WEATHERING OF PLASTICS GLAZING MATERIALS

by Susan M Halliwell

A Doctoral Thesis

Submitted in partial fulfilment of the requirements
for the award of

Doctor of Philosophy of the Loughborough University of Technology

(1996)

ABSTRACT

Plastics glazing materials have properties which allow their widespread use in construction, for example as rooflights. However, they are more susceptible than is glass to degradation by weathering, notably the combined effects of ultraviolet light, heat and moisture. Examples of unacceptable durability have been seen in practice, particularly when high operating temperatures occur in sunlight.

Artificial weathering tests are used to assess plastics glazing materials in a reasonably short time, two main types being utilised in this study. The applicability of ultra-fast methods of accelerated degradation has been shown to depend on the extent to which the mechanisms of degradation simulate practical weathering, since different procedures were found to promote different mechanisms in the materials tested. Misleading information was obtained when the full spectrum of solar UV and much of the visible was not adequately reproduced in the accelerated tests. In particular an established grade of PVC-U performed unexpectedly poorly under fluorescent lamps. Procedures based on xenon arc sources were found to be the most generally applicable because they better reproduce the full solar spectrum range and, hence, the typical effects observed in plastics materials in practice.

Several analytical techniques were used to characterise the virgin polymers and to assess the weathered materials. Two commercial grades of each polymer type (poly[vinylchloride], polycarbonate and poly[methylmethacrylate]) were studied, and measured changes explained in terms of initial polymer properties. Profiling of chemical (e.g. carbonyl index measured by photo-acoustic fourier transform infrared), physical (e.g. molecular weight, surface gloss/roughness), optical (e.g. colour, light transmission) and mechanical properties (e.g. impact resistance) as a function of exposure period and environmental conditions enabled degradation rates and mechanisms to be established for each material. In conducting these tests particular attention was given to the control and effects of sample temperature during weathering, and to the wavelength range of the light source used. Poly(vinylchloride) was affected much more by weathering at higher temperatures, and by exposure to short wavelength radiation, than was polycarbonate, with acrylic being the most durable overall.

Practical applications of this work are through Standards committees primarily, in particular with plastics rooflights (B/542/8 and CEN/TC128/SC9).

ACKNOWLEDGEMENTS

CONTENTS   Page

INTRODUCTION

Organic polymers have become one of the most important groups of materials. Their increasing use in outdoor applications has resulted in the need for satisfactory methods of assessing the weathering performance of materials and of finished products. In general, samples are tested in natural conditions or artificially weathered so that environmental factors such as light intensity, relative humidity and temperature duplicate, as closely as possible, outdoor weathering.

Weather is a general and yet complex term that includes many elements, among which are the effects of sunlight, oxygen, humidity, precipitation, wind and atmospheric impurities. Plastics, like most other materials, are affected by the elements of weather. However, solving plastics weathering problems is complicated since there is a large number of materials, all of which are affected in a different manner by these factors[1]. This leads to difficulties in standardising methods of testing plastics to determine the effects of weather on their mechanical, electrical, physical and chemical properties.

Ultra-violet light is one of the major contributors in the breakdown of plastics[2]. Light of wavelength 290 to 410 nm has quantum energies of the same order as the bond strengths in common monomers and if absorbed and not dissipated as heat or by photo-physical processes, such as fluorescence or phosphorescence, it will initiate photo-degradation. Thus photo-degradation of plastics is wavelength dependent; those polymers, such as aromatic-based types, which absorb wavelengths above 290nm, tend to be more susceptible to degradation than those which are intrinsically transparent. The main source of ultraviolet light is the sun from whence its potential energy is sufficiently high to split all organic molecules, thus leading to obvious degradative effects. The nature and severity of this degradation varies from location to location, and with season, owing to the differences in intensity of solar radiation.

The first signs of changes due to weathering appear on the surface of specimens since this area is most exposed to the direct effects of solar radiation and other climatic factors[3]. The effect of alternating hot days and cold nights can be drastic, often causing crazing of the surface due to excessive expansions and contractions. This is particularly true if internal tensions exist in the material due to earlier thermal treatment during processing or due to reinforcement. As well as these mechanical effects the degradation reactions are accelerated by temperature increases. The action of water is complex and depends on the nature of the

1

polymer and the moulding method. It may wash away soluble degradation products which might otherwise catalyse decomposition. On the other hand it may wash away soluble compounding ingredients such as plasticisers, stabilisers, self-extinguishing additives etc. Unassisted reactions involving oxygen and polymers are slow, but there may be a synergistic effect with elevated temperatures, ultra-violet radiation, moisture etc.

With continued exposure the effects of weathering extend into the material under the surface layer. This may result in changes in surface colour, the gradual formation of cracks, a decrease in transparency, blisters, minor changes in shape or size, or changes in the mechanical or electrical properties or in the solubility. The course of the changes characterises each polymer and its stability.

Polymers currently used on a large scale may be divided into three groups depending on their resistance to photo-degradation:
i) highly photo-stable polymers that are commonly used without photo-stabiliser added e.g. acrylics.
ii) moderately photo-stable polymers that can be used without photo-stabiliser e.g. polycarbonates.
iii) poorly photo-stable polymers which require extensive photo-stabilisation for outdoor uses e.g. poly(vinylchloride).

Complete inhibition of degradation caused by weather is not possible, but the life of a plastics product may be extended by choice of processing stabiliser, pigmentation and light stabiliser. Indeed the general world trend to an increase in the use of plastics materials in external applications has resulted in the introduction of types of polymers, with complex mixtures of basic polymer and additives, to give the required stability of properties in such applications, i.e. a satisfactory service life.

Earlier work[4] illustrates the weathering characteristics of plastics glazing materials when exposed to artificial conditions in a Xenotest-1200. A range of sample mounting methods are available which allow a degree of control over sample surface temperature and give a wide, well spaced range of temperatures attainable in this instrument without changing machine operating conditions. With very durable materials, the additional acceleration achieved at higher temperatures, together with increased thermal shock during rain-spray, may offer the only practical means of assessment in a reasonable time scale.

CHAPTER ONE : BACKGROUND AND LITERATURE REVIEW

This chapter is concerned with plastics glazing materials, with particular reference to weathering and/or associated mechanical effects. The first part of the chapter discusses some applications in the U.K. and typical problems encountered. This is followed by a description of properties of glazing materials and how durability aspects can be investigated and improved. Throughout this chapter it has been attempted to accumulate, correlate and put forward the ideas of workers in the general field of properties of plastics materials.

1.1 BACKGROUND

The service environment generally causes permanent, irreversible changes in the properties of plastics components. Deterioration of most plastics materials starts at the outer surface and may take the form of discolouration, pitting, exudation of ingredients and micro-cracking. Mechanical properties such as tensile strength and impact resistance of most plastics deteriorate when subjected to outdoor exposure[5,6]. Several cases of unacceptable performance of plastics glazing materials have been reported in the U.K.

In 1974 the leisure pool roof of Bletchley Leisure Complex was completed. The roof is pyramid shape consisting of numerous panels each one constructed using an acrylic material[7,8]. Acrylic was used over the pool hall only because it has similar optical properties to tinted glass yet is capable of being formed into large shapes. It also has good impact properties and would not produce dangerous fragments should accidental breakage occur above the pool. Precautions were instituted for the use of acrylic with regard to fire hazards following the Summerland report of 1974[9] which discusses the causes and sequence of events of the fire on the Isle of Man and the factors contributing to the spread of fire and loss of life. In 1987 24 broken or cracked panels were reported. It was deduced that the cracking was caused by impact, possibly children throwing stones. The material otherwise seemed to be in acceptable condition and the panels were not replaced.

The use of PVC rooflights has been widely favoured in the U.K. for reasons of fire performance and as smoke/heat vents. However there is increasing evidence that such rooflights in corrugated and other forms are showing poor durability and weather tightness in practice. Typical cases are shown in Figures 1.1 and 1.2.

Figure 1.1: Frenchway Hospital - Barrel Vault Roof

Figure 1.2 Isle of Wight Ferry Terminal

The barrel-vault roof over the shopping centre in Basildon was glazed using PVC but UV degradation had discoloured the material, reducing light transmission after only a few years, see Figure 1.3. In addition the joints between the glazing and the pressed steel sheeting were leaking owing to differential and extreme thermal movement. The panels were replaced with tinted polycarbonate which has good mechanical, optical and thermal properties. The material chosen also has specially developed UV surface protection.

Figure 1.3: Basildon Shopping Centre - Barrel Vault Roof
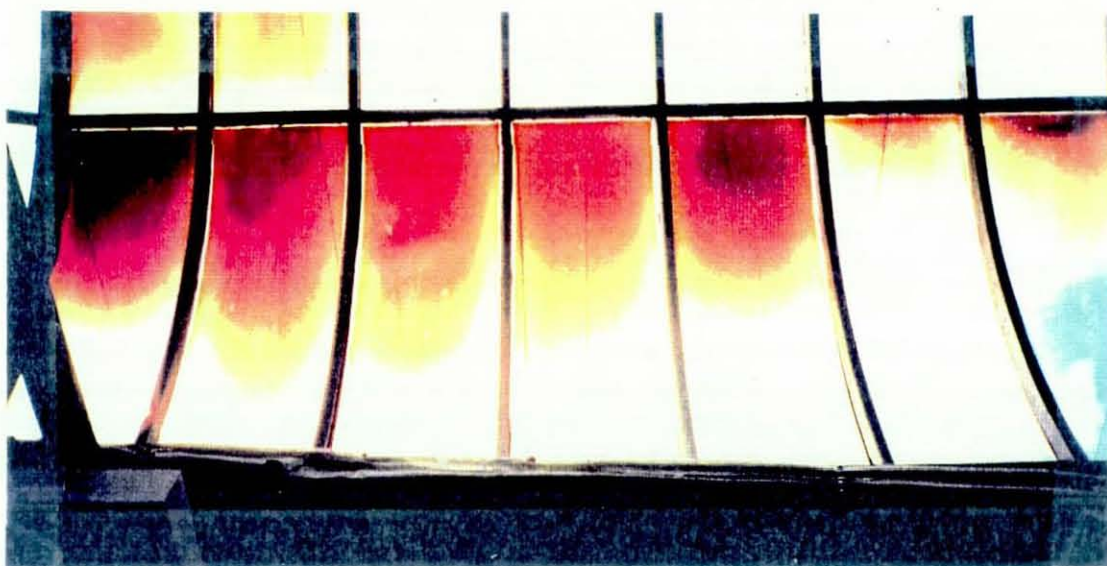
The swimming pool roof at the Dolphin Leisure Centre in Romford, opened in 1982, is enclosed by a four-sided pyramidal roof containing 120 PVC glazing units on each side. The glazing units comprise a four-faced pyramid shaped outer skin of transparent bronze-tinted PVC, and a domed inner skin of clear PVC, clamped together to create a deep rhomboid. During the summer of 1985 several units in the south-facing elevation started to discolour. By February 1987 two of these units had turned almost black and had started to distort, presumably because darkening led to higher temperatures in the sun. Other panels were showing various degrees of discolouration at this stage, see Figure 1.4. During the summer of 1989 several panels turned almost black and started to distort, some distorting so badly that in places their edges had come clear of the glazing framework. In this construction both the bronze colour and the double-skinned feature are likely to contribute to the increased

6

temperatures. Instability to heat may have been induced during the various stages of manufacture of the panels, and work has shown variations in heat stability which correlate well with the observed discolouration of the glazing units when they were on the roof. It is therefore questionable whether PVC is capable of providing acceptable service in a roof construction of this kind.

Figure 1.4: Leisure Pool Roof at Romford

A recent situation was highlighted at a warehouse in Thurrock where PVC rooflights were claimed to be leaking. The rooflights were double-skinned with lateral ribs and falls to long edges for drainage. The extent of weathering after 7 to 8 years was not excessive by visual assessment though there was some variation between panels. The general tendency was a surface 'whitening' over the double-glazed areas, and darkening where the outer PVC overlapped peripheral coated metal and at south and upward facing faces of corrugations in regions of intermediate lap joints. The leading edges of the outer PVC sheet were distorted at their overlaps. Crack formation seen on many panels were long-standing and were commonly associated with screw fixing points. Apparent leaks to building interior might be in part condensation associated with areas of cold bridging around the metal structure, though some water may have penetrated by means of cracks at the edges or by way of the sealant strip which appeared to be in poor condition.

PVC is often used in such construction as highlighted above to act as smoke vents in fire situations. However, if they are not functioning as rooflights it puts the whole practice in question.

1.2 PROPERTIES OF GLAZING MATERIALS

A plastics glazing material can be a single sheet of synthetic plastic material, a combination of two or more such sheets laminated together, or a combination of a plastic material and reinforcement material in the form of fibres or flakes[10]. This material contains as an essential ingredient an organic substance of large molecular weight; is solid in its finished state; and, at some stage in its manufacture, or in its processing into finished articles, can be shaped by flow. Several materials are commercially available for use in glazing applications.

Generally, polymers need to be amorphous to possess good clarity. Crystalline or semi-crystalline polymers tend to scatter light, even if they are of low light absorption, due to regions of varying density and refractive index. Hence, polyolefins are little used for glazing.

Polystyrene in sheet form can have very good clarity but is brittle. It can be impact modified by blending with other polymers but this may be difficult to do whilst retaining clarity because of differences in refractive index. Polystyrene also has rather poor resistance to UV degradation. It is sometimes sold in DIY outlets for lightweight internal secondary double glazing; the outer glass then protects it from the worst effects of short-wavelength UV.

Glass reinforced polyester (GRP) composites are widely used as glazing materials e.g. as

8

corrugated rooflights. However, their composite character makes it very difficult to obtain glass-like clarity and flatness of surface. For this reason and because they involve the use of thermosetting rather than thermoplastic resins GRP glazing materials will not be discussed further.

Poly(ethylene terephthalate) (PET), now widely used for carbonated drinks bottles, is a potential candidate somewhat similar to polycarbonate in character. However, it has yet to be seriously promoted as a glazing material.

In this study three glazing materials are to be considered in detail: poly(methylmethacrylate), poly(vinylchloride) and polycarbonate.

1.2.1 Poly(methylmethacrylate)

Poly(methylmethacrylate) (PMMA) was introduced in the late 1930's and one of its first and main current uses is as a replacement for glass in aircraft transparencies[11]. The reasons why PMMA has retained its strong hold in this field are because of its high stiffness, excellent optical properties and outstanding resistance to weathering. Examples of commercial PMMA sheet are Perspex (ICI), Oroglas (Rohm and Haas, USA) and Plexiglas (Rohm and Haas, Germany).

Polymerisation is carried out, using a syrup of the polymer in monomer with added initiator, by free radical means in large glass cells[12]. This produces high quality cast sheet of very high molecular weight (polymerisation is carried out over many hours). Alternatively, polymerisation is carried out in an extruder, the sheet being shaped by an appropriate die. In this case the molecular weight of the polymer has to be controlled to allow die shaping.

Cast PMMA sheet is more expensive than the extruded form but because its molecular weight is an order of magnitude higher it gives overall better performance. Cast PMMA has superior impact resistance (less notch-sensitive), has better craze resistance and has higher gloss finish than extruded sheet. Cast sheet cannot be processed by methods generally applicable to thermoplastics[12], however, it can be thermoformed by vacuum blowing or plug-assisted methods: deformation is almost entirely high elastic strain and the original sheet is regained if the shaping is heated above the softening temperature (105-120°C).

The principal properties of PMMA are summarised below[12,13]. The absorption of visible light is zero and the light scatter is so low that transparency can be regarded as

9

perfect. Acrylic has high strength, and although it cracks, any fragments formed are less sharp and jagged than those of glass: it is however, brittle and fails at low elongation. Acrylics are very resistant to UV radiation and to other weathering. Resistance may be reduced by residual stress in the shaping which may cause moisture absorption and desorption stresses and thus lead to crazing. Crazing and cracking can also be induced by a number of organic materials e.g. aliphatic alcohols. Mineral acids also attack acrylics but the plastic is resistant to alkalis, water and most aqueous inorganic salt solutions. Acrylics can act as good electrical insulators for low frequency use, but they are inferior to polyethylene and polystyrene.

One of PMMA's least attractive properties is that it is readily flammable with burning drips (the extruded form more so than the cast[14]), and since it depolymerises at temperatures above 170°C to form the monomer which is highly flammable and toxic, the use of the unmodified plastic in building applications is restricted in the U.K. (particularly following the Summerland Fire). However, there are older installations in the U.K. still in use and it is quite widely used on the continent and in the USA. Flame retardant grades have been developed but should they become involved in fires, other toxic products could be evolved and the smoke density will be much higher than with the standard acrylic.

Applications are mainly concerned with transparency and light transmission, with very good weathering performance and with high surface hardness and durability. Hence it is used for aircraft canopies, motor-bike visors, sanitary wear e.g. baths, car light assemblies and optical components, as well as in many external glazing applications.

In recent years, tough and heat-resistant materials closely related to PMMA have been developed. Brittleness for example can be reduced by either copolymerisation of methyl methacrylate with a secondary monomer or blending with a rubber. A very wide range of acrylic polymers are now available with an extremely broad property spectrum.

1.2.2 Poly(vinylchloride)

Poly(vinylchloride) (PVC) is probably the most adaptable of the synthetic polymers[11], and more than any other polymer it has been improved by the use of additives such as processing aids, plasticisers, comonomers and fillers.

The properties of PVC are greatly influenced by method of manufacture. Commercially, PVC is polymerised by free-radical mechanisms in bulk, suspension or emulsion. Polymerisation is carried out at about 50 to 75°C since the general kinetics are

influenced by a significant chain transfer to monomer reaction which increases more rapidly with temperature and is little affected by initiator concentration.

Because of its limited thermal stability together with the low amount of crystallinity, the melt viscosity of PVC is very high at normal processing temperature and so thermal stabilisers and lubricants are essential ingredients for processing[12]. Unplasticised or rigid PVC (PVC-U) is frequently extruded, and is widely used in sheet form which can readily be shaped by thermoforming. PVC-U compound can be injection moulded using a screw pre-plasticiser.

PVC is one of the least stable of commercially available polymers and yet, in terms of tonnage at least, it is one of the most important plastics materials available today. This is largely due to the discovery of suitable stabilisers and other additives which has enabled useful thermoplastic compounds to be produced[12].

PVC polymers are slightly branched molecules with the monomer arranged in a head-to-tail sequence. They are rigid materials and are tough under normal conditions if stress concentrations are absent. The mechanical properties depend on temperature: below -65°C they behave as a brittle material; above this the material becomes increasingly tough with increasing temperature until at about 80°C the material becomes rubbery. At 160°C the flow point is reached, with decomposition releasing HCl occurring above 200°C (100°C for unstabilised PVC). Performance of PVC under load depends on the magnitude of the stress and the length of time for which it is applied.

PVC is difficult to ignite and shows limited flaming or dripping. However, when rigid PVC does burn the amount of hydrogen chloride evolved will give rise to a very pungent atmosphere. These fumes can also lead to the corrosion of metals e.g. electrical circuitry, hence causing disproportionate damage. However, the low softening temperature of PVC is claimed to be an advantage for rooflights since it can release smoke, fumes and heat. PVC is resistant to water and hydrocarbons, and to most aqueous solutions including those of alkalis and dilute mineral acids and so is widely used for pipes.

There is often a price advantage to be gained in using PVC but there are environmental questions against this. These include the current use of heavy metal stabilisers such as barium, lead and tin, and acid production if PVC waste is incinerated. The range of possible PVC formulations is very wide and hence applications are numerous. A large volume of material is used in outdoor applications, for example in the building industry rigid PVC is used for cladding and raingutters, whilst copolymers of PVC and compounds

with ethylene vinyl acetate or acrylic impact modifiers are being used in the construction of window frames.

1.2.3 Polycarbonate

Polycarbonates (PC) were first prepared by Einholm in 1898 but this polymer was not developed until about 1960 when it began to replace glass and acrylic in areas prone to vandalism e.g. subways. The 1980's saw a growth in its use, a main reason for this being that its fire performance is relatively good. Today, commercial polycarbonate resins are being marketed in Germany by Bayer (Makrolon), in the USA by General Electric (Lexan) and Mobay (Merlon), in Italy by ANIC and in Japan by the Taijun Chemical Co, Mitsubishi Edogawa and Idemitsu Kasei.

Polycarbonates may be produced from a wide range of polyfunctional hydroxy compounds. In practice only the diphenyl compounds have proved of much interest and the only commercially important polycarbonate is derived from bis-phenol A.

Although a linear polymer with symmetrical structure, the melt-processed material is difficult to crystallise and polycarbonate articles and components are substantially amorphous and therefore transparent if unpigmented. Grades of polycarbonate are available for injection moulding and for extrusion based processes including blow-moulding. The range of commercial grades of polycarbonate has increased greatly in recent years[14]. The main differences between grades are due to differences in molecular weight, the presence or otherwise of a second polyhydroxy compound, and differences in additives.

Unusually for a rigid amorphous plastic, polycarbonate is generally tough. However, great care must be taken in the design of components since a wide range of factors can lead to embrittlement and premature failure; these include sharp notches, frozen-in stresses, cyclic stressing and a number of organic solvents which promote stress crazing. One of the major attributes of the polymer is its relatively low flammability: the oxygen index of the polymer is 25%[12]. Polycarbonate is more expensive than polyethylene, polystyrene and PVC. A major disadvantage for its use is its limited resistance to chemicals and ultra-violet light; satisfactory weathering resistance is usually only achieved by surface coating e.g. with acrylics.

The largest single field of application is in electronics and electrical engineering: covers for time switches, batteries etc. utilise the good electrical insulation characteristics

12

in conjunction with transparency, flame resistance and durability. The increase in vandalism in recent years has led to the substantial growth of the market for polycarbonate glazing e.g. bus shelters, telephone kiosks, riot squad shields and visors, and lamp housings. However, in these glazing applications the limited scratch and weathering resistance of the polycarbonates are a disadvantage and much research to try to overcome these problems is being carried out. One such development is to coat the polycarbonate sheet with a material glass-like in chemical composition and structure which provides hardness and long-term protection against abrasion and weathering.

1.3 MECHANISMS OF POLYMER DEGRADATION

On exposure to weathering polymer molecules may break (by chain scission), crosslink, or suffer substitution reactions. Substitution is the least common and causes the smallest property changes and will not be considered further in this report. Scission and cross linking both occur under natural weathering conditions and molecular degradation can also take place during processing. There is a general rule that molecular degradation takes place almost exclusively at defects in the molecule. Much research has been carried out into the chemical reactions involved and there are many papers and several reviews on the subject[15-21].

1.3.1 Photo-oxidation

One of the most important processes in polymer degradation is that of photo-oxidation. This proceeds by a radical chain process initiated by either dissociation caused by the collision of a photon with sufficient energy with a polymer molecule, or as a result of some impurity present, for example trace elements from the polymerisation catalyst. Whereas there are important differences between the initiation of thermal and photo-oxidative degradation, in photo-oxidation the chemical reactions which constitute the propagation, branching and termination steps are believed to closely parallel those established for thermal oxidation[11]:

Initiation:

hv

P -> P.   [1]

13

Propagation:

$$P \cdot + O_2 \rightarrow POO \cdot \qquad\qquad [2]$$
$$POO \cdot + PH \rightarrow POOH + P \cdot \qquad\qquad [3]$$

Chain Branching:

$$POOH \rightarrow PO \cdot + HO \cdot \qquad\qquad [4]$$
$$2POOH \rightarrow POO \cdot + PO \cdot + H_2O \qquad\qquad [5]$$
$$PO \cdot + PH \rightarrow POH + P \cdot \qquad\qquad [6]$$
$$HO \cdot + PH \rightarrow P \cdot + H_2O \qquad\qquad [7]$$
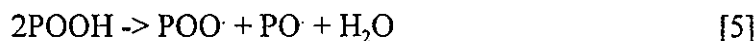
some alternative reactions are given by other authors[22,23] as:

$$POOH \rightarrow P \cdot + \cdot OOH \qquad\qquad [8]$$
$$POOH + PH \rightarrow PO \cdot + P \cdot + H_2O \qquad\qquad [9]$$
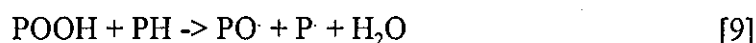
Termination is then normally through the reaction of pairs of radicals. The reaction schemes are affected by trace metal impurities such as polymerisation catalyst residues or contaminants from processing machinery, for these may catalyse some of the degradation reactions, for example [5][24]. Degradation can still occur slowly in the dark through the formation of hydroperoxides through intramolecular back-biting hydrogen abstraction by peroxy radicals[25,26].

Hydroperoxides produced by reaction [3] or by other means can be decomposed by UV radiation with wavelength below 360nm giving a PO· radical, as shown in [4]. The decomposition of hydroperoxides is generally acknowledged to be a key feature in the degradation of polyolefins, though their behaviour in polyethylene, in which they do not accumulate during photo-oxidation, is different to that in polypropylene, in which they do accumulate[27].

The presence of carbonyl groups in a degraded polymer indicates that oxidation has taken place and also warns that the material is vulnerable to further deterioration because they are photo-labile. Aldehyde and ketone carbonyl groups are common products during processing and the effect of processing on the subsequent degradation behaviour has been identified as of significant importance[28]. Two important photolytic decomposition reactions for aliphatic ketones are:

14

Norrish Type I:

$$\underset{\|}{\overset{O}{P_1CCH_2P_2}} \rightarrow \underset{\|}{\overset{O}{P_1C}} + CH_2P_2 \qquad\qquad [10]$$

$$\underset{\|}{\overset{O}{P_1C}} \rightarrow P_1\cdot + CO \qquad\qquad [11]$$

The primary radicals formed may also abstract hydrogen from the polymer (PH):

$$\underset{\|}{\overset{O}{P_1C}} + PH \rightarrow P\cdot + P_1CHO \qquad\qquad [12]$$

Norrish Type II:

$$\underset{\|}{\overset{O}{P_1\text{-}C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}P_2}} \rightarrow \underset{\|}{\overset{O}{P_1CCH_3}} + CH_2=CHP_2 \qquad [13]$$
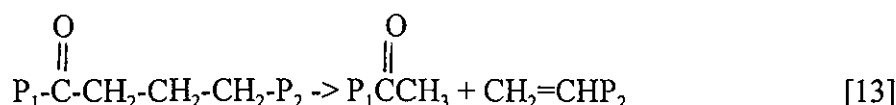
Although most studies of photo-oxidation have centered on UV radiation the need for information on the behaviour of polymers for insulation (polyethylene) and jacketing (PVC) in nuclear installations has stimulated study of the effect of M-radiation. Clough and Gillen[29,30] found that radiation dose and temperature act synergistically in promoting degradation.

1.3.2 Thermal Decomposition and Oxidation

Thermal degradation is of relevance here because damage suffered by the polymer during processing at elevated temperature can accelerate the subsequent effects of photo-oxidation. Thermal degradation is a serious problem with PVC and has been the subject of much research. The initial step in the process of degradation is dehydrochlorination, with hydrogen and chlorine atoms on adjacent chain carbon atoms stripping off to form HCl and leaving behind a double bond in the polymer backbone. Adjacent sites become less stable and more HCl may be stripped off and a conjugated polyene structure develops. This causes yellowing of the material. HCl catalyses the reaction which is therefore auto-accelerating unless steps are taken to remove the HCl. The process is accelerated in oxygen but can occur in the absence of oxygen at temperatures above 120°C[31]. Troitskii and Troitskaya[32] conclude that abnormal unstable fragments have a major influence over

15

thermal degradation of PVC.

Mechanico-chemical degradation may occur during processing, producing free radicals that may then initiate dehydrochlorination in PVC[33]. It is expected that dehydrochlorination will initiate at pre-existing defect sites in the polymer, although there is evidence that it may not be restricted to them[31]. The small amount of oxygen present during processing allows the formation of hydroperoxides by reaction with radicals. After thermal degradation the polymer will suffer further degradation during later stages of processing, or under other conditions favouring thermal oxidation, or even under conditions of photo-oxidation[34]. Even though the shearing action during processing is generally believed to promote molecular damage, the inclusion of lubricants to reduce the viscosity during processing does not produce any significant reduction in the vulnerability of the product to oxidation[29]. The susceptibility to further degradation will depend on the amount of HCl present, the degree of unsaturation and on the hydroperoxide content[35].

Although generally regarded as a lesser problem than with PVC, degradation of polyolefins occurs during processing as well. Mellor et al[36] found that the lifetime under UV exposure was very sensitive to the degree of oxidation that took place during processing on a 2-roll mill and that the rate of UV degradation was related to the increase in melt flow index that occurred in the material.

1.3.3 Hydrolysis

Hydrolytic attack can cause chain scission in some polymers, leading inevitably to a deterioration in properties. A general hydrolysis scheme can be summarised as follows:

$$-CH_2-\underset{O}{\overset{\|}{C}}-O-CH_2- \ + H_2O \ \rightarrow \ -CH_2-\underset{O}{\overset{\|}{C}}-OH + HO-CH_2-$$
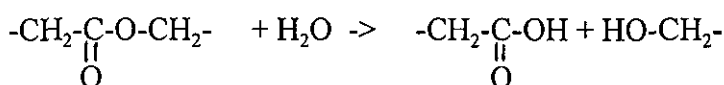
Polymers susceptible to hydrolytic attack include polycarbonate. The reaction can be unacceptably fast at elevated temperature and when water is absorbed in polycarbonate in sufficient quantity it can form disc-shaped defects that act as stress concentrating flaws and cause a serious loss of toughness[37].

16

1.3.4 Specific Mechanisms of Photo-oxidation
1.3.4.1 Poly(methylmethacrylate)

In comparison with many other commercial polymers, acrylics are considered more resistant to photo-oxidation. PMMA begins to absorb at 320nm, the absorption rising rapidly with decreasing wavelength. The presence of monomer and catalyst residues can decrease the stability of PMMA, however these are not normally present in the commercial material, which to achieve the desired optical properties, has to be of the order of 99.8% pure.

Photo-oxidative degradation results in simple chain splitting without side reactions that would lead to the build-up of light-absorbing chromophores such as conjugated diene links which would accelerate the reaction. Degradation leads to changes in mechanical properties. For example, 17 years exposure in New Mexico caused a decrease in flexural strength by 51%, strain at rupture decreased by 66% and the polymer became more brittle due to crack initiation by surface roughness[11]. There is also often a small reduction in Tg due to the chain splitting. A loss in transmission of light may occur though this will tend to be small and mainly due to surface roughness.

Photo-oxidative degradation results in an increase in UV absorption at 280nm due to formation of aldehyde groups in the side chain[14].

$$
\begin{array}{ccc}
CH_3 & CH_3 & CH_3 \\
| \quad hv & | & | \\
-CH_2-C- \quad \longrightarrow \quad -CH_2-C- & \longrightarrow \quad -CH-C- \\
| & | & | \\
COOCH_3 & CO \cdot + \cdot OCH_3 & CHO \\
\end{array}
$$
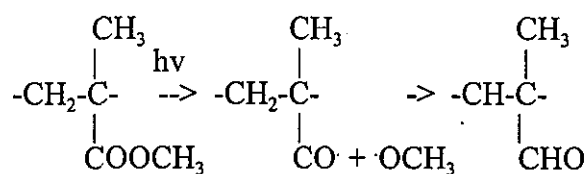
or hydrogen abstraction may also occur from an adjacent chain

$$
\begin{array}{cccc}
CH_3 & CH_3 & CH_3 & CH_2 \\
| & | & | & | \\
-CH_2-C- \; + \cdot CH_2-C- & \longrightarrow \; -CH_2-C- \; + -CH_2-C- \\
| & | & | & | \\
CO \cdot & COOCH_3 & CHO & COOCH_3 \\
\end{array}
$$
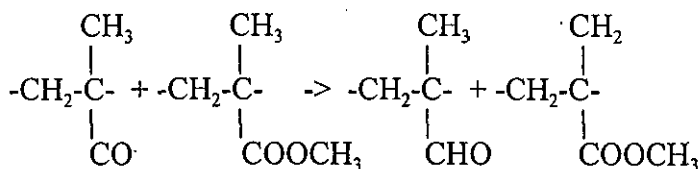
Irradiation of PMMA in a vacuum at normal temperatures results in extensive chain scission. The polymer also exhibits yellowing. Three major reactions are thought to occur simultaneously[14].

1. Random homolytic scission of polymer backbone

$$\underset{[I]}{-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-} \xrightarrow{h\nu} \underset{[II]}{-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\cdot} \quad + \cdot CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-$$
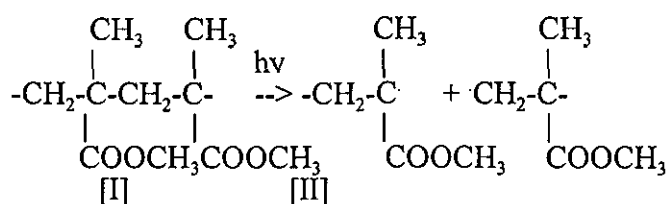
2. Photolysis of methyl side groups

$$-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2- \xrightarrow{h\nu} -CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{\cdot}{}}{C}}-CH_2-$$

3. Photolysis of the ester side groups

$$-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-$$

$$\longrightarrow -CH_2-\underset{\underset{\cdot}{}}{\overset{\overset{CH_3}{|}}{C}}-CH_2- + \cdot COOCH_3 \quad [III]$$

$$\longrightarrow -CH_2-\underset{\underset{CO\cdot}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2- + \cdot OCH_3 \quad [IV]$$

$$\longrightarrow -CH_2-\underset{\underset{COO\cdot}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2- + \cdot CH_3 \quad [V]$$
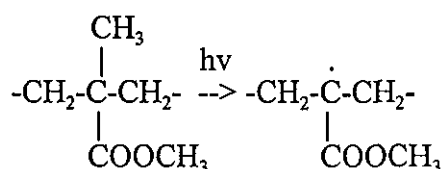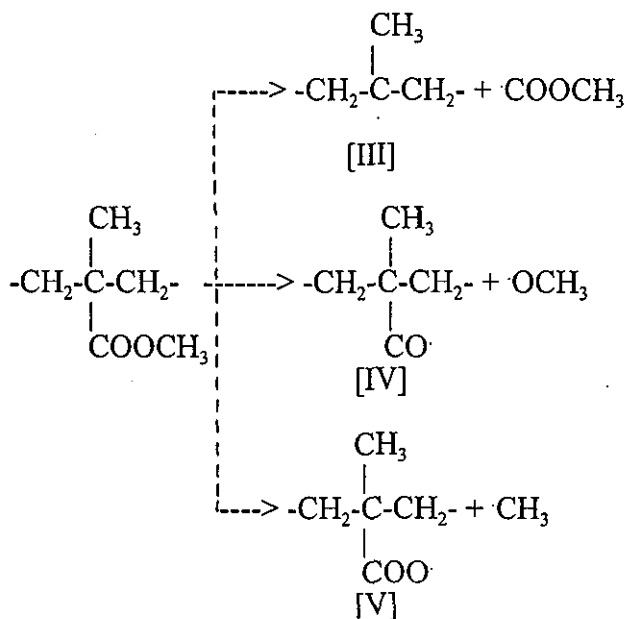
Photo-yellowing is thought to occur on subsequent reactions:

18

$$\begin{array}{ccc} \quad CH_3 & \quad\quad\quad CH_3 \\ \quad | & \quad\quad\quad | \\ -CH_2\text{-}C\text{-} + \cdot COOCH_3 \rightarrow -CH\text{-}C\text{-} + HCOOCH_3 \end{array}$$

[III]

$$\begin{array}{c} CH_3 \\ | \\ -CH=C\text{-} \rightarrow etc. \end{array}$$
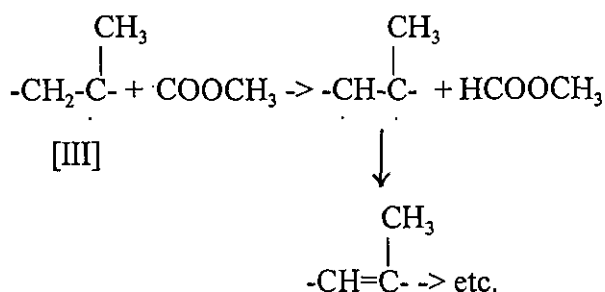
1.3.4.2 Poly(vinylchloride)

On outdoor exposure PVC tends to discolour. This discoloration depends on a large number of factors including solar radiation intensity, thermal cycling, humidity, processing conditions during sheet manufacture, forming conditions of time and temperature, storage conditions prior to use and the design of the structure. Thus several factors can be employed to maximise the time to discoloration; heating should be kept to a minimum during sheet shaping, temperature kept as low as possible (not >60°C), and sheet shielded from the sun and rain when stored.

PVC degrades photochemically at ambient temperature to yield HCl and conjugated polyene structures which are highly coloured and cross-linked. The reaction is accelerated by the HCl produced and by the presence of oxygen (although oxygen can have a bleaching effect caused by the radical oxidation of long-chain polyenes) and is known to produce chain scission[11].

$$\begin{array}{c} \quad\quad\quad\quad -HCl \\ -CH\text{-}CH_2\text{-}CH\text{-}CH_2\text{-}CH\text{-} \cdots\cdots> -CH=CH\text{-}CH\text{-}CH_2\text{-}CH\text{-} \dashrightarrow etc. \\ | \quad\quad | \quad\quad | \quad\quad\quad\quad\quad | \quad\quad | \\ Cl \quad\quad Cl \quad\quad Cl \quad\quad\quad\quad\quad Cl \quad\quad Cl \end{array}$$
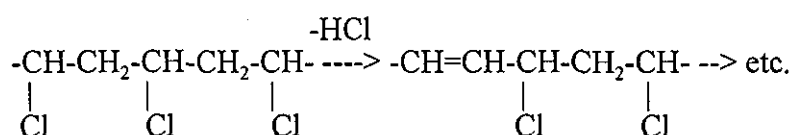
Dehydrochlorination is considered to proceed by a radical process:

19

$$-CH_2\text{-}\overset{\centerdot}{CH}\text{-}CH_2\text{-}CH + \cdot Cl$$
$$\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad Cl$$

$$-CH_2\text{-}CH\text{-}CH_2\text{-}CH\text{-} \;\longrightarrow\; -CH_2\text{-}CH\text{-}\overset{\centerdot}{CH}\text{-}CH + \cdot H$$
$$\quad\;\; |\qquad\quad\; |\qquad\qquad\qquad\qquad |\qquad\quad |$$
$$\quad\; Cl\qquad\; Cl\qquad\qquad\qquad\quad Cl\qquad Cl$$

$$\longrightarrow\; -CH_2\text{-}\overset{\centerdot}{C}\text{-}CH_2\text{-}CH + \cdot H$$
$$\qquad\qquad\qquad\quad |\qquad\quad\; |$$
$$\qquad\qquad\qquad\; Cl\qquad\; Cl$$
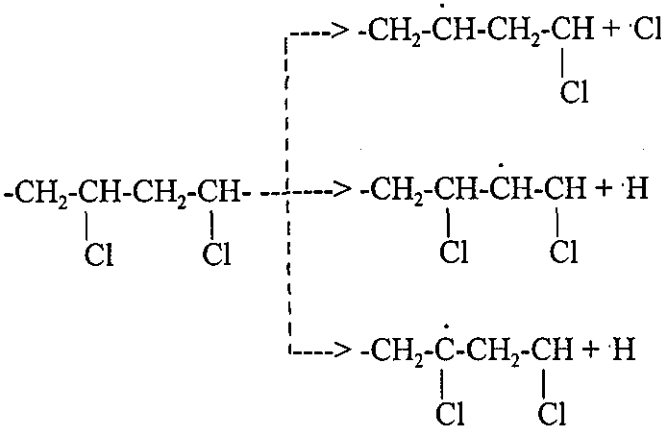
Chlorine radicals then abstract hydrogen:

$$-\overset{\centerdot}{CH}_2\text{-}CH\text{-}CH_2\text{-}CH\text{-} + \cdot Cl \;\longrightarrow\; -CH_2\text{-}CH{=}CH\text{-}CH\text{-} + HCl$$
$$\qquad\quad |\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\; Cl\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad Cl$$
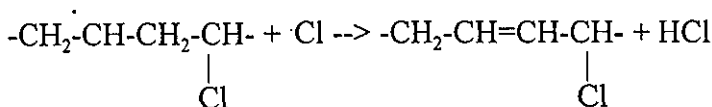
Further dehydrochlorination occurs by a `zipper' process:

$$-CH_2\text{-}CH{=}CH\text{-}CH\text{-} + \cdot Cl \;\longrightarrow\; -CH_2\text{-}(CH{=}CH)_2\text{-}CH\text{-} + HCl$$
$$\qquad\qquad\quad |\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\; Cl\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad Cl$$
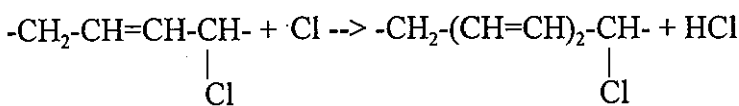
However, there is difficulty in explaining the catalytic effect of HCl. Alternative mechanisms have been suggested in which metal salts such as $FeCl_3$ and $ZnCl_2$ accelerate the rate of dehydrochlorination[38]. A third mechanism has also been considered[14] involving a molecular, cyclic, six-membered transition state.

As previously mentioned, oxygen can also accelerate the breakdown of PVC. Oxygen quenches the free-radicals formed to initiate an oxidative chain reaction that leads to the formation of carbonyl groups (C=O). Rate of formation of carbonyl groups in PVC is independent of both relative humidity and PVC temperature, and is proportional to the intensity of radiation. This implies that the primary production of free radicals determines the rate of production of carbonyl groups[39].

There is strong evidence suggesting that the photo-dehydrochlorination of PVC is

highly complicated. For example, typical inhibitors such as hydroquinone do not affect the rate of dehydrochlorination in a nitrogen atmosphere. Also the accelerating effect of the presence of HCl on the rate of dehydrochlorination is difficult to explain by means of a radical mechanism.

Further complications arise from the fact that the discoloration is confined to a very narrow surface layer which acts as a filter and can reduce the rate of degradation drastically since the bulk of the material is unaffected.

1.3.4.3 Polycarbonate

Unstabilised polycarbonate absorbs ultraviolet light strongly, although degradation effects are confined almost entirely to the surface. The visible surface changes are a darkening in colour and eventual crazing[40].

The key mechanism of photo-aging of polycarbonate involves the photo-Fries reaction.
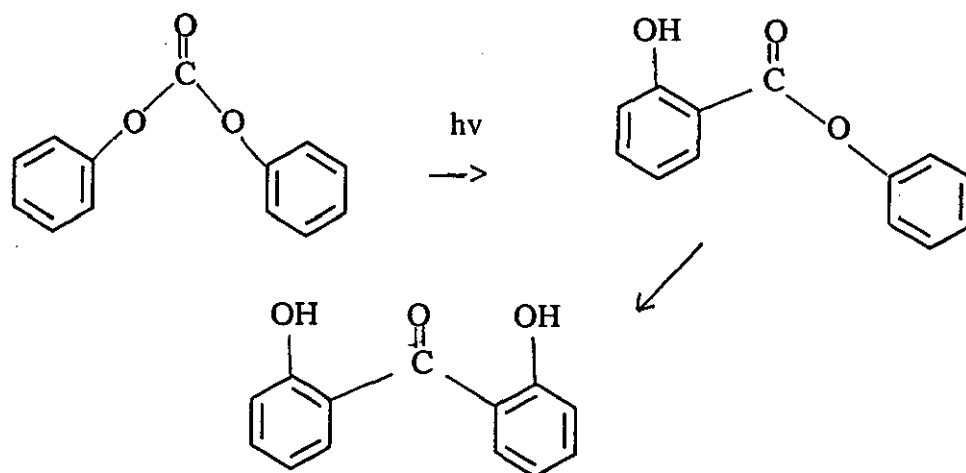
Davis and Golden[41] found that the products of the photolysis of diphenyl carbonate could best be explained by the formation of free-radicals formed by cleavage of both the aryl-oxygen and oxygen-carbonyl bonds, followed by either recombination (Fries reaction) or loss of CO and CO_2 with subsequent recombination to form aryl ethers and phenol. o-Hydroxybenzophenones and related compounds are very efficient UV-absorbers; see section 1.4.1.2.

21

The role of oxygen in photo-aging of polycarbonate is less well understood. Oxygen up-take is known to play an important part in the photo-aging of polycarbonate under accelerated and actual outdoor conditions[42]. The production of free radicals seems to predominate during the induction phase. These reactive intermediates in turn react with oxygen to form hydroperoxides, quinones and ketonic compounds. Other processes such as metal catalysts may also have a role in this early period. Since the products of these primary processes are themselves photo- and thermally-unstable, they in turn decompose in secondary processes and initiate the formation of more unstable products, making an autocatalytic cycle:

$$
\overset{\displaystyle R}{Ar_2CMe_2} \xrightarrow{\quad} \overset{\displaystyle \cdot CH_2}{Ar_2CMe} \xrightarrow{\; O_2 \;} \overset{\displaystyle CH_2O_2H}{Ar_2CMe} \xrightarrow{\quad} \overset{\displaystyle CH_2OH}{Ar_2CMe}
$$

Ar_2CMe (CH$_2$) $\downarrow$

$$
\underset{ArCMe}{ArCH_2} \quad\quad Acids, Esters, Anhydrides
$$

(with H$^+$)

$$
\underset{ArCMe}{ArCH_2} \overset{\displaystyle O_2}{\downarrow}
$$

$$
\underset{\underset{O_2H}{|}}{ArCMe}
$$

$$
ArCO_2H \uparrow
$$

$$
ArCH_2\overset{O}{\overset{||}{C}}OH \uparrow
$$

$$
\underset{O_2}{\swarrow} \qquad \overset{O_2}{\searrow} \; ArC\overset{O}{\overset{||}{}}Me + ArCH_2OH
$$

$$
ArOH + ArCH_2\overset{O}{\overset{||}{C}}Me
$$
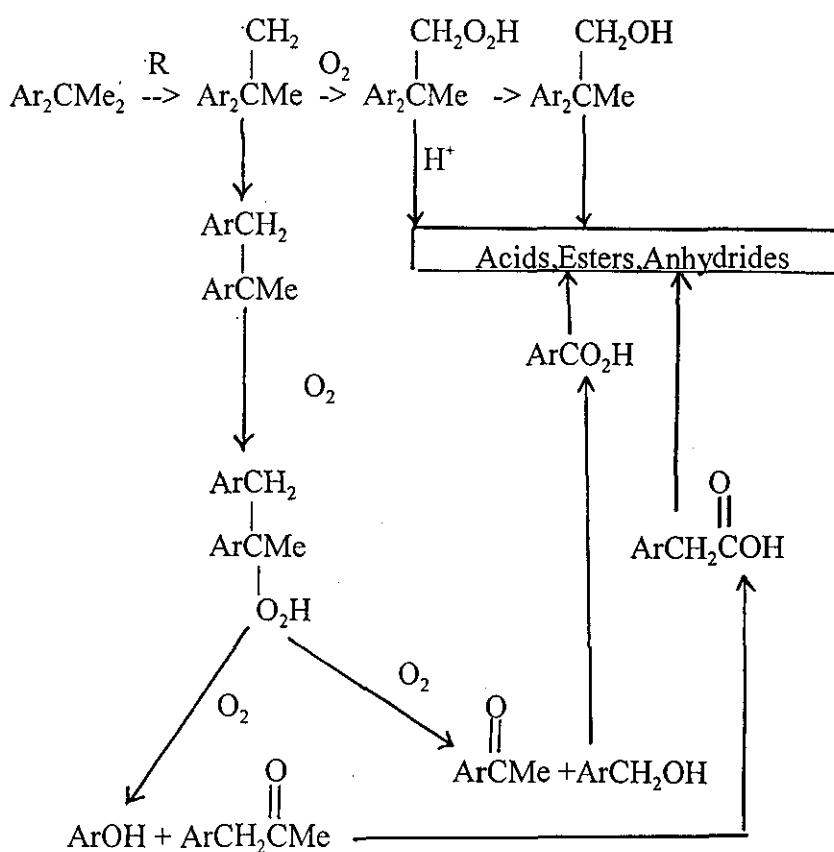
Degradation can be slowed considerably by using ultraviolet stabilisers, or the effect on mechanical properties delayed by using high molecular weight grades. However, since the impact strength of polycarbonate is very sensitive to notch radius and molecular weight, surface crazing and the reduction of molecular weight caused

22

by photolysis can affect the impact strength of polycarbonate severely[40]. One method of reducing the sensitivity of polycarbonate to scratching and UV degradation is to use surface coatings.

1.4 STABILISATION

The inclusion of stabilisers can produce a spectacular improvement in the lifetime of a polymer component. Although a basic understanding of the mechanisms of degradation was needed before effective stabilising systems could be chosen, the study of the effect of these stabilising systems has lead to a more detailed understanding of degradation mechanisms and so to improved stabilising systems.

1.4.1 Photo-stabilisers

The methods that offer protection against photo-oxidation are UV screening, UV absorption, excited state deactivation, free radical scavenging and hydroperoxide decomposition. These are all discussed in a review by Allen et al.[43]

1.4.1.1 UV Screening

This is provided by pigments or by a reflective coating[11]. Carbon black is very effective and is used to stabilise many outdoor grades of polymer. This method of stabilisation causes strong colouration of the polymer and so it is not used for plastics glazing materials.

1.4.1.2 UV Absorption

Additives that are transparent to visible light can provide UV absorption and do not alter the appearance of the product. Transparent compounds can be made; ideally the transmittance should be 100% in the visible range and zero at wavelengths below the visible limit of 400nm, and there exist stabilisers that come remarkably close to this specification[43]. The most common UV stabilisers are the hydrobenzophenones, the hydroxyphenylbenzotriazoles, the hydroxyphenyltriazines and derivatives of phenyl salicylates; their chemical formulae and the trade names of some of the commercial compounds are listed elsewhere[43,44]. The act of absorbing the UV is not the only requirement of a molecule to contribute to stabilisation; it must also dissipate the energy absorbed without damaging the polymer it is meant to protect. Some discussion of how this

23

may happen is given by Allen et al[43]. As with screens, the presence of UV absorbers causes the UV intensity to drop more rapidly as it penetrates into the material and degradation is concentrated even more sharply near the surface[45]. It is most economical if these additives are concentrated at the surface; for example in purpose applied coating.

1.4.1.3 Excited State Deactivation

Quenching provides an alternative method for the dissipation of energy absorbed by a polymer chromophore to the damaging scission reaction. The tendency for carbonyl photolysis to lead to backbone cleavage can be reduced by deactivating excited carbonyl species using transition metal chelates. Allen et al[43] cite studies in which it was shown that the quenching process can operate over a distance up to 19nm, so that protection can be provided by a very low concentration of additive if uniformly dispersed. As with UV absorbers, the quencher must be able to dissipate the acquired energy.

1.4.1.4 Radical Scavengers

These break the oxidation chain, so limiting the damage. Allen et al[43] discuss the chain-breaking donor mechanism and the chain-breaking acceptor mechanism, giving details of the chemical structure of the stabilisers and of the reactions involved in the stabilising process. In the chain-breaking donor mechanism a hydrogen atom is donated to an alkoxyperoxyl radical to form a hydroperoxide. The donor is a hindered phenol or an aromatic amine. Alkyl radicals are the target of the chain-breaking acceptor mechanism. There are many compounds that can be used for this purpose. Free radicals that are relatively stable and do not themselves initiate reactions with the undamaged polymer can be used, reacting with alkyl radicals when they are produced by photo-oxidation. Examples of suitable free radicals are nitroxyls and phenoxyls.

1.4.1.5 Hydroperoxide Decomposition

Hydroperoxide decomposition into inactive products is an important method of stabilisation in polyolefins for it prevents generation of radicals. Hydroperoxides are more potent photo-initiators than carbonyl groups[46]. Decomposition can be achieved by reaction with phosphite esters or nickel chelates, or by a catalytic action by a range of compounds listed by Allen et al[43] and including dithiocarbamates and mercaptobenzothiazoles. Decomposition of hydroperoxides

24

formed during processing is also important for the stabilisation of PVC[47].

It is evident that some classes of chemicals may provide stabilising action through two or more mechanisms. This is of great benefit but may have slowed progress in developing optimal stabilisation systems because of the uncertainty attached to the true mechanism of stabilisation in some cases. Combinations of stabilisers can be used to provide multi-mechanism protection though care must be taken that no antagonism exists between the different components wherein presence of one of them renders the other less effective than when used in isolation. In some cases the combination of two different anti-oxidants provides better protection than would be expected by simply adding the effects produced by them both when used alone, a phenomenon known as synergism.

1.4.2 Thermal Stabilisers

PVC has poor thermal stability; methods to improve this have been discussed in four reviews in a single volume[31,33,48,49]. The features required by a thermal stabiliser have been listed by Ayrey and Poller[31] and include:-

(i) reaction with and removal of HCl liberated during the early stages of degradation;

(ii) replacement of labile Cl atoms or other structural weaknesses by more stable entities;

(iii) interruption of chain reactions such as unzipping or the production and decomposition of peroxides;

(iv) interruption of conjugated polyene sequences (to reduce colour deterioration);

(v) reaction with pro-degradant products of the stabilisation process.

The main classes of thermal stabilisers used in transparent PVC are listed below.

1.4.2.1 Organo-tin Stabilisers

These are effective in preventing chromophore production during processing and may provide some photo-stabilisation in addition[31,50], though Cooray and Scott[33] claim that some compounds may act as pro-oxidants due to photolysis of the stabiliser. Organo-tin stabilisers can be used for clear grades of polymer.

1.4.2.2 Organo-phosphorus Stabilisers

These stabilisers are effective for preserving the original colour in PVC[49]. They decompose hydroperoxides and react with peroxy radicals to terminate kinetic chains. Pobedimski et al[49] give a glossary of phosphites suitable for this application and

25

present some kinetic data for various phosphites reacting with hydroperoxides. They note that transition metal ion-phosphite combinations are synergistic and are effective in scavenging peroxy radicals.

1.4.2.3 Metal Soaps

These and other organic compounds have been used as stabilisers for PVC for many years and have been reviewed by Guyot and Michel[48], however, they are not generally suitable for transparent PVC-U formulations.

1.5 THE ENGINEERING PERSPECTIVE

The ultimate goal is the development of materials with indefinite lifetime. This may never be achieved, but it would be almost as valuable if methods could be developed that would permit an accurate prediction of component lifetime, either from the time of manufacture, or from the time of an in-service inspection.

Studies of degradation mechanisms of polymeric materials have concentrated largely on the chemical reactions that are involved. As a consequence, the understanding of the chemical mechanisms of degradation is quite advanced. The spectacular improvement in polymer lifetime made possible by anti-degradation additives, many of them commercially available and in widespread use, bears testimony to this. Nevertheless many review and research papers on this topic claim that more research should be done in this area. It is evident that engineering aspects of weather-related failure of polymers are not as well understood as the chemical mechanisms of degradation. Many examples are to be found in the literature where a chemical characteristic (e.g. the carbonyl index) is used to monitor the progress of degradation reactions and is found to correlate reasonably well with deterioration of engineering properties (e.g. elongation to break in a tensile test) yet there is very little known about the links between chemical changes and the consequent mechanical changes. It seems that to be able to predict lifetimes of polymeric components a more comprehensive appreciation of the engineering aspects of failure is required and that more insight is needed into the relationship between chemical and mechanical degradation. Only then can predictions of lifetimes based on chemical kinetics and other physico-chemical properties such as diffusion be developed with confidence. Weathering has different effects on the three polymer types studied in this work.

26

1.5.1 Weathering of Poly(methylmethacrylate)

PMMA is claimed to be one of the most weather resistant polymers and there are many instances of its successful use in building applications, especially as a replacement for glass. The advantages of PMMA are its outstanding light transmission, good impact resistance, lightweight, easy handling and installation, and outstanding weatherability and durability. In fact the monomer is used in the manufacture of unsaturated polyester resins since methylmethacrylate retains its optical properties for longer periods than the more usual styrene[51].

Ledbury and Stoke[52] carried out durability tests on a general purpose and a heat stabilised grade of PMMA. After 64 days at 100°C the general purpose grade showed a considerable decrease in tensile strength and elongation at break while the heat resistant grade showed practically no deterioration. Under hot, humid conditions (70°C/100% RH) both grades showed approximately 40% loss in tensile strength after 32 weeks. At 90°C/100% RH the general purpose grade lost its tensile strength rapidly (within 4 weeks) while the heat stabilised grade retained 60% of its strength after 32 weeks.

It has also been found that not more than a 1% decrease in luminous transmittance after 240 hours accelerated ageing and not more than 1% haze increase after the same exposure occurs on grades of PMMA marketed for external use[53].

It has been suggested that the thickness of the sheet and conditions of exposure play a part in the weathering properties of acrylic sheet[54]. Thin pieces of coloured PMMA fade more rapidly than thick ones of the same colour and this applies particularly to transparent and neutral colours. If the thickness of a transparent sheet is reduced from 3mm to 1.5mm the difference in weathering behaviour, it is stated, could more than halve its useful life. Yustein et al[55] studied the light transmission and haze development of PMMA at Panama, New Mexico, New York, Canada and Alaska. The New Mexico samples showed very slight yellowing after 12 months exposure. At New York the 7 month and 12 month samples showed increased haze. At 2 years exposure, no serious impairment of surface properties apart from the effect of yellowing was observed at New Mexico. At the end of the programme the light transmission of the Panama and New York samples had decreased slightly. The haze at all locations had increased slightly, the greatest being a 6% increase at New York. Although Panama and New Mexico samples had yellowed slightly the effect could not be considered serious. This yellowing is thought by the authors to be due to the strong UV radiation in these regions.

27

Trusova and Gudimov[56] state that the mechanical properties of PMMA fall only slightly after 26 months exposure in a subtropical climate. Studies of the ageing of PMMA under stress showed little difference in impact strength and Brinell Hardness between aged and unaged samples.

Rainhart and Schimmel[57] found that after more than 17 years exposure in New Mexico the acrylic material was still transparent and showed little visual evidence of weathering with a loss in transmission of less than 10%. Much of this loss in transmission was due to surface roughness and the original properties could nearly be restored by polishing. Rugger[1] has also shown poor abrasion resistance of PMMA but has indicated that the performance of PMMA when subjected to wind-blown sand is better than the test suggests. This is thought to be due to the ability of the material to yield slightly under sand particle impact.

Schreyer[58] has presented results on the weathering of UV stabilised cast sheet PMMA exposed in Europe for 2 years. Only small changes in the mechanical properties were observed and the molecular weight was shown to remain above the critical value of 10^5. Coloured cast-acrylic sheet has a similar long-life with manufactures estimated life for many grades in excess of 10 years in tropical climates[54].

Samples exposed at Ottawa, Canada (humid continental climate) showed that although the tensile impact strength of high impact PMMA was initially 2.5 times greater than that of PMMA, this advantage reduced with weathering until the difference was nullified after 4 years[59].

The crazing of acrylics exposed to environments such as solvents and the weather has received frequent comment. It is possible to state that almost all forms of crazing and cracking are due to the relieving of stresses. Russell[60] discusses previous work on crazing and then discusses the forms and theories of crazing. According to Russell the variety of patterns produced by crazing of PMMA can be divided into the effect of two factors; stresses, and solvent crazing which is induced by chemicals. Crazing is defined as multiple hair-line surface cracks which, being narrow, relatively deep and sharp at the bottom, act as notches and may cause a serious drop in the mechanical strength of the component. The depth of the crack, it is claimed, may increase with time if the formation of the surface cracks has not relieved the stresses, and could ultimately penetrate through the sheet.

The portion of the transmission loss attributed to diffusion due to surface pitting and abrasion could not be isolated from the UV degradation (yellowing) of the surface layer[60].

28

Rainhart and Schimmel[61] consider the application of an abrasion resistant coating which does not reduce optical transmission, ages well and protects the relatively soft acrylic polymer surface. This coating would minimise the optical diffusion from surface erosion that was evident in the aged specimen. A material considered was a glass resin based on a methylsiloxane network where the methyl groups produce crosslink sites resulting in a very hard thermoset coating.

One of the most important characteristics of PMMA is its ability to transmit light both before and after exposure to weather. The property of good light transmission was a key factor in choosing PMMA to construct skylights to make up the dome of the Houston Astrodome[62]. However, when the first game was played fielders had problems following the ball due to a contrast in light between the panels which showed up bright in sunlight, and the steel girders which showed up dark. Additionally there was the problem of glare. To overcome this Houston authorities painted over the acrylic skylights which minimised the contrast but meant that indoor lighting had to be used even during the day.

A Perspex hemispherical dome was built to house the Astro-swirl ride at Blackpool Pleasure Beach. This was first constructed in 1969 and over 20 years on still looks as good as new. It has withstood over 20 years of seaside weather involving powerful summer sunshine, the corrosive effects of the salty seaside environment, and winds up to 100mph[63]. Neutral-tinted acrylic was selected for the original design because it has high strength with low structural weight and solar heat control, and because of its high resistance to weather.

From the published work it seems that PMMA has been in use in the building industry longer than many other plastics materials and has excellent weathering properties. The life of acrylic products is optimised if all the necessary steps are taken during fabrication and service which help the product to function within its design capabilities.

1.5.2 Weathering of Poly(vinylchloride)

PVC can be compounded at reasonable cost to give acceptable outdoor life over a range of applications, despite its inherent instability to sunlight. In building usage where loadings are small, practical lives of 15 years have been achieved even though the impact resistance during this period may have been greatly reduced[11].

In earlier work, Penn[64] stated that PVC is weather resistant. Plumb[65] suggested that a 15-20 year guarantee on PVC products which are not plasticised could be issued on a

reasonable risk basis. Crowder[66] found that transparent PVC products could lose their light transmission properties after a period of 10 years. Formulation, compounding and processing have to be critically controlled to obtain weatherability in a PVC product[67]. Plumb[65] states that there are five material properties that have to be considered when evaluating the potential use of PVC in building and he names strength, impact strength, weathering resistance, heat resistance and fire resistance as these properties.

According to Hendricks[68] weathering is reflected in many properties; discoloration, tack, spotting, stiffening, physical and electrical properties. Haze or opacity appears to be directly related to humidity. Tensile strength is related to molecular weight and a loss in this property is taken as indicating a reduction in chain length[69]. Loss of modulus and hence increased stiffness is taken to indicate loss of plasticiser. However, retention of elongation is affected by both changes of plasticiser content and chemical structure rearrangement due to decomposition.

Surface finish appears to have an important bearing on the weathering performance of PVC[70]. Blemishes, pores and cracks on the surface are potential sites for degradation. Also light is scattered on a matt surface and therefore will be strongly absorbed whereas a smooth glossy surface will reflect a greater part of the radiation. Moreover dust will cling more easily to a rough surface and is not so easily washed off by rain as it would be from a smooth pore-free finish.

Fedoseeva et al[71] found that the weathering of PVC is restricted predominantly to the surface of the material. They showed that in a specimen 1mm thick, dehydrochlorination occurred mainly at the front and back surface to a depth of about 0.15mm for a composition with no anti-oxidant.

Martin and Tilley[72] found a correlation between yellowness index and total radiation received on a PVC sample. They used this to support a proposal that total radiation data may be used to characterise a site with respect to the rate of photo-oxidation of PVC at that site. Martin[73] furthered the work and suggested that PVC films offered a considerable promise as monitors in estimating UV radiation between the erythemal and visible regions suitable for use in studies on the outdoor weathering of plastics. Provided that about 80% of the incident global radiation exceeds 25mWcm^{-2}, the increase of carbonyl groups in the PVC is directly proportional to the amount of UV radiation to which it has been exposed.

In studies on the tropical weathering of a range of plastics, Gough[74] found a high increase in the stiffness of PVC on exposure. The material became brittle and cracked

easily, also displaying bumps which may have been bubbles. These effects occurred in a relatively short time and were attributed to chemical changes in the material caused by UV since samples under a UV absorbing screen did not show excessive change.

The development of high efficiency MBS (methacrylate/butadiene/styrene) modifiers for clear PVC bottles and other packaging materials has raised the possibility of inexpensive high impact clear modified glazing. Lutz[75] tested MBS modified PVC and clear PVC containing a new all-acrylic clear impact modifier (ACR-3). Both modifiers gave adequate impact resistance to PVC which was maintained for several years on exterior exposure. The all-acrylic modifier also kept adequate `see through' clarity after 4 years exposure whereas the excessive chalking of the MBS-modified PVC contributed to a serious loss in clarity.

Lutz[75] also studied an acrylic modified PVC containing titanium dioxide. The results of these tests suggested an inter-relationship between loss of strength and development of colour. A comparison of performance at three quite different sites shows that exposure in Arizona causes more severe degradation than is the case for exposure in Pennsylvania or Florida and indicates the importance of solar radiation in determining the extent of weathering[75,76]. Similar work has been carried out by Menzel et al[77] showing that impact-modified PVC has significantly better weather resistance than rigid PVC which rapidly loses impact strength on exposure.

Light stability can be improved by processing with a good thermal stabiliser[78]. The function of these stabilisers is to quench the thermo-oxidative component of weathering as well as reducing thermal degradation of the material during fabrication.

Probert[79] has shown that transparent PVC sheet containing reworked material has poor outdoor performance.

To ensure maximum weathering resistance, manufacturing, shaping and storage conditions must be carefully monitored. These factors must be kept in mind when choosing a material for a certain application.

1.5.3 Weathering of Polycarbonate

Polycarbonate is used increasingly as shatter-proof glazing material in public and industrial buildings because of its very high impact resistance and excellent transparency. It does, however, appear to have limited scratch and weather resistance.

Weathering of polycarbonate with no UV stabiliser leads to the development of a

31

yellow colour mainly at the surface which deepens as exposure continues and is eventually accompanied by a loss of gloss[80]. This yellowing or discoloration occurs in two zones[42]. The first zone is a dark crosslinked top surface probably due to the action of the shorter wavelengths of light. The second zone is a thicker yellow under-surface probably caused by the action of the more penetrating longer wavelengths of light.

Irradiation of polycarbonate in an artificial weathering machine (Xenotest) showed that the strong oxidation at the film surface formed a layer with different solubility characteristics than the bulk. This increased the crack formation as a result of internal stresses due to sample heterogeneity[81]. After 2000 hours exposure the polycarbonate film (0.2mm thick) was severely degraded. It was found that the molecular weight had decreased from original values Mn=9140, Mw=40600 to Mn=5300, Mw=20000, where Mn and Mw are number and weight average molecular weights respectively; and this was suggested as a lower limit below which the material is no longer of any practical use. A decrease in molecular weight causes a lowering of the total attractive forces between adjacent polymer chains, and this in turn, lowers the resistance of the material to fracture[82].

Gardner and Martin[83] have also shown that the molecular weight of polycarbonate falls quickly when samples are exposed to hot, humid environments and that the mode of fracture is brittle; unaffected polycarbonate shows ductile failure and at room temperature is more ductile than both PMMA and polystyrene. Plotting time taken to reach the ductile-brittle point versus temperature(K)$^{-1}$ gave a straight line which allows predictions of storage temperature effects on the durability of polycarbonate to be made. Under standard tensile test conditions, the ductile-brittle transition is observed at Mw=33800 and Mn=14300.

The transition is related to the ease of crazing relative to shear yielding. When the stress required for craze initiation falls below the level needed to initiate shear yielding, brittle failure occurs.

Hull and Owen[84] also investigated the transition from ductile to brittle failure in polycarbonate. They showed that brittle fracture is preceded by crazing. Cracks nucleate in the craze and subsequent propagation occurs in association with crazing. Crazes form in tension and so serve as sites for ultimate failure[85]. Morgan and O'Neal[86] also showed that embrittlement is dependent on specimen thickness, molecular weight, thermal history, strain rate and test temperature. The characteristics of surface crazes can control directly the stage of deformation at which fracture occurs and hence the mechanical response of polycarbonate.

32

Surface crazing is enhanced in polycarbonates by environmental factors such as handling[86]. The regions of the polycarbonate surface that have come into contact with finger grease are plasticised and fabrication stresses in such regions relax at a faster rate than those in the unplasticised surroundings. The plasticised, relaxed regions separate from their surroundings producing microcracks which serve as sites for craze initiation and crack growth, and possible embrittlement of the polymer.

Weathering certainly affects the surface of polycarbonate. Scanning electron microscopy pictures show a difference in behaviour between specimens exposed to hot/wet as opposed to hot/dry conditions. At the dry site a more ordered almost unidirectional form of surface cracking occurred, whereas at the wet site the cracking seemed to be more random. UV stabilised polycarbonate shows less cracking at the hot/dry site than non-UV stabilised grades although the cracking of all materials was similar at the hot/wet site[11].

Radiation by itself, or even relatively severe cycling of temperature and humidity without radiation, does not induce microcracking. The surface resin undergoes a gradual reduction in strength owing to a lowering of its molecular weight as a result of photochemical degradation. Cyclic variation of temperature and humidity imposes on the surface material a type of stress fatigue. Such stress fatigue is caused by non-uniform dimensional changes that result from thermal and moisture-content gradients between the surface and the bulk of the resin. When the fatigue limit of the surface material at a microsite becomes lower than the physically induced stresses, the resin cracks[82].

On weathering, the tensile properties of polycarbonate changed very little after 2 years exposure in the U.K. but exposure in the tropics lead to a dramatic fall in elongation at break within 6 months and embrittlement of some samples after 4 years[80]. UV stabilised polycarbonate can retain up to 50% of its original impact strength after 30 months exposure in the tropics whereas non-UV stabilised grades showed the same loss after only 9 months.

Weathered polycarbonates can still retain some level of internal stress as demonstrated by Ledbury[87] who showed that some specimens which had been handled and exposed to perspiration, when removed from exposure, developed cracks inside 24 hours when stored in the control laboratory.

Due to the limited scratch and weathering resistance of polycarbonate, the material is sometimes coated with a material glass-like in chemical composition which provides

33

hardness and long-term protection against abrasion and weathering[14], for example Margard marketed by the General Electric Company of America. Success depends on the priming system used to ensure good adhesion between coating and base material.

1.6 WEATHERING TESTS

The ultimate objective of testing is the prediction of component lifetime under service conditions. The principle behind an investigation concerned with the weatherability of polymers is to expose the sample to the set conditions and to follow changes in the properties of the material. In general, commercial samples are tested in natural conditions or artificially weathered so that environmental factors such as light intensity, relative humidity and temperature duplicate, as closely as possible, outdoor weathering.

1.6.1 Natural Weathering

The outdoor weathering of polymers is dependent on many atmospheric factors such as light intensity, ambient temperature, humidity and wetness, all of which are subject to seasonal, yearly and locational variations. Microbiological growth and soiling are also important factors and cleaning to remove dirt affects the polymer surface.

The UV portion of sunlight from 290 to 400nm which reaches the surface of the earth constitutes about 5% of the total radiation from the sun. It is this spectral region which is most damaging and therefore of interest. The degradation rate of polymers depends markedly on the intensity and energy distribution of the solar spectrum in the UV region, both of which vary with the seasons. Various attempts have been made to normalise this seasonal degradation effect[88] and an equalisation ratio of 1.6:1, between the most severe and least severe, was developed which standardises the light intensity measured in Langleys for each month's exposure.

In most standard natural tests, samples are exposed in such a way throughout the year that they receive the maximum exposure to sunlight. This is generally accepted as an exposure angle of 45° to the horizontal facing the equator for U.K. latitudes. Darby and Graham[89] investigated the effect of exposure angle on plasticised PVC film and found that vertical exposure (90°) gives less degradation than horizontal exposure (0°), and horizontal exposure results in more rapid degradation than the generally accepted 45° angle. The severity of the horizontal position was due to the retention of rain and moisture (e.g. dew

34

and frost) for long periods; it gives less severe exposure to direct solar radiation (unless close to the equator). Horizontal exposure can give more exposure to short wavelength UV radiation than 45° angle, because such radiation is scattered and much of it may be contained in light received by samples from the whole sky. It is better to expose at an angle of at least 5° to the horizontal facing the equator than horizontal to allow water to drain off surfaces. A more general `optimum angle' of exposure than 45° is as contained in ISO 877 (Clause 6.1(a)) "for maximum annual exposure to total solar radiation (i.e. direct beam and scattered light from sky) at most mid-latitude regions of the world the tilt angle from the horizontal shall be the site latitude less 10°".

It is important to realise that even natural weathering does not always reproduce accurately the effects of weathering in building applications, for instance when heat from within the building may have an effect. Because of inclination of the specimens to catch a maximum of solar radiation, there is usually an acceleration of breakdown to a degree which depends on the material.

Although natural weathering is the most practical and valuable test of polymer stability, results are not always reproducible due to variations in season, climate and location. The problem with natural weathering is that the exposure period must be equal or greater than the required service lifetime if the results are to be used with confidence. In an application that demands a lifetime of say 50 years this is unacceptable and some form of acceleration is required. With artificial weathering this is easily arranged but the validity of predictions in service life under natural conditions based on data from such tests is questionable. An alternative strategy is to weather samples in extreme climates and to devise a method to relate the rate of degradation at the test site to that in the service environment. In this way 'natural' weathering conditions are preserved during testing, though the temperature and levels of UV radiation may be quite different from those likely to be met in service. Suzuki et al[90] obtained good agreement between the mechanical degradation results for samples exposed in two different sites in Japan by plotting the total UV dose rather than the time exposed. Further acceleration can be achieved by using mirrors to concentrate the solar radiation onto the test samples and to arrange that the exposure racks track the sun.

All of the popular test sites are located in hot climates with high UV levels. Arizona is popular for studies using a hot dry climate and Florida for a hot damp climate[91,11], but there are many studies in which outdoor exposure has been carried out in other parts of the world, including Australia, Israel and Saudi Arabia. Davis and Sims[11] give details of

the climatic conditions at various test sites and, for comparison, at locations in the U.K. and elsewhere in Europe.

If the results of outdoor weathering are to have any value other than an indication of the expected behaviour of a material at the test site then the climatic conditions should be monitored. The temperature and humidity should be recorded continuously and rainfall should be measured. The radiant exposure should be recorded, preferably the full spectral distribution. To complete the profile of the test site conditions then it is desirable to measure pollutant concentrations, including ozone, sulphur dioxide and nitrous oxides in the air, and the pH of the rain.

1.6.2 Artificial Weathering

Artificial test methods are used for three main reasons:

1. To accelerate but reproduce the effects of exposure to weather, in particular exposure to natural daylight. The effects of this are followed throughout exposure.
2. For quality control purposes to check variations between different batches of material.
3. To evaluate a product using prescribed procedures.

It is particularly important that such tests should identify materials or products not suitable for permanent outdoor use whilst not unfairly distorting the comparative performance of disparate types.

Several artificial weathering devices have been developed to incorporate as many as possible of the outdoor factors in order to obtain a meaningful correlation with outdoor exposure. In principle they allow consistency of conditions but it is essential to identify and control the relevant variables.

1.6.2.1 Temperature

All thermally activated rate processes are accelerated by an increase in temperature and most artificial weathering is conducted at elevated temperature. Unfortunately this may promote degradation that would not occur at lower (ambient) temperatures[91,92,93]. Even if this is not the case there can still be serious problems when several processes are involved in degradation since the rates may not be accelerated proportionally and the various stages in the degradation process do not imitate those in natural conditions. This is particularly the case when sequential reactions involving degradation products are involved or when diffusion of one of the reactants is required to maintain adequate concentration in the reaction zone. For

36

example, at ambient temperatures photo-oxidation in the interior of a thick section may be limited by the depletion of oxygen through reaction whereas at elevated temperatures diffusion of oxygen may be sufficiently rapid to maintain the reaction.

When plastics samples are exposed outdoors on a sunny day they can reach quite high temperatures, the surface facing the sun normally being hotter than the surface facing away from the sun. A significant temperature gradient can be supported because of the low thermal conductivity of polymers and this will lead to the development of thermal stresses. These stresses may provide the driving force for the development of surface cracks that may ultimately provide the site for initiation of a macro-crack by which the component fails. Because of the potential importance of the presence of a temperature gradient in influencing the failure of a polymeric component, consideration should be given to the provision of a temperature gradient across a sample undergoing artificial weathering. This will occur if a water spray is used to simulate rainfall, but more attention needs to be paid to the conditions of spraying than has been the case until the present. It is important that the water cools only the heated side of the test piece and does not flow around the back. The water temperature should be as cold as possible for maximum effect.

In an investigation of the behaviour of polyethylene in a marine environment it was found that the degradation rate was lower when the samples were floating in sea water than when they were exposed out of the water[94,95]. This was attributed to the cooling effect of the water.

The measurement of surface temperature in test conditions presents problems. The temperature of the test piece is determined partly by the absorption of radiation and cannot be taken to be equal to the background temperature of the test surroundings or enclosure. This is true of outdoor exposure too and Davis and Sims[11] report surface temperatures more than 30°C higher than the surroundings. The problem is further exacerbated by the changes in absorption and emission characteristics that will occur during exposure as a result of the chemical and physical changes taking place. To obtain a reproducible measurement of temperature suitable for comparison from test to test a black standard thermometer is used adjacent to the test piece.

37

1.6.2.2 Ultraviolet Light

The major hazard in natural outdoor exposure is the ultraviolet (UV) component of solar radiation. The lower the wavelength the greater is the photon energy and one way of accelerating degradation is to use lamps giving wavelengths below the lower limit (approximately 290nm) of solar radiation. This may lead to reactions that cannot be promoted by solar radiation[91] and tests based on acceleration by this means cannot be used with confidence. A more acceptable means of acceleration is to use a high intensity of irradiation.

There are two sources of UV radiation in common use in artificial weathering of polymers, based respectively on the xenon arc and on fluorescent tubes. These sources have largely replaced earlier sources such as carbon arc and mercury vapour lamps. The xenon arc contains wavelengths shorter than the cut-off level of solar radiation and these must be removed by filters. Xenon lamps also emit a high intensity of infrared radiation and this must also be removed partially to prevent overheating of the samples. The Xenotest-1200 offers water spray, light/dark cycling and humidity control and has gained quite wide acceptance in industry but is expensive to run. The xenon burner and the filters deteriorate with age and their performance must be checked regularly or a suitable strategy must be developed to compensate for this ageing effect[92]. Fluorescent tubes are much cheaper to run and do not have the disadvantage of producing unwanted heat. Tubes are available with several different spectral outputs. The intensity of UV-B tubes peaks strongly around 313nm and the output is very high throughout the lower wavelength end of the spectrum. As a consequence they provide strong acceleration, but the output is also high at wavelengths below the solar radiation cut-off and may lead to unwanted reactions. UV-A tubes do not have this problem and a lamp designated UVA-340 gives a very close match to solar radiation up to 350nm. UV fluorescent tubes emit low levels of visible radiation and no infrared; the heating effect is negligible and a separate source of heat is required to maintain temperature levels at or above those reached outdoors. The spectral output from fluorescent tubes changes with use and the tubes should be checked regularly for spectral output or should be taken out of service after 1600 to 2000 hours[90,96].

1.6.2.3 Water Spray and Humidity Control

The provision of a water spray allows the simulation of rainfall which may promote

38

degradation for a variety of reasons. The impingement of water droplets may cause mechanical erosion; some polymers undergo hydrolysis reactions that may lead to chain scission; the thermal shock produced when cold water falls on a previously warmed surface may cause surface cracking[97]; some polymers are swollen by water, causing residual stresses to form when water is unevenly distributed, as during the initial exposure to water, or soon after the source of water is removed if desorption occurs.

An effective way of providing a suitable spray is to use an atomiser. An alternative method of wetting the sample is by condensation. In the QUV artificial weathering chamber a trough of heated water provides a humid atmosphere and condensation occurs on the samples because they are cooled naturally through the exposure of the unexposed surface to laboratory air[90,96]. The condensation method is not expected to produce the same thermal shock as cold water spray and may produce a temperature gradient quite unlike that caused by rainfall so that it may not provide an adequate test of the resistance of a material to natural exposure to water.

Some polymers absorb water when exposed to moist air and it is necessary to monitor the humidity within the artificial weathering chamber and preferably control it as well.

1.6.3 Correlation Between Natural and Artificial Weathering

There are several critical reviews of the correlation between natural and artificial weathering[90,98,99,100]. There is general agreement that only poor correlation exists between natural and artificial weathering, and this view is even expressed in some of the standards[101]. Even accelerated outdoor weathering using mirrors to provide enhanced exposure has been found to give contradictory information on polyolefins[102]. Gugumus[99] notes that a combination of fluorescent tubes with a back light can often give good correlation with natural weathering but that failure times (to a chosen carbonyl index) of polypropylene films exposed in this way can differ from those obtained with a xenon arc by an order of magnitude. The results of xenon arc tests on polypropylene films did not correlate well with QUV test results. Good agreement was found between xenon arc and natural weathering behaviour of high density polyethylene. Gugumus[99] expresses a strong distrust in tests based on fluorescent lamps and this point of view is supported by the results of Rabinovitch and Butler[103] for PVC.

Even when good correlation is claimed to exist between natural and artificial weathering

39

the agreement is often less than perfect when assessed quantitatively, as, for example, in studies of PVC by Matsumoto et al[104]. The reasons for poor correlation are evident from the discussions of mechanisms of degradation and stabilisation. Gugumus[99] observes that polyethylene and polypropylene light stabilisers generally perform better in outdoor service than is predicted by an accelerated test using xenon arc exposure. This is usually because one of the ingredients in the stabilising system (e.g. a low molecular weight hindered amine) diffuses to the surface during the dark periods to restore some of the protection. For a particular polymer it is often possible to 'recalibrate' the Xenotest, leading to a reasonable correlation between natural and artificial weathering performance. The general consensus of opinion is therefore that accelerated test should only be considered as giving a rough indication of the relationship between natural and artificial weathering.

1.6.4 Review of Standard Procedures

Historically, several different types of light source have been developed for artificial weathering purpose and applied in product performance requirements. The main types are included in the 1981 version of ISO 4892. This international standard has recently been revised to distinguish more clearly between the different approaches. The revision excludes enclosed carbon arc light sources and brings fluorescent lamp devices within the formal scope. The standard has a 4-part structure:

ISO 4892: 1994: Methods of Exposure to Laboratory Light Sources

Part 1: General Guidance

Part 2: Xenon Arc Sources

Part 3: Fluorescent Lamps

Part 4: Open Flame Carbon Arc Lamps

Substantial efforts have been made to reduce the number of optional variations and the intrinsic variability of the recommended procedures. The aim is to provide basic methods which will be more reproducible from time to time and between laboratories and so usable with greater confidence as the basis of product performance specifications and for product development. The main aspects dealt with are:

- radiation spectral distribution, intensity and exposure duration;

- control of temperature through use of black standard thermometers;

- simplification of recommended values for operating conditions.

The revised standard defines two preferred radiation distributions for xenon arc light

40

sources, Method A to simulate direct sunlight and Method B to simulate daylight through window glass with much reduced UV-B levels[135]. A radiation intensity in the wavelength range 300 to 800nm of 550 ± 50 Wm^{-2} is suggested, though other levels may be used. To control the total radiation dose and allow for such variations, it is proposed to express the exposure in terms of total irradiance, integrated over the wavelength range 300 to 800nm for example, in the sample plane. This requires an adequate knowledge of radiation incident on the samples and its variations with time, strictly speaking through continuous measurement. The use of blue wool scales is dropped, certainly for Method A, and account is taken of more recent instrument design permitting the use of one of two methods of controlling the   UV irradiance[136]. The more common, known as narrow band control, maintains a constant irradiance level at a specific wavelength, typically 340nm throughout the life of the lamp. The other, broad band control, keeps the integral of irradiance, 340nm to 400nm constant. Test piece temperature is dependent, amongst other things on the intensity of radiation and the light absorption characteristics of the test piece. Measurement is by means of a black panel thermometer, which is intended to replace the variety of black standard temperatures available previously. This will be better related to surface temperatures reached by plastics components and will provide a more consistent means of controlling the temperature of the weathering device. A white standard thermometer is also specified and may be more relevant to white or transparent test pieces. A black standard temperature of 65 ± 3°C is proposed for normal purposes, being influenced by radiation intensity and controlled by cabinet air temperature and rate of circulation.

Historically, a range of water spray cycles has been used. The revised version of ISO 4892 specifies a single preferred choice of 18 mins ON / 102 mins OFF. This cycle was selected because it allows time for samples to dry off and for well defined maximum operating temperatures to be established. Clearly other cycles may continue to be used for particular purposes. Preferred relative humidities in the dry period are $50\pm5\%$ or $65\pm5\%$ for normal test purposes.

In anticipation of publication of the revision of ISO 4892, the new technical principles have been incorporated in the draft European Standards for plastics materials. The proposed EN for white PVC-U window profiles includes an artificial weathering procedure using xenon arc, as above. The target irradiances over the bandpass 300 to 800nm i.e. UV and visible radiation, are 8 and 12 GJm^{-2}. These values are considered to correspond to 5 years exposure in northern and southern Europe respectively. The proposed EN for transparent

41

plastics sheets[137] also recommends artificial weathering by xenon arc using filtering to keep the spectral distribution as close as possible to that detailed in ISO 4892 : Part 2.

Fluorescent lamps are brought within the formal structure of ISO standards in Part 3 of the revised ISO 4892 standard. This is intended to accommodate both American (ASTM G53) and German (DIN 53384) practice. The former in the form of the UV-condensation cycle devices is the more widely used, but the latter offers more precise control over exposure conditions, with direct water spray being used. The preferred lamp type is the UV-A with peak emission at 340nm, though the more aggressive UV-B type with peak emission at 313nm may also be used. The recommended test cycle for normal purposes is : 4 hours exposure to UV light at 60°C followed by 4 hours condensation at 50°C, following American practice, using UV-A lamps with peak output at 340nm. However, this may be an excessive temperature for PVC products. Fluorescent lamps will not produce the range of temperature differentiation with sample colour characteristic of sunlight or xenon arc lamps. Other cycles may be used, but a certain minimum excess of condensation temperature over room temperature is essential if efficient condensation is to result on plastics test pieces which may have rather low thermal conductivity.

1.7 CHARACTERISATION OF WEATHERED POLYMERS

Methods of assessing the changes that are promoted by weathering are of great importance. They are used to indicate the kind of chemical degradation that has taken place and can be used to determine the rate of reaction[105]. They are required to assess the action and effectiveness of stabilisers. The most sensitive methods may indicate that degradation has occurred long before it is apparent in the engineering properties. There are many techniques available, some of which require sophisticated, expensive, equipment, found only in specialised research laboratories, and some which are widely available and can be applied routinely without extensive operator training. The techniques reviewed below cover those available at the Building Research Establishment and/or Loughborough University of Technology.

1.7.1 Infra-red Absorption

Infra-red absorption is used for functional group determination. The absorbed energy causes the molecule to vibrate, the most useful vibrations occurring in the 4000 to 650 cm^{-1} range. Functional groups have vibration frequencies, characteristic of that

functional group, within the well-defined regions of this range. This makes identification simple and rapid by infra-red spectroscopy.

Infrared absorption is used to monitor the oxygen uptake in polymers during weathering[106]. The extent of oxygen uptake is followed by measuring the carbonyl absorption at 1710 to 1740cm^{-1}, normalising the value by dividing by the signal at a part of the spectrum well removed from any strong absorption resonance from any of the components of the sample or ratioing against a peak which is not likely to change. This procedure selects the oxygen that has reacted to form carbonyl groups and does not indicate the amount of oxygen reacted in any other way or simply physisorbed. With modern instrumentation using Fourier self-deconvolution of the carbonyl absorption it is possible to separate the different contributions (ketones, saturated carboxylic acids etc.)[107]. The carbonyl index is a more valuable quantity, however, because this type of modification provides a chromophore that may take part in further degradation reactions. Marks and Butters[108] found that attenuated total reflection (ATR) monitoring of carbonyl build-up was the most sensitive and reliable method for studying weathering of rigid PVC and reported that changes were apparent before any change was detected by other techniques.

Depth profiling can be performed by photoacoustic spectroscopy[109], exciting different frequencies to provide information at different depths, of the order of tens of microns. This technique has the advantage of fairly simple sample preparation and has been applied to the accelerated weathering of PVC[110].

1.7.2 Changes in Molecular Weight

Deterioration is often the result of chain scission that follows the oxidation of the polymer. Hence change in molecular weight is an important parameter to follow. The technique most favoured for making molecular weight measurements for weathering studies is gel permeation chromatography[106,111]. This method provides the molecular weight distribution from which the number average (Mn) or weight average (Mw) molecular weights can be derived as convenient parameters to follow the progress of degradation. Other methods give averages directly but do not provide the distribution of molecular weight; study of the changes in the distribution of molecular weight can sometimes reveal information about the underlying reactions.

Shlyapnikov[112] has emphasised the need for caution when interpreting the results of molecular weight measurements. Fragments with low molecular weight may not register

in the molecular weight measurement and if several scissions occur close together on a molecule the result may be indistinguishable from a single scission.

1.7.3 Glass Transition Temperature

The glass transition temperature, Tg, is determined mainly by the molecular structure of the repeat unit in a polymer. In the early stages of degradation the majority of the repeat units remain unchanged but there are important secondary factors that may alter Tg, including molecular size, the extent of cross linking, and the concentration of plasticiser. Chain scission creates more free chain ends and lowers Tg; increasing the crosslink density increases Tg, as does a decrease in plasticiser concentration, through diffusion and/or volatilisation. All these effects change with distance from the surface and the most meaningful measurements are made using samples from narrow bands at chosen depths.

The most convenient way of measuring Tg is by differential scanning calorimetry (DSC) or differential mechanical thermal analysis (DMTA)[106,113]. In DTA the temperature rises at a constant rate except when a physical transition, such as a phase transition, is taking place, or when a chemical reaction is occurring. In DSC the temperature of the sample is held at a target value at all times by altering the power input to compensate for exotherms and endotherms using a sensitive feedback system. The glass transition temperature is shown by a change in slope of the thermogram[106,114,115]. Tg fell about 20° after one year's outdoor exposure in Jeddah with both poly(vinylchloride) and polystyrene[116,117].

1.7.4 Surface Topography

The appearance of the surface of a polymer article usually changes during weathering. This itself may be sufficient to render the article unserviceable in some applications. The change in surface appearance may indicate the extent of degradation and the imminence of mechanical failure. Study of the surfaces of failed components can assist the determination of the mechanism of failure.

Scanning electron microscopy has superior resolution and depth of field compared to the light microscope. Light microscopy is simple and easy to use and is usually non-destructive. The most common feature of interest on the surface of a weathered polymer is fine cracking. This is usually well within the resolution capability of a light microscope and the cracking is often located on flat surfaces so that the depth of field limitation is not

44

a serious handicap. Fracture surfaces show much greater variations in depth and light microscope images are almost always inferior to scanning electron microscope images.

1.7.5 Impact Resistance

Although some plastics have good impact resistance, they are not unbreakable. A hard blow can cause fracture but plastic glazing breaks into large, dull-edged fragments rather than sharp fragments that may fly from a smashed glass window. Moreover, the light weight of the plastic imparts little momentum to the broken pieces so the injury hazard is greatly reduced[5].

BS 6206:1981 specifies methods for determining impact resistance of safety glazing by striking a large sample held in a frame once in a pendulum arc, the impactor being a leather bag filled with lead shot. Three drop heights can be used and to meet safety requirements and it is stated that, `if when breakage occurs, numerous cracks and fissures may develop but no shear or opening through which a 3 inch diameter sphere can pass may form, or if disintegration occurs then the ten largest crack free particles must weigh no more than the equivalent of 10 square inches of the original test specimen.' The standard does not however specify any requirements for durability and only assesses the ability of the new material to withstand specific impacts in order to qualify as a safety glazing material.

The ability of a thermoplastic to serve as an exterior building component depends to a large extent on its impact strength and the retention of this property during service. On exposure to weather the mechanical properties, including impact resistance, deteriorate rendering the material more brittle. This occurs as the material is less able to undergo plastic deformation probably caused by a decrease in molecular weight since it is known that thermoplastics undergo chain scission on exposure to solar UV radiation[59].

Impact resistance can be tested by various methods. A commonly used test is the Charpy impact test as specified in BS 2782 Method 359:1984. In this method the samples are tested with the notched edge in tension. The material is considered acceptable for safety glazing if impact strength is not reduced by more than 25% as a result of outdoor exposure, however, the single-notch method is not very suitable for looking at changes caused by a weathered face. The relevant variant is the double edge notch sample where the sample is struck on the face between the notches and bends along that line. In this case it is important to strike the unweathered face so that the weathered face is put in

45

tension (the test piece is not clamped so is free to bend).

Another method for testing impact resistance is the falling weight type of test[16], as described in ISO 6603-1:1985. In this test a standard weight is dropped onto a bar or sheet from a known height. The tests run under conditions such that the falling weight barely has enough energy to crack or break the specimen. This type of test generally correlates much better with field tests and practical experience than does the pendulum type. The tests can, if necessary, measure just the energy to form a crack rather than the energy to completely fracture the specimen and, in fact, in many applications the plastic object can be considered as having failed as soon as the first crack forms.

1.7.5.1 Effects of Abrasion on Impact Resistance

Loss of surface quality can be caused by scratching or abrasion during service as well as by several types of surface deterioration caused by exposure to the environment. Scratching is the main cause of surface damage of plastics sheets not subjected to outdoor weathering. Scratches are caused by contact with rough surfaces or airborne particles whose hardness is greater than the plastic surface, and may also be induced during cleaning processes. Pitting and scratching, if extensive, may not only impair the appearance and light transmission of the plastic but may also affect the mechanical properties by acting as stress concentrators. In the long term the durability of the plastics material will be affected.

1.7.5.2 Effect of Temperature on Impact Resistance

The impact resistance of thermoplastics is temperature dependent, generally falling with temperature. With some tougher materials it is often the case that impact strength declines quite markedly over a more or less narrow temperature range. The impact strength of polymers such as polystyrene or PVC can be improved by blending with a second, rubbery, polymer and this commonly lowers the temperature at which embrittlement occurs. For glazing purposes, consideration must be given in preparing such blends to differences in refractive index between the polymers used, to ensure that transparency is not lost.

1.7.6 Light Transmission

Depending on the type of plastic and service exposure, light transmission, which can be important in certain applications, may be affected in different ways; in extreme cases it may be completely obstructed. Light transmission may be reduced by loss of surface

46

quality and/or by changes in the bulk of the plastic material. Loss of surface quality can be caused by scratching, abrasion and/or, more often, by surface deterioration from exposure to the environment. The surface flaws cause the incident light to scatter, decreasing the portion of light being transmitted. Light transmission may also be reduced by changes in the bulk of the plastic, such as discoloration of the resin and colour changes in the pigments or dyes, i.e. increased absorption.

1.7.7 Development of Colour

Colour changes are often a useful assessment of the degradation of polymers. Such changes are not necessarily accompanied by changes in mechanical properties but are important particularly in decorative applications. In the case of transparent materials colour development may inhibit light transmission. Colour measurement is usually done by means of comparators or by electronic devices.

Typical commercial colourimeters measure tristimulus values X, Y, Z and calculate from these the colour co-ordinates (L*, a*, b*)[118,119]. By calculation of these co-ordinates for a weathered sample and its unweathered reference sample the change in colour can be determined (δL*, δa*, δb*). These express numerically any lightening or darkening, any change in the red to green ratio and yellowing or loss of yellowness; see Section 2.6.

1.7.8 Changes in Gloss

Reduction or loss of gloss often occurs when samples are exposed to the outdoor environment. Gloss, the property of surfaces that causes them to have a shiny or lustrous appearance, is generally the result of specular reflection of light by the surface of a sheet or object. This reflective ability can be measured[120] and usually varies with the surface smoothness and flatness. A roughening of the surface material caused by overall breakdown during exposure results in reflection of the impinging light being more diffuse and, consequently, in a loss of gloss.

1.7.9 X-ray Fluorescence Spectroscopy

X-ray fluorescence spectroscopy is also a useful analytical technique for examining chemical changes on the sample surface[121]. The technique measures the change in surface concentration of relevant elements produced by weathering rather than an absolute measure of concentration as such. It can also be useful for determining the presence of elements,

47

thus providing information on stabiliser type for example.

1.7.10 Optical Microscopy

Light microscopy is effectively used to examine surface changes due to exposure. Surface roughening can be examined and it is a particularly useful method for examining surface crazing and cracking.

1.8 OBJECTIVES

To compare different methods of artificial weathering and give recommendations to Standards committees to improve current standards procedures. In particular to investigate the application of the principles and recommendations of the revised version of ISO 4892 on glazing materials, and to apply this experience to defining performance requirements for plastics glazing product standards.

Studies of degradation mechanisms of polymeric materials concentrated largely on the chemical reactions that are involved. The aim of this work is to expand previous work [4] to examine the effect of artificial weathering on commercial grades of acrylic, polyvinylchloride and polycarbonate glazing materials so as to better understand the surface mechanisms involved.

It is evident that engineering aspects of weather related failure of polymers are not as well understood as the chemical mechanisms of degradation. Hence, this work investigates and develops different methods of material characterisation and the effective application of these techniques for studying durability aspects of plastic glazing materials.

CHAPTER TWO : EXPERIMENTAL

In Chapter One it was observed that surface appearance is a very important factor in the utilisation of plastics glazing materials. In the appraisal of weathered specimens therefore, much of the experimental investigation is of an optical/surface condition nature. Six materials have been selected, artificially weathered and changes characterised. This chapter describes sample preparation, and the test equipment used. Artificial weathering techniques are explained in detail. Further details of experimental procedure are given in Appendix A.

2.1 MATERIALS USED

Polymers currently used in the construction industry on a large scale may be divided into three groups depending on their resistance to photodegradation:

1. highly photostable polymers that are commonly used without photostabiliser added e.g. poly(methylmethacrylate)
2. moderately photostable polymers that can be used without photostabiliser e.g. polycarbonate
3. poorly photostable polymers which require extensive stabilisation for outdoor uses e.g. poly(vinylchloride).

Two commercial makes of each of the three above polymer types were investigated. Details, as given in the product literature, of the materials used are in Table 2.1.

Table 2.1: Materials Used

POLYMER	GRADE	THICKNESS	MATERIAL DETAILS
PMMA-1	Clear	2mm, 3mm	Cast acrylic sheet does not absorb UV light
PMMA-2	Clear	2mm, 3mm	Extruded acrylic sheet impact modified absorbs UV light
PVC-1	Clear	2mm, 3mm	Pressed PVC sheet completely unplasticised absorbs UV light
PVC-2	Clear	2mm	Calendered and pressed PVC sheet impact modified absorbs UV light
PC-1	Clear	2mm	Extruded PC sheet indoor glazing grade absorbs UV light
PC-2	Clear	2mm, 3mm	Extruded PC sheet UV stabilised absorbs UV light

2.2 WEATHERING PROCEDURES

Modern artificial weathering procedures in principle allow consistency of conditions. The

objective of ISO 4892 : Methods of Exposure to Laboratory Light Sources[132], is to identify and control the relevant variables. It is intended that this should correspond with methods being prepared for paints and rubbers.   Applications to rooflights pose the particular challenge of defining an artificial weathering procedure which can fairly be applied to a wide range of materials e.g. PVC, acrylic and polycarbonate. The effects of surface coating and of thermoforming need to be taken into account[133,134]. Standards development in CEN/TC128 is moving towards European Standards for light transmitting plastics rooflights materials. Temperature control of samples is critical, especially for PVC; significant failures have occurred in practice with PVC rooflights mounted in ways which tend to raise operational temperatures, for example, double glazed units and shapes which trap heated air but lack ventilation. There is a need to be able to simulate such effects in artificial weathering procedures.

2.2.1 Artificial Weathering Devices

Several accelerated weathering devices have been developed to incorporate as many as possible of the outdoor factors in order to obtain a meaningful correlation with outdoor exposure. In particular it is essential that the UV spectral intensity should correspond as closely as possible to that of the irradiation source to which the polymers will be exposed in practice.

The electromagnetic energy from sunlight is normally divided into ultraviolet light, visible light, and infra-red energy. Figure 2.1 shows the spectral energy distribution (SED) of noon mid summer sunlight (Cleveland, Ohio, 1986).

Figure 2.1: The Sunlight Spectrum
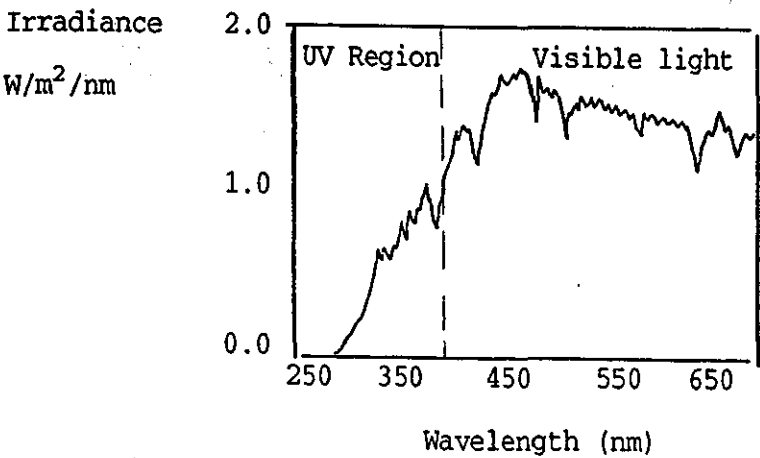
Infra-red energy consists of wavelengths longer than the visible red wavelengths and starts above about 760nm. Visible light is defined as radiation between 400nm and 760nm. Ultra-violet light consists of radiation below 400nm. The international commission on illumination (CIE) further subdivides the UV portion of the spectrum into UV-A, UV-B and UV-C[135].

The effects of the various UV wavelength regions can be summarised as shown in Table 2.1.

Table 2.1: Wavelength Regions of the UV

UV-A 400-315nm	Causes polymer damage
UV-B 315-280nm	Includes the shortest wavelengths found at the earth's surface; responsible for severe polymer damage; absorbed by glass
UV-C 280-100nm	Found only in outer space; filtered out by the earth's atmosphere; germicidal

The principal artificial sources of UV radiation are carbon arcs, xenon arcs, mercury lamps and fluorescent lamps. To ensure that the light source in artificial exposure produces the same type of photochemical reaction in the plastic as is produced by natural exposure, it is important that the spectral energy distribution of the light source is as close as possible to that of daylight. Publication CIE No. 85-1989[135] is the international criterion for comparison of artificial sources with natural daylight.

Figure 2.2 shows that only the xenon arc, when appropriately filtered, produces radiation with a spectral energy distribution in the ultraviolet range similar to that of natural sunlight.

The radiation must be filtered to ensure that samples are not exposed to any radiation of shorter wavelength than that found at the Earth's surface. Filters can also be used so that a specimen can be exposed to particular spectral regions to which plastics may be specially sensitive. Plastics are particularly sensitive to radiation in the UV portion of the spectrum, hence when defining periods of exposure it is important to measure not only the total radiation but the UV wavelength band of the light source.

Figure 2.2: Spectral Energy Distribution of UV Sources

a Sunlight
b Xenon arc
c Mercury lamp
d Fluorescent lamp
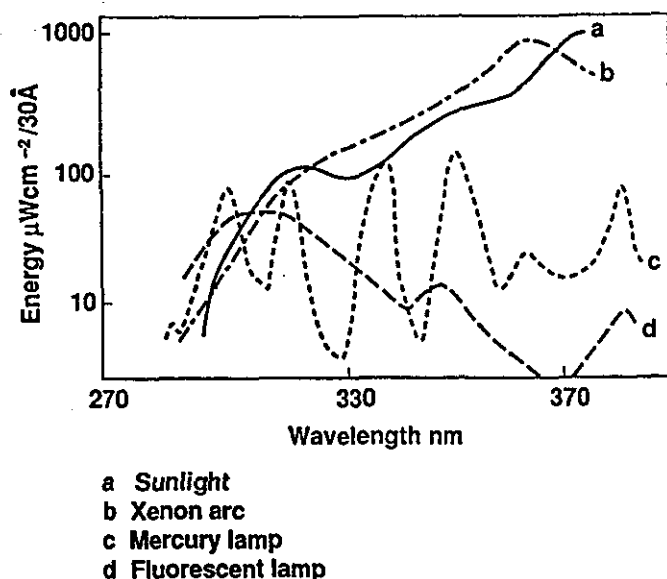
Photochemical degradation is caused by photons of light breaking chemical bonds. For each type of bond there is a critical threshold wavelength of light with enough energy to cause a reaction. Light of any wavelengths shorter than the threshold can break the bond, but longer wavelengths of light cannot break it - regardless of their intensity. Therefore, the short wavelength cut-off of a light source is of critical importance. For example, if a particular polymer is only sensitive to UV light below 295nm (the solar cut-off point), it will never experience photochemical deterioration outdoors. If the same polymer is exposed to a laboratory light source that has a spectral cut-off of 280nm, it may deteriorate. Although light sources that produce shorter wavelengths accelerate degradation, there is a possibility of anomalous results if a tester has a wavelength cut-off too far below that of the material's end use environment. In this report the use of fluorescent lamps is examined and the results obtained compared to those from exposure in a Xenotest-1200.

Since all artificial weathering devices vary in their application it is important when reporting durability results to detail the apparatus and conditions used. In this study the use of fluorescent and xenon lamps is examined and the results compared.

Fluorescent UV Lamps

Radiation from a fluorescent lamp is produced by the re-emission at longer

wavelengths of the light from a low-pressure mercury vapour discharge source. This is achieved by a 'phosphor' coating on the inner surface of the tubes. The broad spectral distributions obtained correspond to the output from the phosphor which either converts or filters most of the original mercury light. While fluorescent tubes can be used to investigate the photostability of materials, chambers are commercially available which have been designed with the objective of simulating the deterioration caused by rain or dew as well as that caused by sunlight. The instrument used in these trials is called the Q-UV, a schematic cross-section is shown in Figure 2.3[138].

The ultra-violet radiation source is an arrangement of fluorescent lamps. Condensation is produced by exposing the test surface to a heated saturated mixture of air and water vapour while the reverse side of the test specimen is exposed to the cooling influence of ambient room air. Specimens are alternately exposed to ultraviolet radiation and condensation and the conditions may be varied by selection of the ultraviolet lamp, the timing of the ultraviolet and the condensation exposure periods, and the temperature.

Figure 2.3: Cross-section of the Q-UV Artificial Weathering Chamber
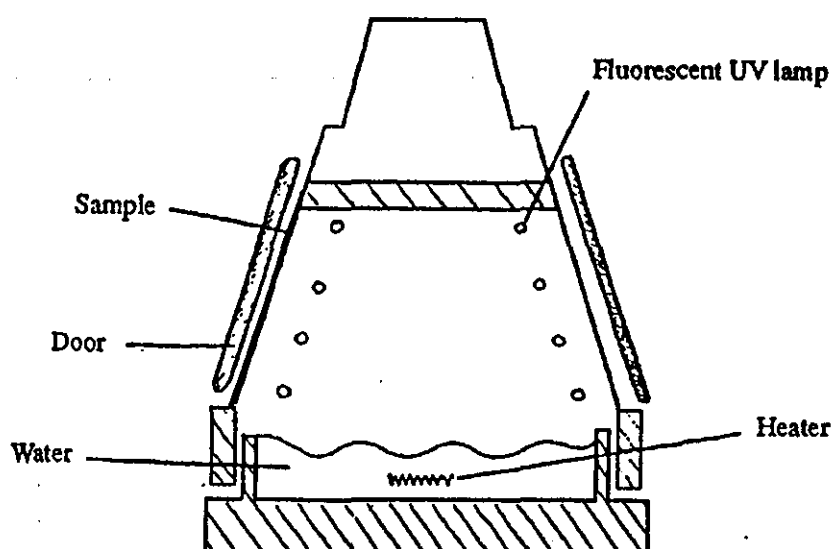
Several types of fluorescent lamps may be used, each type giving light of a different spectral distribution. In these experiments one side of the Q-UV chamber was

fitted with UV-A lamps with maximum emission at 340nm and the other side with UV-B lamps with maximum emission at 313nm; a divider separated the two halves of the chamber. The spectral distribution of these lamps is shown in Figure 2.4.

Figure 2.4: Energy distribution of fluorescent lamps and sunlight
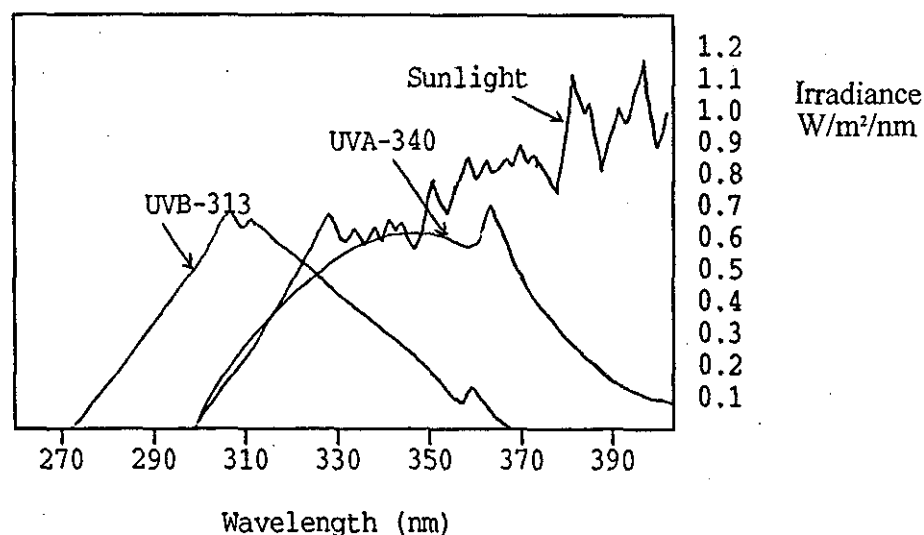
Xenotest 1200

In the Xenotest 1200 radiation is generated by three xenon lamps each with a rating of 4500W. These lamps are arranged in the centre of the test chamber and emit radiation similar to that of natural sunlight. However, xenon sources tend to emit radiation with a high proportion of infra-red and so this has to be filtered out. To meet these requirements a lamp and filter system as shown in Figure 2.5 is employed. The UV cut-off of this system is 300 nm[139].

The three xenon burners are surrounded by mirrors which reflect visible and UV light but transmit most of the infra-red. This infra-red is absorbed by water cooled metallic fins behind the mirrors. The ultra-violet and visible radiation passes through a quartz cylinder which has a reflective coating that allows the required visible and UV radiation to pass through but reflects any short-wave infra-red radiation. The quartz cylinders form

57

a water jacket through which purified cooled water is circulated via a heat exchanger. This both cools the filter system and absorbs some of the near infra-red radiation. Outer UV-filters are fitted, either using `Suprax' glass to simulate direct sunlight or window glass as appropriate.

Figure 2.5: Lamp and Filter Arrangement of the Xenotest 1200
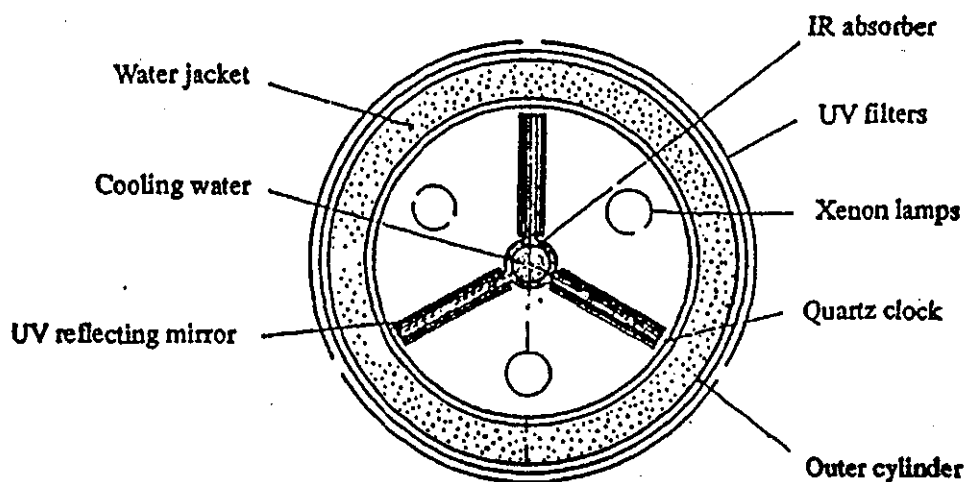
Specimens are mounted on a frame which rotates at 2 rev min^{-1} around the lamp system and so compensates for spatial fluctuations in radiation.

2.2.2 Experimental
Operating Conditions of Q-UV

Samples were cut to size 75mm x 270mm and mounted in holders backed by aluminium plates. During these trials an exposure cycle of 4 hours UV / 4 hours condensation was employed. Two sets of trials were carried out, one set at temperatures of 45°C UV/50°C condensation and the other set at 60°C UV/ 50°C condensation. Two types of fluorescent lamps were used, one type either side separated by a divider: UV-A lamps with maximum emission at 340nm; and UV-B lamps with maximum emission at 313nm. Samples were exposed for up to 2000 lamp hours.

Operating Conditions of Xenotest-1200

Xenon arc exposures were conducted in a Xenotest-1200 U using borosilicate filters to provide a light distribution as close as possible to ISO 4892 : Part 2 : Method A and

with a light intensity in the wavelength range 300 to 800nm of approximately 800 GJm^{-2} in the sample plane. Cabinet air was controlled at 28±1°C, 65±5% RH using a recirculatory cooling unit, which provided a maximum black standard temperature of 65°C in the dry period. The water spray cycle was 18 mins ON / 102 mins OFF. Sample size was 200x65mm mounted so as to face the lamps continuously and both with no backing at all (open-backed) and with black backing allowing a 3mm air gap ventilated top and bottom (black-backed)[4]. Thus two sample surface temperature ranges were achieved. Samples in open-back holders typically reached surface temperatures of 30°C whereas samples on black PVC backing reached surface temperatures of 50 to 60°C with highest temperatures developed towards the centre of each test piece. Samples were exposed for a minimum of 1500 to 2000 lamp hours (4.4-5.8 GJm^{-2}) with exposure periods extended if necessary.

Sample surface temperatures were measured using a non-contact infrared thermometer. Non-contact temperature measurement is made possible by the fact that all objects emit infrared energy. It is thought that this infrared energy is emitted from the outer few tens of microns of the surface and this is the part of the sample most likely to be affected by weathering. The amount of energy emitted is proportional to the objects' temperature and emissivity. Emissivity (ϵ) depends on the material being measured and its surface finish. The emitting and reflecting character of the material is quantified by emissivity, which can have values ranging from 0.10 to 1.00 (for most plastics ϵ=0.90-0.95). Infrared instruments provide temperature readings by sensing the total energy coming from a target which is composed of emitted energy, reflected energy and transmitted energy. For most objects transmitted energy is zero. Using the given emissivity value (0.95 in the standard Raytek model used), the unit calculates the emitted energy and compensates for the effects of reflected energy. The temperature is then calculated from the amount of emitted energy. The entire process takes place in a fraction of a second. This enables fast temperature measurements, 'hot-spot' location and establishment of temperature gradients.

2.3 CHARACTERISATION TECHNIQUES

Practically all of the major newer analytical techniques, and many of the older classical techniques, have been used to examine plastics and their additive systems. Qualitative elemental

59

analysis is normally the first step when attempting to identify a polymer, followed by functional group analysis.

Various elements occur in polymers, both metallic and non-metallic, and these can be divided into three categories:

1. Elements which are a constituent part of the monomers used in polymer manufacture.

2. Elements which occur in substances deliberately included in the polymer formulation.

3. Elements which occur as adventitious impurities in the polymer.

For a variety of reasons, ranging from control during the manufacturing process to the identification of unknown polymers, it is necessary to be able to determine accurately the elements in polymers, and many different types of techniques have been evolved for this purpose. Generally the techniques used come under two broad headings:

1) adaptations of classical techniques

2) instrumental techniques such as X-ray Fluorescence.

As in the case of elemental analysis, functional groups can occur in polymers over a wide range of concentration ranging from a few parts per million to the percentage range. A wide range of physical and chemical techniques have been employed in such analyses. These fall under two main headings:

1) chemical methods e.g. techniques based on colourimetric procedures

2) physical methods e.g. procedures based on infra-red spectroscopy.

Many methods exist for carrying out molecular weight measurements. Polymers are polydisperse i.e. they consist of a mixture of molecules with a range of molecular weights. Molecular weight and molecular weight distribution may be measured and both may change during degradation.

Thermal methods of analysis of polymers are important in that these techniques can provide information about the thermal stability of polymers, their lifetime under particular conditions, phases and phase changes occurring in polymers, and information on the effect of incorporating additives in polymers.

2.3.1 Elemental Determination by X-ray Fluorescence Spectroscopy

X-ray fluorescence spectroscopy was used to look for elements present in unweathered samples, thus helping to identify additives.

Background

X-ray fluorescence (XRF) spectroscopy is a powerful physical technique for elemental analysis. It is based on the fact that the chemical elements emit characteristic radiations when subjected to appropriate excitation. The emission of characteristic line spectra can be induced either by a) the impact of accelerated particles such as electrons, protons, alpha particles and ions; or by b) the impact of high energy radiations from an x-ray tube or from a suitable radioactive source. For reasons of sensitivity and versatility, the combination of the classical high power sealed x-ray tube and wavelength dispersion by selected crystals remains the practical and preferred technique for quantitative x-ray fluorescence analysis[123].

When a sufficiently energetic X-ray photon interacts with an atom, several phenomena take place. One interaction involves the transfer of the photon energy to one of the electrons of the atom (for example a K shell electron) resulting in its ejection from the atom as in Figure 2.6. The distribution of electrons in the ionised atom is then out of equilibrium and within an extremely short time returns to the normal state, by transitions of electrons from outer shells to inner shells. Each such electron transfer, e.g. from the L shell to the K shell, represents a loss in the potential energy of the atom, this energy reappears as a photon (in this case a $K\alpha$ photon) whose energy is the difference between the binding energies of the two shells.

Figure 2.6: Ionisation of the K Shell by an Incident X-ray Photon
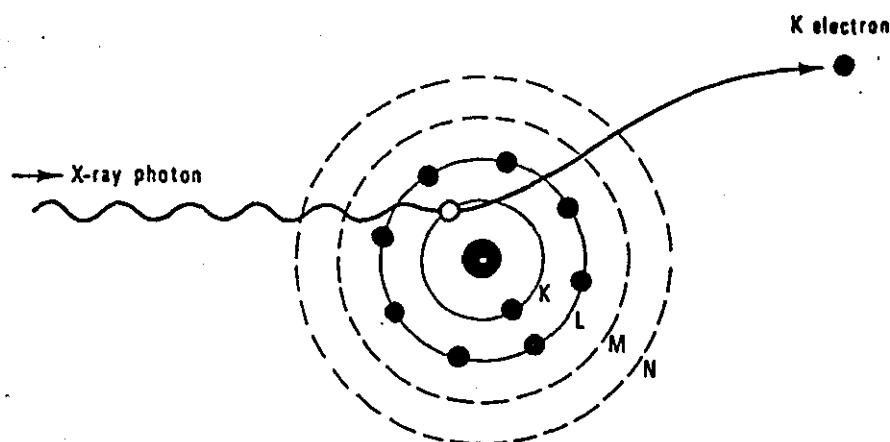
One of two processes can then take place, namely (i) the x-ray photon escapes from

the atom and contributes to a characteristic radiation of the atom; or (ii) the photon is absorbed within the atom itself on its way out and ionises the atom in an outer shell; for example a Kα photon can eject an L, M or N electron; this is called the Auger effect. Again, the ionised atom becomes a source of radiation as before. These electronic transfers give rise to x-ray spectral lines from which elemental identification can occur.

By convention, the various series in x-ray spectra are named as follows: lines are named by a capital letter indicting the final level of the transition involved. For example, the K spectrum corresponds to electron transitions that finalise on the K shell. Similarly the L spectrum corresponds to all the electron transitions that finalise on the L_1, L_2 and L_3 levels. Each particular line is differentiated after Siegbahn[124], by adding a lower case Greek letter and a numerical subscript after the capital letter e.g. α_1, β_3, δ_6 etc. these symbols usually reflect the relative intensities of the lines, α_1 being the strongest line in a given spectrum. This notation is widely accepted but it bears no relation to the transfer that gave rise to the line; it is preferable to describe a line by the final and initial levels of the electron transition, as in Table 2.2.

Table 2.2: Notation of the Characteristic Lines of the K Spectrum

Line (Siegbahn)	Transition	
	Empirical Notation	Quantum Notation
$K\alpha_1$	KL_3	$2p_{3/2} - 1s$
$K\alpha_2$	KL_2	$2p_{1/2} - 1s$
$K\beta_1$	KM_3	$3p_{3/2} - 1s$
$K\beta_3$	KM_2	$3p_{1/2} - 1s$
$K\beta_2$	$KN_{2,3}$	$4p_{1/2} - 1s$
		$4p_{3/2} - 1s$

Each characteristic line can be represented by the difference between the binding energies of the final and initial transition levels. Thus for the $K\alpha_1$ line

$$E_{K\alpha1} = \delta E = E_K - E_{L3}$$

therefore the corresponding wavelength is

$$\lambda_{K\alpha 1} = \frac{12.398}{E_{k\alpha 1}} = \frac{12.398}{E_K - E_{L3}}$$

There is an obvious relation between the emission wavelengths and the atomic number.

When a beam of photons strikes a volume of matter, the emission of x-rays will depend on a number of probabilities. The intensity of a particular emission, $L\alpha_1$, for example, depends on the product of three factors:

a) the probability that the incident photons will ionise an atom in the L_3 level;

b) the probability that the vacant site created on L_3 will be filled by an M_5 electron; and

c) the probability that the $L\alpha_1$ photon will leave the atom without being absorbed within the atom itself.

The relative intensities in the K spectrum are known with accuracy and vary only slightly with atomic number. However, the variations in the relative intensities within the L and M spectra are more noticeable.

Experimental

The spectrometer used was a Philips PW1480 which is a sequential x-ray spectrometer system capable of measuring elements in the range from boron to uranium. Its layout is given in fig 2.7.

Figure 2.7: Philips PW1480 X-ray Fluorescence Spectrometer
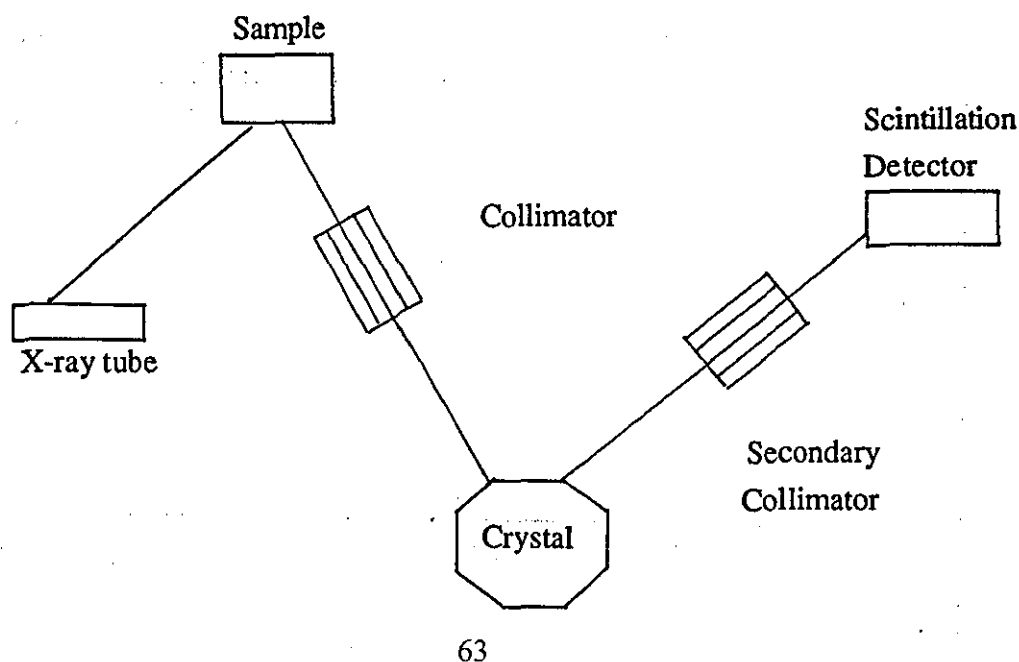
As previously stated, the primary radiations from the x-ray tube excite atoms in the sample, resulting in the emission of characteristic radiations in every direction. The fraction of this radiation that passes through the slit collimator is in the form of a parallel beam which is directed onto the analysing crystal. The crystal disperses the beam as a function of wavelength which relates to the Bragg equation $n\lambda = 2d\sin\theta$ where λ is the wavelength, d is the interplanar spacing of the crystal, θ is the reflection of diffraction angle and n is the order,1,2,3 etc. of the reflection. As a rule the first order (n=1) is of more interest as it corresponds to higher intensities.

The reflected radiation emerges at an angle of 2θ with respect to the incident beam and the 2θ value at which maximum intensity is detected enables the wavelength of that particular characteristic radiation and hence the element of origin to be determined.

To record a spectrum of an unknown sample the crystal is rotated at a constant speed through a range of θ values and the relative intensities recorded at the detector. Two types of detector are used (i) scintillation counter for short wavelengths and (ii) gasflow counter for longer wavelengths.

Samples were cut from 2mm thick sheet and analysed using a qualitative program which scans from sodium to uranium.

2.3.2 Determination of Functional Groups by Infra-red Spectroscopy

Infra-red spectroscopy was used to study functional groups at the surface of the unweathered and weathered samples. Two techniques were used; attenuated total reflectance and photo-acoustic spectroscopy.

Background

Fourier transform infrared spectroscopy (FTIR) has many advantages over the traditional dispersive technique[125]. The main difference between the two techniques is that FTIR uses an interferometer which has only one moving part, a mirror; dispersive instruments have many moving parts. This difference means that FTIR is faster, has greater energy throughput, eliminates the problem of stray light and enables photometric repeatability. FTIR spectroscopy uses sampling techniques which involve little sample preparation. Since sample preparation time determines sample throughput, FTIR enables quick analysis times. Sampling techniques used in FTIR

64

spectroscopy include attenuated total reflectance, specular reflectance, diffuse reflectance and photo-acoustic.

Fourier Transform spectrometers contain a source, an interferometer and a detector. The fundamental difference between dispersive and FTIR instruments is that the interferometer replaces the monochromator and the mode of operation in FTIR is single beam. An interferometer measures all the frequencies in the infra-red radiation simultaneously, rather than splitting it into individual spectral components, as in dispersive instruments. The interferogram, produced by the interferometer is then mathematically treated by a process known as a Fourier transform to yield the spectrum of the sample.

Configuration of a typical FTIR spectrometer is given in Figure 2.8.

Figure 2.3 : FTIR Spectrometer Configuration
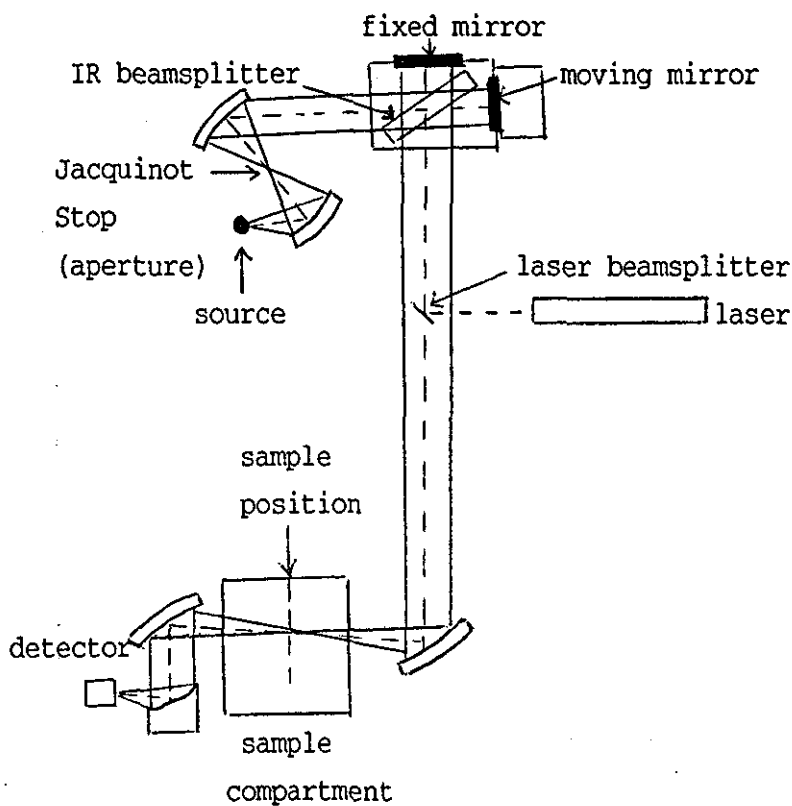
The beamsplitter is designed to transmit 50% of the IR light onto the moving mirror

and reflect 50% onto the fixed mirror in the interferometer. The fixed mirror reflects radiation back to the beam splitter, while the moving mirror also returns the IR radiation, but creates a path difference between two mirrors. As the moving mirror moves through its full displacement, the interference (both constructive and destructive for all frequencies in the IR source) is measured with respect to the position of the moving mirror and the interferogram is produced. It can therefore be stated that the interferogram is the sum of both constructive and destructive interferences for each component wavelength in the IR source. The sources used in FTIR instruments are the same as those used in dispersive spectroscopy. The only difference is the shape of the beam produced, most FTIR spectrometers produce a circular beam rather than a rectangular beam as in dispersive instruments.

An important advantage of FTIR spectroscopy is the speed at which an instrument can scan a sample, this is achieved since the rate determining step is simply the movement of a mirror a short distance in the interferometer. The absence of energy restricting slits in an FTIR spectrometer means that most of the energy supplied by the IR source reaches the detector. This results in a substantial increase in the sensitivity of the instrument and enables difficult samples to be handled with ease. Since an FTIR spectrometer uses a laser as a reference for data sampling, the wavelength accuracy of FTIR instruments is far higher than could be achieved in a dispersive instrument.

The number of different sampling accessories available for recording IR spectra on an FT instrument mean that almost any material regardless of its shape or form can be analysed.

Attenuated Total Reflectance

Attenuated total reflectance (ATR), also referred to as multiple internal reflection (MIR), is a technique for analysing smooth, flat surfaces. The sample is held in intimate contact with a high refractive index crystal. An infrared beam entering the crystal is multiply internally reflected and this creates an evanescent wave which extends into the sample (Figure 2.9).

In regions of the infrared spectrum where the sample absorbs energy the evanescent wave will be attenuated (absorbed). The condition which must exist to obtain total internal reflectance is that the angle of incident radiation, θ, must exceed the critical angle θ_c. The critical angle is a function of the refractive indices of the

66

sample and ATR crystal and is defined as

$$\theta_c = \sin^{-1} \frac{n_2}{n_1}$$

where n_1 is the refractive index of the ATR crystal and n_2 is the refractive index of the sample. High refractive index materials are chosen for the ATR crystal to minimise the critical angle. A property of the evanescent wave which makes ATR a powerful technique is that the intensity of the wave decays exponentially with distance from the surface of the ATR crystal. The distance, which is of the order of microns, makes ATR generally insensitive to sample thickness, allowing for the analysis of thick or strongly absorbing samples.

Figure 2.9: ATR Principle
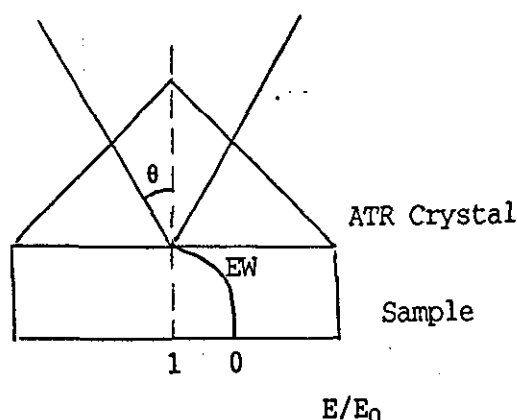
The penetration of depth of the infrared energy into the sample is wavelength dependent. As the wavelength of the infrared radiation increases, the depth of penetration also increases. It is often convenient to discuss this in terms of wavenumbers: the depth of penetration decreases when wavenumber increases. This causes the relative band intensities in the ATR spectrum to decrease with increasing wavenumbers when compared to a transmission spectrum of the same sample. Since band positions and shapes are nearly identical for the ATR and transmission spectrum, many spectrometers have an 'ATR correction' program which makes the ATR spectrum appear more like a transmission spectrum.

The refractive index of the ATR crystal has two effects on the ATR spectrum obtained. The first is that by increasing the refractive index of the crystal material, the critical angle is decreased. This is important when working with samples which have a high index of refraction. Distortions in the infrared spectrum of the sample will be observed if the angle of incidence does not greatly exceed the critical angle. The refractive index also affects the depth of penetration of the evanescent wave into the sample. By increasing the refractive index of the ATR crystal, the depth of penetration will decrease. This will decrease the absorbance intensity of the spectrum.

Changes in the angle of incidence of the infrared radiation have three effects on the ATR spectrum of a sample.

1. The first is that the angle of incidence must be chosen to exceed the critical angle in order to obtain an ATR spectrum. For example, for ZnSe θ_c=38.7° and for Ge θ_c=22.0°. If an angle of incidence of less than 38.7° was chosen for the ZnSe crystal, internal reflection would not occur and a spectrum of the material would not be obtained. An angle of incidence should be chosen to exceed greatly the critical angle such as a 45° crystal in this example.

2. The angle of incidence also has an effect on the number of reflections in the ATR crystal which affects the infrared absorbance intensity of the spectrum. As the angle of incidence increases, the number of reflections decreases and the absorbance intensity decreases.

3. Changing the angle of incidence also changes the depth of penetration. If the angle of incidence is increased, the depth of penetration will be decreased and the absorbance intensity will be decreased.

Another factor which affects the quality of an ATR spectrum is the efficiency of sample contact. Because the evanescent wave decays rapidly with distance from the surface, it is important to have the sample in intimate contact with the crystal. This is easily achieved with most liquids since they wet the surface of the ATR crystal. For solids, it is important to use a pressure device which presses the sample against the crystal. For very hard materials, care must be taken when increasing the pressure on the crystal so as not to crack the crystal.

The area of sample contact directly affects the intensity of the absorbance spectrum. If the entire crystal surface is not covered, the intensity of the absorbance spectrum will decrease. To ensure maximum reproducibility, the entire crystal surface

68

should be covered by the sample.

The material from which the ATR crystal is made will affect the refractive index, the infrared transmission range, as well as the chemical properties of the crystal. A crystal material must have a high refractive index to allow internal reflection. Materials with a refractive index greater than 2.2 are normally chosen as ATR crystals. The material most commonly used for ATR crystals is ZnSe. ZnSe has a refractive index of 2.4 making it suitable for most organic materials and it has a transmission range from 20,000 to 650 cm^{-1}. This material is insoluble in water but should not be used in acidic or strong alkaline solutions.

Experimental Procedure

A Nicolet 510P infra-red spectrometer was used with a zinc selenide crystal ATR attachment. Samples were cut from 2mm thick sheets so as to be just big enough to cover the whole crystal surface. A clamping device was used to ensure efficient contact with the crystal, but care was taken so as not to apply undue pressure which may crack the crystal. Spectra were obtained and an ATR correction procedure performed on each sample using computer software before analysis.

2.3.3 Photo-acoustic Spectroscopy

Photo-acoustic spectroscopy was used to examine the surfaces of weathered samples for changes in functional group properties. It was used in preference to ATR because of the rough nature of the surface of the weathered samples.

Background

The photo-acoustic phenomenon was first observed by Alexander Graham Bell in the early 1880's. He found that when a gas placed within a sealed compartment was illuminated with pulsed radiation, pressure fluctuations could be detected by a sensitive microphone inside the compartment. In infra-red photo-acoustic spectroscopy a microphone is used to detect the acoustic signal generated by the IR radiation (modulated by the interferometer) falling onto a sample as shown in Figure 2.5[127].

IR radiation absorbed by a solid sample heats its surface which in turn heats the boundary layer of gas surrounding the sample. Modulated radiation produces expansion and contraction of the boundary layer which is detected as sound. To

remove the absorptions due to atmospheric water vapour the photo-acoustic cell is purged with dry gas prior to sealing. Due to its high thermal conductivity helium is the best purge gas for both elimination of water vapour and improved signal-to-noise ratios. Spectra can be obtained from solids, liquids and gases.

Figure 2.5 : Principle of Photo-acoustic Spectroscopy
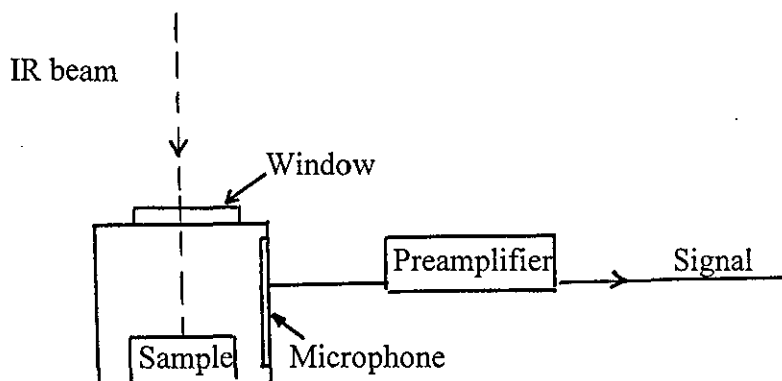
Photo-acoustic measurements provide spectral information about the surface of a sample. The depth to which the infrared beam penetrates the sample is proportional to the heat capacity and the thermal conductivity of the sample and the modulation frequency of the incident radiation. To achieve this the FTIR spectrometer must be capable of achieving stable slow mirror velocities in the region of 0.1cm/sec.

Photoacoustic spectra are typically referenced to a highly absorbing background spectrum obtained using carbon black to ratio out the FTIR's instrument profile. The sampling depth depends on both the thermal and optical properties of the material. The samples studied in this report are optically transparent. The thermal diffusion length, μ, is calculated by

$$\mu = \left(\frac{2\alpha}{W}\right)^{1/2}$$

where α is the thermal diffusivity of the sample (determined for each sample for reliable results) and W is the modulation frequency of the radiation, which is dependent on the mirror velocity in the interferometer, V, and the infrared wavenumber, ν, expressed as $W = 4\pi\nu V$. α is dependent on the thermal conductivity,

density and specific heat of the sample and is defined as

$$\alpha = \frac{\text{thermal conductivity}}{\text{density x specific heat}}$$

For the materials tested α values may be evaluated as follows

Polycarbonate $\alpha = \dfrac{0.21 \ Wm^{-1}K^{-1}}{1.2 \ gcm^{-3} \ x \ 1.17 \ kJkg^{-1}K^{-1}}$

$\therefore \underline{\alpha = 1.50 \ x \ 10^{-7} \ m^2s^{-1}}$

PMMA $\alpha = \dfrac{0.18 \ Wm^{-1}K^{-1}}{1.17 \ gcm^{-3} \ x \ 1.47 \ kJkg^{-1}K^{-1}}$

$\therefore \underline{\alpha = 1.05 \ x \ 10^{-7} \ m^2s^{-1}}$

PVC $\alpha = \dfrac{0.15 \ Wm^{-1}K^{-1}}{1.40 \ gcm^{-3} \ x \ 0.85 \ kJkg^{-1}K^{-1}}$

$\therefore \underline{\alpha = 1.26 \ x \ 10^{-7} \ m^2s^{-1}}$

Thus the following depths of penetration in Table 2.3 can be calculated.

Table 2.3 : Depth of Penetration for Varying Mirror Velocity

Sample	Mirror Vel=0.16cms^{-1}	Mirror Vel=0.16cms^{-1}	Mirror Vel=0.63cms^{-1}	Mirror Vel=0.63cms^{-1}
	400cm^{-1}	4000cm^{-1}	400cm^{-1}	4000cm^{-1}
PC	19 μm	6 μm	10 μm	3 μm
PMMA	16 μm	5 μm	8 μm	3 μm
PVC	18 μm	6 μm	9 μm	3 μm

The mirror velocity in the interferometer varies from 0.16 cms^{-1} to 0.63 cms^{-1}. Depth

71

of penetration is thus highest at slower mirror velocities and lower wavenumber. By using varying mirror velocities the modulation frequencies vary and depth profiling information can be obtained from different depths of penetration into the sample.

Experimental

Samples were cut to fit large sample cups approximately 8mm diameter. Carbon black was used for background scans and the photoacoustic cell was purged with helium.

Scans were taken on reference and weathered materials to examine any differences; spectra were taken with mirror velocity set to 0.3 cms^{-1} (medium) so as to enable examination of the surface only. Depth profiling was also carried out on PVC samples.

2.3.4 Molecular Weight Determination by Gel Permeation Chromatography

Gel permeation chromatography was used to quantify the molecular weight distributions for unweathered samples and then look for changes in the weathered samples.

Background

Polymers normally do not consist of a particular molecule with a unique molecular weight, but rather are a mixture of molecules with a molecular weight range. With some types of polymers the picture is further complicated by the appearance of crosslinks. Crosslinking will increase the molecular weight of a polymer and decrease its solubility in organic solvents (fully cross-linked samples will be insoluble and have a molecular weight of ∞).

Gel permeation chromatography (GPC)[128,129] is a technique where a solution of the polymer is passed down a column packed with a gel (beads) which separates the polymer into fractions based on molecular weight by means of a sieving action. The larger polymer molecules dissolved in solvent carrier cannot diffuse into the pores and are rapidly eluted, while the smaller ones penetrate further into the gel with decreasing size and are retarded correspondingly. Thus, the larger molecules leave the column first and the smaller ones last because they travel a much longer path. Each fraction is detected by a suitable detector and a chromatogram is obtained for the

72

sample which shows the difference in refractive index of the eluent from the sample column to that from the reference column. The recorded reading is a function of the elution volume and the refractive index of the dissolved species eluting.

In interpreting a GPC chromatogram in terms of its averages, it is important to consider which average molecular weight has the most significance in relation to the property of the sample which is of interest. The most common molecular weight averages computed from GPC chromatograms are:

Number Average Molecular Weight (Mn). This is the molecular species population molecular weight average. It correlates well with properties that are dependent on mole fraction.

Weight Average Molecular Weight (Mw). This average is weighted towards the mass of the individual species comprising the sample. It correlates well with properties that are dependent on mass fraction such as mechanical properties.

Z-Average Molecular Weight (Mz). The Z-average molecular weight is weighted towards the higher weight population of the molecular weight distribution. It correlates well with material properties which are dependent on the very high molecular weight component of the sample.

Experimental

A mixed gel column was used to separate the polymer samples. About 10mg was scraped from the surface of the glazing sample, the depth of the sample being no greater than 0.3mm from the surface, and dissolved in 20ml tetrahydrofuran (THF). The sample is separated on the basis of molecular weight. The THF solution was injected into the THF solvent flowing through the column at constant rate. The eluted solvent was monitored using a refractive index detector and results were analysed using a BBC microcomputer.

Five polystyrene standards were dissolved in tetrahydrofuran (THF) and a calibration obtained.

2.3.5 Thermal Analysis

Thermal analysis techniques were used to determine glass transition temperatures for the six test materials, also transitions below Tg. This then gives information on molecular

mobility. Differential Thermal Analysis was also used to assess fusion levels in the PVC samples.

Background

Thermal methods of analysis of polymers are important in that these techniques can provide information about the thermal stability of polymers, their lifetime or shelf-life under particular conditions, phases and phase changes occurring in polymers, and information on the effect on incorporating additives in polymers.

Differential Thermal Analysis

When a substance undergoes a physical or chemical change a corresponding change in enthalpy is observed. This forms the basis of the technique known as differential thermal analysis in which the change is detected by measuring the enthalpy difference between the material under study and an inert standard.

The sample is placed in a heated block and warmed at a uniform rate. The sample is then monitored by means of a thermocouple and compared with the temperature of an inert reference such as an empty sample pan, which is subjected to the same linear heating programme. As the temperature of the block is raised at a constant rate the sample temperature T_S and that of the reference T_R will keep pace until a change in the sample takes place. If the change is exothermic T_S will exceed T_R for a short period, but if it is endothermic T_S will temporarily lag behind T_R.

A DuPont 2000 Thermal Analyser, fitted with a differential scanning calorimetry (DSC) cell was used. The polymer sample was heated at a controlled rate ($10\,°C/min$) from $40\,°C$ to $240\,°C$ using a pre-programmed method, the temperature of the sample being continually monitored. The data was analysed by computer and transition temperatures determined ; when the sample undergoes a phase change heat is either produced or absorbed which can be identified on the heat flow vs temperature trace. For the two PVC samples heats of fusion were also calculated; the method for this is discussed in chapter 4.

Dynamic Mechanical Analysis

Dynamic mechanical analysis is the most sensitive thermal analytical technique for detecting transitions associated with movement of polymer chains. The technique involves measuring the resonant frequency and mechanical damping of a material forced to flex at a selected amplitude. Mechanical damping is the amount of energy dissipated by the sample as it oscillates, while the resonant frequency defines Young's

(elastic) Modulus or stiffness. As a polymer is viscoelastic it can exhibit both elastic and viscous (fluid) responses. Elastic materials convert mechanical work into potential energy which is recoverable. No energy is converted into heat during cycling, so that no damping is experienced. Liquids flow if subjected to stress. They do not store energy, but dissipate it as heat, thus possessing damping characteristics. Thus viscoelastic polymers exhibit both elastic and damping behaviour.

The technique is based on the assumption that polymeric materials can be modeled as behaving in the same way as a combination of perfect springs and perfect dashpots when subjected to a sinusoidally varying input of either stress or strain. Hence, if a sinusoidal stress is applied to a linear viscoelastic material, the resulting stress will also be sinusoidal, but will be out of phase and lag behind when there is energy dissipation or damping in the polymer as shown in Figure 2.11.

Figure 2.11: Application of Sinusoidal Stress to Viscoelastic Polymer
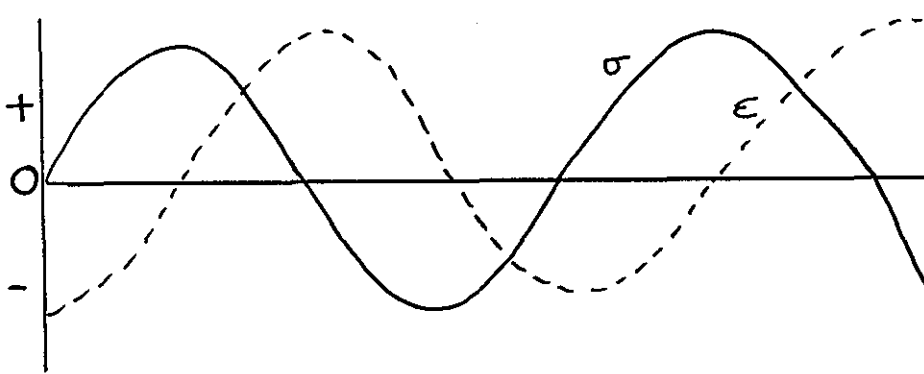
The resulting strain may be described in terms of its angular frequency, ω, and the maximum amplitude, ε_0, using complex notation:

$\varepsilon^* = \varepsilon_0 \exp(i\omega t)$ $\qquad\qquad$ $\omega = 2\pi v$; $\quad v$ = frequency; $\quad i = -1$

thus the relationship between alternating stress and strain is:

$\sigma^* = \varepsilon^* E^*(\omega)$ $\qquad\qquad$ E^* = complex dynamic modulus

$E^* = E'(\omega) + iE''(\omega)$

Thus the dynamic modulus is composed of two components:

$E'(\omega)$ is the real part in phase with the strain - the storage modulus

$E''(\omega)$ is the loss modulus, defined as the ration of the component 90° out of phase with the stress to the stress itself.

Hence, $E'(\omega)$ measures the amount of stored energy and $E''(\omega)$ is a measurement of

75

the energy dissipated by the material.

The damping of the system can be measured by the loss tangent, tanδ. This is a measure of internal friction

$$\tan\delta = \frac{1}{\omega\tau} = \frac{E''(\omega)}{E'(\omega)}$$

Therefore, $E'' = E'\tan\delta$.

In general, modulus and frequency, as well as damping, change more dramatically than heat capacity or thermal expansion during secondary transitions. Thus this is a very sensitive method.

The sample was clamped in the apparatus at each end. One end was held stationary in the reaction frame and the other end was attached to the drive mechanism that applies the movement. The required amount of movement was induced by passing a sinusoidal current through the coil. A frequency of 1Hz was used. The amplitude of deformation was constant at 0.75mm. The following procedure was used: a sample of dimension 30mm x 13mm x 2mm was heated from -100°C to 180°C at a rate of 5°C/min.

2.3.6 Colour Measurement

In weathering trials most plastics materials undergo surface colour changes due to degradation and so this becomes a useful method for following the weathering characteristics of a material.

Background

Colours have three basic subjective attributes which are defined as follows:

<u>Brightness (or Value)</u> - attribute of a visual sensation according to which an area appears to exhibit more or less light.

<u>Hue</u> - attribute of a visual sensation according to which an area appears to be similar to one, or to proportions of two, of the perceived colours red, yellow, orange, green, blue and purple.

<u>Colourfulness</u> - attribute of a visual sensation according to which an area appears to exhibit more or less chromatic colour.

Although all colours can be described in terms of brightness, hue and colourfulness, the recognition of coloured objects is often dependent not so much on

76

colourfulness as on saturation.

Saturation (or chroma) - the colourfulness of an area judged in proportion to its brightness.

The most basic objective measure of colour stimuli are their spectral power distributions. Because perceived colours have three basic attributes, it is necessary to weight the spectral power distributions in three different ways. This is achieved by using the CIE colour matching functions, x(M), y(M), z(M) to obtain the psychophysical tristimulus values X, Y, Z.

$$X = k(P_1x_1 + P_2x_2 + P_3x_3 + ...)$$
$$Y = k(P_1y_1 + P_2y_2 + P_3y_3 + ...)$$
$$Z = k(P_1z_1 + P_2z_2 + P_3z_3 + ...)$$

Where P_1, P_2, P_3 etc. are the radiances at wavelengths M_1, M_2, M_3 etc.

The Y tristimulus is proportional to the luminance L which correlates to brightness (value). The value of k is usually chosen so that Y = 100 for a suitably chosen reference white; hence for other colours, Y is the percentage luminance relative to white, that is, the percentage reflectance or transmittance. The psychophysical chromaticity co-ordinates, x, y, where

x = X/(X+Y+Z) and y = Y/(X+Y+Z), are often quoted instead of X and Z. Colorimetric specifications may therefore consist of values of X, Y, Z and L or x, y, Y and L. X and L are related to brightness; X, Z, x and y are related to combinations of hue and saturation.

CIELAB is the official abbreviation for the equation system defined as the CIE 1976 L*, a*, b* colour space. CIELAB defines each colour in terms of three co-ordinates L*, a* and b*. (Figure 2.12)

The L co-ordinate represents the lightness/darkness of the sample in a scale ranging from 0 (black) to 100 (white).

The a co-ordinate represents the greenness/redness of the sample. In this case 'green' colours are represented by negative values and 'red' by positive values.

The b co-ordinate represents the blueness/yellowness of the sample. 'Yellow' colours being represented by positive values and 'blue' by negative values.

77

Figure 2.12 : Solid L* a* b* Colour Chart
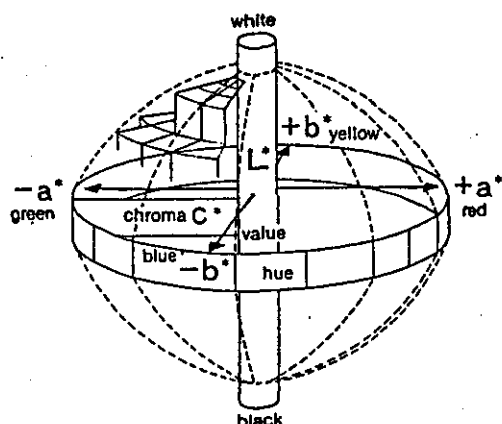
The calculation of these values from the tristimulus values is accomplished as follows:

$$L^* = 100(Y^*)$$
$$a^* = 500(X^*-Y^*)$$
$$b^* = 200(Y^*-Z^*)$$

where $X^* = \left(\dfrac{X}{X_0}\right)^{1/3} - \dfrac{16}{116}$

$$Y^* = \left(\dfrac{Y}{Y_0}\right)^{1/3} - \dfrac{16}{116}$$

$$Z^* = \left(\dfrac{Z}{Z_0}\right)^{1/3} - \dfrac{16}{116}$$

X_0, Y_0 and Z_0 are the tristimulus co-ordinates of the standard illuminant (obtained by tristimulus calculation using samples with reflectance 1, i.e. 100% reflectance, at all wavelengths).

Colour measurements were made using a Macbeth 1010S colorimeter. The Macbeth operates with diffuse illumination and with viewing at 8° to the normal as shown in figure 2.13.

78

Experimental

Measurements were done with specular reflectance (effect due to gloss) included because the samples generally have variable levels of specular reflectance and surface texture which are likely to change on weathering quite independently of colour changes. This is the preferred geometry, because to quote BS 3900:Part D9:1986 (Colour measurement)[118] 'If the gloss changes without a visually perceptible change in colour, for example after weathering, the tristimulus values measured including the specular reflectance will generally not be influenced.' The instrument uses xenon flash giving high illumination levels essential for work in brightly lit laboratories and outdoors.

Figure 2.13 : Principle of Optical Structure of Macbeth Colorimeter

Photo receiver
Filters
Measuring channel
Optical cable
Reference channel
Xenon flash lamp
Shutter
Integrating sphere
Measuring orifice
Sample
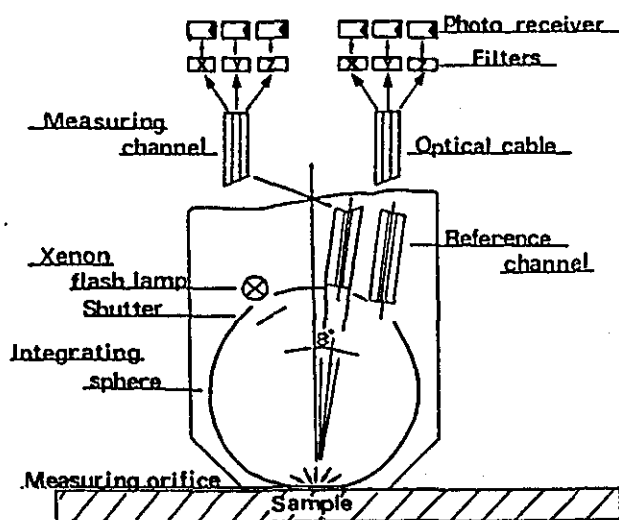
The Macbeth calculates colours as if using CIE Standard Illuminant C (resembles North daylight i.e. blue-rich). The field of measurement is 20mm in diameter. For the purpose of measuring colour changes in transparent materials a standard white tile was placed behind the glazing sample before a reading was taken. Colour data was transferred from the Macbeth onto files on a BBC micro computer where a suitable programme was used to calculate colour changes. Two programmes were available

for use: either calculation of colour change with reference to a separate unweathered sample; or calculation of colour change with reference to initial measurements made on the sample before it was weathered. Samples were measured after every 250 hours exposure in the Xenotest-1200 and at more frequent intervals for exposure to UVB and UV-A radiation.

Colour changes are represented by the values:

δL^* positive value indicates lightening of the sample
   negative value indicates darkening of the sample

δb^* positive value indicates yellowing or fading of blueness of the sample
   negative value indicates a loss of yellowness or an increase in blueness

δa^* positive value indicates an increase in redness or fading of greenness
   negative value indicates an increase in greenness or fading of redness

δE^* always a positive value and indicates overall colour change

$$\delta E^* = \sqrt{(\delta L^{*2} + \delta b^{*2} + \delta a^{*2})}$$

2.3.7 Gloss Measurement

Gloss is an optical phenomenon of value when evaluating the appearance of a surface. The evaluation of gloss describes the capacity of a surface to reflect directed light and so can be used to follow changes in the surface of a sample upon weathering.

Background

Different types of surfaces have different reflection behaviour under direct illumination. For glossy surfaces, gloss is defined as the direct reflection on the first surface. In cases of high gloss surfaces, light reflected from the surface follows the reflection law (angle of illumination = angle of reflection). For glossy surface with haze the dominant part of the light is reflected in the main direction of reflection(specular). A small amount of light is scattered in directions adjacent to the direction of specular reflection. This scattered light of low intensity causes haze. For medium to matt surfaces in this case the light is not only reflected in the direction of specular reflection, but also in other directions. The capacity of a surface to reflect a light source or other images is strongly reduced. The more evenly the intensity is distributed in all directions, the less glossy a surface will appear.

Experimental

Changes in gloss were also used to follow the weathering behaviour of the glazing samples. The changes in 60° specular reflectance were followed using apparatus complying with BS 3900:PartD5:1986[120]. Gloss readings were taken from samples with black felt backing. Because only a small area is measured each time, generally three readings were taken per sample to give a more accurate indication of any changes. However, because the samples are transparent, high gloss values were obtained due to double/multiple reflections of the light in the sample. The strength of reflections from the lower surface depends on the transparency of the material. Loss of gloss on the upper surface causes a diffusion of transmitted light and weakens the multiply-reflected signal also; so the method, as with colour, is very sensitive to small changes.

In principle a 20° gloss head could have been used in the same way but this tends to require surfaces to be flat and parallel.

2.3.8 Light Transmission

Depending on the type of plastics and service exposure, light transmission, which can be important in certain applications, may be affected in different ways; in extreme cases it may be completely obstructed. Light transmission may be reduced by loss of surface quality and/or by changes in the bulk of the plastics material. Loss of surface quality can be caused by scratching, abrasion and/or, more often, by surface deterioration from exposure to the environment. The surface flaws cause the incident light to scatter, decreasing the portion of light being transmitted. Light transmission may also be reduced by changes in the bulk of the plastic, such as discolouration of the resin and colour changes in the pigment or dyes.

Background

The scattering of light as it passes through a material which is essentially transparent leads to two effects: aberration of the image (loss of clarity), and reduction in contrast of the image. The former is associated with scattering at very small angles, whilst the latter occurs with scattering at high angles; both are aspects of transparency and both are caused by variation of refractive index within the material.

Transparency may be quantified by considering a narrow beam of light of specified

81

frequency falling normally on to the plastics material. A fraction of the light is reflected, and some is scattered by imperfections at the surface as shown in Figure 2.14.

Figure 2.14 : Reflection and Scattering of Light at a Surface
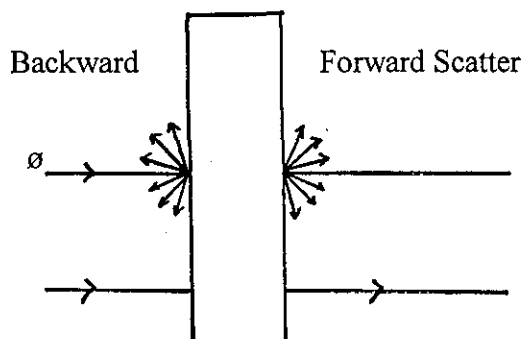
The direct transmission factor, T, also known as the specular transmittance, is defined by the ratio:

$$T = \frac{\varnothing_{undev}}{\varnothing}$$

where $\varnothing$ is the flux in the absence of a plastics specimen, and $\varnothing_{undev}$ represents the undeviated flux when the sample is included in the measurement cell.

The difference between these two quantities represents the sum of the flux absorbed ($\varnothing_A$) and the scattered component ($\varnothing_{Sc}$)

$$\varnothing_{undev} = \varnothing - \varnothing_A - \varnothing_{Sc}$$

For comparatively low concentrations of the scattering species, and for relatively thin specimens (<3mm thick), the relationship between the direct transmission factor and the thickness (b) can be approximated by

$$T = \exp[-b(\sigma+K)]$$

σ is a measure of the light scattered, and is known as the scattering coefficient, or turbidity. For most polymers $\sigma >> K$. It is the fraction of the light flux scattered in passing through unit thickness of the material. K is the fraction of light energy absorbed in passing through unit thickness of the material. The sum ($\sigma+K$) is known as the attenuation or extinction coefficient.

The scattered radiation is the sum of that scattered forward ($\varnothing_{Sc}^{f}$), between 0 and 90°, measured from the direction of the incident beam, and that scattered backwards.

The total flux transmitted ($\emptyset_T$) is given by:

$$\emptyset_T = \emptyset_{undev} + \emptyset_{Sc}^{f}$$

The forward scattered fraction χ_{Sc}^{f} is : $\chi_{Sc}^{f} = \dfrac{\emptyset_{Sc}^{f}}{\emptyset_T}$

The lower contrast when viewing an object through a scattering medium is due to the light scattered forwards at high angles, which is conveniently expressed as the forward scattering fraction, and is often termed haze. Clarity is the capacity of the sample for allowing details in the object to be resolved in the image; it is perfect only when the scattering is zero, and is dependent on the angular distribution of the scattered intensity, and on the geometry of the optical system.

For colour-tinted sheet plastics products such as roofing panels, reference should be made to transmission spectra to cover the entire visible and near-UV regions, since the extent of light transmission will be very sensitive to the absorption characteristics of the pigmentation system.

For an incident beam the transmission intensity (I) of radiation through a plastics medium is also dependent upon thickness and the concentration of the absorbing species. This is most frequently described by the Beer-Lambert law:

$$I = I_o e^{-kCb}$$

I is the light intensity after passing through a specimen thickness b, I_o is incident intensity, k is a coefficient relating to the efficiency of the absorbing medium, and C is its concentration. Many spectrometers function on the basis of this principle. If the appropriate absorption spectra of a given material are known, such that the wavelength and intensity of the incident radiation can be specified, photometric techniques can be developed to measure and relate the intensity of transmitted light to the thickness and/or concentration of absorbent.

Experimental

UV/visible absorption spectra were measured using a Pye-Unicam SP8-200 spectrometer which is a double-beam, ratio-reading instrument, incorporating a microprocessor for instrument control and data handling.

Two source lamps are used - a 12V quartz halogen lamp in the visible and near infrared region and a deuterium lamp at shorter wavelengths. Changeover occurs automatically at a wavelength of 325nm. Filters are inserted in the beam over certain wavelength ranges to reduce the effects of stray light:

83

Blue (BG3)   greater than 730nm

Red (OG 570)   greater than 572.5nm

Black (UG 11) 325-370nm

The wavelength of the monochromator is set using an Ebert grating. The bandwidth is set by means of a servo system which selects one of six pairs of fixed slits, each of a different width.

For transparent glazing materials an integrating sphere was used to compensate for any scattered light. A pair of rotating mirrors deflects the beam so that the beam passes alternately through the sample and reference (air), after which the two beams converge at the end window of the photomultiplier tube which converts the light into electrical signal.

Charts of % transmission versus wavelength were obtained and values tabulated. Average % light transmission values were calculated by reading % transmission at 10nm intervals and averaging over the wavelength range.

2.3.9 Optical Microscopy

Samples of the six materials exposed to the different radiation types at the lower temperature operating conditions were studied using an optical microscope to identify any crack formation or other surface break up.

2.3.10 Impact Testing

Some plastics materials lose impact resistance on weathering. In safety and construction applications this can thus shorten a product's service life. Loss of impact strength is generally associated with loss of surface quality such as microcrack formation on weathering, hence an abrasion test has been developed to attempt to predict whether a material will lose impact resistance on exposure.

Background

Failure in its widest sense is the inability of a material or an object to fulfil its intended function[130]. Plastics materials and items made from them are not outstandingly strong in comparison with other classes of material of construction,

except where special processing routes have been used to create highly favourable molecular orientations. There are essentially three modes of failure, namely ductile, brittle and mixed mode. However, there is only a loose correlation between failure characteristics and strength; a high strength is not necessarily associated with ductility nor is a low strength necessarily associated with brittleness. Strength is variously classified as brittle strength, yield strength, fatigue strength and impact strength.

A plastics product is more likely to fail when it is subjected to an impact blow than if the same force is applied more slowly because in the latter case the material has greater opportunity to undergo compensating motion. . Due to this potentially damaging aspect of viscoelasticity, impact tests have been developed which provide quantitative data on material characteristics and reflect the likely behaviour of real products subjected to impact abuse in service.

Impact tests are designed to establish the unit amount of impact energy which can be sustained by plastics materials subjected to high strain rate loading conditions. Since the ability to absorb energy is dependent upon the shape, size and particularly thickness of the component, it is important that all tests are standardised so that an impact strength parameter (e.g. energy absorbed per unit area of failure) can be obtained. Clearly this is not feasible for many fabricated products so several different impact tests have developed where the measurement principle examines either a material property or a characteristic of the product, considering not only the material characteristics, but also the effects of processing, design and dimensional fluctuation.

The impact event is displayed as the force-displacement curve, and a typical impact involves initiation and propagation(Figure 2.15).

Figure 2.15 : Impact Event

85
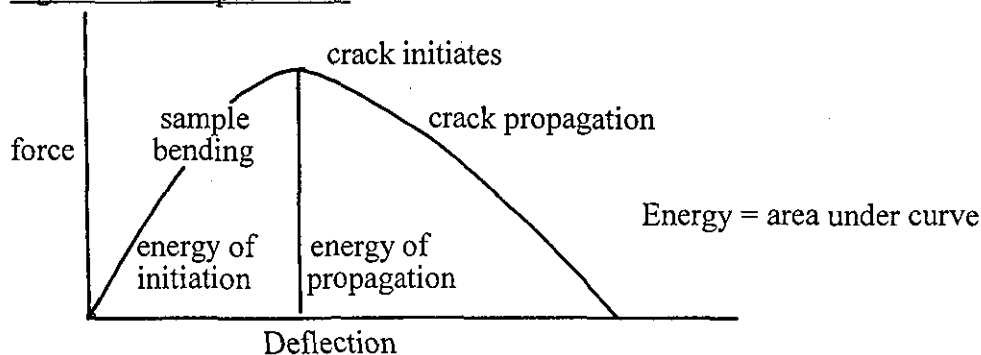
Brittle failure starts with linear viscoelastic behaviour until fracture grows. This means that one of the first activated flaws is transferred immediately into unstable growth and thus triggers off the fracture. Thus the first sign of a drop in force applied is taken as the failure point on the material.

Falling Weight Tests

Normally a loaded striker is dropped from a known height onto a flat sample surface imposing multiaxial stress. In multiaxial impact tests failure does not actually occur over a well-defined area of fracture so that, unlike in the uniaxial or biaxial tests, it is not usually feasible to derive an impact strength as such. However, the multiaxial procedure is useful for assessing changes in impact resistance by comparing, for example, weathered pieces with unweathered controls. A major advantage with this method is that actual products can be used as the test specimen; this is particularly useful if the interaction of processing and material is to be tested such as in quality control, or product specifications. In the test the height of the striker is generally fixed

(Figure 2.16) to fix the velocity and its mass is altered to change the energy.

Figure 2.16: Falling Weight Impact Test
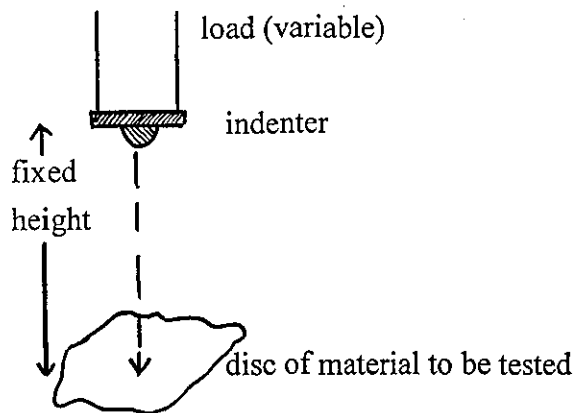
Two methods are then employed to assess the impact strength of a material or product; either the staircase method or the Probit method. With the staircase method the mean input of energy for about 20 trials which fall within the range of `possible failures' is recorded. The Probit method records the fraction of specimens which fail (or fracture) at each energy level; the value corresponding to 50% failure is

recorded as the impact strength of the material or product.

The Instrumented Falling Weight Test is frequently used in quality control and product specifications. A transducer is fitted to the impactor head, which measures the force created by the resistance of the specimen to the high-velocity blow, throughout the few milliseconds associated with the impact event. These force-time data are fed through a charge amplifier, stored on a transient recorder, and can be examined on an oscilloscope.

The total potential energy available at the test initiation point is chosen so that conditions of excess energy exist; that is, the energy absorbed during fracture is much lower than the total kinetic energy of the weight when contact is made. Assuming constant impact-head velocity during failure under these conditions, the read-out can be transposed from force-time to force-deflection, allowing stress, strain and impact energy throughout impact to be calculated.

The type of impact in which an object impinges and rubs or scrapes across the surface of another is a common one in many building operations. For plastics materials resistance to such damage depends on surface hardness and flexibility. Abrasive damage to surfaces includes marring, abrasion and scoring. Such damage, whilst causing deterioration in aesthetic appearance of a component may also provide potential sites of reduced impact resistance. This type of damage may thus have a detrimental effect on subsequent product performance.

Abrasion is also investigated in this study as a method of predicting whether a material will lose impact resistance due to surface cracking on weathering.

Experimental

Samples of 2mm thickness were used to assess the effect of weather on impact resistance. They were exposed in open-back holders in the Xenotest-1200, and under UV-A and UV-B lamps in the Q-UV, as described in section 2.2. Impact testing was carried out with the weathered face in tension, all samples were tested at 23 °C. The instrumented falling weight impact test method was employed. The apparatus used and dimensions are shown in Figure 2.17. Three pieces of each sample type at each exposure were tested.

Samples of nominally 2mm and 3mm thickness were used to test the effect of abrasion on impact resistance. Samples were abraded using the BRE abrasive impact pendulum apparatus[31] and then tested for impact resistance using the

instrumented falling weight method. The abrasive pendulum apparatus comprises a heavy, rigid pendulum that can be dropped from various heights up to $1m^2$. It was used to produce a uniform and reproducible scratch on the surface of the plastic. Samples were scratched with Grade Zero (G0) and grade Two (G2) emery paper. To test reproducibility of the results three materials were chosen on which nine impact test were made.

Figure 2.17 : Instrumented Falling Weight Impactor
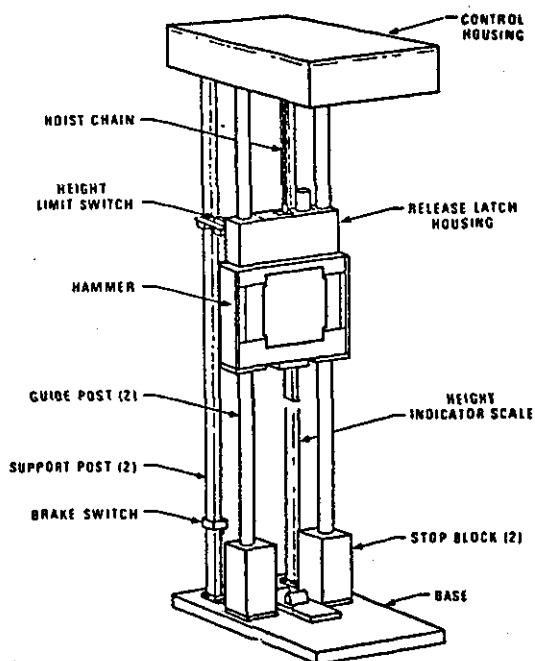
The test equipment consisted of a framework for carrying a guide for the falling dart and a ring to support the samples being tested. To process the data there was a charge amplifier, transient recorder, oscilloscope, recorder, microprocessor and printer. The hemispherically headed dart had a diameter of 12.5mm and the support ring 25mm. The dart of weight 10kg always struck the specimen from a height of 0.431m, weathered face down, with the same impact velocity of $3ms^{-1}$ and a total energy of 45J. The force on the specimen, energy absorbed, time and specimen deflection were all calculated. The whole of the falling dart apparatus was surrounded by a protective

cage and the temperature of the room was kept at a constant 23°C.

Abraded samples were tested scratched face down so that the abraded surface was placed in tension on impact.

CHAPTER THREE : RESULTS

This chapter is constructed into three main sections. The first two deal with characterisation of materials, and characterisation of changes on weathering, each being further sub-divided to include results for the techniques used in each case. The last section concerns the effect of abrasion on impact resistance of unaged samples and shows the significance of such surface changes.

3.1 CHARACTERISATION OF MATERIALS

A number of techniques were used to characterise the composition of the glazing panels as fully as possible. Initially, a qualitative elemental analysis was carried out, followed by functional group analysis. The molecular weight , impact resistance, thermal and optical properties of the materials were also investigated.

3.1.1 Elemental Determination

X-ray fluorescence was used for determining the presence of elements, thus providing information on stabiliser type and other additives. XRF data are given in Tables 3.1-3.3.

Table 3.1 XRF Analysis of Acrylics

Sample	Crystal	2θ	kCts/s	Type
PMMA-1	LiF200	99.9	7.8	2Cu $K_{\alpha1,2}$
		102.9	0.5	I $\quad L_{\alpha1}$
		113.2	0.6	Ca $\quad K_{\alpha1,2}$
	Ge	92.9	0.4	Cl $\quad K_{\alpha1,2}$
		110.8	0.1	S $\quad K_{\alpha1,2}$
	PE	109.2	0.2	Si $\quad K_{\alpha1,2}$
PMMA-2	LiF200	100.1	7.6	2Cu $K_{\alpha1,2}$
		118.2	2.0	K $\quad K_{\beta1}$
		136.1	8.5	K $\quad K_{\alpha1,2}$
	Ge	92.9	0.3	Cl $\quad K_{\alpha1,2}$
		100.8	0.1	S $\quad K_{\beta1}$
		110.8	2.4	S $\quad K_{\alpha1,2}$
	PE	109.2	0.1	Si $\quad K_{\alpha1,2}$
	PX1	22.9	0.2	Mg $\quad K_{\alpha1,2}$

Table 3.2 : Analysis of PVC

Sample	Crystal	2θ	kCts/s	Type
PVC-1	LiF220	19.8	21.5	Sn $K_{\alpha1}$
	LiF200	104.1	0.2	Sn $L_{\beta2}$
		113.1	0.5	Ca $K_{\alpha1,2}$
		114.4	1.1	Sn $L_{\alpha2}$
		136.8	0.2	K $K_{\alpha1,2}$
	Ge	84.7	78.3	Cl $K_{\beta1}$
		92.8	1107.6	Cl $K_{\alpha1,2}$
		141.2	0.2	P $K_{\alpha1,2}$
PVC-2	LiF220	17.5	3.8	Sn $L_{\beta3}$
		19.8	13.0	Sn $K_{\alpha1}$
	LiF200	104.1	0.6	Sn $L_{\beta2}$
		113.1	0.5	Ca $K_{\alpha1,2}$
		126.8	5.3	Sn $L_{\alpha1}$
		136.7	0.3	K $K_{\alpha1,2}$
		84.7	73.6	Cl $K_{\beta1}$
	Ge	92.8	1047.7	Cl $K_{\alpha1,2}$
		100.7	0.2	S $K_{\beta1}$
		110.7	4.5	S $K_{\alpha1,2}$
		141.0	0.3	P $K_{\alpha1,2}$

Table 3.3 : XRF Analysis of Polycarbonates

Sample	Crystal	2θ	kCts/s	Type
PC-1	LiF200	136.8	0.4	K $K_{\alpha1,2}$
		100.2	1.0	Cu $K_{\alpha2}$
		92.9	0.5	Cl $K_{\alpha1,2}$
		110.8	0.1	S $K_{\alpha1}$
		141.2	0.1	P $K_{\alpha1,2}$
	PE	108.2	0.2	Si $K_{\alpha1,2}$
PC-2	LiF200	100.3	7.4	Ca $K_{\beta1}$
		113.8	0.9	Ca $K_{\alpha1,2}$
		136.8	0.3	K $K_{\alpha1,2}$
	Ge	92.9	0.7	Cl $K_{\alpha1,2}$
		110.8	0.1	S $K_{\alpha1,2}$
	PE	109.2	0.3	Si $K_{\alpha1,2}$
	PX1	22.9	0.3	Mg $K_{\alpha1,2}$

3.1.2 Functional Group Determination by ATR-FTIR

A computer programme was used to calculate peak heights. The programme is based on drawing a baseline for each peak and calculating the maximum peak height relative to that baseline. Spectra are given in Figures 3.1-3.7, peak absorbance data are given in Appendix B1.

Figure 3.1 ATR Spectrum of PMMA-1
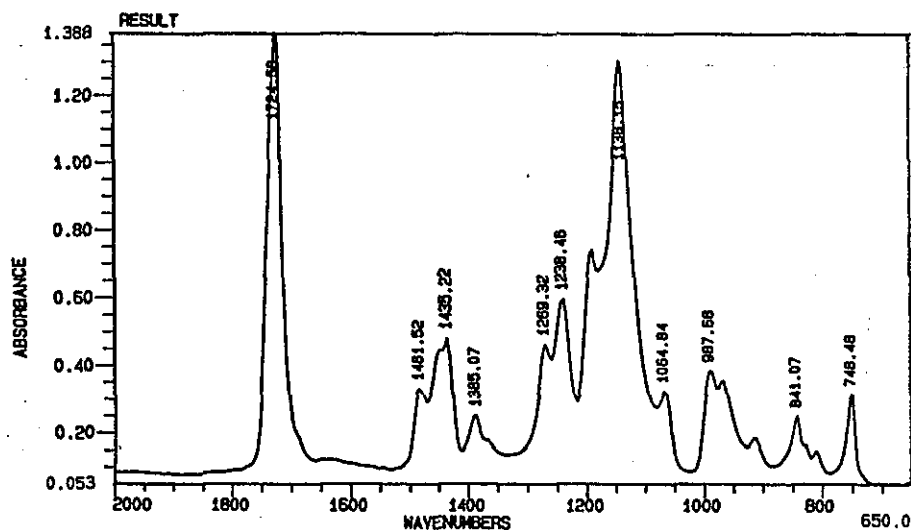
The strong band at 1725cm^{-1} due to the C=O stretching is at relatively high frequency due to the adjacent electronegative oxygen. C-O stretching occurs in the 1300-1020cm^{-1} region. The peaks are characteristic of O=C-O-C stretching.

Figure 3.2 ATR Spectrum of PMMA-2

Figure 3.2 ATR Spectrum of PMMA-2
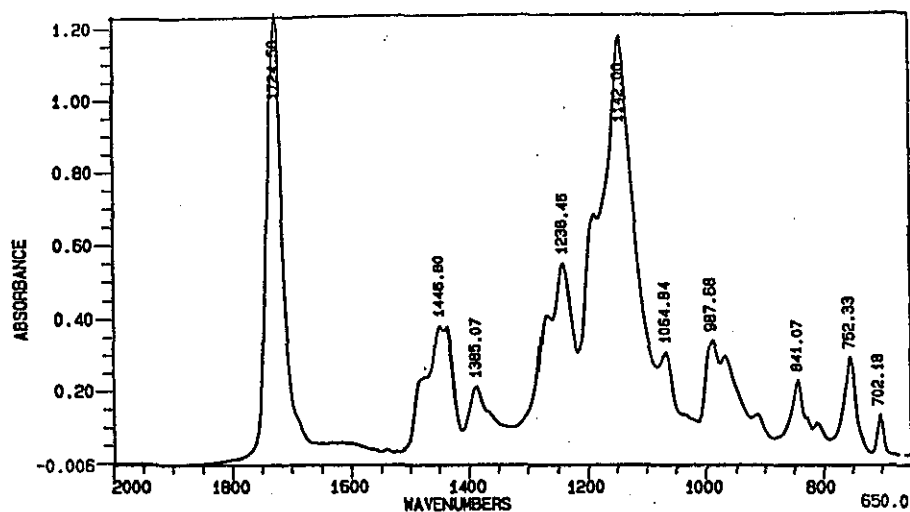
By subtracting pure PMMA (library spectrum) from the spectrum of PMMA-2 it is possible to identify some additives. The subtraction spectrum is shown below:

Figure 3.3: Subtraction Spectrum for PMMA-2

Figure 3.3: Subtraction Spectrum for PMMA-2
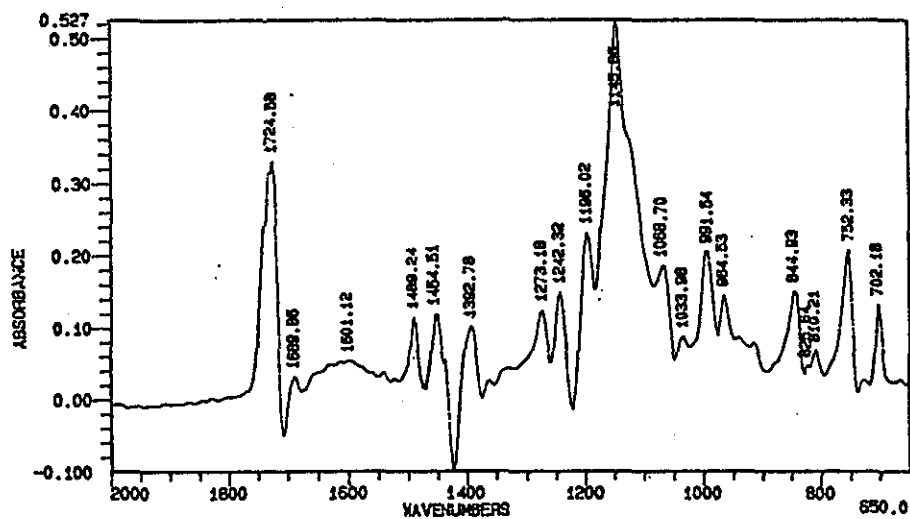
The band at 1725cm^{-1} is indicative of acrylate C=O whilst that at 1145cm^{-1} suggests C-O

94

stretches.

Figure 3.4 ATR Spectrum of PVC-1
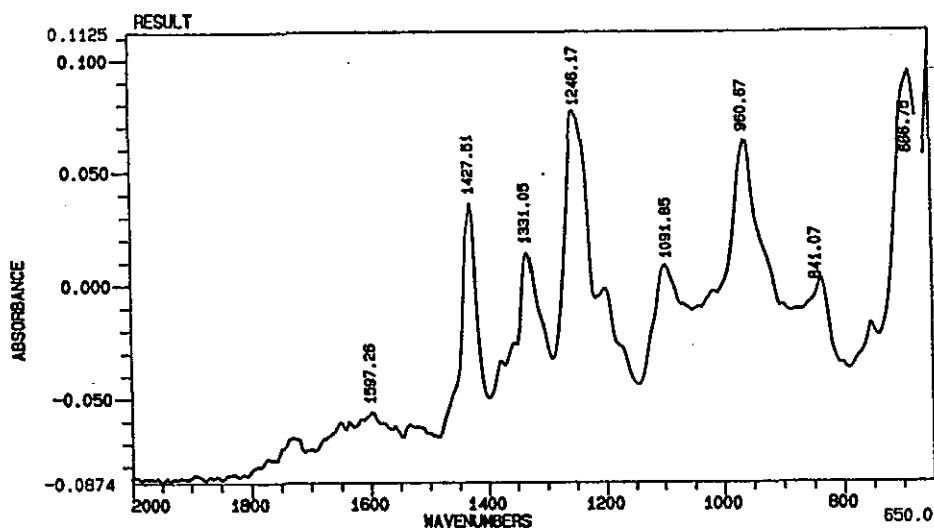
Figure 3.5 ATR Spectrum of PVC-2
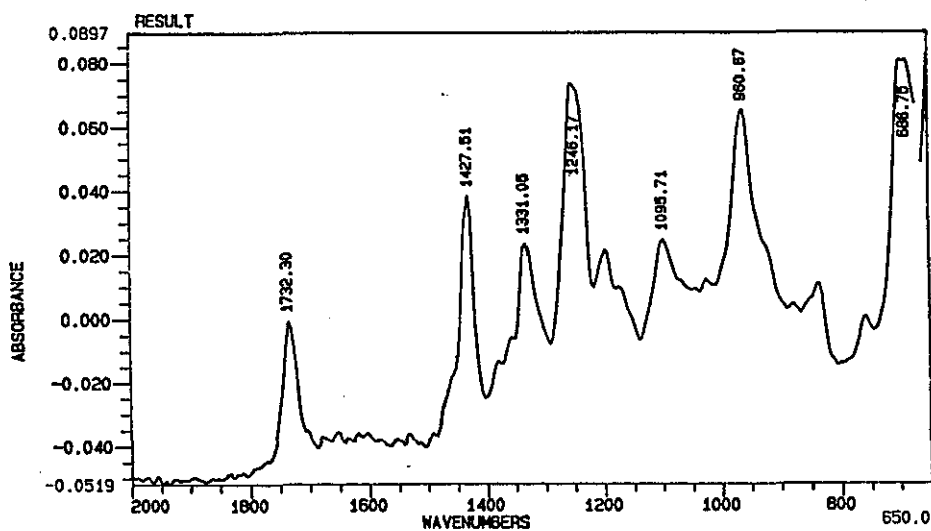
The strong band at $1427 cm^{-1}$ is typical of CH deformation in the CH_2 group and that at $960 cm^{-1}$ of CH deformation in the C-O group. C-Cl stretches are observed at $841 cm^{-1}$ and $686 cm^{-1}$. There also appears to be C=O stretching in the PVC-2 spectrum.

By computer subtracting pure PVC (library spectrum) from the spectra for PVC-1 and PVC-2, it is possible to identify peaks due to the presence of additives. The spectra are given in Appendix B1, a summary of the 'subtraction' peaks is given in Tables 3.4 and 3.5.

Table 3.4 : PVC-1 Subtraction Spectrum

Peak cm^{-1}	Assignment	Peak cm^{-1}	Assignment
2960	>CH$_2$, -CH$_3$	1440	CH$_3$
1730	methacrylate C=O	1110	C-O
1640	C=C	970	C-H, HC=CH
1590	C=O (adjacent to Sn)	840	methacrylate C-H
1510	benzene ring		

Table 3.5 : PVC-2 Subtraction Spectrum

Peak cm^{-1}	Assignment	Peak cm^{-1}	Assignment
2940	>CH$_2$, -CH$_3$	1130	C-O
1730	C=O of ester group, methacrylate group	1090	C-O
1510	benzene ring	970	C-H
1460	CH$_3$	840	C-H

96

Figure 3.6 ATR Spectrum of PC-1

Figure 3.6 ATR Spectrum of PC-1

Figure 3.7 ATR Spectrum of PC-2
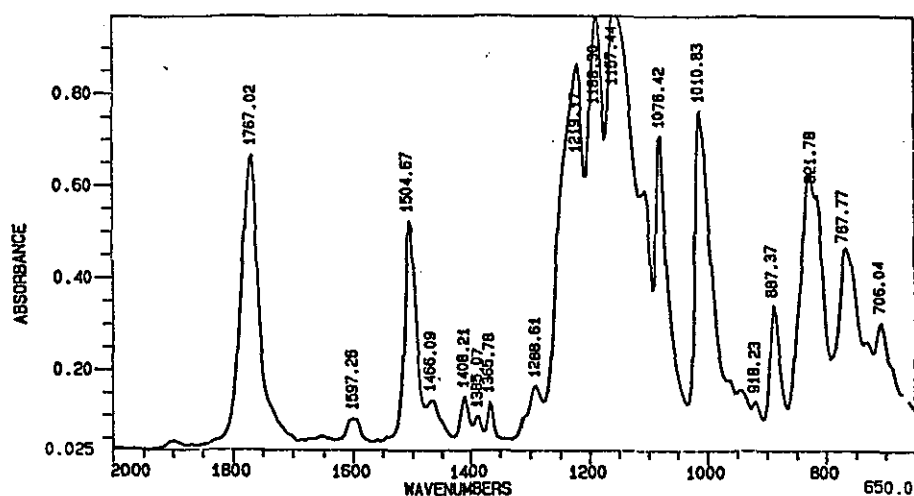
Figure 3.7 ATR Spectrum of PC-2
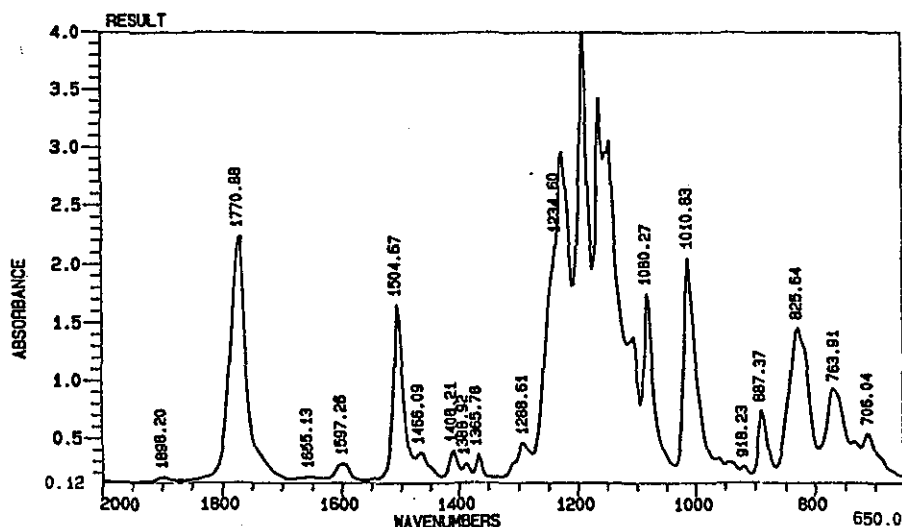
Aromatic groups are characterised by the weak C-H stretching near 3000cm^{-1} and by the strong band at 1504cm^{-1}. The strong band at 821cm^{-1} is characteristic of a p-disubstituted benzene ring, this band is due to the out-of-plane bending vibrations of the C-H groups. The stretching of the C=O group is at relatively high frequency (1770cm^{-1}) due to the electronegative effects of the two adjacent oxygens. The several strong bands in the region 1050cm^{-1} to 1250cm^{-1} are due to the C-O stretches and are characteristic of the O=C-O-C type group.

97

3.1.3 Molecular Weight Distribution Analysis

Results obtained from gel permeation chromatography are summarised in Table 3.6. Full data is given in Appendix B2. The following K and a values were used in the calculation of molecular weight:

PMMA K=1.28E-5 a=6.90E-1

PVC   K=1.50E-5 a=7.70E-1

PC   K=1.04E-5 a=6.97E-1

Table 3.6: MWD Data

Sample	Mn	Mw	Mw/Mn
PMMA-1	694000	2280000	3.29
PMMA-2	46000	98500	2.14
PVC-1	34900	82900	2.37
PVC-2	40500	87000	2.15
PC-1	31100	81800	2.63
PC-2	31500	78800	2.58

3.1.4 Determination of Tg and other Transitions

Tg results obtained using the DuPont thermal analyser with DSC cell are given in Table 3.7. Traces are given in Appendix B3.

Table 3.7: Glass Transition Temperatures

Material	Tg Value °C
PMMA-1	119
PMMA-1	105
PVC-1	72
PVC-2	72
PC-1	145
PC-2	147

Fusion levels and processing temperatures also obtained for PVC samples on the same apparatus are given in Table 3.8.

98

Table 3.8: Fusion Levels in PVC

Sample	Heat of Fusion (J/g)	Processing Temperature (°C)
PVC-1	2.594	189.55
PVC-2	2.382	177.95

To identify other transitions, such as β transitions, DMA was used. The results are given in Table 3.9. DMA traces are given in Appendix B3.

From the DMA results obtained, the storage modulus was observed to decrease with increasing temperature. The loss modulus increased with increasing temperature due to increasing molecular motion. Thus tanδ also increased to a maximum with increasing temperature. The tanδ maximum corresponds to the glass transition temperature of the material at the measured frequency.

Table 3.9: DMA Results

Sample	E' (Gpa) at 30°C	E"$_{max}$ (MPa)	Tg (°C)	Tanδ_{max}
PMMA-1	3.7	271 (125.4°C) 326 (22.4°C)	142.3	1.45
PMMA-2	2.2	153 (112.0°C) 271 (0.9°C)	132.8	1.35
PVC-1	6.0	650 (83.6°C) 276 (-33.4°C)	90.7	0.86
PVC-2	2.7	274 (83.4°C) 128 (-29.0°C)	90.2	0.85
PC-1	2.3	422 (164.3°C)	173.0	1.25
PC-2	2.4	426 (162.1°C)	166.6	1.23

3.1.5 Light Transmission

Levels of light transmission for unaged samples in the UV and visible regions are

given in Table 3.10. The low UV-light transmission values for PMMA-2, both PVC and both polycarbonate samples suggests the presence of UV absorbers. The values given are % light transmission.

Table 3.10: Mean Light Transmission Values

Sample	290-400nm	410-790nm
PMMA-1	53.3	92.9
PMMA-2	14.0	91.1
PVC-1	4.4	84.9
PVC-2	6.9	82.7
PC-1	3.7	88.4
PC-2	4.5	88.6

3.1.6 Impact Resistance

Table 3.11 summarises the impact values for each polymer tested as 2mm thick sheets at 23°C; the values are an average of three readings. The high impact resistance of PMMA-2 suggests the presence of an impact modifier. Typical traces obtained for the two modes of failure are shown in Figures 3.8 and 3.9.

Table 3.11: Impact Resistance Data

Sample	Force at Failure (N)	Displacement to Failure (mm)	Energy at Failure (Nm)	Failure Mode
PMMA-1	283±8	0.81±0.02	0.10±0.0	brittle
PMMA-2	2309±317	5.18±0.11	5.10±0.54	brittle
PVC-1	2707±286	4.97±0.15	5.31±0.78	ductile
PVC-2	2674±26	5.12±0.08	5.27±0.09	ductile
PC-1	2365±99	5.36±0.68	5.13±0.53	ductile
PC-2	2643±102	5.35±0.25	5.81±0.39	ductile

Figure 3.8: Brittle Failure (PMMA-1) Figure 3.9: Ductile Failure (PVC-1)
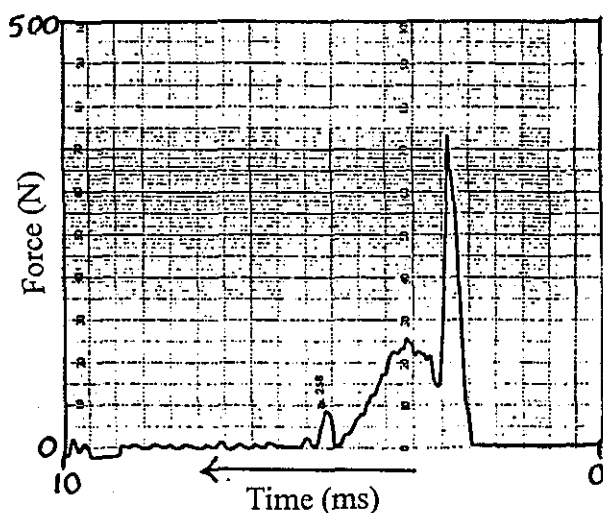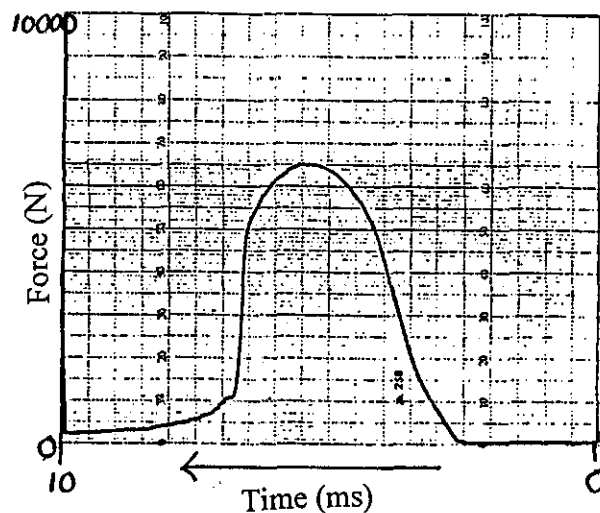
3.2 CHARACTERISATION OF CHANGES ON WEATHERING

Characterisation of chemical, physical, optical and mechanical properties as a function of exposure period and environmental conditions is of key importance. This enables degradation rates and mechanisms to be established for each material in the different regimes.

3.2.1 Analysis of Functional Group changes by PAS-FTIR

Photo-acoustic FTIR was used for examining weathered samples because efficient sample/crystal contact could not be achieved for all samples with the ATR method, resulting in very noisy spectra, as shown in Figure 3.10.

Photo-acoustic spectroscopy gives the best spectral reproducibility for weathered samples since it does not rely on a flat or smooth surface. Earlier work has shown that spectra of reference samples compare well with library spectra[140]. Full results are given in Appendix C1.

Figure 3.10: Comparison of ATR and PAS Spectra for Weathered Materials

PC-2 1500 HOURS EXPOSURE
ATR SPECTRUM

PC-2 1500 HOURS X-1200
PAS SPECTRUM
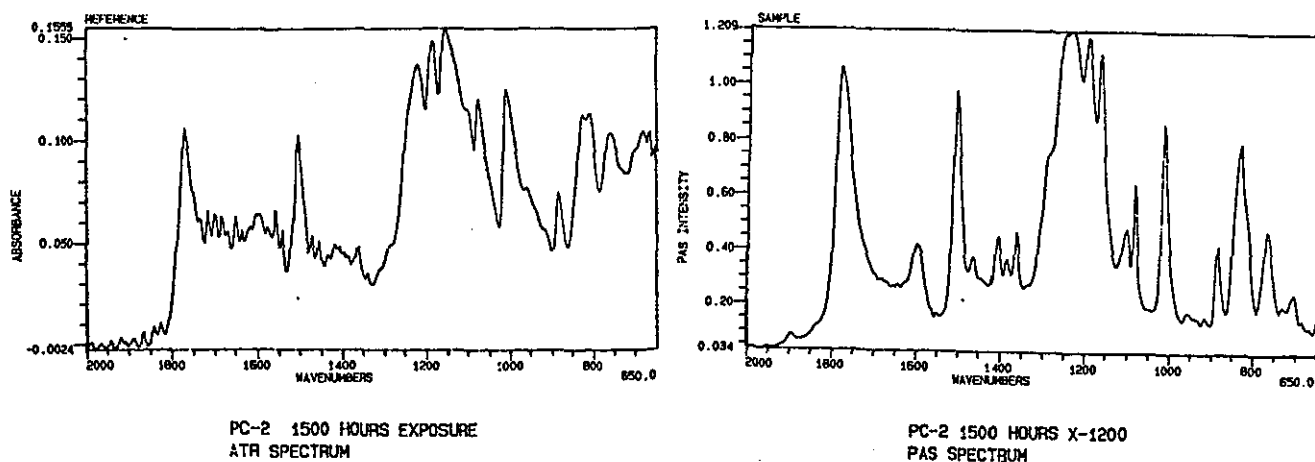
Subtraction spectra were obtained where the sample spectrum is first normalised against a peak in the reference spectrum which is known to be unaffected by exposure to weathering. Negative peaks are observed in some instances; this could be due to a slight shift in peak position or a broadening of the peak due to weathering. The reference spectrum is then subtracted from the sample spectrum to identify any differences. Interpretation of results is given in Chapter 4.

3.2.1.1 Poly(methylmethacrylate)

No detectable difference was identified for PMMA-1 after 14500 hours exposure in the Xenotest 1200. However, there appears to be a slight increase in peaks in the carbonyl region ($1700cm^{-1}$) after exposure in the Q-UV under both UV-A and UV-B lamps as shown in figure 3.11.

102

Figure 3.11 : Subtraction Spectrum for PMMA-1 UV-B Exposure (2000hrs)

Figure 3.11 : Subtraction Spectrum for PMMA-1 UV-B Exposure (2000hrs)
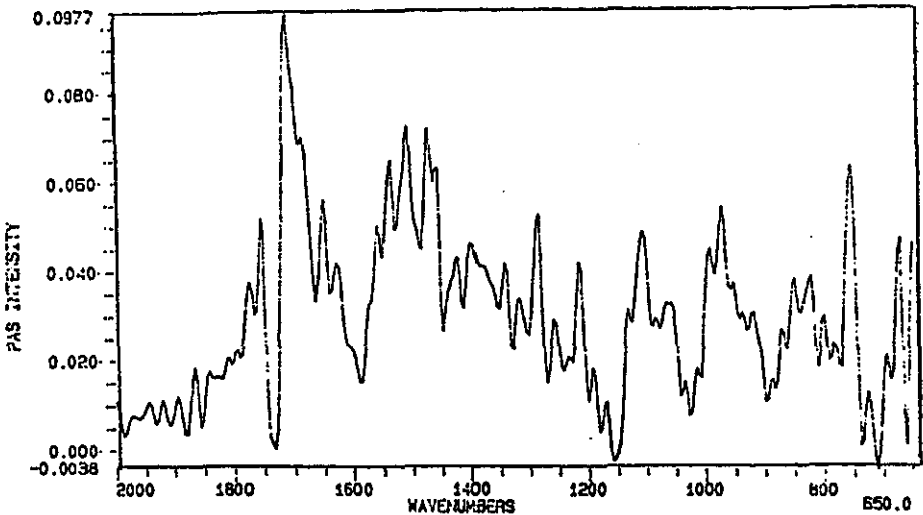
With PMMA-2, after 6750 hours exposure in the X-1200 and 2000 hours in the Q-UV there appears to be an increase in C-O bonding and a slight broadening of the C=O peak. This is more clearly seen in figures 3.12 and 3.13.

Figure 3.12 : Subtraction Spectrum for PMMA-2 X-1200 Exposure(6750hrs)

103
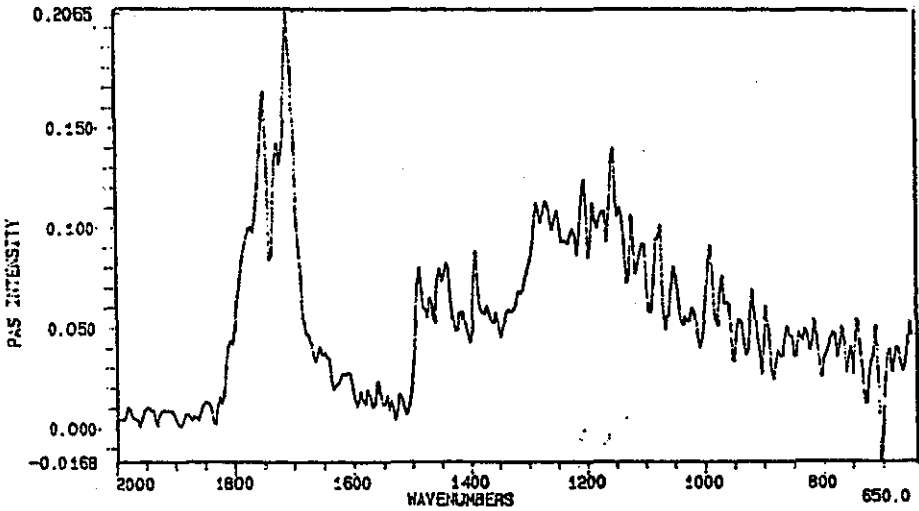
Figure 3.13 : Subtraction Spectrum for PMMA-2 UV-B Exposure (2000hrs)
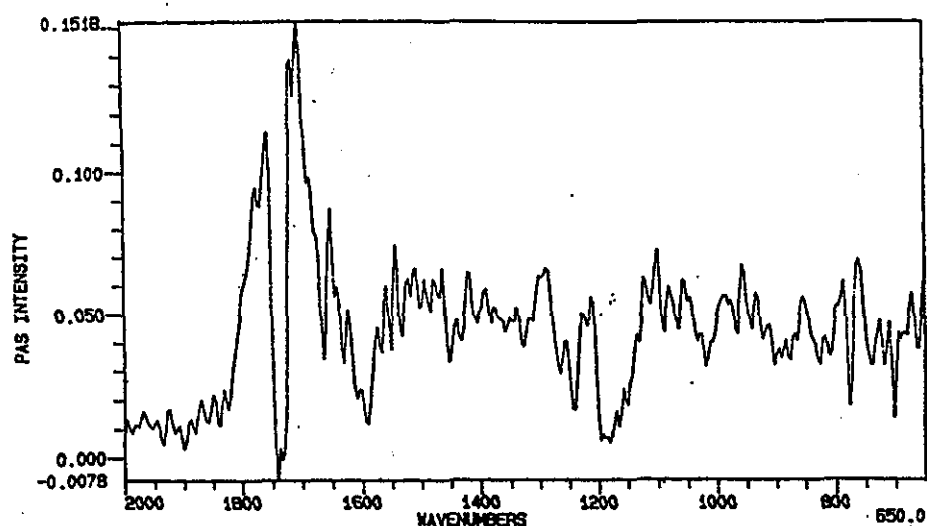
The increase in C-O bonding is seen around 1160 cm^{-1} on and there are apparently two 'new' peaks in the carbonyl region at 1705 cm^{-1} and 1740 cm^{-1}, although it is thought that these could be due to broadening of the original sharp carbonyl peak.

3.2.1.2 Polycarbonate

Subtraction spectra for both polycarbonate samples after exposure in the Xenotest 1200 show several differences between weathered and reference samples (figures 3.14 and 3.15). This suggests complicated photo-oxidation.

Figure 3.14 : Subtraction Spectrum for PC-1 Xenotest 1200 Exposure(2000hrs)
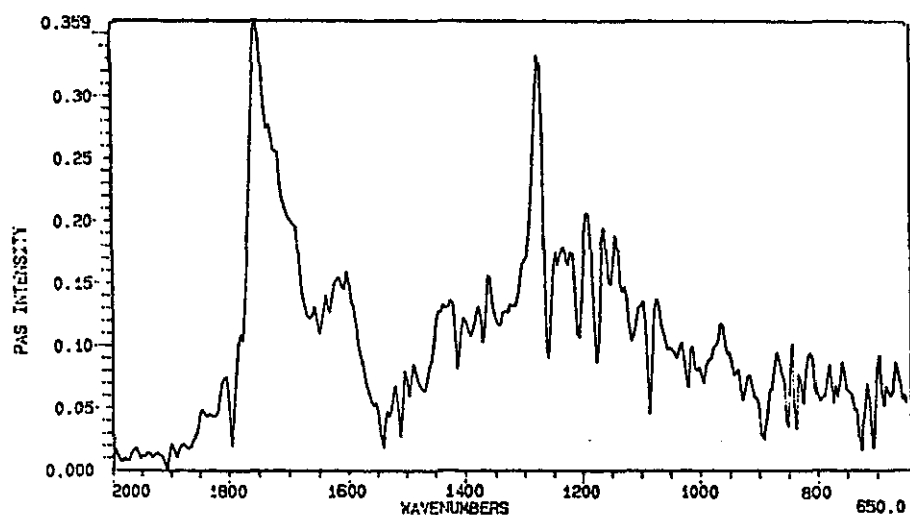
Figure 3.15 : Subtraction Spectrum for PC-2 Xenotest 1200 Exposure(2000hrs)
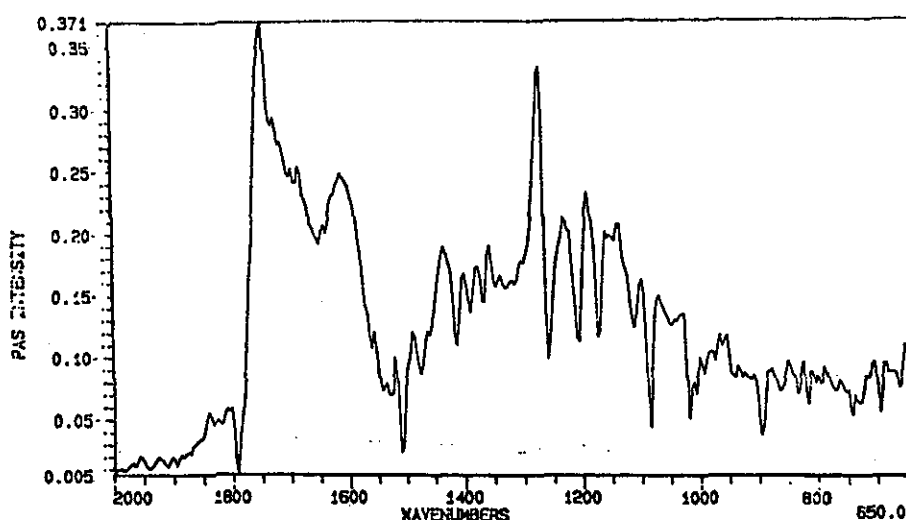
There appears to be less well defined differences between weathered and reference samples for exposure in the Q-UV. UV-A and UV-B exposures produce samples with very similar subtraction spectra. That for exposure to UV-B is shown in figure 3.16, for the subtraction spectrum of UV-A exposure see Appendix C1.

Figure 3.16 : Subtraction Spectrum for PC-1 UV-B Exposure (2000hrs)
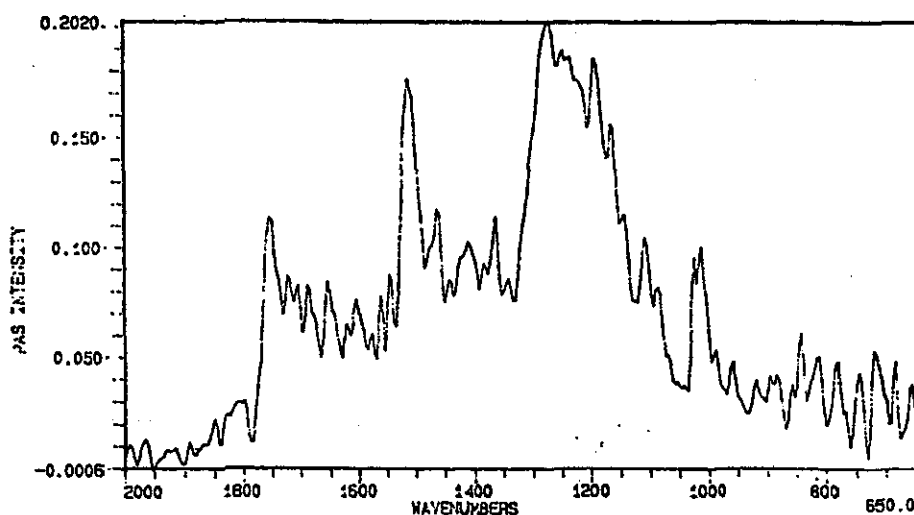
3.2.1.3 Poly(vinylchloride)

Comparison of spectra for reference and weathered samples of PVC-1 exposed in

105

the Xenotest 1200 shows significant changes in the carbonyl absorption region. The subtraction spectra (figure 3.17) shows reduction of a peak at 690 cm^{-1} which could be loss of C-Cl, this would support the view that dehydrochlorination is a significant degradation process for PVC.

There appears to be evidence of C=C formation with an increase in absorption between 700 and 1000 cm^{-1}, again this would support dehydrochlorination leaving polyene sequences.

Four new bands are evident in the carbonyl region at 1715, 1730, 1755 and 1785 cm^{-1}. Q-UV exposure of PVC-1 produces more significant increases in absorptions in the carbonyl region of the spectrum as seen in figure 3.18.

Figure 3.17 : Subtraction Spectrum for PVC-1 X-1200 Exposure (8000hrs)
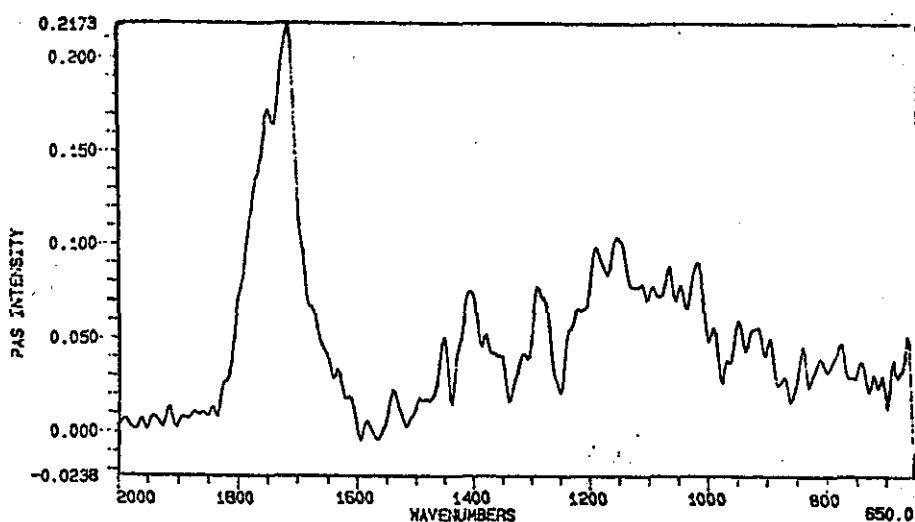
Figure 3.18 : Subtraction Spectrum for PVC-1 UV-B Exposure (2000hrs)
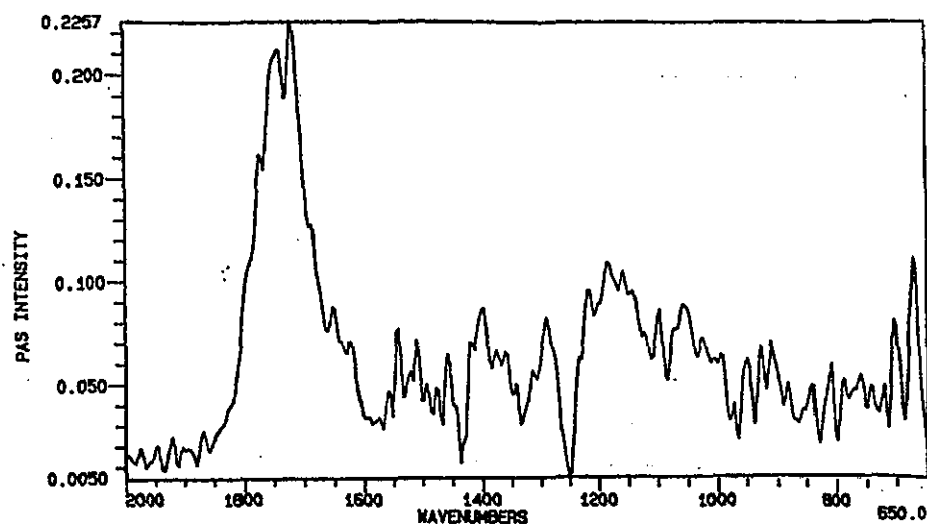
Although exposure to all three light sources causes increases in the same peak absorptions (carbonyl species) the relative intensities of these peaks depends on the lamp type used as shown in Table 3.12.

Table 3.12: Relative Intensity of Carbonyl Species in PVC-1

Peak Abs.cm^{-1}	X-1200	UV-A	UV-B
1718	1.0	1.0	1.0
1730	0.97	0.94	0.98
1755	0.69	0.72	0.95
1785	0.42	0.46	0.55

Exposure also causes an increase in C-O absorption (1150-1200cm^{-1}).

PVC-2 again shows a possible loss of C-Cl which suggests dehydrochlorination (figure 3.19).

107

Figure 3.19 : Subtraction Spectrum for PVC-2 X-1200 Exposure (1500hrs)
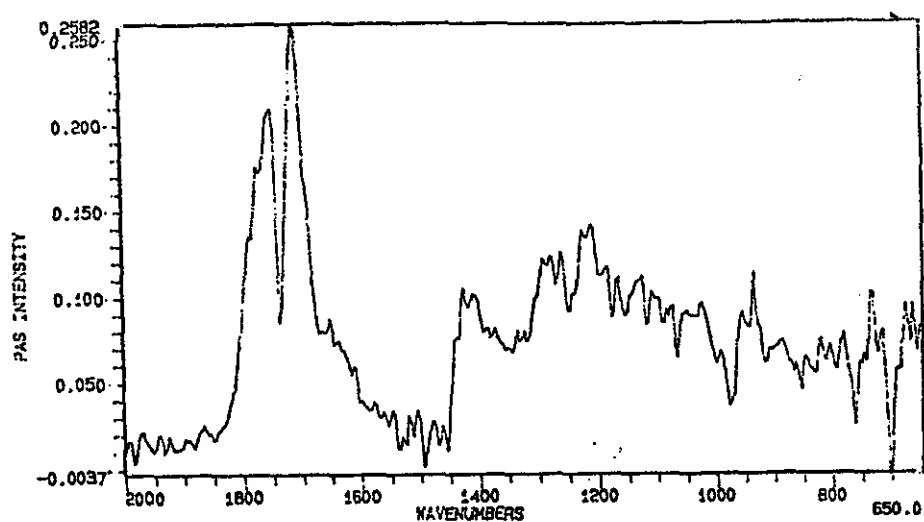
Figure 3.20 : Subtraction Spectrum for PVC-2 UV-B Exposure (2000hrs)
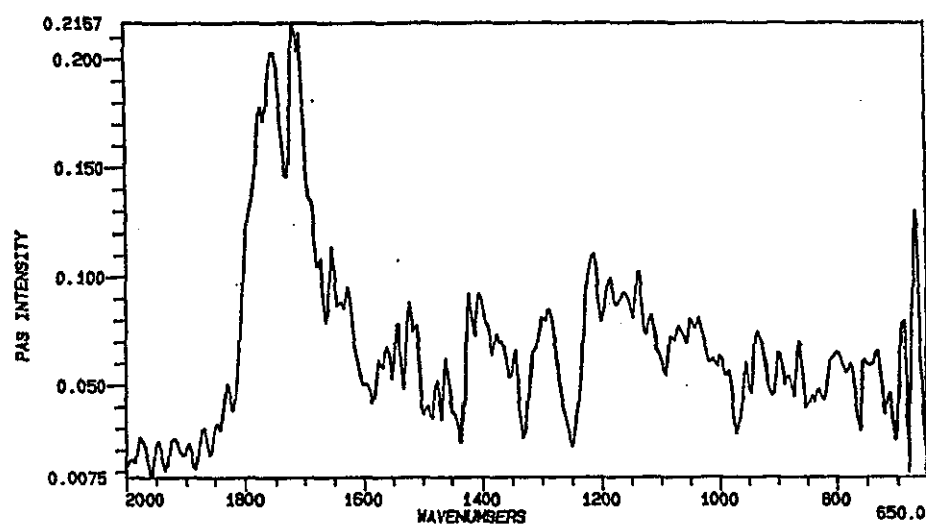
The weathered samples on exposure to all three lamp types show a broadening of the carbonyl peak.

3.2.1.4 Depth Profiling of PVC Samples

For depth profiling studies examination was concentrated on the carbonyl region of the IR spectrum. Figures 3.21 and 3.22 show the spectra obtained for each sample.

108

Figure 3.21 : Depth Profiling PVC-1 (8000hrs)
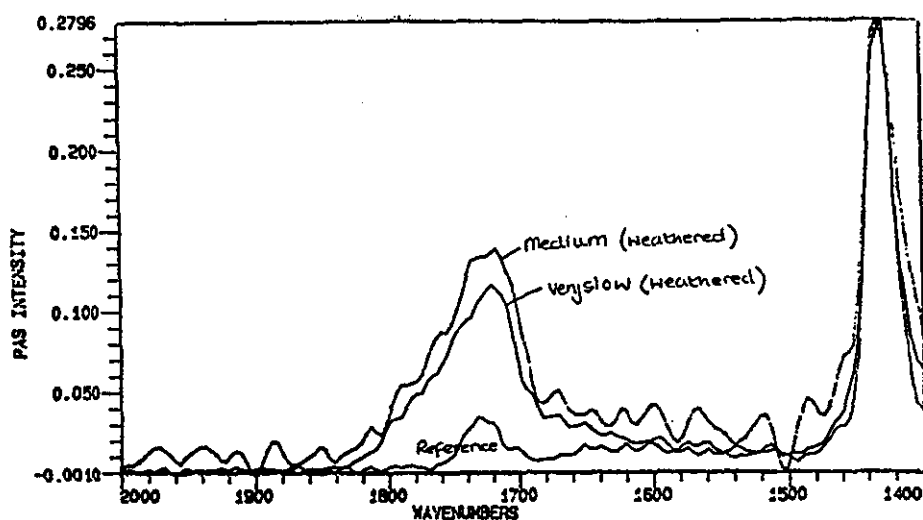
Figure 3.22 : Depth Profiling PVC-2 (1500hrs)
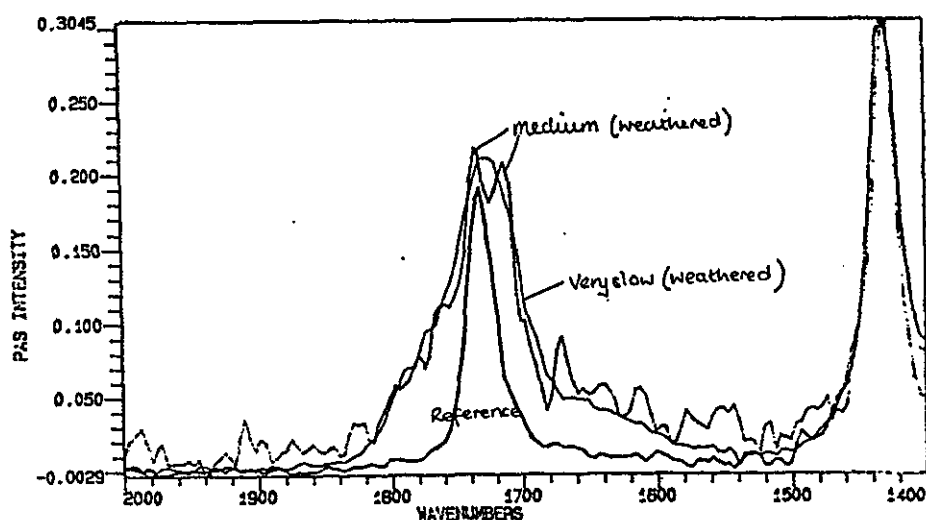
Results are more easily interpreted for PVC-1 where it can be seen that the effects due to weathering are clearly present in the spectrum collected at very slow mirror velocity (0.16 cms^{-1}) i.e. that which allows greatest depth of penetration. This suggests that the weathered layer extends at least 5-20μm into the sample. It was felt that depth profiling in these cases was not sufficiently sensitive to warrant extensive study.

109

3.2.2 Molecular Weight Distribution Analysis

Results obtained from Gel Permeation Chromatography are given in Table 3.13; those for PMMA-1 are also represented in figure 3.23. Traces are given in Appendix C2.

Table 3.13 : MWD Data for Exposed Samples

Sample	Exposure (hrs)	Mn	%ref	Mw	%ref	Mw/Mn
PMMA-1	1000 X-1200	340000	49	765000	34	2.25
	2000	167000	24	510000	22	3.05
	4000	159000	23	399000	18	2.50
	6000	124000	18	299000	13	2.41
	12000	73800	11	225000	10	3.06
	2000 UV-A	132000	19	357000	16	2.70
	2000 UV-B	101000	15	257000	11	2.54
PMMA-2	6750 X-1200	42000	91	81700	83	1.94
PVC-1	8000 X-1200	28700	82	74000	89	2.58
PVC-2	1500 X-1200	33500	83	82400	95	2.46
PC-1	1750 X-1200	24000	77	72100	88	3.00
PC-2	1500 X-1200	25700	82	75700	96	2.94

Figure 3.23: Plot of Mn vs Exposure Time for PMMA-1

110
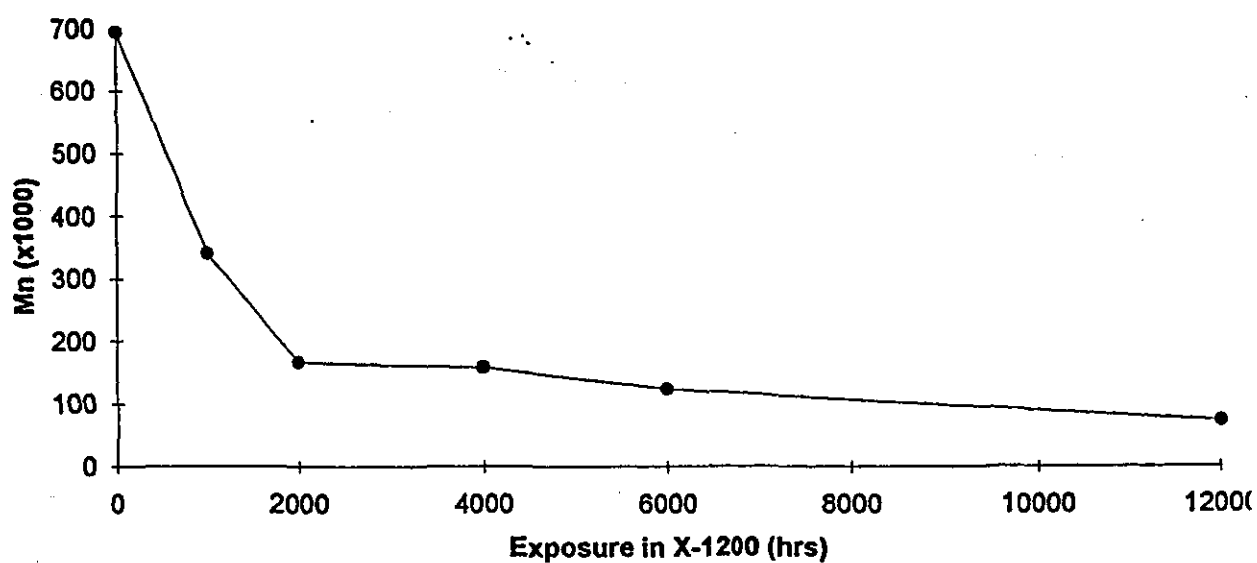
3.2.3 Thermal Analysis

Results from the DuPont thermal analyser with DSC cell are given in Table 3.14. A very slight decrease in Tg was observed for all samples. Traces are given in Appendix C3.

Table 3.14 : Tg Values for Samples Exposed in Xenotest-1200

Material	Exp (hrs)	Tg value
PMMA-1	14500	118
PMMA-2	6750	103
PVC-1	8000	71
PVC-2	1000	70
	1750	69
PC-1	1500	142
PC-2	1500	144

3.2.4 Colour and Gloss Data

Changes in surface gloss, yellowness (δb^*) and overall colour (δE^*) are given in Tables 3.15-3.17. Changes in gloss are given as a percentage of the initial value and colour changes are given as a measured change compared to the initial reference. Full data is given in Appendix C4.

111

Table 3.15: Comparison of Changes in 60° Gloss as Percentage of Initial Value

Device	Xenotest-1200		Q-UV (UV/Condensation Cycle)			
Type	Xenon Arc		UV-A Lamps		UV-B Lamps	
Exposure	Open-back	Black-back	45°/50°	60°/50°	45°/50°	60°/50°
PMMA-1						
500	99.0	99.3	98.2	97.5	97.5	97.5
1000	99.8	99.7	97.3	97.2	97.0	95.7
1500	99.9	99.7	97.8	96.2	97.5	95.2
2000	99.1	99.5	98.0	96.0	97.7	95.0
PMMA-2						
500	98.1	97.7	98.5	95.6	94.8	87.8
1000	100.0	99.5	96.4	79.7	89.2	81.3
1500	100.2	97.1	94.8	77.3	86.1	71.8
2000	99.1	95.7	93.8	76.1	80.3	-
PVC-1						
500	100.1	95.2	100.0	97.2	85.9	58.1
1000	100.9	98.7	98.5	33.6	5.2	12.2
1500	100.8	98.6	72.2	5.8	4.2	9.1
2000	100.8	94.4	27.9	3.3	4.1	7.5
PVC-2						
500	94.4	83.6	89.8	80.1	39.7	32.1
1000	91.3	34.8	75.8	8.0	3.7	12.4
1500	87.1	2.2	19.6	2.2	2.4	5.3
2000	84.5	-	4.7	2.3	1.9	6.0
PC-1						
500	100.5	77.9	97.4	92.3	95.3	91.4
1000	97.2	56.9	86.3	80.9	84.1	84.8
1500	84.0	29.0	80.0	77.8	58.3	75.7
2000	74.9	26.7	70.8	74.4	38.7	70.1
PC-2						
500	98.8	95.6	96.2	93.8	81.8	91.9
1000	96.9	8.7	84.6	80.1	46.2	86.1
1500	88.9	3.1	76.7	74.7	33.6	76.8
2000	86.0	3.9	65.1	70.4	20.7	72.6

Table 3.16 : Comparison of Changes in Yellowness (Db*)

Device	Xenotest-1200		Q-UV (UV/Condensation Cycle)			
Type	Xenon Arc		UV-A Lamps		UV-B Lamps	
Exposure	Open-back	Black-back	45°/50°	60°/50°	45°/50°	60°/50°
PMMA-1 500 1000 1500 2000	0.24 0.31 0.72 0.85	0.47 1.36 1.49 1.45	3.53 4.90 4.83 3.28	4.38 4.56 4.48 3.55	5.71 5.98 5.91 4.67	6.22 6.23 6.92 6.23
PMMA-2 500 1000 1500 2000	-0.48 -0.45 -0.45 -0.35	-1.11 -1.15 -0.39 -0.52	0.71 1.05 1.06 1.01	0.93 1.57 2.26 2.72	1.31 2.12 2.81 3.28	2.12 3.51 5.71 -
PVC-1 500 1000 1500 2000	-1.14 -1.22 -1.13 -1.22	-2.04 -1.90 -1.81 -1.29	-0.41 1.85 5.06 7.35	2.50 14.87 19.15 22.49	7.06 13.74 12.33 12.54	14.47 18.04 19.68 20.47
PVC-2 500 1000 1500 2000	7.06 8.45 8.45 11.88	20.62 33.27 34.13 -	15.49 21.47 27.67 33.73	27.22 36.25 37.38 35.52	32.02 34.95 37.97 39.04	36.09 36.30 30.95 29.80
PC-1 500 1000 1500 2000	1.61 5.66 9.49 8.96	4.19 6.21 7.74 7.79	4.68 8.88 9.62 10.63	6.73 10.64 10.99 11.31	8.39 10.98 10.58 10.98	10.92 11.68 11.81 11.94
PC-2 500 1000 1500 2000	2.65 7.81 10.11 10.89	5.89 17.38 17.00 14.42	6.12 11.28 12.17 12.63	8.75 13.83 14.53 15.18	12.41 13.72 17.00 17.03	12.99 14.06 14.50 14.92

Table 3.17 : Comparison of Total Colour Difference (DE*)

Device	Xenotest-1200		Q-UV (UV Condensation Cycle)			
Type	Xenon Arc		UV-A Lamps		UV-B Lamps	
Exposure	Open-back	Black-back	45°/50°	60°/50°	45°/50°	60°/50°
PMMA-1						
500	0.30	0.60	3.75	4.77	6.07	6.68
1000	0.42	1.43	5.13	4.90	6.31	6.73
1500	0.86	1.57	5.14	4.90	6.29	7.46
2000	0.98	1.61	3.49	4.12	4.96	6.88
PMMA-2						
500	0.51	1.42	0.72	1.30	1.39	2.57
1000	0.50	1.40	1.13	2.29	2.42	4.47
1500	0.52	0.80	1.19	3.35	3.37	6.87
2000	0.50	0.87	1.29	4.08	4.26	-
PVC-1						
500	1.26	2.60	0.88	2.92	7.71	17.44
1000	1.33	2.56	2.25	18.69	21.16	23.11
1500	1.19	2.36	5.81	26.45	18.88	25.61
2000	1.33	1.79	11.63	31.08	19.18	27.79
PVC-2						
500	8.35	22.00	15.96	28.90	35.77	44.60
1000	9.72	44.39	22.56	47.50	42.96	49.28
1500	10.13	45.26	32.78	51.80	50.16	53.04
2000	13.84	-	40.56	51.88	51.64	54.68
PC-1						
500	1.74	4.57	4.88	7.13	8.78	11.47
1000	5.98	7.63	9.34	11.23	11.45	12.31
1500	10.15	9.61	10.22	11.69	11.12	12.46
2000	9.78	9.19	11.41	12.17	11.62	12.72
PC-2						
500	2.85	6.23	6.39	9.20	12.98	13.57
1000	8.25	22.12	11.81	14.46	14.36	14.68
1500	10.81	21.64	12.81	15.34	17.83	15.15
2000	11.70	18.68	13.48	16.17	17.93	15.68

3.2.5 Changes in Light Transmission

Spectra were obtained for reference and weathered samples (exposed at the lower temperature cycles) and the average light transmission calculated. Data tables are given in

114

Appendix C4. Figures 3.24-3.29 represent the measured changes.

Figure 3.24: PMMA-1. % Remaining Light Transmission

PMMA-1 UV region 290-400nm

PMMA-1 Visible region 410-790nm

115
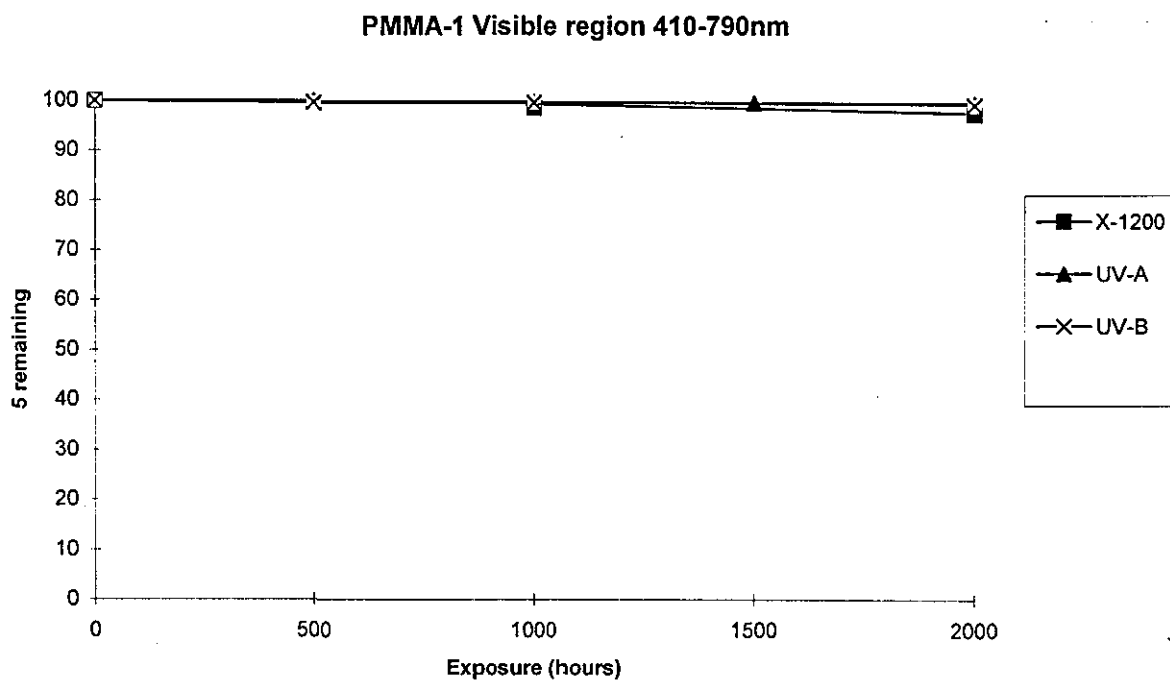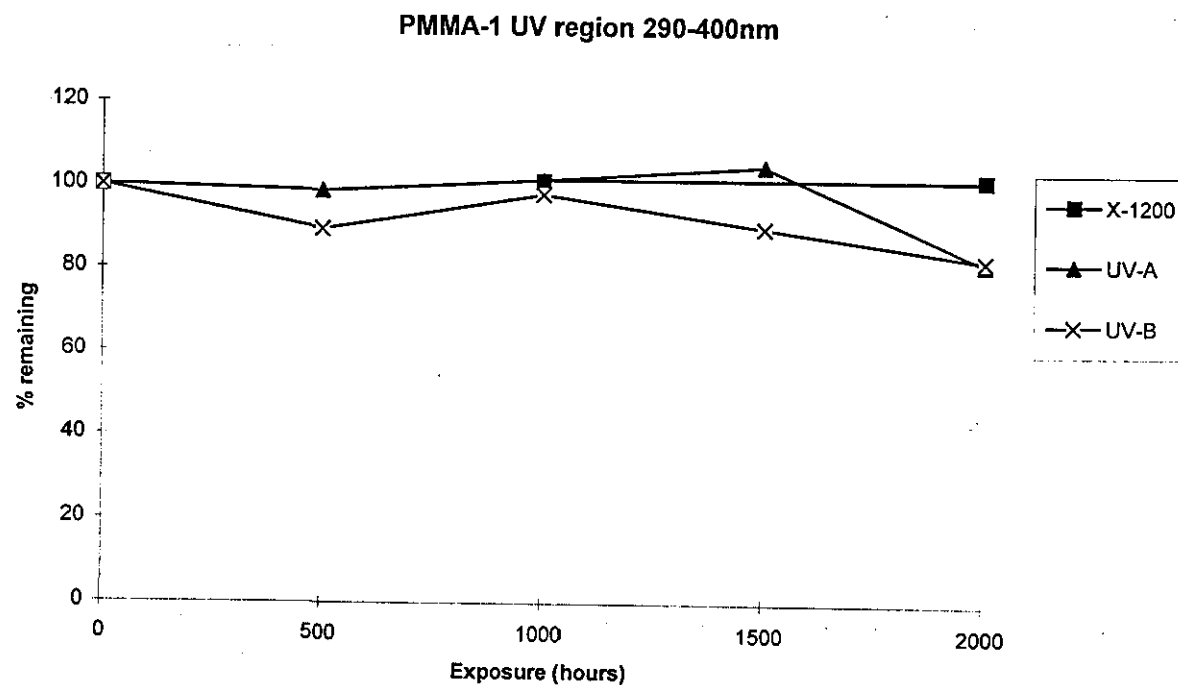
Figure 3.25: PMMA-2. % Remaining Light Transmission

PMMA-2 UV region 290-400nm

PMMA-2 Visible region 410-790nm

116

PVC-1 UV region 290-400nm

PVC-1 Visible region 410-790nm

117
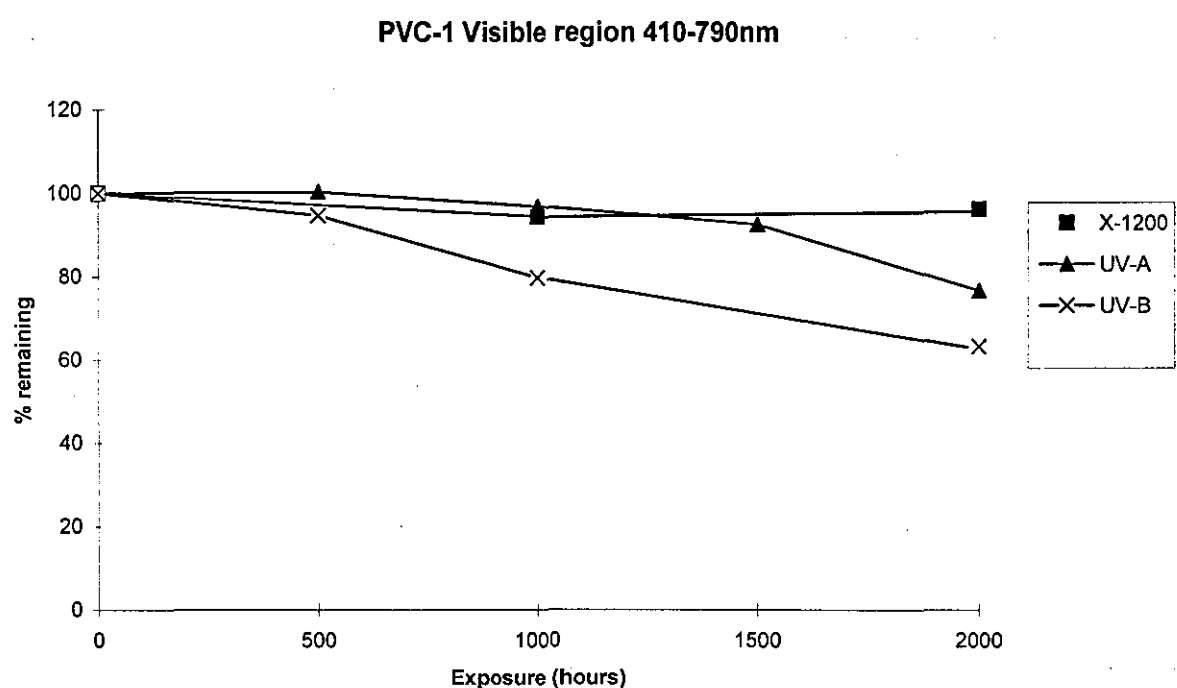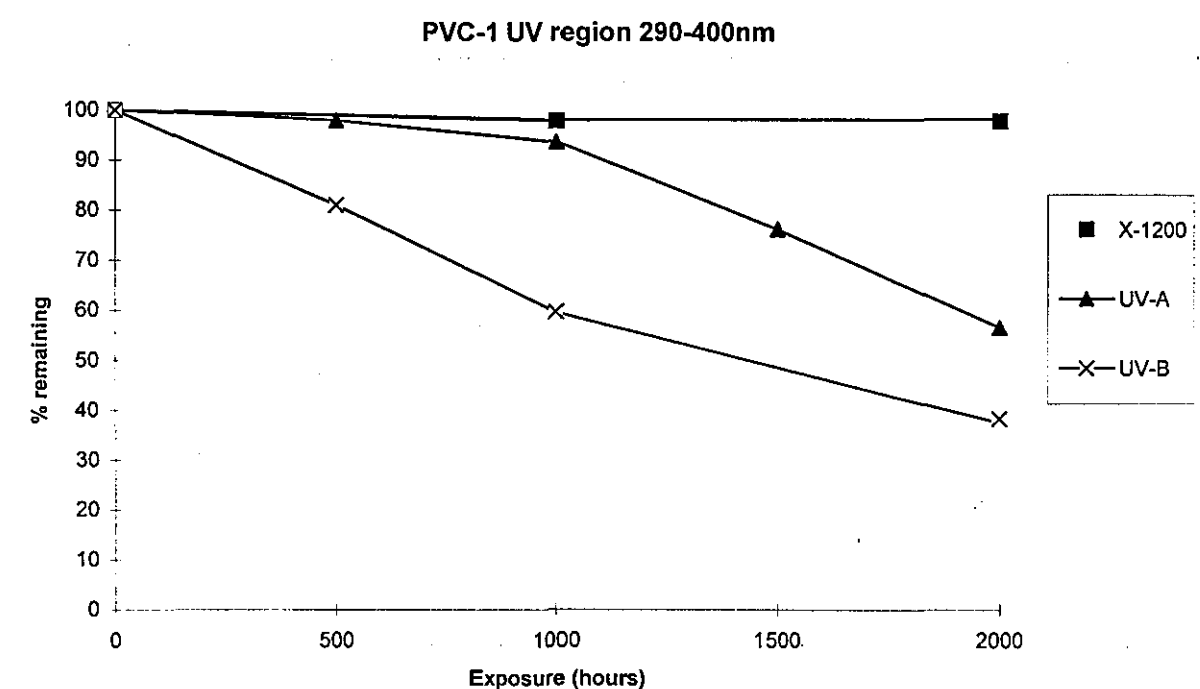
Figure 3.27: PVC-2. % Remaining Light Transmission

PVC-2 UV region 290-400nm

PVC-2 Visible region 410-790nm
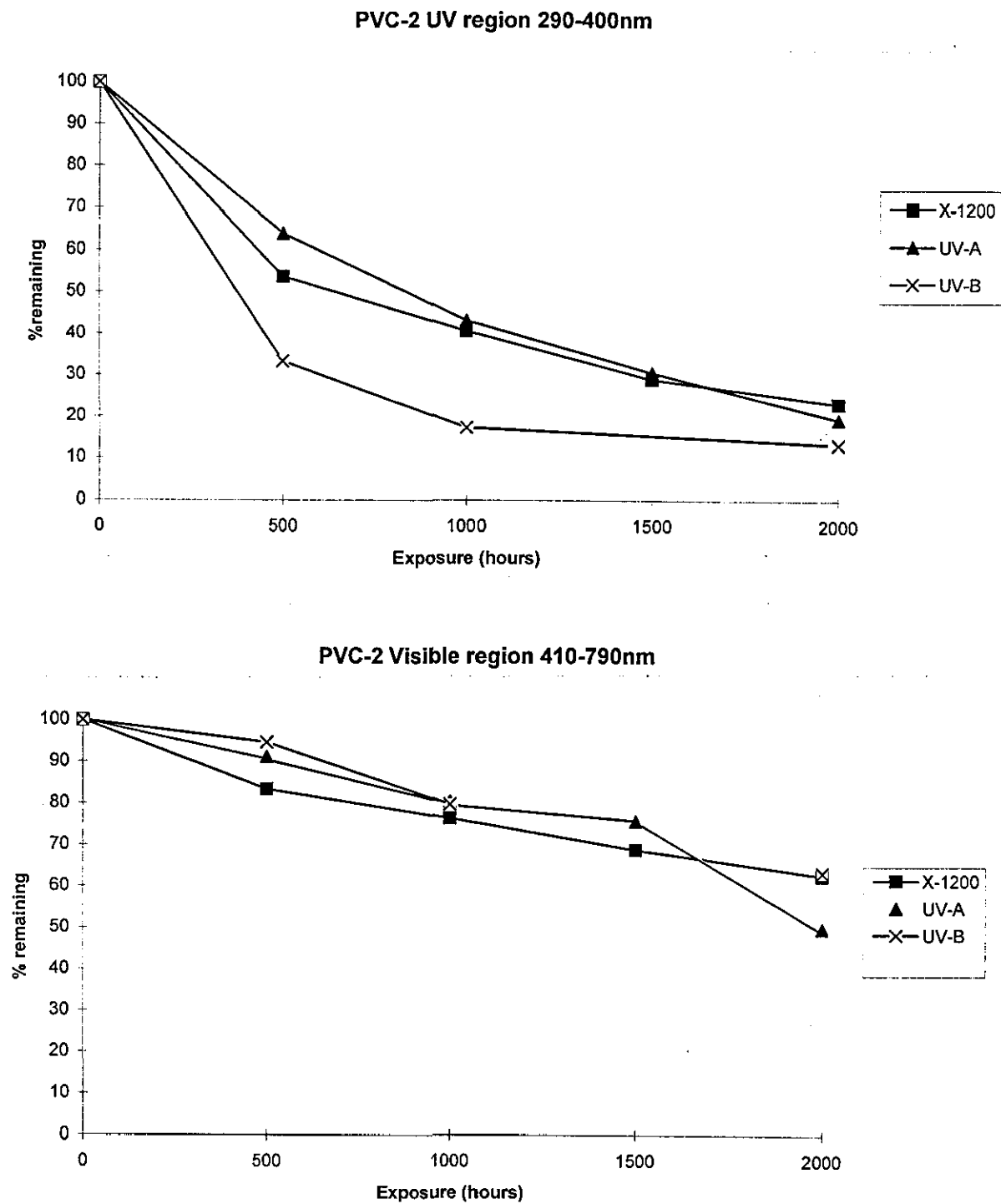
Figure 3.28: PC-1. % Remaining Light Transmission

PC-1 UV region 290-400nm

PC-1 Visible region 410-790nm
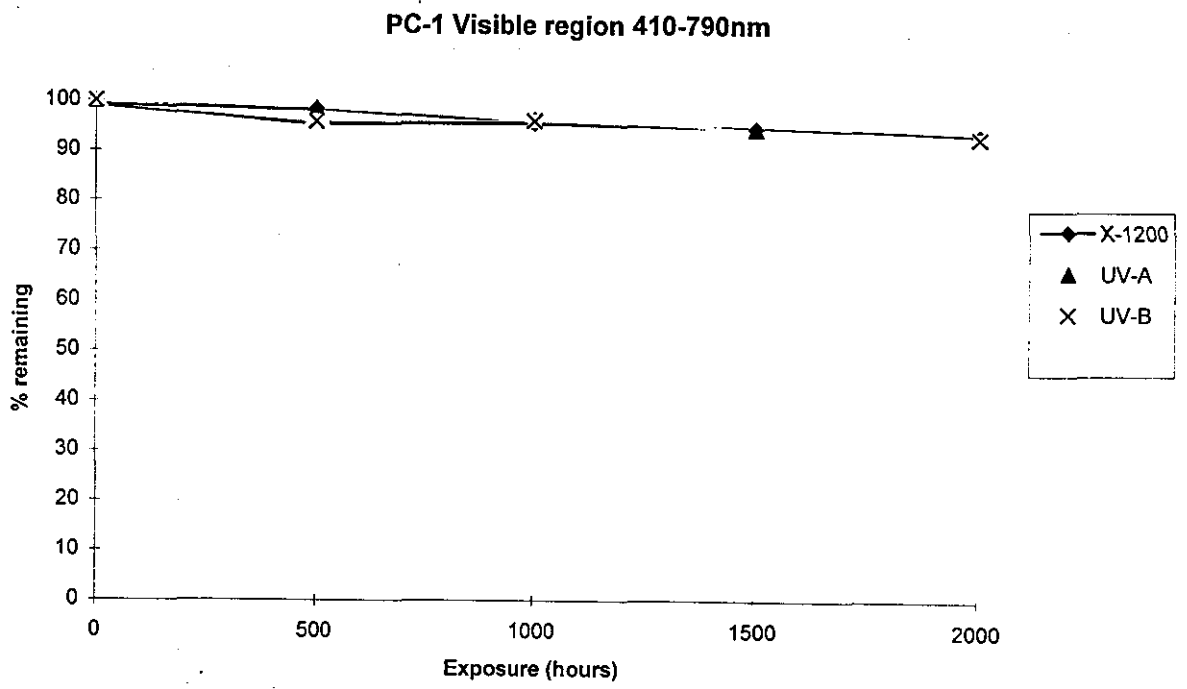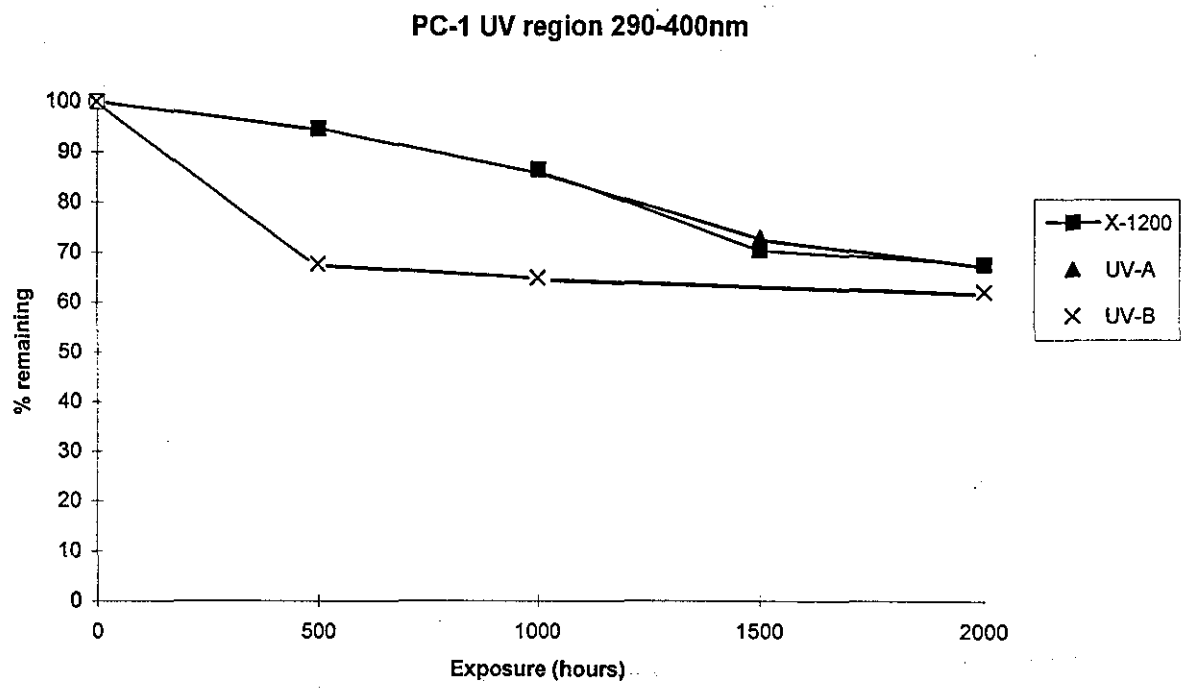
Figure 3.29: PC-2. % Remaining Light Transmission

PC-2 UV region 290-400nm

PC-2 Visible region 410-790nm
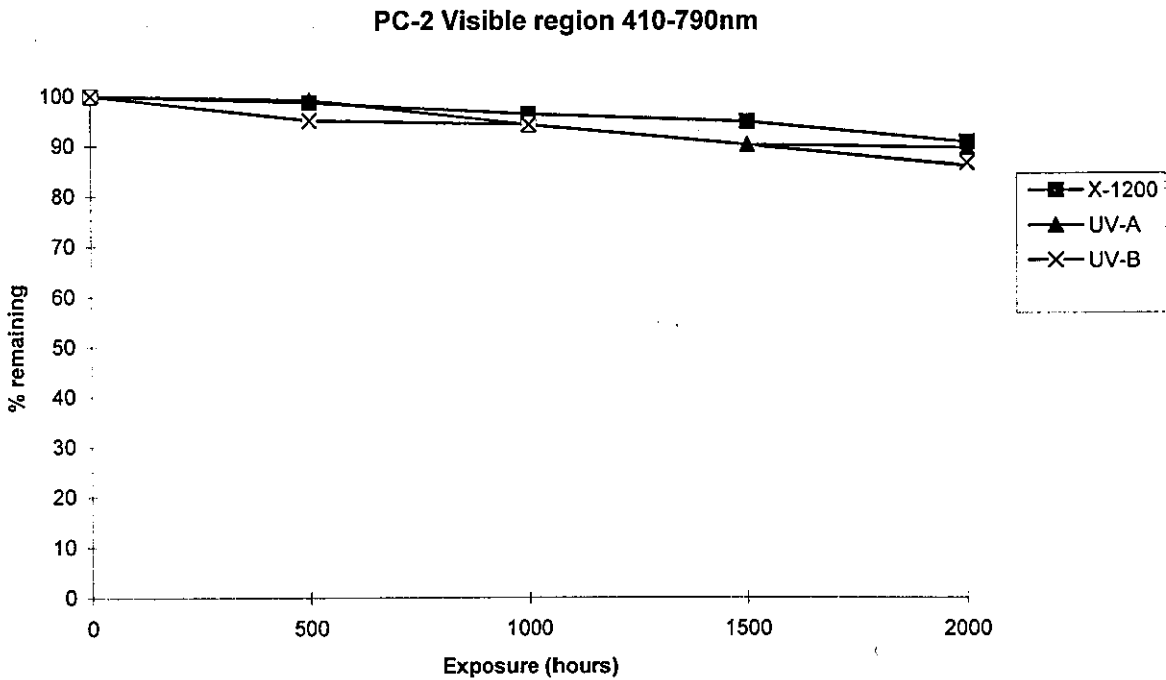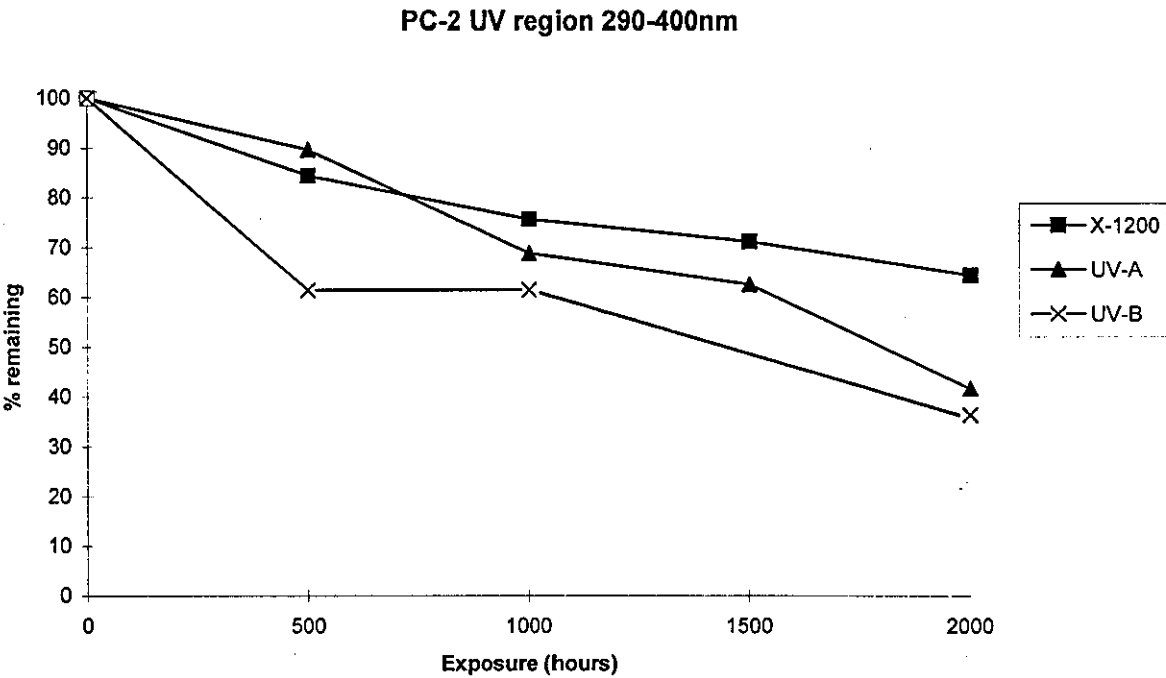
3.2.6 Optical Microscopy

Samples were examined at 500x magnification to identify surface cracking or other defects. Results are summarised in Table 3.18, results for Q-UV samples are for the lower temperature exposure cycle (45°C /50°C) and for the open-back Xenotest cycle. Typical surfaces are represented in Figures 3.30-3.43. The unexposed face of each sample showed no cracking. The scale is each micrograph represents an area 70 microns by 50 microns.

Figure 3.30: Surface Micrograph of PMMA-1, 2000hrs X-1200
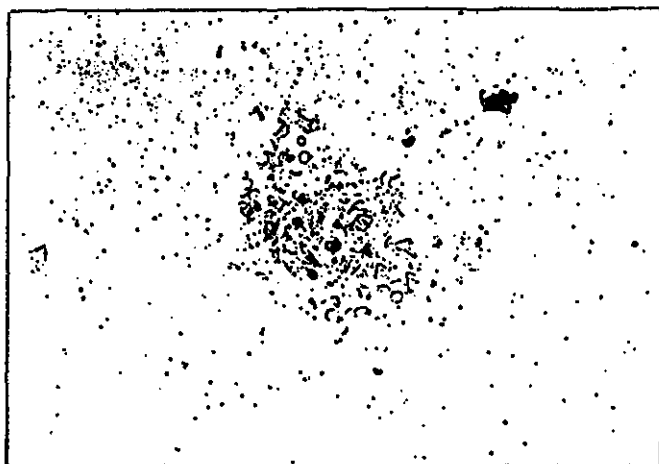
Figure 3.31: Surface Micrograph of PMMA-2, 2000hrs X-1200
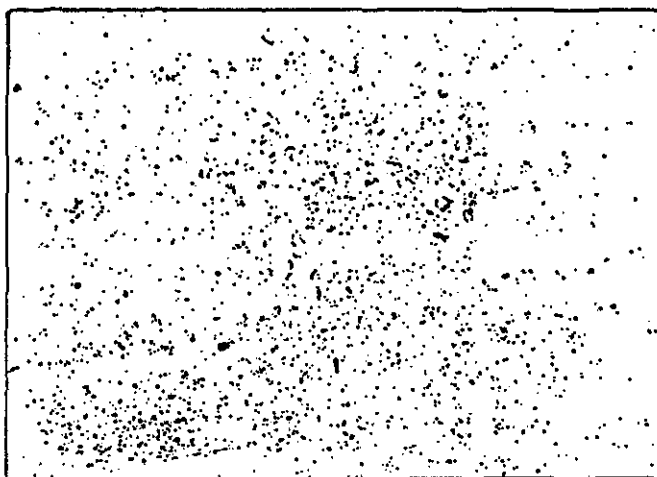
Figure 3.32: Surface Micrograph of PVC-1, 2000hrs X-1200
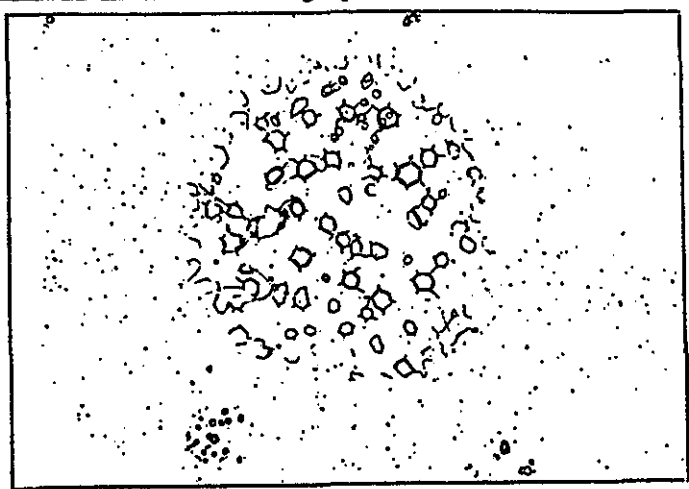
Figure 3.33: Surface Micrograph of PVC-1, 2000hrs UV-A
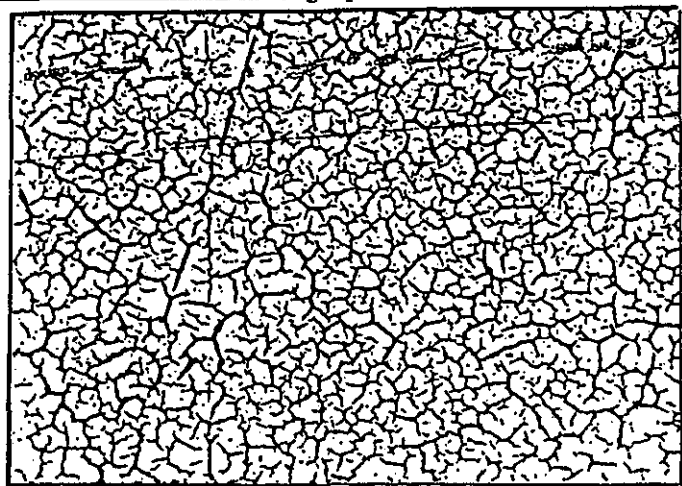
Figure 3.34: Surface Micrograph of PVC-1, 2000hrs UV-B
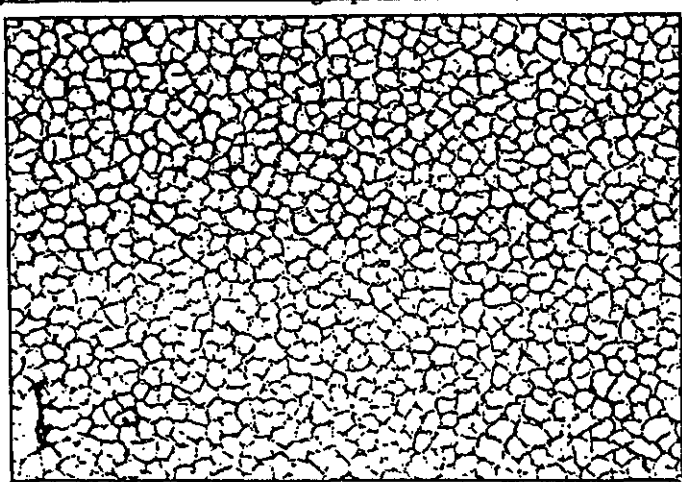
Figure 3.35: Surface Micrograph of PVC-2, 500hrs UV-B
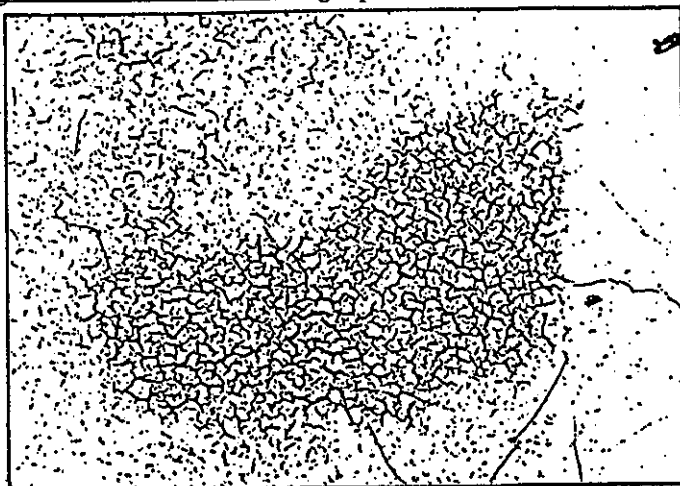
Figure 3.36: Surface Micrograph of PVC-2, 1000hrs UV-B
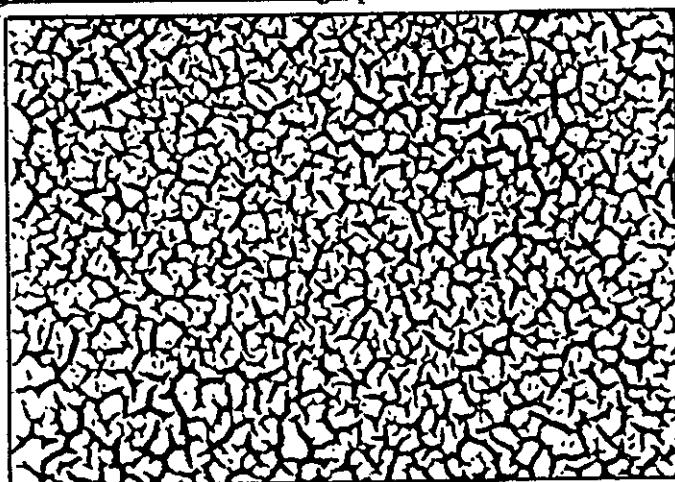
Figure 3.37: Surface Micrograph of PVC-2, 2000hrs UV-B

123
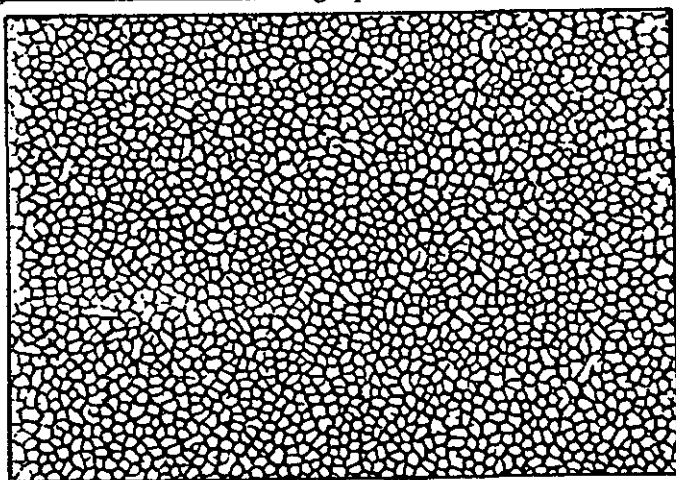
Figure 3.38: Surface Micrograph of PC-1, 2000hrs X-1200

Figure 3.39: Surface Micrograph of PC-1, 3500hrs X-1200
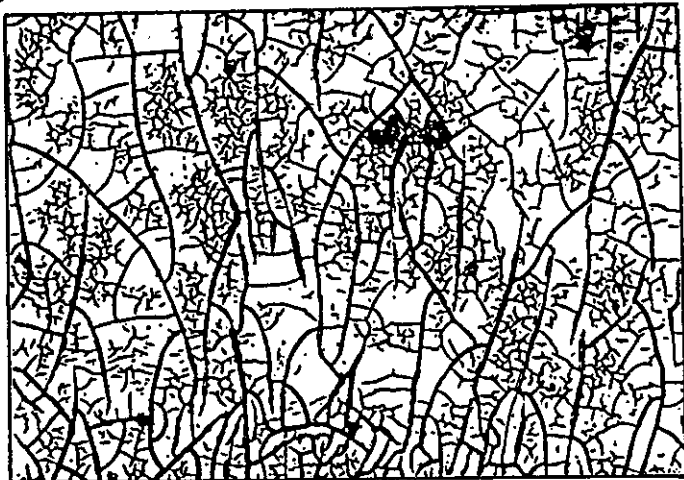
Figure 3.40: Surface Micrograph of PC-1, 2000hrs UV-A
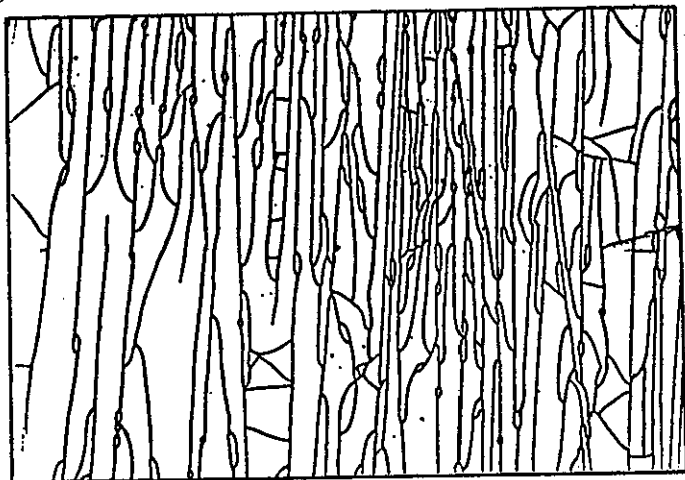
Figure 3.41: Surface Micrograph of PC-2, 2000hrs X-1200

Figure 3.42: Surface Micrograph of PC-2, 2000hrs UV-A
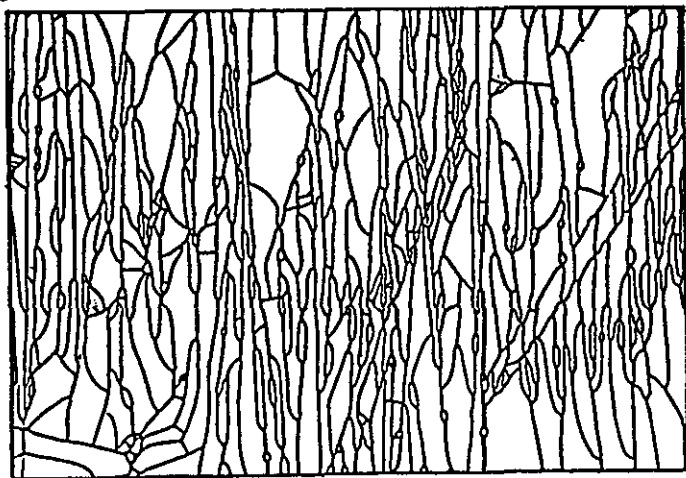
Figure 3.43: Surface Micrograph of PC-2, 2000hrs UV-B
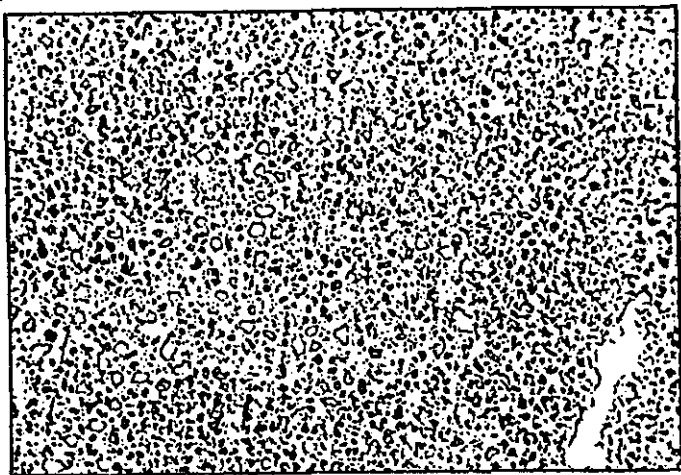
Table 3.18: Summary of Microscopy Results

Sample	Exposure		Observations
PMMA-1	X-1200 OB UV-A/UV-B	2000hrs 2000hrs	small areas of surface breakdown no detectable changes
PMMA-2	X-1200 OB UV-A/UV-B	2000hrs 2000hrs	beginnings of surface breakdown no detectable changes
PVC-1	X-1200 OB UV-A UV-B 	1000hrs 2000hrs 4000hrs 1000hrs 2000hrs 500hrs 1000hrs 2000hrs	many small cracks, uniform direction fewer cracks, areas of surface degradation surface completely degraded surface O.K. surface cracked surface O.K. surface cracked surface completely degraded
PVC-2	X-1200 OB UV-A UV-B 	250hrs 1000hrs 2000hrs 1000hrs 1500hrs 2000hrs 500hrs 1000hrs 2000hrs	some fine cracks, uniform direction fewer cracks, surface degraded surface totally degraded some small fine cracks surface very cracked, larger cracks surface totally degraded areas of small fine cracks whole surface cracked, larger cracks surface totally degraded
PC-1	X-1200 OB BL UV-A UV-B	1000hrs 2000hrs 3500hrs 500hrs 750hrs 1000hrs 2000hrs 2000hrs	small fissures in some areas fine cracks and thicker cracks, joining up larger cracks with smaller cracks branching off surface O.K., some areas of fine cracks very high density of large cracks faint 'spotting' in background, some fine random cracks higher density of fine cracks which seem more oriented 'spotting' of surface, some evidence of fine long cracks
PC-2	X-1200 OB UV-A UV-B	1000hrs 2000hrs 3500hrs 1000hrs 2000hrs 2000hrs	very small fissures, many joined together cracks much longer, also some fine cracks large cracks with small cracks branching off network of fine random cracks higher density of fine cracks 'spotting' of surface

3.2.7 Effects on Impact Resistance

Tables 3.19 to 3.21 summarise impact data for weathered samples (2mm thick) tested with the weathered face in tension. Samples were weathered using the lower temperature cycles.

Table 3.19 : Effect of Xenotest-1200 Weathering on Impact Properties

Sample Exp.(hrs)	Force at Failure (N)	Displacement to Failure(mm)	Energy at Failure (Nm)	Energy Retained[*] (%)	Failure Mode
PMMA-1 14500	281 ± 34	0.92 ± 0.03	0.11 ± 0.0	100	Brittle
PMMA-2					
250	2361 ± 211	4.45 ± 0.49	4.33 ± 1.35	85	Brittle
750	2343 ± 153	4.17 ± 0.28	4.18 ± 0.54	82	Brittle
1000	2224 ± 446	4.10 ± 0.66	3.86 ± 1.16	76	Brittle
1250	850 ± 223	2.49 ± 0.29	1.05 ± 0.31	20	Brittle
4250	579 ± 12	1.79 ± 0.03	0.47 ± 0.03	9	Brittle
8000	145 ± 25	1.37 ± 0.30	0.13 ± 0.04	3	Brittle
PVC-1					
500	3392 ± 43	4.80 ± 0.15	6.35 ± 0.11	120	Ductile
750	3575 ± 102	4.39 ± 0.01	6.77 ± 0.13	127	Ductile
1000	3637 ± 69	4.68 ± 0.23	7.19 ± 0.06	135	Ductile
1000	980	1.81	0.94	17	Brittle
1250	883 ± 104	1.75 ± 0.21	0.71 ± 0.19	13	Brittle
2500	246 ± 53	2.75 ± 0.17	0.36 ± 0.14	7	Brittle
8000	254 ± 26	2.32 ± 0.28	0.35 ± 0.07	7	Brittle
PVC-2					
110	2829 ± 47	4.90 ± 0.15	5.59 ± 0.11	104	Ductile
250	2835 ± 2	5.63 ± 0.28	5.84 ± 0.16	109	Ductile
250	337 ± 42	1.50 ± 0.34	0.27 ± 0.12	5	Brittle
390	447 ± 47	1.91 ± 0.33	0.47 ± 0.13	9	Brittle
500	337 ± 35	1.80 ± 0.40	0.53 ± 0.13	9	Brittle
3750	356 ± 48	2.03 ± 0.48	0.41 ± 0.17	7	Brittle
PC-1					
3750	2573 ± 117	4.56 ± 0.03	4.88 ± 0.17	95	Ductile
5750	2628 ± 46	4.84 ± 0.02	5.08 ± 0.10	99	Ductile
PC-2					
3750	2608 ± 36	4.71 ± 0.07	5.09 ± 0.06	88	Ductile
5750	2853 ± 4	4.96 ± 0.08	5.60 ± 0.04	96	Ductile

* see Table 3.11 for unweathered control values. Energy retained is the energy at failure for a weathered sample expresed as a percentage of the energy at failure for the control sample. The values are an average of 3 readings with ± standard deviations quoted. Full data and failure details are given in Appendix C5.

Table 3.20 : Effect of Q-UV UV-A Weathering on Impact Properties

Sample Exp. (Hrs)	Force at failure(N)	Displacement to failure(mm)	Energy at failure (Nm)	Energy Retained*(%)	Failure Mode
PMMA-1					
500	360 ± 28	1.83 ± 0.77	0.36 ± 0.23	360	brittle
1000	280 ± 4	1.04 ± 0.02	0.12 ± 0.00	120	brittle
1500	253 ±12	1.10 ± 0.06	0.12 ± 0.01	120	brittle
PMMA-2					
500	2402	5.18	4.78	94	brittle
1000	1699 ± 153	3.84 ± 0.28	2.56 ± 0.36	50	brittle
1500	1000 ± 393	2.85 ± 0.76	1.28 ± 0.69	25	brittle
PVC-1					
500	3264	4.69	6.02	113	ductile
1000	227 ± 123	1.22 ± 0.02	0.14 ± 0.05	3	brittle
1500	193 ± 5	1.11 ± 0.08	0.10 ± 0.01	2	brittle
PVC-2					
500	595 ± 323	3.78 ± 2.23	1.34 ± 1.28	23	brittle
1000	535 ± 77	3.07 ± 0.04	0.88 ± 0.00	15	brittle
1500	339 ± 29	1.95 ± 0.27	0.34 ± 0.09	6	brittle
PC-1					
500	2801 ± 23	4.71 ± 0.14	5.44 ± 0.12	106	ductile
1000	2837 ± 18	4.77 ± 0.06	5.49 ± 0.00	107	ductile
1500	2676 ± 60	4.69 ± 0.06	5.17 ± 0.12	101	ductile
PC-2					
500	2931 ± 69	4.97 ± 0.02	5.71 ± 0.16	98	ductile
1000	2830 ± 222	4.78 ± 0.15	5.57 ± 0.58	96	ductile
1500	1209	4.19	2.28	39	ductile

* see Table 3.11 for unweathered control values

128

Table 3.21 : Effect of Q-UV UV-B Weathering on Impact Properties

Sample Exp (hrs)	Force at failure (N)	Displacement to failure (mm)	Energy at failure (Nm)	Energy Retained*(%)	Failure Mode
PMMA-1 250 500 1000	257 ± 17 303 ± 1 319 ± 40	1.08 ± 0.04 0.98 ± 0.02 1.49 ± 0.17	0.12 ± 0.00 0.13 ± 0.01 0.25 ± 0.07	120 130 250	brittle brittle brittle
PMMA-2 250 500 1000	2373 ± 319 683 ± 13 420 ± 69	5.01 ± 0.03 2.85 ± 0.31 3.23 ± 2.41	4.50 ± 0.74 0.93 ± 0.07 0.83 ± 0.79	88 18 16	brittle brittle brittle
PVC-1 250 500 1000	539 ± 27 195 ± 27 430 ± 24	1.52 ± 0.12 1.06 ± 0.12 1.49 ± 0.04	0.33 ± 0.03 0.10 ± 0.03 0.25 ± 0.02	6 2 5	brittle brittle brittle
PVC-2 250 500 1000	425 ± 79 518 ± 16 505 ± 99	2.58 ± 1.24 2.52 ± 0.00 2.65 ± 0.64	0.56 ± 0.37 0.71 ± 0.02 0.71 ± 0.30	10 12 12	brittle brittle brittle
PC-1 250 500 1000	2719 ± 111 2710 ± 9 2722 ± 69	4.78 ± 0.06 4.82 ± 0.17 4.81 ± 0.03	5.26 ± 0.21 5.34 ± 0.02 5.25 ± 0.27	103 104 102	ductile ductile ductile
PC-2 250 500 1000	2797 ± 28 2837 ± 18 2820 ± 32	4.87 ± 0.29 4.77 ± 0.06 4.86 ± 0.14	5.57 ± 0.00 5.65 ± 0.07 5.52 ± 0.05	96 97 95	ductile ductile ductile

* see Table 3.11 for unweathered control values

Figure 3.44 : Effect of Weathering on the Impact Properties of PMMA-2(X-1200)
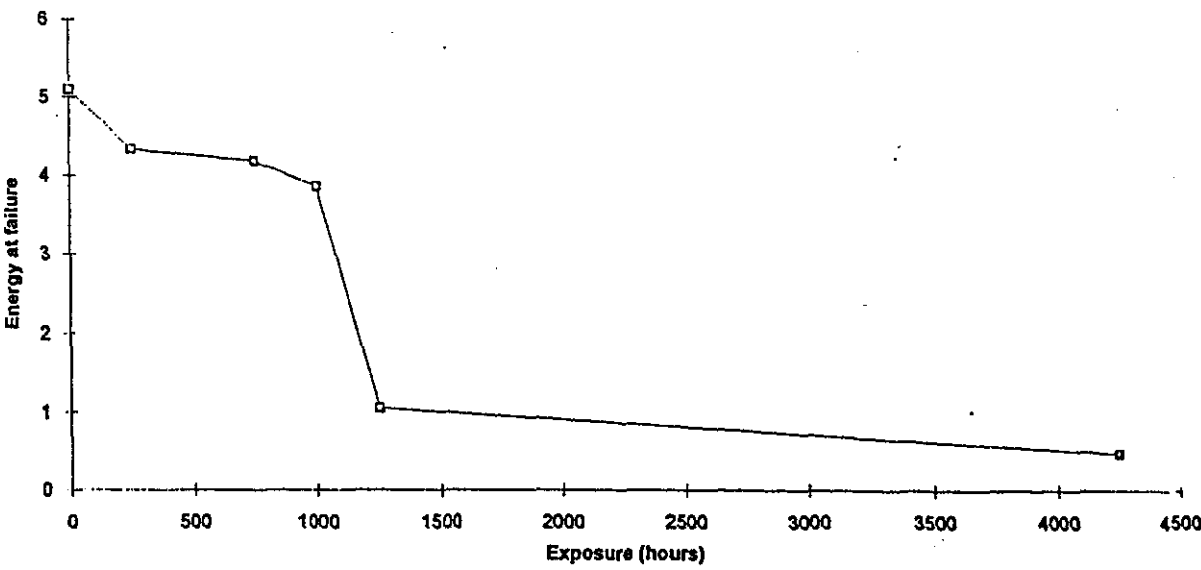
Figure 3.45: Effect of Weathering on the Impact Properties of PMMA-2(Q-UV)
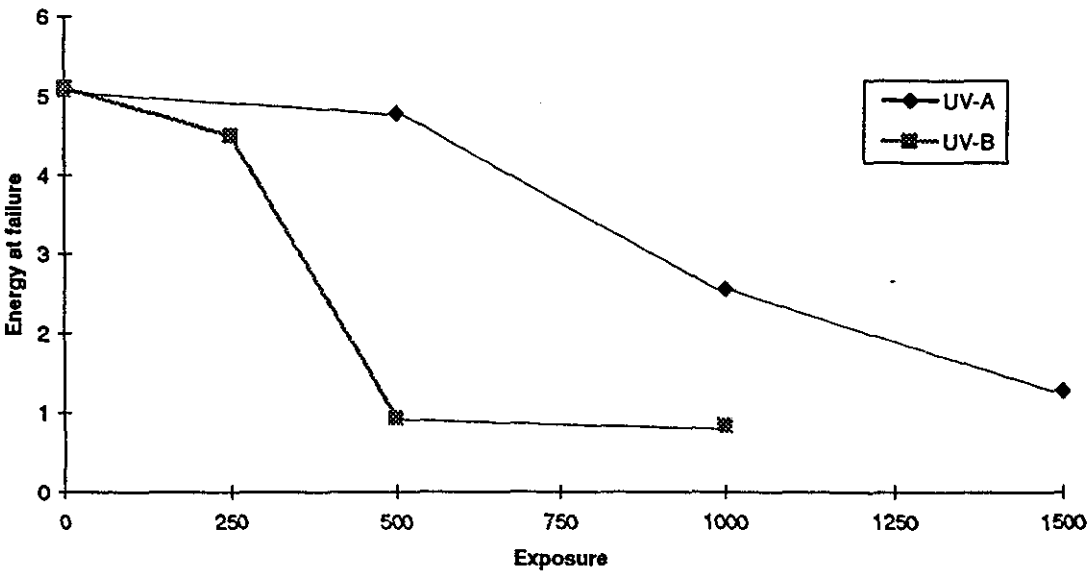
Figures 3.46 and 3.47 show there are two modes of failure at 1000 hours exposure for PVC-1 and 250 hours exposure for PVC-2.

Figure 3.46 : Effect of Weathering on the Impact Properties of PVC-1 (X-1200)
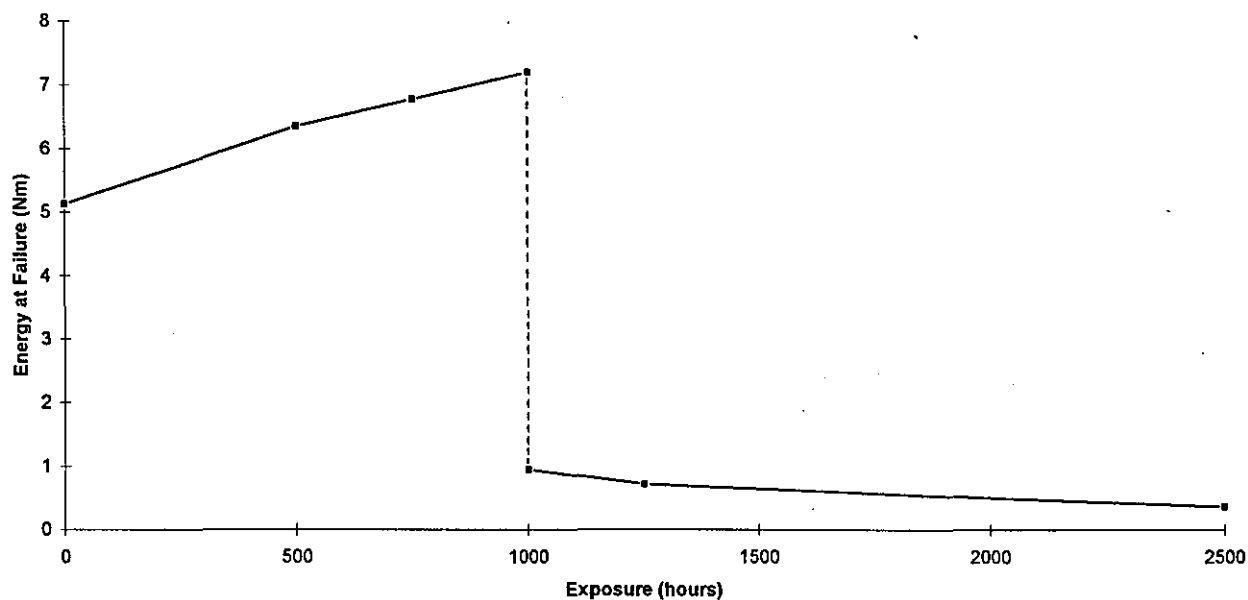
Figure 3.47 : Effect of Weathering on the Impact Properties of PVC-2 (X-1200)
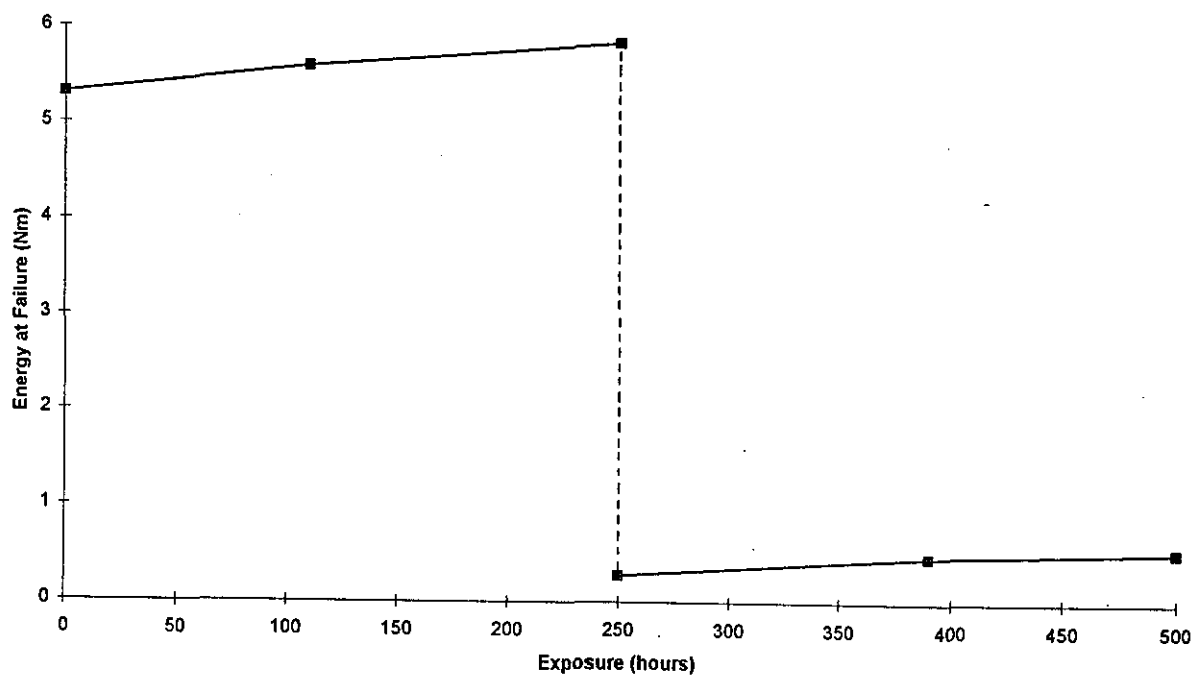
3.3 THE EFFECT OF ABRASION ON IMPACT RESISTANCE

Values given in Tables 3.22 and 3.23 are an average of 3 test measurements. Table 3.24 illustrates the reproducibility of impact test data (full results in Appendix D), values given are an average of nine test measurements. Data are quoted with ± standard deviations. Scratched test pieces were impacted scratched face down.

UN = unscratched material

G0 = Grade Zero scratch (fine scratch)

G2 = Grade Two scratch (coarse scratch)

Table 3.22 : Summary of Impact Test Data For 2mm Thick Samples

Sample		Force at Failure (N)	Displacement to Failure (mm)	Energy at Failure (Nm)	Energy Retained(%)	Failure Mode
PMMA-1	UN	283 ± 8	0.81 ± 0.02	0.10 ± 0.00		brittle
	G0	243 ± 17	0.86 ± 0.09	0.10 ± 0.02	100	brittle
	G2	318 ± 12	1.03 ± 0.19	0.19 ± 0.06	190	brittle
PMMA-2	UN	2309 ± 317	5.18 ± 0.11	5.10 ± 0.54		brittle
	G0	357 ± 4	1.36 ± 0.07	0.25 ± 0.02	5	brittle
	G2	304 ± 24	1.26 ± 0.03	0.20 ± 0.01	4	brittle
PVC-1	UN	2707 ± 286	4.97 ± 0.15	5.31 ± 0.18		ductile
	G0	313 ± 55	1.07 ± 0.17	0.15 ± 0.05	3	brittle
	G2	283 ± 49	0.83 ± 0.05	0.10 ± 0.02	2	brittle
PVC-2	UN	2647 ± 26	5.27 ± 0.08	5.72 ± 0.09		ductile
	G0	342 ± 53	1.86 ± 1.29	0.33 ± 0.29	6	brittle
	G2	306 ± 26	1.47 ± 0.40	0.22 ± 0.09	4	brittle
PC-1	UN	2365 ± 99	5.36 ± 0.68	5.13 ± 0.53	-	ductile
	G0	2484 ± 120	5.32 ± 0.31	5.33 ± 0.42	104	ductile
	G2	2471 ± 91	5.31 ± 0.20	5.31 ± 0.32	104	ductile
PC-2	UN	2643 ± 102	5.35 ± 0.25	5.81 ± 0.39		ductile
	G0	2533 ± 208	5.34 ± 0.20	5.55 ± 0.53	96	ductile
	G2	2666 ± 34	5.49 ± 0.10	5.95 ± 0.10	102	ductile

Energy retained is the energy to failure for a scratched sample expressed as a percentage of the energy to failure for the unscratched control sample.

Table 3.23 : Summary of Impact Test Data for 3mm Thick Samples

Sample		Force at Failure (N)	Displacement to Failure (mm)	Energy at Failure (Nm)	Energy Retained(%)	Failure Mode
PMMA-1	UN	693 ± 79	0.86 ± 0.22	0.31 ± 0.13		brittle
	G0	637 ± 43	0.99 ± 0.18	0.36 ± 0.07	116	brittle
	G2	676 ± 15	1.15 ± 0.04	0.46 ± 0.00	148	brittle
PMMA-2	UN	3259 ± 154	4.50 ± 0.15	6.80 ± 0.43		brittle
	G0	848 ± 49	1.20 ± 0.14	0.50 ± 0.04	7	brittle
	G2	685 ± 2	1.30 ± 0.22	0.52 ± 0.13	8	brittle
PVC-1	UN	5758 ± 113	5.63 ± 0.24	16.08 ± 0.18		ductile
	G0	1157 ± 148	1.01 ± 0.10	0.52 ± 0.10	3	brittle
	G2	655 ± 155	0.80 ± 0.08	0.23 ± 0.06	1	brittle
PVC-2	UN	3915 ± 230	5.95 ± 0.36	10.51 ± 0.80		ductile
	G0	4094 ± 190	5.99 ± 0.11	11.17 ± 0.46	106	ductile
	G2	4144 ± 150	5.98 ± 0.04	11.33 ± 0.39	108	ductile

Table 3.24 : Reproducibility of Impact Test Data (2mm thick samples)

Sample		Force at Failure (N)	Displacement at Failure (mm)	Energy at Failure (Nm)
PMMA-1	UN	298 ± 15	0.85 ± 0.05	0.11 ± 0.01
	G0	272 ± 27	0.90 ± 0.05	0.10 ± 0.03
PVC-1	UN	2855 ± 253	5.08 ± 0.12	5.71 ± 0.70
	G0	357 ± 72	1.28 ± 0.25	0.20 ± 0.07
PC-1	UN	2648 ± 53	5.51 ± 0.24	5.86 ± 0.23
	G0	2620 ± 124	5.39 ± 0.13	5.75 ± 0.34

CHAPTER 4 : DISCUSSION

This chapter is divided into five sections based on the main areas under investigation. The first section deals with the analysis and characterisation of unexposed samples of each of the six materials. The second section involves a detailed comparison of the three weathering devices and six weathering regimes utilised in this study. It gives a critical appraisal of each, considering in particular recommendations of the revised version of ISO 4892. Section three involves a more detailed appraisal of the effects of weathering on the properties of glazing materials; and the fourth section considers the effect of abrasion on impact resistance, an important factor in many applications of these materials. Finally, a General Discussion is included to link the main points and key findings together.

4.1 ANALYSIS OF UNEXPOSED MATERIALS

4.1.1 Identification of Additives

The bulk properties of a polymer can often be altered considerably by the incorporation of additives[13]. In some cases an additive may be encountered in a variety of polymers for a wide range of end uses, for example certain antioxidants. In other instances the additive may be very specific to a certain polymer for a particular end use.

Improvements in one property can, however, lead to deteriorations in others and consequently it is the overall performance of an additive in a given formulation which determines the final choice. With transparent materials it is crucial that the refractive index of the additive is similar to that of the polymer in order to maintain transparency. Commercially, the most important requirement of any additive is that it should be effective for the purpose for which it has been designed, at an economic level.

It is possible to identify the additives present in each polymer and these are summarised in Table 4.1.

Poly(methylmethacrylate) may be blended with a number of additives. Two particular requirements are, first, that when used in castings they should not affect the polymerisation reaction and, second, that they should have good weathering resistance. Important additives are pigments which should be stable to both processing and service conditions. Further improvement in light stability may be achieved by the addition of small quantities of UV-absorber; PMMA-2 is known to contain such an additive from light transmission data (Table 3.10). Infrared analysis of PMMA-2 identified the presence of a polyacrylate (see Figure 3.3) which is incorporated as an impact modifier and

135

accounts for the high initial

Table 4.1 : Identification of Additives

Polymer	Method Used	Additive	Role in Polymer
PMMA-1	XRF	Cu pigment	optical pigment
	XRF	Ca stearate	lubricant
PMMA-2	XRF	Cu pigment	optical pigment
	ATR/FTIR	Poly(butylacrylate)	impact modifier
PVC-1	XRF	Ca stearate	lubricant
	XRF	Phosphite	secondary antioxidant
	XRF, ATR/FTIR	Alkyl tin carboxylate	heat stabiliser
	ATR/FTIR	MBS modifier	impact modifier
PVC-2	XRF	Ca stearate	lubricant
	XRF	Phosphite	secondary antioxidant
	XRF, ATR/FTIR	Alkyl tin mercapto-carboxylate	heat stabiliser
	ATR/FTIR	MBS modifier	impact modifier
PC-1	XRF	Cu pigment	pigment
	XRF	Chlorinated paraffin	flame retardant
	XRF	Phosphate	stabiliser
PC-2	XRF	Ca stearate	heat stabiliser
	XRF	Chlorinated paraffin	flame retardant

impact resistance of PMMA-2 compared to PMMA-1. PMMA-2 is thus a two phase

material in which the glassy phase consists of poly(methylmethacrylate) and the rubbery phase an acrylate polymer (usually 15% poly(butyl acrylate)[13]).

In the massive form poly(vinylchloride) is a colourless rigid material with limited heat stability and with a tendency to adhere to metallic surfaces when heated. For these, and other, reasons it is necessary to compound the polymer with other ingredients to make useful plastics materials. It is a known fact that heating PVC at temperatures above 70°C has a number of adverse effects on the properties of the polymer. At processing temperatures used in practice (Table 3.11) sufficient degradation may take place to render the products useless. Certain materials known as stabilisers are thus incorporated to moderate the degradation reaction. Many stabiliser systems can be used, infra-red and XRF analysis of the two PVC materials identified the presence of organo-tin compounds which are commonly used in transparent PVC[13]. PVC-2 contains a tin mercapto-carboxylate stabiliser, identified from carbonyl groups in the IR spectrum and XRF identified tin and sulphur:

$$R \diagdown \atop R \diagup Sn \diagup^{SCH_2COOR'} \diagdown_{SCH_2COOR''}$$
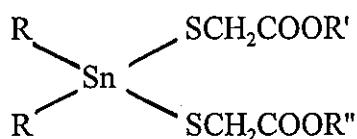
Carbonyl groups are also present in PVC-1 but no sulphur is evident which suggests a dialkyl tin maleate stabiliser in this material:

$$R \diagdown \atop R \diagup Sn \diagup^{OOC=CH} \diagdown_{OOC=CH}$$
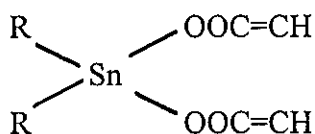
To prevent sticking of the PVC compound to processing equipment, internal lubricants are widely used. Calcium stearate is commonly used in the U.K. since it is a material of limited compatibility which will thus sweat out during processing to form a film between the bulk of the compound and the metal surfaces of the processing equipment.

Unplasticised PVC has a high melt viscosity leading to some difficulties in processing. The finished product is also too brittle for some applications. In order to overcome these problems it has become common practice to add certain polymeric additives to the PVC.

137

The impact modifiers generally are semi-compatible and often somewhat rubbery in nature. In applications where tough materials of high clarity are required a methacrylate-butadiene-styrene (MBS) terpolymer is often used, indeed this was identified in the IR spectra of both PVC materials by the presence of methacrylate C=O, and the benzene ring of styrene. MBS has sufficiently different solubility parameters from PVC for it to exist in the dispersive phase but has a very similar refractive index to PVC so that light scattering at the interface between the two phases is at a minimum.

The two polycarbonate samples appear to contain fewer additives than PVC or PMMA. Pigments, heat and light stabilisers and fire retardants are used and can be identified in the two polymers, but the range of materials available is very restricted because of the high processing temperatures involved[13]. Light transmission results suggest both materials also contain UV absorbers.

4.1.2 Molecular Interpretation of Tg and other Transitions

Glass transition temperature, Tg, is only observed in amorphous polymers but since no polymer is fully crystalline, all polymers will have a Tg[128].

The glass transition temperature of a polymer is sensitive to molecular weight and its distribution. As the molecular weight of a polymer increases, so does the glass transition temperature of that polymer. Hence PMMA-1 has a high Tg, and the Mw/Mn index indicates a high ratio of large, high molecular weight chains. This occurs because the larger the molecule, the more difficult mobility becomes and consequently the greater the temperature required to give the polymer sufficient energy to move in a way appropriate to the rubber state. A low molecular weight polymer has a greater number of chain ends in a given volume than a high molecular weight polymer. The chain ends are less restricted and can become more active than segments in the centre of a molecule and cause a polymer mass to expand. This gives the molecules greater mobility and they can be taken to a lower temperature before the thermal energy of the molecules is too low for the segments to rotate. Thus, it is the molecular weight of the polymer that determines the value of the glass transition temperature, and this is reflected in the values obtained. There is little difference in Tg between the two types of PVC or the two types of polycarbonate, but there is a considerable difference between the two types of acrylic.

The intrinsic chain flexibility is determined by the nature of the chain backbone and by the nature of the groups directly attached to the backbone. Chain flexibility determines

138

chain mobility and hence influences glass transition temperature. Chains based on aliphatic C-C and C-O bonds are quite flexible whereas the introduction of ring structures such as the p-phenylene group into the chain has a marked stiffening effect. The glass transition temperatures of the two polycarbonate samples are thus very high because of the presence of such phenylene groups.

The presence of polar groups or atoms such as chlorine tends to raise the glass transition point; hence, the value for PVC is much higher than for polyethylene[129]. The introduction of n-alkyl groups in separating the polymer chains decreases the inter-chain attraction more than it increases the inherent chain stiffness; this stiffening effect of the methyl groups in the acrylic samples thus raises the value of the glass transition point.

' Transitions additional to the glass transition occur because at temperatures below the glass transition point, side chains, and sometimes small segments of the main chain, require less energy for mobility than the main segments associated with the glass transition temperature. Various types of nomenclature are used, one of the most common being to label the transitions α, β, δ, and so on in descending order of temperature, the α-transition normally corresponding to the glass transition temperature[13]. It must be stressed that simply to label a transition as a β-transition does not imply any particular type of mechanism and the mechanism for a β-transition in one polymer could correspond to a δ-transition in a second polymer. Both acrylic samples exhibit a strong secondary transition, as seen on their DMA traces in E" values (which enhances transitions seen in the rubbery region); at 22.4°C in PMMA-1 and at 0.9°C in PMMA-2, the differences in temperature being attributable to the differences in molecular weight as previously discussed. This secondary transition is attributable to the onset of hindered rotation of the side group. Values of tanδ and storage modulus are also higher for PMMA-1 indicating a more rigid polymer structure. PVC-1 and PVC-2 also show secondary transitions, albeit smaller, at -33.44°C and -29.03°C respectively. Values of E' and E" for PVC-1 are much higher than for PVC-2, possibly due to the incorporation of impact modifier in PVC-2.

4.1.3 Level of Fusion and Processing Temperature

The degree of fusion of PVC has a profound influence on its mechanical, physical and chemical properties. Failure to achieve the necessary degree of fusion has often been suggested as the cause of product failure. The optimum degree of fusion is not 'complete' fusion or total homogeneity of the material, indeed this can lead to 'over-processing' of

the material.

Differential thermal analysis can be used to evaluate thermal history and level of fusion of processed PVC samples[141]. Figure 4.1 shows a typical thermogram for PVC-1.

Gilbert et al[141] found that at any given processing temperature, lower-melting crystallites melt while higher crystallites are annealed, so that their melting temperature increases to produce a small endotherm (labeled B) at a higher temperature than Tg. At processing temperatures of 160°C and above there is enough melted material to allow recrystallisation on cooling and an additional endotherm (labeled A) appears, the energy of which increases with processing temperature i.e. higher processing temperature leads to a better fused sample. The heats of fusion for the PVC samples suggest, according to Gilbert et al, fusion levels of approximately 26% for PVC-1 and 24% for PVC-2 ie not significantly different.

Figure 4.1: Thermogram for PVC-1
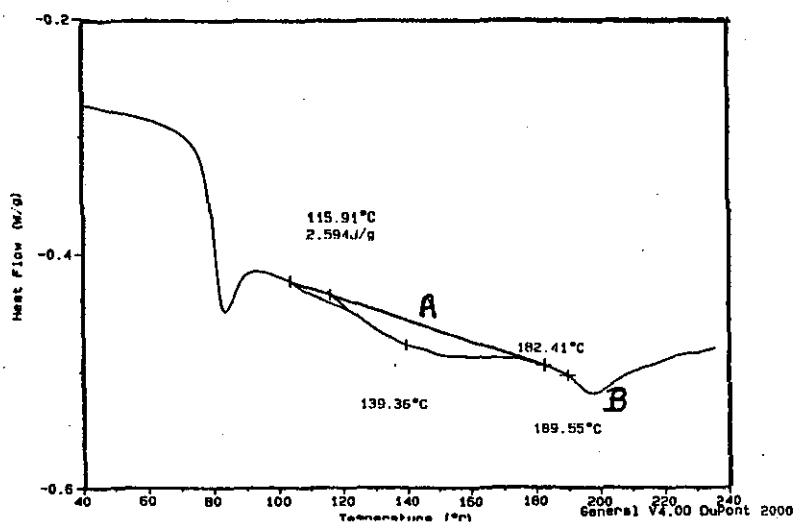
The B-endotherm was shown by Gilbert et al to correspond to the processing temperature of the material i.e. 190°C for PVC-1 and 178°C for PVC-2. Since PVC-1 has the higher processing temperature, it is expected to be the more durable of the two materials.

PVC has low crystallinity levels but the crystalline segments act as rigid areas in comparison to the amorphous regions, and as such, they can act like additives in increasing the strength of the polymer. With this increased strength usually comes

140

increased brittleness. Indeed, PVC-2 has slightly higher absorbed energy at failure than PVC-1 (Table 3.11).

4.2 COMPARISON OF WEATHERING DEVICES

Polymeric materials are particularly susceptible to bond breakage by UV light in the 300-400nm wavelength range. The penetrating power of the UV light is usually limited, except for PMMA-1 without added UV absorbers, so the destruction is mainly a surface phenomenon. Light absorption in a molecule consists of a specific interaction of a certain chromophoric group with a photon of energy. Saturated compounds possessing bonds such as: C-C, C-H, O-H, C-Cl etc., have absorption maxima between 200 and 300nm[142]. Although only a small number of the important polymers are capable of absorbing solar radiation, quite frequently commercial polymers contain impurities capable of absorbing sunlight.

All wavelengths shorter than the threshold have sufficient energy to break bonds, but longer wavelengths of light cannot break them regardless of their intensity. Thus if a polymer is only sensitive to UV light below 295nm (the solar cut-off point) it will never experience photochemical degradation outdoors. If the same polymer is exposed to a laboratory light source that has a spectral cut-off of 280nm, it will deteriorate. Although light sources that produce shorter wavelengths allow faster tests, there is a possibility of anomalous results if the wavelength cut-off is below that of the material's end use environment.

4.2.1 Optical Measurements

The observed changes in gloss are summarised in Table 3.15 for the six test materials. The initial 60° gloss measurements were high because specular reflection from both upper (weathered) and lower surfaces were detected. If the transparent materials darken in colour during weathering this will reduce the intensity of the light from the lower face of the test piece and so may register as a small loss of gloss. Where substantial losses of gloss are recorded this is due to erosion of the upper, weathered surface.

Changes in colour of these transparent materials were measured using a reflectance technique with a white tile as backing. This method is very sensitive for comparative purposes, but exaggerates the absorption that would be experienced by light passing once through the material. It is expected that substantial loss of gloss in the weathered surface

141

would affect the measured colour change to some extent, although the optical arrangement of the colorimeter should minimise such effects. The colorimeter utilises diffuse illumination and viewing at 8° to normal. In this case inclusion of diffuse reflection reduces the sensitivity of the colour difference measured to changes in gloss, see ISO 7724[118].

Comparison of Tables 3.16 and 3.17 show that the principle contributor to changes in total colour (δE^*) was generally in yellowness; thus a positive value of δb^* in Table 3.16 denotes an increase in yellowness. The negative δb^* for PVC-1 exposed to xenon arc radiation is due to long wavelength UV bleaching of the yellow-coloured species produced during processing. At wavelengths greater than 400nm PVC undergoes bleaching[142]. The bleaching process can be explained in terms of several mechanisms, including photo-addition of HCl to polyenes resulting in reduced average sequence lengths in conjugated polyenes, quenching of growing conjugate double-bond sequences by oxygen, and reaction between oxygen and polyenyl radicals. While the reaction of HCl with conjugated double bonds is the most plausible mechanism, it is likely that more than a single mechanism accounts for the process.

4.2.2 Temperature Effects

The two artificial weathering devices used cause heating of the sample surface in different ways:

1)Transparent samples exposed to a xenon arc lamp will transmit much of the incident energy, causing any backing to heat up, which in turn may heat the test piece. The effect of method of mounting samples, in the Xenotest-1200, on sample temperature is discussed in previous work[4]. In the Xenotest-1200, transparent samples in the open-backed mode achieve surface temperatures of about 30°C, little above cabinet air. Introduction of a black backing with limited air circulation raises the temperature of the outer test piece surface to 50-60°C, much closer to the black standard temperature of 65°C.

2)In the case of the UV-condensation (Q-UV) apparatus there is limited potential for radiation heating since the radiant intensity is much lower. Most samples will absorb all the incident radiation, and their surface temperatures are close to air temperature which is either 45°C or 60°C in the two test cycles used here. A common condensation temperature of 50°C was used for both cycles.

142

4.2.3 Comparison of Polymer Types and Test Cycles

In order to assess the validity of each test it is useful to rank the materials according to their exposure behaviour (chemical and physical changes on weathering for each material are discussed in detail in Section 4.3). Colour change and changes in gloss are used to evaluate the procedures. The materials are ranked in order of decreasing durability, 1 being the most durable material.

Tables 4.2 and 4.3 show the relative rankings for gloss and colour retention for the six materials tested based on performance up to 2000 hours in the 6 test regimes (lowest number = least change). It is important that, in trying to define a test procedure capable of application to a wide variety of polymer types and surfaces used for glazing purposes, no disproportionate bias should be introduced for or against any particular type. At the same time, it will be helpful to be able to investigate the effects of design variables, such as surface temperature, which are likely to be encountered in practice.

Table 4.2 : Materials Ranked by Loss of Gloss

| Rank | Xenon Arc | | UV-A | | UV-B | |
	OB	BL	45/50	60/50	45/50	60/50
1	PVC-1	PMMA-1	PMMA-1	PMMA-1	PMMA-1	PMMA-1
2	PMMA-1	PMMA-2	PMMA-2	PMMA-2	PMMA-2	PC-2
3	PMMA-2	PVC-1	PC-1	PC-1	PC-1	PC-1
4	PC-2	PC-1	PC-2	PC-2	PC-2	(PMMA-2)
5	PVC-2	PC-2	PVC-1	PVC-1	PVC-1	PVC-1
6	PC-1	PVC-2	PVC-2	PVC-2	PVC-2	PVC-2

Table 4.3 : Materials Ranked by δb* Value

| Rank | Xenon Arc | | UV-A | | UV-B | |
	OB	BL	45/50	60/50	45/50	60/50
1	PVC-1	PVC-1	PMMA-2	PMMA-2	PMMA-2	(PMMA-2)
2	PMMA-2	PMMA-2	PMMA-1	PMMA-1	PMMA-1	PMMA-1
3	PMMA-1	PMMA-1	PVC-1	PC-1	PC-1	PC-1
4	PC-1	PC-1	PC-1	PC-2	PVC-1	PC-2
5	PC-2	PC-2	PC-2	PVC-1	PC-2	PVC-1
6	PVC-2	PVC-2	PVC-2	PVC-2	PVC-2	PVC-2

Considering the two xenon arc cycles first, these were designed to simulate two extremes of operating conditions: first that of free ventilation in which sample temperature is close to external air temperatures; and second that in which the surface temperature of the material is raised by virtue of hot air trapped behind. The latter condition can be encountered in practice in structures such as poorly ventilated barrel vault roofs, for example. Comparison of the yellowing induced by the xenon arc exposure, Table 4.3, shows the same ranking order for both low temperature (open-backed) and higher temperature (black-backed) exposure modes. However, the extreme discoloration of PVC-2 under the higher temperature xenon arc condition does not necessarily register as yellowing. Much the same order is seen for gloss retention, bearing in mind that the better samples show little change in gloss. However, the use of the higher test temperature significantly affects the gloss retention of PVC-2 and PC-2 relative to PC-1. Account of this needs to be taken in defining xenon arc exposure conditions for transparent materials of this kind. By comparison, the main effects on ranking order of using fluorescent lamps is by down-rating the performance of the exterior grade PVC-1 and upgrading PC-2. These effects are most noticeable with the UV-B lamp and at 60°C. However, even with the UV-A lamp at 45°C PVC-1 rates poorly on gloss retention. A UV-exposure temperature of 45°C is about as low as can consistently be maintained using Q-UV equipment in a normal laboratory. This temperature may be more appropriate than 60°C for this purpose. In general the use of UV-A fluorescent lamps, which is the preferred option in ISO 4892 : Part 3 as revised, and especially at the lower operating temperature, comes closest to giving the same ranking order as seen with xenon arc equipment but

144

tends to be more severe on PVC relative to polycarbonate. The tendency of PMMA to yellowing may also be exaggerated.

4.2.4 Effect of Moisture and Temperature Cycles

Although temperature effects on polymer degradation are important, equally significant effects are the thermally induced expansion and contraction imposed on a plastic material structure. Cyclic variation of humidity causes absorption and desorption of moisture, and this, in turn, results in alternate swelling and shrinkage of the surface material; cyclic variation of temperature induces alternate expansion and contraction. The combined effects of these dimensional changes can cause severe deterioration in the form of surface cracks in plastics structures.

Exposure in the Q-UV apparatus induces two cycles of dimensional change. During the condensation cycle, when the environment in the chamber is hot and humid, the plastics sheets undergo thermal expansion at the same time as swelling caused by water absorption; when the lamps are on and humidity off the chamber environment is hot and dry, and the sheets undergo thermal expansion but also shrinkage because of water desorption. Although the amount of water absorbed by the materials will be relatively low, the volume changes induced by moisture may be significant, especially when thermal expansion also occurs. The amount and rate of water absorption will change with time as a result of surface cracking, formation of hydrophilic groups by hydrolysis, and reduction in molecular weight.

Shortly after the rainspray comes on in the Xenotest-1200 the top-most layer of the plastic material will be cooled because of the lower temperature of the water; at the same time because of the low thermal conductivity of plastics materials, the layer at 10-20μm depth will still be hot (at the surface temperature prior to the rain spray). Consequently, the resin in the top layer tends to contract, but it is restrained by the underlying layers which are still in an expanded state. This produces tensile stresses in the top layers. These stresses are greater in the exposed surface of samples mounted over black backing. The black backing causes the sample temperature to be hotter (~60°C) than in the open-backed mode (~30°C)[4] so the cooling effect of rainspray and air means that the exposed surface is in a higher state of tension as shown in Figure 4.2.

145

Figure 4.2: Cause of Tensile Stresses in Exposed Sample Face

black   3mm   glazing
backing   gap   material
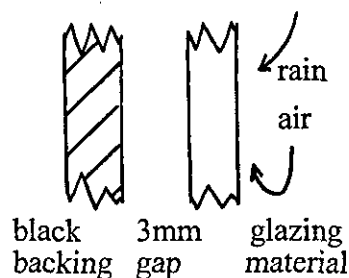
4.2.5 Correlation between Light Sources

Lack of agreement between the solar spectrum and that of the artificial light source is a common cause of poor correlation between different types of exposure but it is one that can be overcome by the use of filters. Although mismatch in the infrared region can cause the surface temperatures of natural and artificially exposed samples to be quite different, and lack of agreement in the visible range can result in poor correlation for coloured materials, it is differences in the UV region which are likely to cause deviation. The output of many lamps, in particular fluorescent UV-B lamps, extends below 295nm, the cut-off of solar radiation, resulting in the possible occurrence of reactions in the artificial chamber which are not possible outdoors. This results in alteration of the degradation profile and accentuates the surface nature of the degradation.

Compared with outdoors, artificial weathering offers a relatively stable and controllable environment for the systematic study of polymer stability. Q-UV weathering devices can be effectively used for comparative work, for example when comparing the durability of coated material to an uncoated sample. Because of the intense UV lamp used results can be obtained very quickly, but it is difficult to determine how many hours in the Q-UV instrument equals a year of outdoor exposure.

It is somewhat less difficult to establish the approximate equivalence of xenon arc artificial weathering to natural exposure, since the spectral energy distribution of xenon arc radiation is very close to that of natural sunlight at least over the UV and visible ranges (i.e. 300-800um). It is important to establish an equivalence in order to recommend exposure times for assessing durability to severe and moderate climates. The two climates are defined in terms of the total annual solar energy falling on a horizontal surface:

moderate climate $< 5GJm^{-2}$

severe climate $> 5GJm^{-2}$

For the purposes of this calculation the following values will be used:

moderate = 4GJm⁻² severe = 6GJm⁻²

In artificial weathering it is the UV and visible regions that are important i.e. the 300-800nm range, this is about 60% of the total solar radiation energy. A further correction of 67% is applied to allow for the fact that not all this radiation is acting at higher summer temperatures and so will be less damaging to the affected surfaces. The recommended radiation doses are therefore as shown in Table 4.4.

Table 4.4: Radiation Doses for Artificial Weathering

	moderate	severe
1 year	1.6 GJm⁻²	2.4 GJm⁻²
5 years	8.0 GJm⁻²	12.0 GJm⁻²

For an artificial weathering device with an average irradiance of I Wm⁻² in the range 300-800nm, exposure times equivalent to 5 years will be:

moderate = $2.2 \times 10^6 / I$ (hours)

severe = $3.3 \times 10^6 / I$ (hours)

In the Xenotest used in this study $I \approx 800$Wm⁻² therefore exposure times would be: moderate ≈ 2750 hours and severe ≈ 4000 hours. It is of course accepted that this represents very approximate means of estimation. However, it does put the requirements on some sort of logical basis bearing in mind that natural weathering itself is a very variable phenomenon depending on location, aspect, shading and so on.

These figures can also be used to estimate the service life of a component from artificial weathering data. Current standards allow a δE* value of 7 for white PVC profiles after exposure to artificial weathering, however, there are proposals to lower this value to 5. If we were to apply this to the glazing samples tested the information given in Table 4.5 on relative service life, as regards discolouration, could be obtained; for full colour data see Appendix B. This assumes changes in other material properties would not cause the polymer to fail earlier, often not the case; for glazing materials other factors such as light transmission, loss of gloss would also need to be considered in practice. However, the exercise allows a qualitative comparison of relative durability of the materials tested.

147

Table 4.5 shows that PVC and polycarbonate are not suitable for outdoor glazing applications unless they are appropriately stabilised. Acrylics have far superior weathering properties in terms of discolouration.

Table 4.5 : Estimated Lifetimes in Moderate Climates

Sample	Open-backed			Black-backed		
	δE^*	Exp (hours)	Estimated years	δE^*	Exp (hours)	Estimated years
PMMA-1	4.55	21000	>40	4.84	10500	21
PMMA-2	3.92	8000	15	4.96	6000	12
PVC-1	4.41	7250	14	5.66	3250	6
PVC-2	7.6	250	<0.5	17.30	250	<<0.5
PC-1	3.3	750	1.5	4.57	500	1
PC-2	4.3	750	1.5	2.62	500	1

4.3 CHANGES INDUCED BY WEATHERING

Although some slight changes in the chemical nature of plastics may take place during processing, the most significant degradation occurs during exposure to the service environment. Conditions during processing are relatively severe (e.g. excessive heat, molecular shearing) but exposure to them is of short duration. Temperature changes, humidity and mechanical stresses are usually lower in the service environment than during fabrication, but the time of exposure is considerably longer. In addition, natural conditions normally fluctuate in contrast with the more constant conditions of fabrication.

Chemical changes induced by weathering in plastics materials are generally the result of a complex set of processes in which the combined action of UV light causes disruption of the chemical bonds in a polymer which can lead to one or more of the following chemical changes: cleavage into smaller molecules (chain scission), cross-linking, elimination of small

148

molecules (e.g. hydrogen chloride, carbon dioxide, carbon monoxide, water), formation of double bonds in the main chain (e.g. in PVC as a result of dehydrochlorination) and light induced hydrolysis. The most frequent light-induced chemical degradation processes in polymeric materials are chain scission and cross-linking, with concomitant formation of functional groups such as carbonyl (C=O), carboxyl (-COOH), hydroxyl (-OH) and peroxides (-O-O-).

4.3.1 Optical Properties
4.3.1.1 Colour and Gloss

For all samples exposed, those under UV-B lamps showed increased degradation compared to those under UV-A lamps, and, in general, those under UV-A lamps showed increased degradation compared to those under xenon arc lamps.

Poly(methylmethacrylate)

PMMA-1 contains no added UV-absorber but exhibits measurable absorption towards the shorter UV end of the solar spectrum. It has a long history of end use in the U.K. and normally shows good durability in practice. The performance in the xenon arc device is in line with this expectation, even at the higher temperature of test. Whilst the fluorescent lamp exposures also indicate good weathering properties, an appreciable level of discolouration was observed (see Tables 3.16 and 3.17). This was most evident with the UV-B lamps and at the higher exposure temperature.

PMMA-2 performed comparably in the xenon arc device, and fluorescent lamp exposures also indicate good durability, although at the higher temperature exposure with UV-B lamps there was evidence of surface deterioration; this is indicative of molecular weight reduction and it is expected that the sample will have lost impact strength.

PMMA begins to absorb at 320nm, the absorption rising rapidly with decreasing wavelength. The deterioration observed on exposure to UV radiation was a slight darkening as well as some yellowing. Little gloss change was evident. Photo-oxidative degradation is thought to result in an increase in UV absorption due to formation of aldehyde groups in the side chain, with yellowness being attributed to reaction of radicals following photolysis of the ester side groups on the polymer chain which lead to conjugated species in the chain. Such changes are evident in the IR spectra of weathered samples of PMMA-1 under QUV conditions (Figure 3.11) and

149

PMMA-2 under both Xenotest-1200 and QUV exposure (Figures 3.12 and 3.13); in spectra of both samples a broadening of the carbonyl peak is evident which supports formation of aldehyde groups.

Poly(vinylchloride)

PVC-1 is a pressed PVC-U sheet, thought to contain efficient stabilisers. Again it has a long history of use in the U.K. and was expected to perform well under test, at least at operating temperatures below about 45°C. As with PMMA-1, it performed well, even at the higher surface temperature in the xenon arc device. However, it proved very prone to surface deterioration on exposure to the fluorescent lamps. PVC-1 showed some loss of yellowness under UV-B lamps at the lower temperature cycle but this was not observed at the higher temperature cycle (Table 3.16). Yellowness is thought to be due to dehydrochlorination at the surface leaving conjugated chains, the longer these chains the more severe the discolouration. The degradation rates for exposure to all three radiation types were increased at higher temperature, indicating the temperature sensitivity of PVC if inadequately stabilised. The apparent loss of yellowness in some of the samples may be due to the formation of crosslinks at the surface thus leading to shorter conjugated chains.

PVC-2 was an interior grade and, as might be expected, showed significant and rapid discoloration under all six test conditions. After 1000 hours exposure at the higher temperature cycle loss of yellowness in PVC-2 was observed although the sample continued to darken whereas, under UV-A radiation, although degradation was fast it was much slower than under UV-B radiation (Table 3.16). In the X-1200 degradation of PVC-2 was severe at the hotter sample temperature but much less so at the cooler temperatures. This may be because at the hotter exposure conditions sample temperatures are nearing the T_g value for the material, resulting in greater mobility of the polymer chains. It is thought that molecular mobility is important for dehydrochlorination because the polyene sequences associated with discolouration need to be coplanar to achieve conjugation, whilst the original polymer chains are unlikely to be coplanar. If chain scission was the most important factor this would probably not favour discolouration at higher temperatures because the polyene sequences would be shortened. Cross-linking is liable to reduce molecular mobility and ought not to favour discolouration. Under all regimes the higher temperature exposure conditions caused earlier deterioration. There is a history in the U.K. of

150

similar early failures, within 4 to 6 years, of inadequately stabilised PVC-U rooflights which are constructed so as to promote high operating temperatures in sunlight[144]. This effect is highly dependent on aspect to the sun. It is important that a test cycle be available which will give early warning of susceptibility to high operating temperatures. The effects of exposure to UV lamps are similar to that of PVC-1. It seems that none of the fluorescent lamp cycles used adequately differentiates between these two materials.

It is considered that the poor performance of PVC-1 under fluorescent lamp exposure is unrepresentative of the practical performance of the product. The precise reasons for this are not clear, but the following differences between xenon and fluorescent lamp exposures may contribute:

- prolonged high temperature of exposure in the Q-UV
- presence of short wavelength UV light in the output from UV-B lamps
- absence of longer wavelengths in the outputs from the fluorescent lamps. These longer wavelengths may cause further oxidation of the yellow chromophores produced thus causing a bleaching effect.
- differences in leaching of hydrogen chloride by water spray as compared to condensation cycles. Hydrogen chloride is a by-product of PVC degradation on which it has an autocatalytic effect.

Polycarbonate

According to the respective manufacturers literature, PC-1 is an indoor glazing grade, whilst PC-2 is a bulk stabilised grade suitable for external use. Their relative performance on exposure to the various weathering cycles was not consistent with this, especially at the higher operating temperature. Thus PC-2 showed greater and more rapid deterioration than PC-1, particularly at higher operating temperatures (see tables 3.15 to 3.17). Exposure to UV-A lamps caused comparable discolouration of the two with limited loss of gloss, even at the higher UV exposure temperature. Under UV-B lamps the polycarbonate samples degraded rapidly to a high level of darkening and yellowing and there was little change thereafter, similarly on exposure in the X-1200 although some yellowness seemed to be lost on prolonged exposure. Reasons for this loss of colour are thought to be loss of weathered material due to surface erosion or decrease in conjugated species on the surface. Degradation was slightly more gradual under UV-A lamps but a similar level of colour change was reached.

151

Exposure in the X-1200 resulted in a higher loss of gloss than exposure to either UV-B or UV-A lamps which indicates that surface erosion occurs with the development of excessive discolouration. This is thought to match the long term natural weathering of polycarbonate in practice. The behaviour of PC-1 and PC-2 under UV-B exposure is odd. Both show greater loss of gloss (Table 3.15) at the lower temperature cycle. This could be due to photo-Fries reaction giving UV protection to the surface by forming hydroxybenzophenone groups.

4.3.1.2 Light Transmission

The observed changes in light transmission are summarised in Figures 3.17 - 3.22. PMMA-1 is the only material which does not contain an added UV-absorbing substance. In the visible region PMMA-1 and PMMA-2 have similar light transmitting properties; the materials can be ranked as follows where 1 indicates the highest light transmission.

Table 4.6 : Materials ranked according to Initial Light Transmission

Rank	290-400nm	410-790nm
1	PMMA-1	PMMA-1
2	PMMA-2	PMMA-2
3	PVC-2	PC-2
4	PVC-1	PC-1
5	PC-2	PVC-1
6	PC-1	PVC-2

The UV-visible spectra of PVC-1 and PVC-2 indicate the presence of light absorbing species at 580nm and 630nm (PVC-1). Such a species is also evident in PC-2 with a peak at 680nm (see Appendix B4.)

Light transmission characteristics of a material depend largely on two factors: a) the intensity of light scattered both at the surface and within the material, and, b) the concentration of light absorbing species in the material. Tables 4.7 and 4.8 show ranking of materials according to their light transmission properties after 2000 hours exposure to each of three weathering regimes. The materials are ranked in order of decreasing durability, 1 being the most durable material.

152

Table 4.7 : Ranking of Materials - Visible Region 410-790nm

Rank	X-1200, OB	UV-A 45/50	UV-B 45/50
1	PMMA-2	PMMA-1	PMMA-1
2	PMMA-1	PMMA-2	PMMA-2
3	PVC-1	PC-1	PC-1
4	PC-1	PC-2	PC-2
5	PC-2	PVC-1	PVC-1
6	PVC-2	PVC-2	PVC-2

Table 4.8 : Ranking of Materials - UV Region 290-400nm

Rank	X-1200, OB	UV-A 45/50	UV-B 45/50
1	PMMA-1	PMMA-1	PMMA-1
2	PVC-1	PMMA-2	PMMA-2
3	PMMA-2	PC-1	PC-1
4	PC-1	PVC-1	PVC-1
5	PC-2	PC-2	PC-2
6	PVC-2	PVC-2	PVC-2

As samples are weathered, the outer surface becomes roughened and a greater proportion of incident light is scattered at the surface. Comparing the rankings in Tables 4.7 and 4.8 with those in Table 4.2, where materials are ranked according to gloss, there are certain similarities in as much that the acrylics rank high and PVC-2 ranks low. There is very good correlation for the two Q-UV weathering regimes with both Table 4.2 (gloss) and Table 4.3 (δb^* value). The development of unsaturated species which act as chromophores is also an important influence. These absorb UV/visible radiation of varying wavelength and give the sample the observed discoloured appearance. This, in turn, affects the intensity of light transmitted through the samples.

After exposure to each of the three weathering regimes the degraded samples show a reduction in light transmission in the visible region, the extent of which seems to

correlate with changes in colour and loss of surface gloss. This strongly supports the formation of light absorbing species such as C=C conjugated chains in PVC, and carbonyl species in the polycarbonates.

PVC-1 is little affected by exposure to xenon arc radiation but is strongly affected by fluorescent lamps, in particular exposure to UV-B radiation. It is thought that, as with the severe colour changes induced under this regime, this type of behaviour is unrepresentative of the practical performance of the material. UV-B radiation also imparts highest loss of light transmission in PVC-2 and caused high initial loss of light transmission for samples of PC-1 and PC-2. The two acrylic samples were little affected by exposure and the slight reduction in transmitted light is thought to be largely due to loss of surface gloss resulting in increased light scatter, but reflects the excellent weathering properties of these materials.

4.3.1.3 Surface Microcracking

Microcracking only occurs in the presence of radiation - the unexposed side of weathered samples examined by optical microscopy showed no evidence of surface cracking (Section 3.2.6).

Initially, the polymeric material in the surface has a stress-fatigue limit higher than the environmentally induced stresses and thus undergoes repeated reversible deformation without fracture. Owing to the action of the UV portion of radiation, the material of the exposed surface layers undergoes photo-oxidation which leads to a gradual decrease in molecular weight (Table 3.15, Table 3.6 for unweathered samples). This decrease does not occur in the bulk material nor in the surface layers of the side not exposed to radiation. A decrease in molecular weight causes a lowering of the total attractive forces between adjacent polymer chains, and this, in turn, lowers the resistance of the resin to fracture. When the fatigue limit at a given site becomes lower than the environmentally induced differential stresses, fracture of the surface resin occurs, producing micro-cracks. Because of gradients in the stresses involved, the cracks will grow from the surface inwards and are v-shaped.

The six materials all behaved differently under the different weathering regimes. Optical microscopy examination revealed little change in appearance of the exposed surfaces of both acrylic samples weathered under UV-A and UV-B lamps but there were small areas of surface breakdown on the surface of Xenotest-1200 exposed samples (Figures 3.30 and 3.31).

154

Severe surface cracking was observed in samples of both PVC materials exposed under UV-B lamps (Figures 3.34 and 3.37), and in PVC-2 under UV-A lamps (AppendixB4); this cracking led to complete surface degradation on prolonged exposure. It seems that UV-B lamps have the effect of etching fused material away from around the PVC particles leaving the particle cores exposed. The particle size of PVC-1 appears to be greater than for PVC-2. The changes observed occurred at shorter exposure periods to UV-B radiation than UV-A, suggesting cracking is promoted by the shorter wavelengths of the spectrum. Very little cracking was observed in PVC samples exposed in the Xenotest-1200 although areas of surface breakdown were evident, this occurring at shorter exposure periods with PVC-2 than with PVC-1 (Figures 3.32 and 3.35).

Both polycarbonate materials showed severe cracking on exposure to xenon arc radiation (Figures 3.38 and 3.41) with much higher crack density being observed in samples exposed over black backing, i.e. those reaching higher sample temperatures. This is also associated with early loss of gloss, especially for PC-2 (Table 3.15). Finer cracks were seen in both materials when exposed to UV-A radiation (Figures 3.40 and 3.43), but there was no evidence of crack formation under UV-B radiation (Figures 3.39 and 3.42) suggesting in the case of polycarbonate, wavelengths of 340nm and longer promote cracking.

4.3.2 Physical and Mechanical Properties

4.3.2.1 Molecular Weight Distribution

After exposure in the X-1200 analysis shows a marked decrease in Mn and Mw values for PMMA-1 (Table 3.13) which suggests the breakdown of high molecular weight species into lower molecular weight species. This decrease is rapid during the first 2000 hours exposure in the Xenotest-1200 when the value of Mn is reduced to 24% its initial figure; after a further 2000 hours there is only a small further decrease. The values for samples exposed under fluorescent lamps for 2000 hours are of the same order of magnitude as for xenon arc exposure; however, there is a small, but significant, difference with UV-B exposure causing the largest decrease in molecular weight, UV-A exposure is approximately half way between the values for xenon-arc and UV-B exposures. As discussed in section 4.1.1, PMMA-1 does not contain a UV-absorbing additive. It absorbs little radiation greater than 400nm but absorption

155

increases with decreasing wavelength. Hence, lamps with higher levels of short wavelength UV will have the biggest effect on the exposed surface. The literature suggests (section 1.3.4.1) that photo degradation in this case results in simple chain splitting which would cause a decrease in surface molecular weight. A decrease in Mw/Mn value supports this indicating a higher proportion of lower molecular weight species.

The other five materials show a small decrease in molecular weight on exposure to xenon arc radiation (Table 3.13).

4.3.2.2 Thermal Analysis

After exposure in the X-1200 there was little or no apparent change in Tg for all samples. This is due to the fact that Tg only starts to decrease at low polymerisation levels. Thus in the weathered samples tested, although MWD of PMMA-1 was found to decrease, the molecular weight was still too high to have any effect on the glass transition temperature of the material and it remains still much higher than the value for PMMA-2.

4.3.2.3 Changes in Impact Resistance

The failure mode was found to differ for the six materials examined. Initially all materials, except PMMA-1 and PMMA-2, failed in a ductile manner (Table 3.11). PMMA-2 failed in a brittle mode despite high values of force and absorbed energy at impact. Ductile failure is, by definition, failure at high strain. Ductility reflects a materials ability to undergo large scale, irreversible plastic deformation when under stress, and the yield stress describes the load intensity at which such effects occur. The yield stress has direct relevance to product design for two reasons: 1) it represents the point at which the external stress reaches a critical level, allowing enough molecular motion to cause large scale, irreversible deformation; 2) it occurs before ultimate failure, although for many plastics yielding may progress to failure relatively quickly. Of the six materials tested, those failing in a ductile manner exhibit necking - there is a pronounced yield point and when it is exceeded the stress drops appreciably. In this case the failure is calculated from the yield point e.g. PC-1, PC-2.

PVC-2 reference samples show a region of stress whitening extending both inside and outside the striker zone, which is drawn along the striker barrel as the striker penetrates. A circular flap occurs on the inside of the whitened region, resulting in the formation of a central flap. The impact test on this kind of material is essentially a

puncture test with high speed deformation in the region of the striker. PVC-1 reference sample also showed a similar result but there was no evidence of stress whitening.

Brittle failure is a low energy process characterised by failure at low strain, with little or no permanent deformation. Components contain small, crack-like defects which can act as stress-concentration features; these microcracks grow under load and may lead to failure. Brittle failure or multiple splinter failure is characterised in the material by a primary break generally perpendicular to the direction of loading, fracturing the material into tiny splinters within a break-zone e.g. PVC-2 on weathering and PMMA-2 on exposure to UV-A lamps. Besides this, several secondary fractures often occur which can run in any direction through the test piece and have a smooth, glass-like appearance e.g. PVC-1 on weathering and PMMA-2 on exposure to UV-B lamps. Alternatively, samples may fail without a yield point with simple fracture e.g. PMMA-1.

In determining the impact energy of a sample it is noted that some specimens fracture in a progressive and complex manner. The various peaks on the force-time curve relate to various fracture events and the changing compliance of the specimen as damage accumulates. The broad second peak in brittle fracture (and thus the majority of the total energy involved) is concerned with secondary fracture events and the dynamics of fractured fragments. For these trials the first peak is taken as the failure point of the sample.

One of the most useful criterion for determining the service life of a material is the point when the ability to accommodate deformation disappears and the originally tough material becomes brittle. All samples (except PMMA-1 which has low impact resistance before weathering) showed a decrease in impact resistance on exposure to all three artificial weathering regimes.

Two materials, PVC-1 and PVC-2, underwent ductile/brittle transitions on weathering when impacted at 22°C. The transition occurred after short exposure periods, particularly on exposure to fluorescent lamps. These changes in impact behaviour are largely due to the changes in the surface nature of the weathered samples discussed previously. Surface changes can have a significant effect on the impact behaviour of a material as demonstrated and discussed in Section 4.4 with abrasion effects. These effects are most significant if the affected surface is tested in

157

tension. Surface changes caused by weathering generally result in reactions such as chain scission or crosslinking, which leads to a decrease in chain mobility and hence a decrease in surface strength.

PMMA-2 loses strength gradually on exposure to UV radiation. The gradual decrease is thought to be due to the type of impact modifier incorporated. In this case there is no association between loss of impact strength and the development of surface crazing. Prolonged exposure to the xenon arc light source eventually lowers the impact strength to a level somewhat below that caused by abrasion (seeTables 3.19 and 3.22). The impact modifier used in PMMA-2 has been identified as an acrylate polymer which constitutes a rubbery phase in the material. With rubber-modified polymers long-term exposure leads to the formation of a degraded surface layer containing cross-linked rubber particles in a matrix of reduced molecular weight. Cross-linked rubber is ineffective as a toughening agent so the embrittled surface may serve as a site for brittle crack initiation. At lower exposure periods when low levels of the rubbery phase are cross-linked, much of the tensile stress induced by impact is absorbed by the bulk polymer so a slight loss in impact resistance is observed. Cross-links are weaker than the bonds in the main polymer chains and so will slip under localised high stress concentrations. This will reduce the stress concentrations by causing the applied load to be shared over neighbouring chains and thereby permits the deformed network as a whole to bear a higher stress than expected. As more of the rubbery phase cross-links the impact resistance decreases so that at longer exposure virtually none of the initial impact resistance remains. Shorter wavelength radiation increases the extent of cross-linking[13] and so reduction in impact resistance occurs at shorter exposure to fluorescent lamps than under xenon arc lamps (Figures 3.44 and 3.45).

PVC-1 and PVC-2 show an increase in impact resistance on short exposure periods before the ductile/ brittle transition occurs. This is thought to be due to crosslinking in the polymer. As the extent of crosslinking increases the impact resistance of the polymer increases until a threshold value is reached and a sharp ductile/brittle transition occurs, further crosslinking leads to embrittlement. Embrittlement results from a) crosslinking which reduces mobility so the greater the crosslinking the lower the impact strength, b) molecular chain scission which is one of the processes occurring during photo-oxidation, or c) craze formation which results in

158

increased stress concentrations and allows a crack to follow behind the craze. The sharp transition from ductile to brittle behaviour appears to be associated with the development of surface crazing for both samples (Tables 3.18 and 3.19). Exposure to shorter wavelength UV radiation causes ductile/brittle transitions to occur at shorter exposure periods (Tables 3.20 and 3.21). Both PVC-1 (at 1000 hours Xenotest-1200) and PVC-2 (at 250 hours Xenotest-1200) pass through a phase where replicates fail in both ductile and brittle modes. The brittle failures have energies to failure very similar to surface abraded samples (Table 3.22).

PMMA-2 shows brittle behaviour similar to that of PVC-2 on exposure to UV-A or xenon arc lamps. Here a hole of similar size to the base hole is punched out of the sample with little crack propagation through the rest of the sample. This is probably an effect due to the incorporated impact modifier in these materials. On exposure to UV-B radiation however, crack propagation is observed in samples of PVC-2 and PMMA-2. PVC-2 demonstrates extensive crack propagation through the sample when failing in the brittle mode.

A slight decrease in absorbed energy at failure was observed in weathered samples of both polycarbonate materials although it is thought that at lower temperatures greater reduction would be apparent (especially at temperatures below -40°C where the β-transition occurs[145]).

Both polycarbonate materials substantially retained their impact strength on weathering even though both developed significant surface cracking and crazing on exposure to artificial weathering. This is in line with the impact behaviour of surface abraded test pieces (Table 3.22), which show full retention of impact strength for both abrasive papers used.

At least for the six samples tested, the abrasion/impact test is accurately predictive of the effects of long term artificial weathering. It requires further work to validate this as a generally predictive procedure. It would be very useful to have such a predictive procedure since weathering with periodic destructive impact testing is a time consuming procedure. The abrasion/impact test is only indicative of the ultimate effects of weathering, however, it gives no indication of the length of exposure to weathering needed to induce embrittlement.

159

4.3.3 Changes in Functional Group
4.3.3.1 The Advantages of Using Photo-acoustic Spectroscopy

Attenuated Total Reflectance (ATR) works best on optically flat plastics glazing materials before weathering has caused surface roughening; the technique thus gave clear spectra for reference samples with good reproducibility.

Photo-acoustic spectroscopy was found to give the best spectral reproducibility for weathered samples since it does not rely on a flat or smooth surface. Earlier work showed spectra of reference samples compared extremely well with library spectra[140]. An advantage is that only a small sample is required. Depth of sampling is the order of 5-15μm for the operating conditions available, compared to ATR sampling at 0.3-3μm; however, the technique is sufficiently sensitive to ensure one is looking at the weathered surface only with no interference from the bulk polymer.

4.3.3.2 Poly(methylmethacrylate)

No differences were observed in the IR spectrum of PMMA-1 exposed in X-1200 for 14500 hours. Slight increases in peaks in the carbonyl region (1700cm^{-1}) were found following exposure in the Q-UV under both UV-A and UV-B lamps (Figure 3.11).

For PMMA-2, after 6750 hours exposure in the X-1200 or 2000 hours in the Q-UV there appears to be an increase in C-O bonding around 1160cm^{-1} and a slight broadening of the C=O peak, with two new peaks at 1705cm^{-1} and 1740cm^{-1} (Figures 3.12 and 3.13).

Aldehyde formation could cause an absorption at around 1700cm^{-1} which supports the mechanism:

$$\begin{array}{ccc}
CH_3 & CH_3 & CH_3 \\
| & | & | \\
-CH_2\text{-}C\text{-} \xrightarrow{h\nu} & -CH_2\text{-}C\text{-} \xrightarrow{h\nu} & -CH\text{-}C\text{-} \\
| & | & | \\
COOCH_3 & CO^{\cdot} + {^{\cdot}}OCH_3 & CHO
\end{array}$$

$$1705cm^{-1}$$
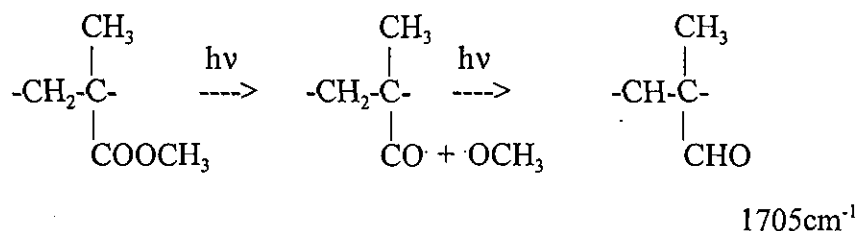
Hydrogen abstraction would lead to a slight shift in the absorption of the C=O bond which may be the cause of the peak at 1740cm^{-1}, by the mechanism:

160

$$CH_3 \qquad CH_3 \qquad\qquad\qquad CH_3 \qquad\qquad \cdot CH_2$$

$$| \qquad\qquad | \qquad\qquad\qquad\qquad | \qquad\qquad\qquad |$$

$$-CH_2\text{-}C\text{-} \; + \; -CH_2\text{-}C\text{-} \qquad \text{---->} \qquad -CH_2\text{-}C\text{-} \qquad + \; -CH_2\text{-}C\text{-}$$

$$| \qquad\qquad | \qquad\qquad\qquad\qquad | \qquad\qquad\qquad |$$

$$CO\cdot \qquad\quad COOCH_3 \qquad\qquad\qquad CHO \qquad\qquad COOCH_3$$

$$\text{1705cm}^{-1} \qquad\qquad \text{1740cm}^{-1}$$
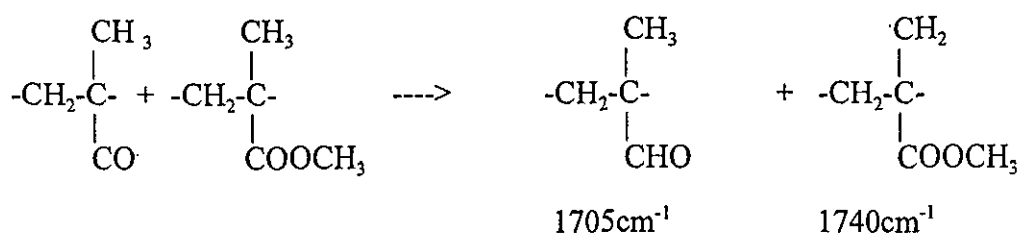
The presence of two peaks supports the hydrogen abstraction mechanism. Under UV-B exposure both PMMA samples show a small increase in the peak at 1650cm^{-1} (Figures 3.4 and 3.5) which can be attributed to formation of conjugated species in the molecular chain. The reaction to form such species follows photolysis of the ester side groups. This explains the slight yellowing observed in samples following exposure to short wavelength UV radiation (Section 4.3.1.1).

4.3.3.3 Polycarbonate

IR spectra for both polycarbonate materials show several differences between weathered and reference samples. This suggests complicated photo-oxidation. The observed absorptions are assigned for each spectrum in Table 4.9[41,42].

Table 4.9 : PC-1 X-1200 Exposure (Figure 3.14)

Peak Abs cm^{-1}	Assignment	Peak Abs cm^{-1}	Assignment
1825	anhydride	1590	subst. phenol
1770		1500	benzene ring
1750	phenyl ester	1270	
1720	aliphatic acid	1230	subst. phenol
1700	aromatic acid	1200	subst. phenol
1620	subst. phenol	1160	subst. phenol

Changes in peak absorbance with exposure are plotted in Figure 4.3. The values plotted are peak absorbance ratioed against that at 1500cm^{-1}.

161

Figure 4.3 : Structural Changes in PC-1, X-1200 Exposure
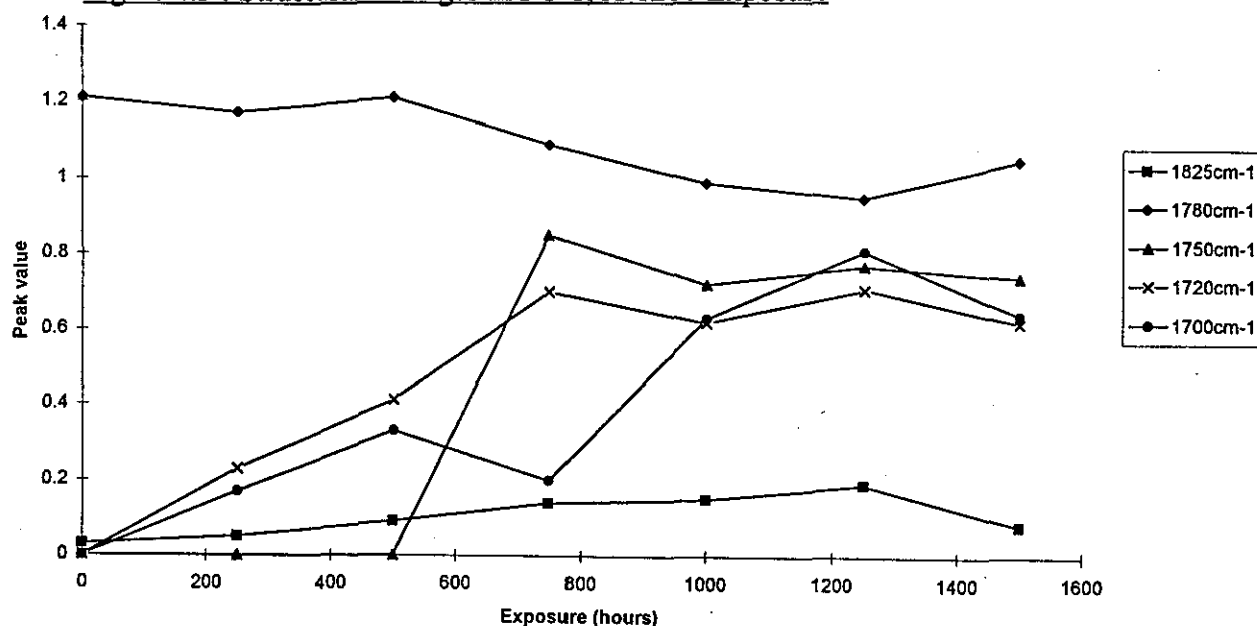
After 1250 hours there is a decrease in photo-oxidation products. Between 1000-1500 hours the glossiness of the material decreases which suggests erosion of the surface causing an increase in surface roughness and thus a less deep weathered layer (Table 3.15). Surface crazing is also evident at this stage (Table 3.18).

Table 4.10 : PC-2 X-1200 Exposure (Figure 3.15)

Peak Abs cm^{-1}	Assignment	Peak Abs cm^{-1}	Assignment
1840	anhydride	1630	subst. phenol
1750	phenyl ester	1600	subst. phenol
1720	aliphatic acid	1240	subst. phenol
1680	aromatic acid	1200	subst. phenol
1650	aromatic acid	1150	subst. phenol

Possible aliphatic acids are : CH_3CO_2H HCO_2H

Possible phenol groups are:
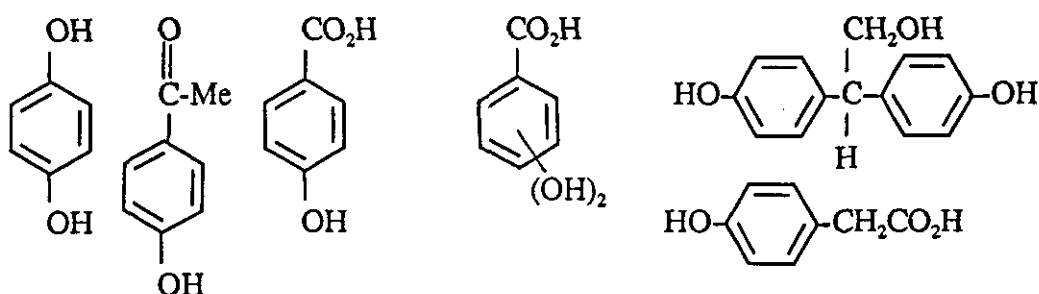
There is also evidence to support photo-Fries reaction with the formation of the following products:

Phenyl ester

Aromatic ketone
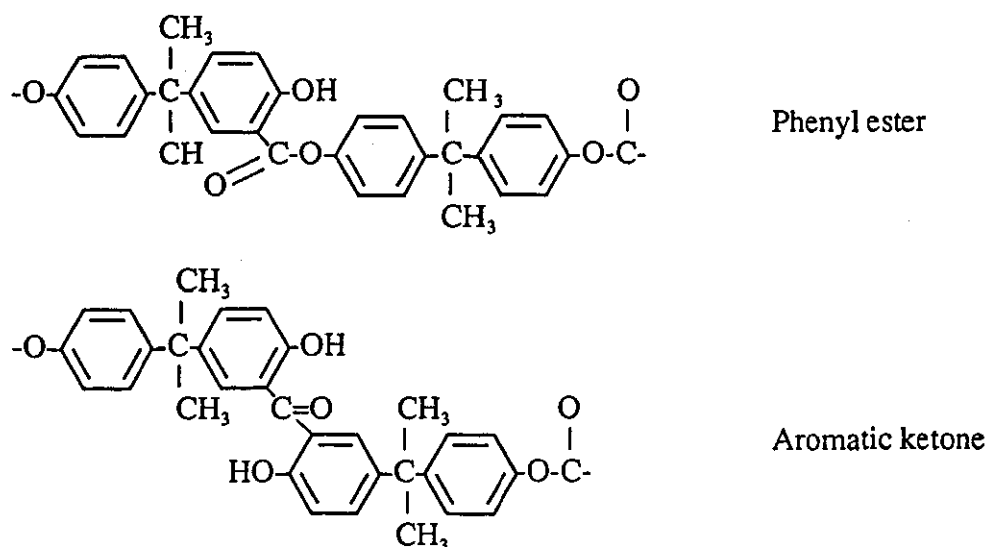
There appear to be less well defined differences between weathered and reference samples for exposure in the Q-UV. UV-A and UV-B exposures produce samples with very similar IR spectra. For both exposures there is an increase in absorption in the carbonyl region. The observed absorptions are assigned as follows:

163

<u>Table 4.11 : PC-1/PC-2 Q-UV Exposure</u> (Figure 3.16)

Peak Abs cm^{-1}	Assignment
1750	Phenyl ester
1720	Aliphatic acid
1700	Aromatic acid
1680	Aromatic acid
1650	Aromatic ketone
1620	Subst. phenol

This supports the photo-Fries reaction but there is little evidence of formation of substituted phenols.

4.3.3.4 Poly(vinylchloride)

Comparison of spectra for reference and weathered samples of PVC-1 exposed in the Xenotest-1200 shows significant changes in the carbonyl absorption region (Figure 3.17). There is also reduction of a peak at 690cm^{-1} which could be loss of C-Cl, and evidence of C=C formation with an increase in absorption between 700 and 1000cm^{-1}; these two changes support dehydrochlorination leaving polyene sequences.

Polyene systems that are formed must be coplanar in order to be conjugated and this must involve considerable, possibly quite complex, movements on the part of the polymer chains to achieve this. Photo-oxidation need not involve much molecular mobility by the polymer chain as a whole. Indeed photo-oxidation can promote effects such as chain scission and cross-linking which would probably tend to inhibit extensive polyene formation.

Hydrogen chloride may cause dehydrochlorination by participating in cyclic mechanisms such as:
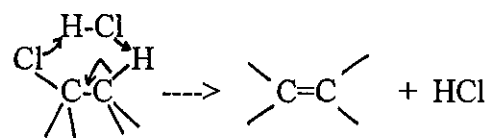
A coplanar transition state gives cis elimination. A further planar transition state in the next step can be envisaged to give a diene

164
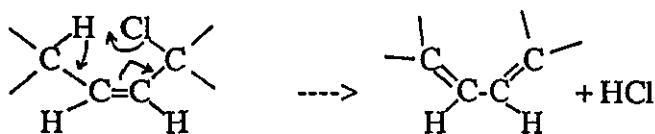
Further dehydrochlorination may depend on allylic chlorine atoms coming into the plane of the growing polyene , for example:
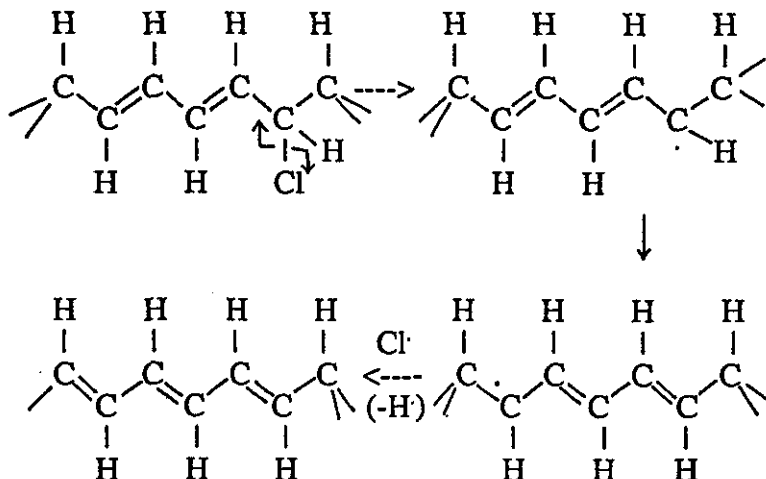
The need for coplanarity in polyene formation also requires molecular mobility so it will be strongly favoured at higher temperatures of exposure to UV, particularly if the Tg is exceeded. In sunlight and xenon arc exposures, the darker the PVC test piece becomes the hotter it will get, because abundant longer wavelengths will be absorbed.

Four new bands are evident in the carbonyl region at 1715, 1730, 1755 and 1785cm^{-1}. Q-UV exposure of PVC-1 produces more significant increases in absorptions in the carbonyl region of the spectrum (Figure 3.18). Although exposure to all three light sources causes increases in the same peak absorptions (carbonyl species) the relative absorbance of these peaks depends on the lamp type used.

Table 4.12 : Ratio of Carbonyl Peak Absorptions for PVC-1 (2000 hours)

Peak Abs (cm$^{-1)}$	X-1200	UV-A	UV-B
1718	1.0	1.0	1.0
1730	0.87	0.94	0.98
1755	0.69	0.72	0.95
1785	0.42	0.46	0.55

Exposure also causes an increase in C-O absorption (1150-1200cm^{-1}). These spectra suggest acid chloride and chloroketone formation from photolysis of hydroperoxides. Photolysis of a tertiary hydroperoxide leads to formation of an acid chloride:

$$\begin{array}{cc}
\text{Cl} & \text{Cl} \\
| & | \\
\text{-CHCl-CH}_2\text{-C-CH}_2\text{-CHCl-} \xrightarrow{h\nu} & \text{-CHCl-CH}_2\text{-C-CH}_2\text{-CHCl-} \\
| & | \\
\text{OOH} & \text{O}^{\cdot}
\end{array}$$

$$\downarrow \begin{array}{l}\beta\text{-scission} \\ +\text{O}_2 + \text{PVC}\end{array}$$

$$\begin{array}{cc}
\text{-CHCl-CH}_2\text{-C=O} + & \text{-CHCl-CH}_2\text{-C=O} \\
| & | \\
\text{OH} & \text{Cl}
\end{array}$$

β-chloro-carboxylic acid   β-chloro-acid chloride
1718cm^{-1} 1785cm^{-1}
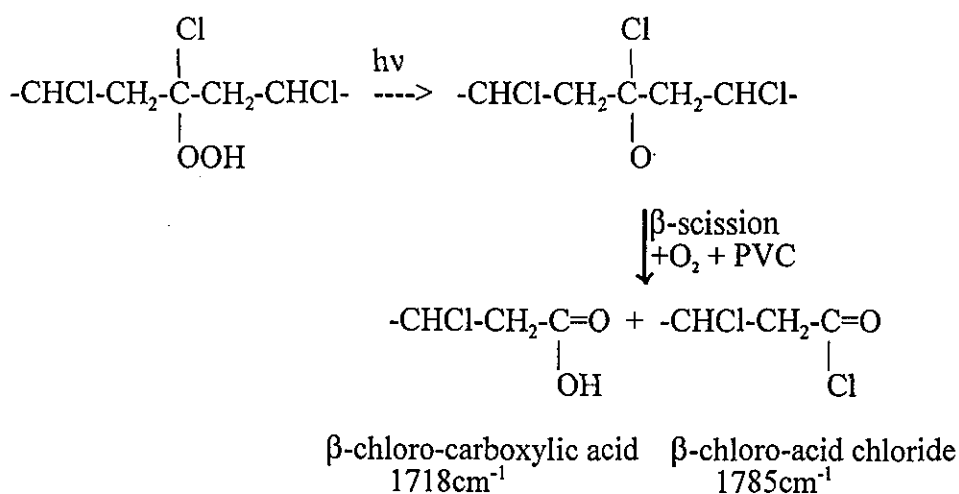
Photolysis of a secondary hydroperoxide leads to formation of a dichloroketone:

$$\begin{array}{ccc}
\text{-CHCl-CH-CHCl-} \longrightarrow & \text{-CHCl-CH-CHCl-} \xrightarrow[\text{reaction}]{\text{cage}} & \text{-CHCl-C-CHCl-} \\
| & | & || \\
\text{OOH} & \text{O}^{\cdot}\ {}^{\cdot}\text{OH} & \text{O}
\end{array}$$

α,α'-dichloroketone
1755cm^{-1}
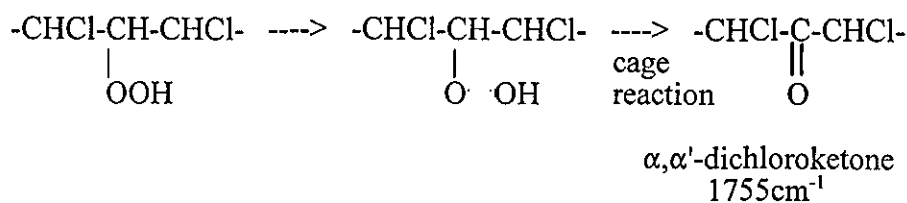
A secondary hydroperoxide can also lead to formation of a fourth photolysis product:

$$-CH_2\text{-}CHCl\text{-}\overset{\displaystyle\overset{\textstyle H}{|}}{C}\text{-}CHCl\text{-} \ \xrightarrow{\ h\nu\ } \ -CH_2\text{-}CHCl\text{-}\overset{\displaystyle\overset{\textstyle H}{|}}{C}\text{-}CHCl\text{-}CH_2\text{-} \ \xrightarrow[O_2]{\ \beta\text{-scission}\ } \ -CH_2\text{-}CHCl\text{-}C{=}O$$

-CH₂-CHCl-C-CHCl- with OOH below; -CH₂-CHCl-C-CHCl-CH₂- with O· and ·OH below; -CH₂-CHCl-C=O with OH below

α-chloro-carboxylic acid
1730cm⁻¹
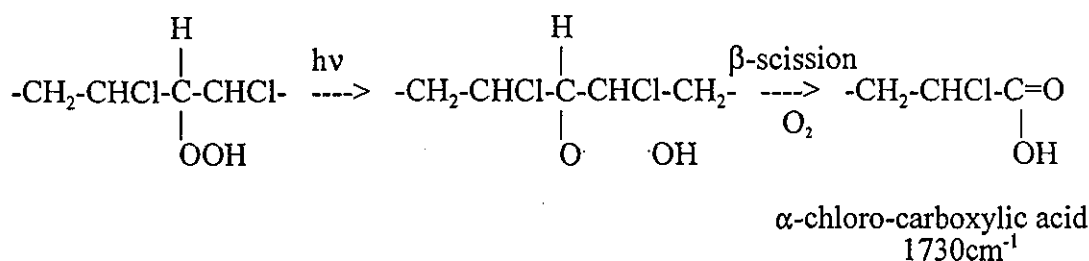
Figures 4.4 and 4.5 show plots of formation of photo-oxidation products versus exposure time to UV-B radiation. The values plotted are peak absorbance ratioed against that at 1430cm⁻¹.

Figure 4.4 : Structural Changes in PVC-1 UV-B Exposure
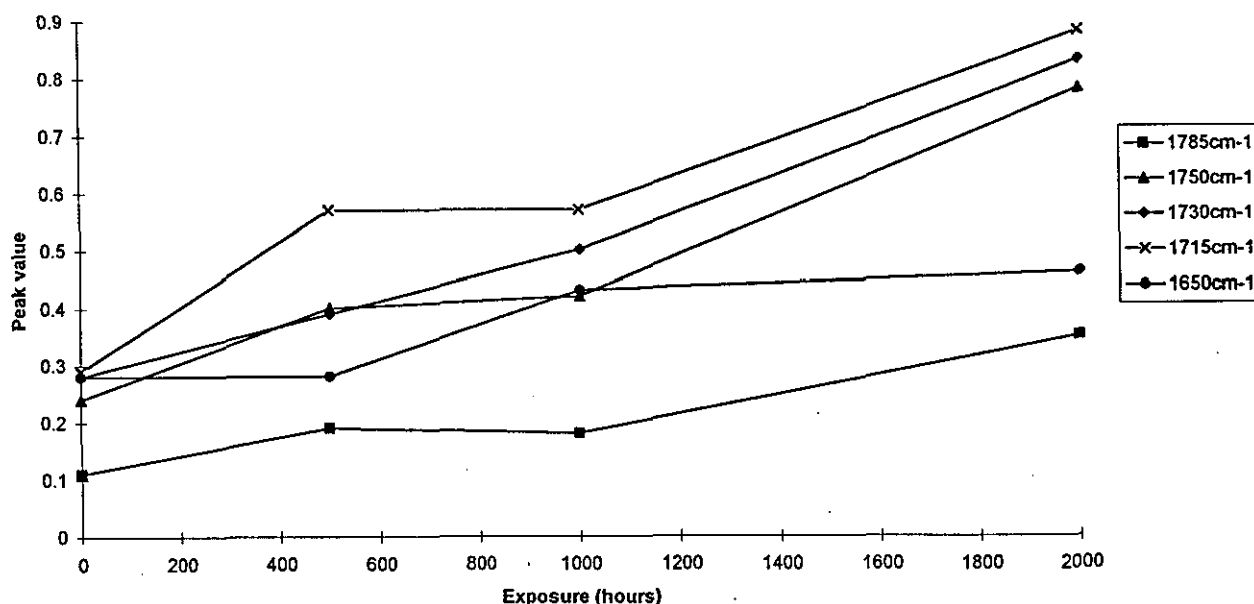
With PVC-1 there is a plateau in carbonyl peak formation between 500-1000 hours exposure but an increase in conjugated C=C groups (peak at 1650cm⁻¹); this correlates with colour data which shows the main colour change occurs in the material before 1000 hours, similarly transmission of light in the 290-400nm (UV) region decreases rapidly during this period.

With PVC-2 the largest changes occur up to 1000 hours exposure followed by a relatively gradual change; this correlates with colour data and transmission of UV light

which is reduced to 15% of the initial after 1000 hours exposure.

Figure 4.5 : Structural Changes in PVC-2 UV-B Exposure
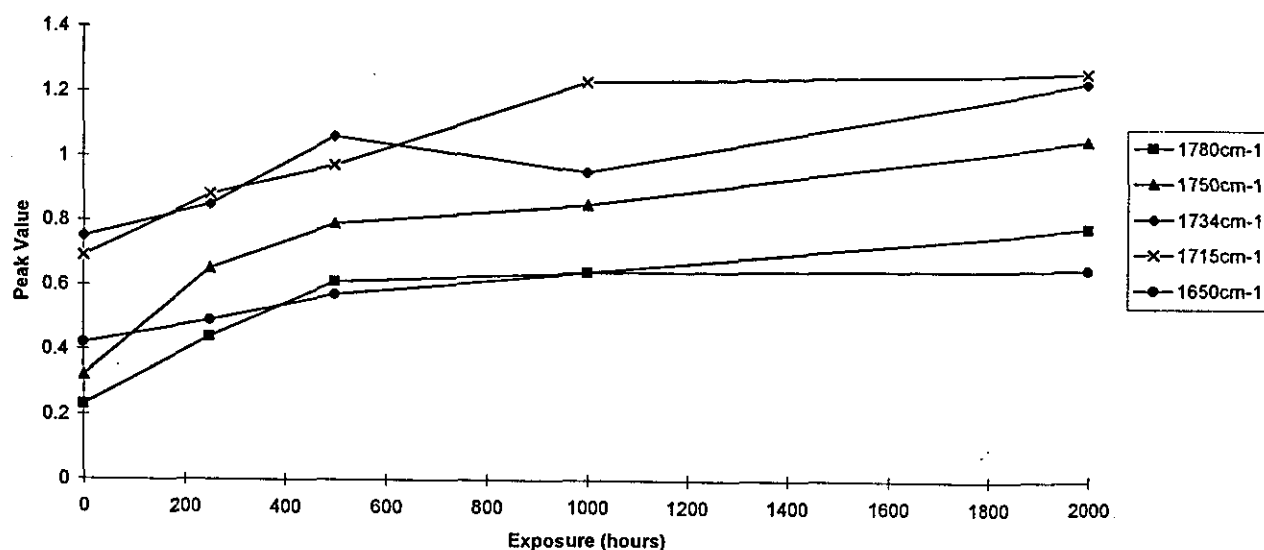
PVC-2 shows a possible loss of C-Cl which suggests dehydrochlorination. The weathered samples on exposure to all three lamp types show a broadening of the carbonyl peak; three main peaks are apparent and can be assigned as follows:

Table 4.13 : PVC-2 Carbonyl Species

Peak Abs cm^{-1}	Assignment
1715	β-chlorocarboxylic acid
1750	α,α'-dichloroketone
1785	β-chloroacid chloride

Depth profiling of the two PVC samples did not give as clear results as was hoped but it was possible to estimate that the weathered layer extends into the sample by about 20μm. For very short exposure periods the option of using higher mirror velocities (not available at present) could be advantageous so that sampling depths of 3-7μm may be achieved.

168

4.4 EFFECT OF ABRASION ON IMPACT RESISTANCE

For tests at 23°C scratching the surface of polymer samples was shown to reduce the energy required for failure in PMMA and PVC specimens (Tables 3.22 and 3.23). PMMA-2, which contains an impact modifier, showed considerably higher impact resistance than PMMA-1; although scratched samples of both materials showed similar impact resistance, that of PMMA-2 being reduced to only about 5% its initial value. Unabraded PVC fails in a ductile manner, however, scratched samples of both PVC materials failed in a brittle manner, the impact resistance being reduced to about 5% the initial values. This suggests notch sensitivity in these materials. Although little difference was observed between scratched and unscratched polycarbonate, it is thought that testing at lower temperatures may produce significantly different results[147].

Introducing a notch into a sample introduces a region of high stress into the specimen[148]. In this case a scratch can be considered as a series of notches. Thus the energy required to initiate a crack is reduced and propagation is much easier. A sharp notch reduces the impact strength more than a blunt notch, as stress concentration is increased by `corners' and sharp edges.

Some materials such as PVC appear to be `notch sensitive'. This occurs where a material has reasonable impact properties until a notch, or crack of critical length, is introduced. Then the material becomes brittle.

When the notch is very sharp it can be assumed that the energy necessary to initiate the crack is small and the main contribution to the impact strength is propagation energy. Failure in abraded samples is thus likely to initiate at the deepest, sharpest scratch on the sample where the stress concentration is greatest.

4.5 GENERAL DISCUSSION

Artificial weathering tests vary considerably and Standard methods have been, and are currently being, developed through various Standards committees. There is no clear correlation between natural and artificial weathering in relation to quantitative prediction of durability. However, correlation between natural and accelerated testing on a qualitative

169

basis is good in some cases but may depend on the specific test conditions.

The applicability of ultra-fast methods of accelerated degradation depends on the extent to which the mechanisms of degradation simulate practical weathering. Present evidence suggests that these are different but some reasonable correlation with the xenon arc test and with natural weathering has been reported in the literature[149,150]. It is not true that polymer degradation generally occurs primarily from solar UV between 290 and 350nm[151]. Therefore, simulation of the long wavelength UV and visible radiation is just as important as simulation of the short wavelength UV radiation. Misleading information is obtained when the full spectrum of solar UV and much of the visible is not adequately reproduced in accelerated tests. This was particularly evident for PVC-1, an established grade of the polymer. With fluorescent lamps, those of the UV-A type are preferred, operating at temperatures lower than suggested in ISO 4892: Part 3, for example 45°C. The output from UV-B lamps extends below 295nm, the solar cut-off, so reactions may occur that would not be seen outdoors.

Considerable care is needed in interpreting the results of fluorescent lamp exposures, especially when a range of polymer types is being compared. None of the fluorescent lamp conditions tested produce the type of behaviour seen with PVC-2 in the black-backed xenon-arc mode. This type of behaviour, typically involving rapid and severe discolouration following a more or less prolonged period of little change, has been seen in practice in the U.K. where PVC-U rooflights are widely used. It is associated with high surface temperatures of the glazing units, usually rooflights, in sunlight[152].

It is important when defining a test that it is applicable to a wide variety of polymer types and surfaces used for glazing purposes. No disproportionate bias should be introduced for or against any particular type. It is also necessary to be able to investigate the effects of design variables, such as surface temperature, that are likely to be encountered in practice. Sample temperature plays a significant role in the weathering of polymers, particularly PVC materials. In testing transparent materials in xenon arc weathering devices it is particularly important to specify and control the method of mounting[4]. These methods reported here, 'open-backed' and 'black-backed', represent the extremes of temperature which can result from such variations. One point requiring further consideration is that different xenon arc devices may need to be set at significantly different cabinet air temperatures in order to reach a given black standard thermometer temperature. It follows that the surface temperatures reached by transparent materials in the open-backed mode are likely to vary considerably.

It is believed that cyclic variation of temperature and humidity in artificial (and natural)

weathering imposes a type of stress fatigue on the material. This physically induced stress fatigue is caused by the non-uniform dimensional changes that result from thermal and moisture content gradients between the surface and the bulk resin and from inhomogeneities and defects inherent in the material. With weathering, the resin of the exposed surface undergoes gradual photochemical degradation that reduces its strength. When the fatigue limit at a microsite becomes lower than the physically induced stresses, the resin undergoes fracture to produce microcracks. Microcracking only occurred under the influence of radiation: short wavelengths promoted surface cracking in PVC; longer wavelengths promoted surface cracking in polycarbonates. Thus the polymer surface seems to fail by a form of stress fatigue induced by radiation. Only very small visual or measured colour changes were observed in either of the two acrylic materials on long exposure to xenon arc radiation, even in cases where the sample temperature was raised by the method of mounting. Similar results were observed under fluorescent lamps although the higher operating temperatures had a more significant effect. The mechanism of degradation was found, by FTIR-PAS analysis, to be wavelength dependent. Longer wavelength radiation resulted in aldehyde formation; with shorter wavelengths present conjugated species were also formed which caused yellowing of the material. The most significant change for PMMA-1 was in molecular weight, the large decrease being attributed to extensive chain splitting to form radicals which then undergo photolysis. PMMA-2 lost virtually all its initial impact strength on exposure due to cross-linking reactions of the incorporated rubbery-type impact modifier; shorter wavelength exposure again produced the most rapid change in properties.

Both PVC materials showed reduction in light transmission and in impact resistance on weathering, two of the most important properties for glazing materials. Both samples were shown to have notch sensitive impact resistance. Short wavelength UV radiation promoted surface cracking which led to reduction in impact resistance after only short exposure periods. On exposure to xenon arc radiation under lower temperature exposure conditions photo-oxidation predominated resulting in formation of carbonyl groups ($-CH_2COCH_2-$) along the polymer chain. When higher temperatures were used dehydrochlorination set in leading to the formation of polyene sequences. High temperatures are needed because the mechanism is under steric control and depends on molecular mobility of the polymer chains for conjugated polyene sequences to form and cause yellowing. The glass transition temperatures of both PVC samples are close to the higher temperature operating conditions which means the polymer chains are very mobile. It is unlikely that polyene formation is

171

initiated at points of weakness in the polymer chain caused by photo-oxidation or thermal damage encountered in processing etc. Chromophores have to be present capable of absorbing and utilising UV energy. Once polyene formation has set in, the chromophores themselves will be subject to destruction by photo-oxidation; under fluorescent lamps, ie. shorter wavelength radiation, photo-oxidation is the dominant mechanism. It seems quite a delicate balance which process dominates or whether an equilibrium is established. If the chromophores develop sufficiently to absorb significant amounts of visible light this will cause heat absorption and a further rise in temperature. This will give rise to increased molecular mobility and the formation of presumably very large polyene systems causing blackening.

Polycarbonate materials degraded rapidly when subjected to UV radiation and lost a high percentage of their light transmission. The degradation or rate of discolouration was rapid on initial exposure but decreased with increased irradiation time. Complicated photo-oxidation took place. Under xenon arc radiation, ie. longer wavelengths present, many substituted phenols were formed supporting an autocatalytic cycle as discussed in Section 1.2.4.3; there was also some evidence of photo-Fries reaction. With fluorescent lamp exposure, ie. shorter wavelength present, no substituted phenol formation was observed and the predominant mechanism was photo-Fries reaction. The resulting photo-products in this case will be very strong UV absorbers and unless themselves degraded (possibly by longer wavelengths present in xenon arc weathering devices or sunlight) will have a protective effect which may account for the good gloss retention shown by PC-1 and PC-2 exposed to fluorescent lamps accompanied by marked yellowing.

CHAPTER 5 : CONCLUSIONS

Artificial weathering test methods vary considerably, their applicability depending on the extent to which the mechanisms of degradation simulate practical weathering.

Misleading information is obtained when the full spectrum of solar UV and much of the visible is not adequately reproduced in accelerated tests. Unless it is known that the long wavelength UV and visible radiation have no effect whatever on the durability of the materials tested, it is essential to adequately reproduce solar radiation.

Profiling of chemical (e.g. carbonyl index for polycarbonate and PVC), physical (e.g. molecular weight for cast PMMA) and mechanical properties (e.g. impact resistance for PVC and extruded PMMA) as a function of exposure period and environmental conditions is a key requirement for quantifying the rate of degradation.

FTIR is a powerful technique for polymer analysis. FTIR-ATR works best on optically flat materials before weathering has caused surface roughening. FTIR-PAS was found to give the best spectral reproducibility for weathered samples.

The acrylics tested in the trials show very good weathering characteristics. The cast acrylic underwent surface breakdown (probably chain scission) resulting in formation of lower molecular weight species. Extruded acrylic sheet underwent surface reaction by a hydrogen abstraction mechanism.

PVC-1 shows good durability to xenon arc radiation, but does not perform well under fluorescent lamps. PVC-2, as predicted, shows poor durability under all conditions used. Degradation rate is temperature dependent, higher temperatures resulting in increased degradation. Degradation mechanism is wavelength dependent. Short wavelength radiation (Q-UV exposure) results in predominantly photo-oxidation although some dehydrochlorination also occurs. Exposure to longer wavelength radiation (xenon arc exposure) results predominantly in dehydrochlorination although some photo-oxidation also occurs. Shorter wavelength UV promotes surface cracking in PVC, so loss of impact resistance occurs early on exposure.

Polycarbonate materials show rapid degradation under all exposure conditions. The

degradation mechanism is wavelength dependent. Under short wavelength radiation the predominant mechanism is photo-Fries reaction; when longer wavelength UV and visible radiation is also present substituted phenols are formed in addition. Longer wavelength radiation promotes surface cracking which is more severe under high temperature exposure.

Surface microcracking only occurs on samples under the influence of radiation. The polymer surface fails by a form of stress fatigue induced by radiation. There appears to be an association between microcracking of exposed PVC-U and loss of impact strength.

It is considered that artificial weathering using suitably filtered xenon arc lamps as defined in ISO 4892: Part 2: Method A, offers the most suitable approach to comparative weathering tests which involve direct comparison of a wide range of polymer types. When operated at higher temperatures this device gives early warning of material susceptibility to high temperatures outdoors.

The different methods of mounting samples in the Xenotest-1200 allow a degree of control over sample surface temperature. The use of such methods allows the effects of increased temperature on weathering to be assessed and hence the implications for various practical applications which tend to impose high service temperatures. This is particularly useful for assessing PVC double-skin glazing systems. Also, with very durable materials, the additional acceleration achieved at higher temperatures, together with increased thermal shock during rainspray, may offer the only practical means of assessment in a reasonable time scale.

The use of UV-A lamps should lead to fewer apparently anomalous results for glazing materials than UV-B lamps. An operating temperature of 45°C is recommended rather than 60°C as cited in ISO 4892: Part 3.

There is a strong association, for the six materials tested, between loss of impact strength on prolonged exposure to weathering and loss of impact strength induced by surface abrasion using an impact/abrasion device. The latter appears to offer a potentially valuable means of predicting the ability of plastic glazing materials to retain strength on weathering. However, it would provide no guidance on the duration of weathering needed to cause embrittlement.

175

Further Work

1. To investigate the surface temperatures reached by transparent materials in the open-backed mode in other xenon arc weathering devices and the effect of this on polymer degradation.

2. To study the effect of test temperature on the impact resistance of glazing materials.

3. To expand the study to include coated and bulk-stabilised glazing materials. It is thought that coating with an acrylic layer, whilst it will improve light transmission retention and reduce photo-degradation of the bulk polymer, it may, on longer exposures reduce the impact resistance of the component as the acrylic layer will become embrittled on exposure to UV radiation.

4. To look at the possibilities of using two different polymers in double-skin structures, for example, and outer skin of acrylic will absorb most of the long wavelength UV to which PVC is most sensitive. This may have important significance in many building applications where double-skin structures have been used and are currently giving problems.

5. To investigate the possibility of developing the impact/abrasion test to predict the ability of plastic glazing material to retain strength on weathering.

REFERENCES

1. G R Rugger. Mat Design Eng, 59, 1, 70, (1964).

2. A King. Plastics and Polymers, June, 195, (1968).

3. R Vesely and F Erben. Int.Poly.Sci.Tech., 5, T/77, (1978).

4. S M Firth. MSc Thesis, Effect of Weather on the Durability of Plastics Glazing Materials, 1990.

5. A Blaga. Canadian Building Digest. 213, Oct, (1980).

6. A Blaga. Durability of Building Materials and Components. ASTM STP 691, 827, (1980).

7. Anon. Architects J., July, 80, (1973).

8. Anon. Architects J., Sept., 608, (1974).

9. Anon. Building, Feb., 53, (1975).

10. ANSI Z97:1-1984:Safety Glazing Materials used in Buildings.

11. A Davis and D Sims. Weathering of Polymers, Applied Science Publishers Ltd, (1983).

12. A W Birley, R J Heath and M J Scott. Plastics Materials, 2nd Ed, Blackie, Edinburgh, (1988).

13. J A Brydson. Plastics Materials 4th Ed, Butterworth Scientific, (1982).

14. ICI Tech Service Note PX31, (1980).

15. N Grassie and G Scott. Polymer Degradation and Stabilisation, Cambridge University Press, Cambridge, (1988).

16. J F Rabek. Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers (Theory and Applications), Wiley, Chichester, (1987).

17. G Scott. Polym.Degrad.Stab., 10, 97-125, (1985).

18. N C Billingham and P D Calvert. Degradation and Stabilisation of Polyolefins (Chapter 1). Ed. N S Allen, Appl.Sci.Publs., London, (1983).

19. P Vink. Degradation and Stabilisation of Polyolefins (Chapter 5). Ed. N S Allen, Appl.Sci.Publs., London, (1983).

20. E T Denisov. Developments in Polymer Stabilisation (Chapter 2). Ed. G Scott, Appl.Sci.Publs., London, (1982).

21. P E Cassidy and J M Aminabhvi. J.Macromol.Sci.-Rev.Macromol.Chem., C21, 89-133, (1982).

22. S H Hamid, A G Maadhah, F S Qureshi and M B Amin. Arabian J.Sci.Eng., 13, 503-531, (1988).

23. S G Kiryushkin and Yu A Shlyapnikov. Polym.Degrad.Stab., 23, 185-192, (1989).

24. A J Chirinos-Padron, P H Hernandez and F A Suarez. Polym.Degrad.Stab., 20, 237-255, (1988).

25. Z Osawa, S Wu and F Konoma. Polym.Degrad.Stab., 22, 97, (1988).

26. F Severini. R Gallo and S Ipsale. Polym.Degrad.Stab., 22, 185-194, (1988).

27. F Gugumus. Polym.Degrad.Stab., 27, 19-34, (1990).

28. F P La Mantia. Polym.Degrad.Stab., 15, 283-290, (1986).

29. R L Clough and K T Gillen. J.Polym.Sci.,Polym.Chem.Ed., 19, 2041-2051, (1981).

30. R L Clough and K T Gillen. Radiat.Phys.Chem., 18, 661-669, (1981).

31. G Avery and R C Poller. Developments in Polymer Stabilisation (Chapter 1). Ed. G Scott Appl.Sci.Publs., London, (1980).

32. B B Troitski and L S Troitskaya. Intern.J.Polymeric.Mater., 13, 169-178, (1990).

33. B B Cooray and G Scott. Developments in Polymer Stabilistion (Chapter 2)., Ed. G Scott, Appl.Sci.Publs., London, (1980).

34. B B Cooray and G Scott. Polym.Degrad.Stab., 3, 127-135, (1980).

35. J B Adeniyi and G Scott. J.Polym.Mater., 5,57-66, (1988).

36. D C Mellor, A B Moir and G Scott. Eur.Polym.J., 9, 219-225, (1973).

37. M M Qayyum and J R White. J.Appl.Polym.Sci., 43, 129-144, (1991).

38. G Ayrey, B C Head and R C Poller. J.Polym.Sci.-Macromol.Chem., 8, 1, (1974).

39. K G Martin. Br.Polym.J., 5, 443, (1973).

40. A Davis and J H Golden. J.Macromol.Sci.-Revs.Macromol.Chem., C3(1), 49, (1969).

41. A Davis and J H Golden. J.Chem.Soc.(B)., 425, (1968).

42. A Factor and M L Chu. Polym.Degrad.Stab., 2, 203, (1980).

43. N S Allen, A Chirinos-Padron and T J Henman. Polym.Degrad.Stab., 13, 31-76, (1985).

44. G M Conroy and K R Wursthorn. J.Vinyl.Tech., <u>10</u>, 37-40, (1988).

45. A R Schultz and A L Andrady. J.Appl.Polym.Sci., <u>33</u>, 2249-2252, (1987).

46. D J Carlsson, A Garton and D M Wiles. Developments in Polymer Stabilisation-1 (Chapter 7)., Ed. G Scott, Appl.Sci.Publs., London, 219-259, (1979).

47. J B Adeniyi and G Scott. J.Polym.Mater., <u>4</u>, 207-213, (1987).

48. A Guyot and A Michel. Developments in Polymer Stabilisation-2 (Chapter3)., Ed. G Scott, Appl.Sci.Publs., London, 9-124, (1980).

49. D G Pobedimskki. N A Mukmeneva and P A Kirpichnikov. Developments in Polymer Stabilisation-2 (Chapter 4)., Ed. G Scott, Appl.Sci.Publs., London, 125-184, (1980).

50. J W Burley. Review: Mechanistic aspects of the thermal stabilisation of PVC by organotin compounds, Appl.Organometallic Chem., <u>1</u>, 95-113, (1987).

51. G R Rugger. Paper 16, Conf. on Plastics in Building Structures, London, June, (1965).

52. K J Ledbury and A L Stoke. U.K. Ministry of Aviation, Explosives Res.and Dev.Est., Tech.Memo 18/M/64, (1965).

53. S E Yustein, R R Winnians and H J Start. ASTM Bulletin, <u>196</u>, 29, (1954).

54. ICI Plastics Division. Tech.Data PXTD 206-7, 2, (1981).

55. S E Yustein, R R Winnians and H J Start. ASTM Bulletin, <u>173</u>, 31, (1951).

56. K I Trusova and M M Gudimov. Soviety Plastics, <u>9</u>, 39, (1962).

57. L G Rainhart and J Schimmel. Inter.Solar Energy Soc.Paper. (US Sect.), (1974).

58. G Schreyer. Die Angerwandte Makro Chemie, 11, 159, (1970).

59. R S Yamasaki and A Blaga. JTEVA, 10, 4, 156, (1982).

60. E W Russell. Nature, 165, 91, (1950).

61. L G Rainhart and W P Scimmel. Solar Energy, 17, 4 259, (1975).

62. Anon. Modern Plastics, Aug., 89, (1965).

63. Technical Services Group. ICI Acrylics.

64. W S Penn. Plastics in Building Handbook, Maclaren, London, (1964).

65. D S Plumb. Mod.Plast., Feb., 75, (1965).

66. J Crowder. Rubb.Plast.Age, 46, 7, 809, (1965).

67. H M Leeper and I L Gomez. Mod.Plast., May, 257, (1966).

68. J G Hendricks. Plast.Tech., 81, (1955).

69. J B Decoste, J B Howard and V T Wallder. Ind.Chem.and Eng.Data Series, 3, 131, (1958).

70. U Moritz. Kunst., 65, 290, (1975).

71. G T Fedoseeva et al. Int.Polym.Sci.and Tech., 8, T1, (1981).

72. K G Martin and R I Tilley. Br.Polym.J., 3, 36, (1971).

73. K G Martin. Br.Polym.J., 5, 443, (1973).

74. M C Gough. Appl.Polym.Symp., 35, 387, (1979).

75. J T Lutz. SPE Tech.Papers, 23, 146, (1977).

76. J B Decoste and V T Wallder. Ind.Eng.Chem., 47, 314, (1955).

77. G Menzel, G Hundertmark and A Polte. Kunst., 67, 339, (1977).

78. H O Wirth and H Andreas. Pure and Appl.Chem., 49, 627, (1977).

79. C Probert. BRE (Garston). Unpublished Data.

80. Ministry of Defence. DRIC S & T Memo 13/73, (1973).

81. K B Abbas. J.Appl.Polym.Sci.;Polym.Symp., 35, 345, (1979).

82. A Blaga and R S Yamasaki. J.Mat.Sci., 11, 1513, (1976).

83. R J Gardner and J R Martin. J.Appl.Polym.Sci., 24, 1269, (1979).

84. D Hull and T W Owen. J.Polym.Sci.;Poly.Phys.Ed., 11, 2039, (1973).

85. R J Morgan and J E O'Neal. Polymer, 20, 375, (1979).

86. R J Morgan and J E O'Neal. J.Polym.Sci.;Poly.Phys.Ed., 14, 1053, (1976).

87. K J Ledbury. Plastics and Polymers, 41, 162, (1973).

88. Fisher Body Division General Motors Corporation, Test Method No. 30-32, Jan, (1966).

89. J R Darby and P R Graham. Mod.Plast., 148, (1962).

90. S Suzuki, O Nishimura, H Kubota, K Yoshikawa and T Shiroya. Proc.23 Japan Congress on Materials Research, Kyoto 293-300, (1980).

91. D Kockott. Polym.Degrad.Stab., 25, 181-208, (1989).

92. D Kockott. Angew.Makromol.Chem., 137, 1-13, (1985).

93. K S Minsker, S V Kolesov and G E Zaikov. Degradation and Stabilisation of Vinyl Chloride-based Polymers (Chapter11)., Pergamon, Oxford, (1980).

94. A L Andrady. J.Appl.Polym.Sci., 39, 363-370, (1990).

95. J E Pegram and A L Andrady. Polym.Degrad.Stab., 26, 333-345, (1989).

96. D M Grossman. J.Vinyl.Tech., 3, 38-47, (1981).

97. A Gilchrist and N J Mills. J.Mater.Sci., 22, 2397-2406, (1987).

98. R P Brown. Polymer Testing, 10, 3-30, (1991).

99. F Gugumus. Symp. on Polymer Stabilisation and Degradation: Problems, Techniques and Applications, Manchester, Sept., (1985).

100. H M Quackenbos and S H Samuels. Appl.Polym.Symp., 4, 155-165, (1967).

101. BS 3900 Paints: Parts F3-F5 Resistance to Artificial Weathering.

102. R J Martinovitch and G R Hill. Appl.Polym.Symp., 4, 141-154, (1967).

103. E B Rabinovitch and R S Butler. J.Vinyl.Tech., 13, 42-46, (1991).

104. S Matsumoto, H Ohshima and Y Hasuda. J.Polym.Sci.-Polym.Chem.Ed., 22, 869-871, (1984).

105. L E Nielsen. Mechanical Properties of Polymers, Reinhold Publishing Co., (1962).

106. D Campbell and J R White. Polymer Characterisation, Chapman and Hall, London, (1989).

107. W F Maddams and S F Parker. J.Appl.Polym.Sci., 27, 1691-1698, (1989).

108. G C Marks and G Butters. J.Macromol.Chem., A12, 569-586, (1978).

109. M Ganzarolli, O Pessoa, Jr H Vargas and F Galembeck. J.Appl.Polym.Sci., 35, 1791-1802, (1988).

110. M E Abu-Zeid, E E Nofal, M A Marafi, L A Tahseen, F A Abdul-Rasoul and A Ledwith. J.Appl.Polym.Sci., 29, 2431-2442, (1984).

111. F W Billmeyer Jr. Textbook of Polymer Science, Wiley, New York,(1984).

112. Yu A Schlyapnikov. Intern.J.Polym.Mater., 13, 1-16, (1990).

113. J N Hay. Analysis of Polymer Systems (Chapter 6), Eds. L S Bark and N S Allen, Appl.Sci.Publs., London, (1982).

114. M J Richardson. Polymer Testing, 4, 101-115, (1984).

115. M J Richardson and N G Savill. Polymer, 16, 753-757, (1975).

116. M M Qayyum and J R White. J.Mater.Sci., 20, 2557-2574, (1985).

117. M M Qayyum and J R White. Arab.Sci.Eng., 13, 545-556, (1988).

118. BS 3900: Part D9: 1986: Determination of Colour-Measurement. (ISO 7724-2:1984)

119. BS 3900: Part D10: 1986: Determination of Colour-Calculation. (ISO 7724-3:1984)

120. BS 3900: Part 5: 1986:Measurement of Specular Gloss of non-metallic paint films at 20°, 60° and 85°. (ISO 2813:1994)

121. S M Firth, D Gardiner and J L Whitcombe. PRI/BPF Conf., FILPLAS, April, (1989).

122. L Mascia. The Role of Additives in Plastics, Edward Arnold Publs. Ltd, London, (1974), ISBN 0-7131-3328-7.

123. R Tertian and F Claisse. Principles of Quantitative X-Ray Flourescence Analysis, Heyden and Sons Ltd, UK, (1982), ISBN 0-85501-709-0.

124. K M Siegbahn. Spektroscopie der Rontgenstrahlen, Springer, Berlin, (1931).

125. P R Griffiths and J A deHaseth. Fourier Transform Infrared Spectroscopy, John Wiley and Sons, (1986), ISBN 0-471-09902-3.

126. D H Williams. Spectroscopic Methods in Organic Chemistry, 3rd Ed., McGraw-Hill, (1980), ISBN 0-07-084108-X.

127. J R Andrews, D H Chenery and R C Milward. Int.Labmate, Vol XIII, 5, (1988).

128. J M Evans. Gel Permeation Chromatography : A Guide to Data Interpretation. RAPRA Bulletin Nov 1972.

129. T R Crompton. Analysis of Polymers, Chapter 7, Pergamon Press, (1989), ISBN 0-08-033936-0.

130. S Turner. RAPRA Review Report Vol4 No5, 'Failure of Plasics'.

131. G W Rothwell. BRE CP 4/82, A Method for the Determination of Abraisve-Impact Resistance of Coatings on Galvanised Steel.

132. BS 2782 : Part 5 : Method 540D : 1995; Plastics : Methods of Exposure to Laboratory Light Sources. (ISO 4892:1994)

133. S M Halliwell and D Gardiner. Construction and Building Materials, 8, 4, 233-241, (1994).

134. S M Halliwell and D Gardiner. 6th Int. Conf. Durability of Building Materials and Components, 2, 741, Japan, (1993).

135. CIE Publication No 85 : 1989; Technical Report - Solar Spectral Irradiance.

136. K P Scott. 1st Symp.Weatherability, Materials Life Society, Japan, (May 1992).

137. EN 1013 : Light Transmitting Profiled Plastics Sheets for Single Skin Roofing. General Requirements and Methods of Testing.

138. D M Grossman. Q-Panel Co Publication. `Know your Enemy : The Weather and how to Reproduce it in the Laboratory.'

139. Original Hanau Publication, Xenotest 1200.

140. S M Halliwell and D Gardiner. Evaluation of FTIR Techniques for Studying the Photo-degradation of Plastics Glazing Materials. BRE Note N108/94.

141. M Gilbert, D A Hemsley and A Miadonye. Plastics and Rubber Processing and Applications, 3, 343, (1983).

142. Anon. Atlas Sunspots, 12, 28, (1982).

143. A Andrady, A Toriaki and K Fueki. J.Appl.Poly.Sci., 37, 935, (1989).

144. C Decker and M Balandier. Env.Polym.J., 18, 1085, (1982).

145. M Parvin and J G Wiliams. J.Mat.Sci., <u>10</u>, 1883, (1975).

146. W Brostow et al. Failure of Plastics, Hanser, 1986, ISBN 3-446-14199-5.

147. S Halliwell and D Gardiner. The Effect of Abrasion on the Impact Resistance of Plastics Glazing Materials. BRE Note N84/94.

148. A Birley, B Haworth and J Batchelor. Physics of Plastics, Hanser Publ., New York (1992).

149. L F E Crewdson. Atlas Sunspots, <u>23</u>, 46, (1993).

150. L F E Crewdson. 2nd Int.Symp. Weatherability, Lilia, Sept.1994.

151. N D Searle. Atlas Sunspots, <u>24</u>, 48, (1994).

152. H Brown. Architects Journal, (Nov 1991).

APPENDIX

APPENDIX CONTENTS

APPENDIX A: EXPERIMENTAL PROCEDURES

A1: Weathering Procedures

<u>Xenotest-1200</u>

Samples of size 200x65mm were mounted in open-back holders and also on metal holders with black acrylic backing (a 3mm air gap was achieved between backing and sample by positioning 10mm wide strips of white PVC-U at either side between sample and backing). The samples were exposed in facing mode using the following machine conditions:

- $28\pm1\,^{\circ}C$ cabinet air temperature
- $65\pm5\,^{\circ}C$ relative humidity during the dry cycle
- water spray cycle 18 mins on / 102 mins off
- light intensity approximately 800 GJm^{-2} in the wavelength range 300 to 800nm

Samples were exposed for a minimum of 1500 lamp hours with exposure periods extended if necessary.

<u>Q-UV</u>

Samples of size 270x75mm were mounted in holders backed by aluminium plates. An exposure cycle of 4 hours UV / 4 hours condensation was employed. Two trials were carried out using the following conditions:

- $45\,^{\circ}C$ UV / $50\,^{\circ}C$ condensation
- $60\,^{\circ}C$ UV / $50\,^{\circ}C$ condensation

Two types of fluorescent lamps were used

- UV-A with maximum emission at 340nm
- UV-B with maximum emission at 313nm

Samples were exposed for up to 2000 lamp hours.

A2: X-ray Fluorescence Spectroscopy

The spectrometer used was a Philips PW1480 which is a sequential x-ray spectrometer system capable of measuring elements from boron to uranium.

Internal monitor standards were used to calibrate the instrument before samples were run using the computer-run calibration programme.

One 30x30mm square was cut from each 2mm thick sheet of material and placed in an aluminium cup with a 20mm diameter mask (giving a measured area of about $315mm^2$). The cups were then lined up in order on the automated sampling bench. The qualitative programme was selected on the computer to measure all the samples against all crystals and over all 2θ values. This meant 8 scans were done in all:

Crystal: LiF220, 2θ range 13.00 to 40.04

Crystal: LiF220, 2θ range 38.50 to 140.02

Crystal: LiF200, 2θ range 70.00 to 130.04

Crystal: LiF200, 2θ range 85.00 to 100.05

Crystal: LiF200, 2θ range 95.00 to 120.06

Crystal: Ge, 2θ range 73.00 to 142.06

Crystal: PE, 2θ range 90.00 to 145.84

Crystal: PX1, 2θ range 20.00 to 60.08

This enabled the samples to be scanned from sodium to uranium. Two types of detector were used ; a scintillation counter for short wavelengths and a gas flow detector for longer wavelengths; these were switched in/out automatically by the instrument during each run. The spinner was manually set to 'on' to ensure even exposure of the sample surface to the radiation. For each crystal 2θ values were calculated by computer and listed with signal level and most likely elemental identification. Quantitative values were not calculated and so external monitors were not used.

A3: Infra-red Spectroscopy

A Nicolet 510P infra-red spectrometer bench was used. The instrument is controlled by computer using Nicolet software series 2.1 (menu driven software).

ATR

A zinc selenide crystal was used with a bench ATR attachment. The attachment sits in a holder attached to a base plate to ensure reproducible readings. A background spectrum on the crystal was taken before every sample measurement. Samples 10x60mm were cut from 2mm thick sheets of control materials. These were then placed on the crystal and clamped using a screw-down pressure device - care being taken to apply even pressure to the crystal. Spectra were obtained over 34 scans with gain set at 16, speed set to slow and resolution set at 8cm^{-1}. A computer ATR correction was applied to spectra and the corrected spectra analysed. ATR was used for reference materials only as the weathered samples had too rough a surface to ensure efficient sample-crystal contact. To identify additives etc library spectra were subtracted from the reference spectra by manual subtraction (the fraction was determined and set manually for each spectrum). The remaining peaks could then be identified and molecular structures assigned.

PAS

The photo-acoustic cell was placed in the sample compartment of the IR bench with its own unique base plate. A helium line was attached and the cell purged for 20 seconds with the gas and then sealed before each background and sample measurement. Background measurements were taken before every sample measurement - an 10mm cup filled with carbon black powder was used as a background. Samples approximately 8mm in diameter were cut from virgin and weathered samples using a bandsaw. These were placed in 10mm cups and measured with the photo-acoustic cell. Background and sample spectra were obtained over 34 scans with gain set at 1 on the bench top and 64 on the charge amplifier attached to the cell (used to boost the signal), resolution of 8cm^{-1} was used with the mirror velocity set to medium.

PAS was used to examine the effects of weathering. Virgin samples were measured and analysed to create reference data, and these subtracted from weathered spectra using the same procedure as above.

A4: Gel Permeation Chromatography

Approximately 5mg was scraped off the surface of each sample with a razor blade and dissolved in 10ml THF, measured using a syringe. A mixed gel column was used to separate the polymer samples. The pump, detector, computer and printer were switched on. The systems disc was inserted in drive 0 and a data disc in drive 1. A flow rate of 1.0ml/min was used. Instructions on the computer were followed to prepare the data file for column calibration - run identification CALIB and file name RA for calibration standards (a solution of 5 polystyrene standards having known molecular weights)sensitivity on the detector was set to 8. With the injection valve on 'load' a syringe was used to inject 50µl of standard solution, leaving the syringe in position the injection valve was turned to 'inject' and the start button on the signal convertor pushed. Once the peaks had been recorded, cursors were used to find maximum positions for each peak and the elution volume for each molecular weight noted. The instruction on the computer were followed to set up and print the calibration file. The programme was then run to analyse sample solutions, using the same experimental procedure as before and replacing K and a values with those appropriate for the sample being run. The elution plots were analysed by computer.

A5: Thermal Analysis

Differential Thermal Analysis

A Dupont 2000 thermal analyser fitted with a differential scanning calorimetry cell was used. 10mg of sample was cut off the sample, weighed and placed in the sample cup, and the lid fitted. The reference cell was pre-filled with an inert material. The sample and reference cells were then placed on the heating pads in the sample compartment, the compartment lid fitted and the glass dome placed over the top. The samples were heated at a controlled rate ($10°C/min$) from $40°C$ to $240°C$ using a pre-programmed method. The temperature of the sample and reference materials were continuously monitored using thermocouples. The temperature differential (ΔT) between the sample and inert material were fed in e.m.f. form to a recorder to plot ΔT against temperature (T). The data was analysed by computer using an analysis programme.

Dynamic Mechanical Analysis

The DMA instrument (Thermal Analysis Ltd equipment) was first calibrated with standard calibration samples using the computer led calibration procedure. Test samples 30mmx13mm were cut from 2mm thick sheets of each control material. These were clamped at each end in the sample compartment of the DMA apparatus. One end was held in the reaction frame and the other end was attached to the drive mechanism that applies the movement. The test run was computer driven. A frequency of 1Hz was used to achieve the required amount of movement. The amplitude of deformation was constant at 0.75mm. The samples were cooled to $-100°C$ using liquid nitrogen and then heated at a rate of $5°C/min$ from $-100°C$ to $180°C$. Data was fed to a computer for analysis.

A6: Colour and Gloss Measurement and Light Transmission

Colour Measurements

These were done using a Macbeth 1010S colorimeter attached to a BBC computer. The colorimeter was calibrated before each set of measurements were taken using a standard white calibration tile. The calibration was then checked with white and grey standard tiles. Measurements were taken over a 20mm diameter area on all specimens and L* a* b* values calculated by the computer programme. A standard white tile was held behind each transparent sample as the colour measurement was taken. Weathered samples were measured against pre-recorded control values and differences of $\Delta L^*, \Delta a^*, \Delta b^*$ and ΔE^* calculated by the computer programme. The colorimeter was operated with specular reflectance included. Generally, 3 readings were taken on each sample at each measurement stage and an average value calculated.

Gloss Measurements

60° specular reflectance was measured for all samples on a 20mm diameter area of sample. The gloss meter was calibrated on a standard gloss tile before each set of measurements was taken. Three readings were taken per sample and an average calculated.

Light Transmission

Samples 40mmx65mm were cut from weathered samples and from control pieces. These were held in the Pye-Unicam SP8-200 spectrometer in a sample holder. An integrating sphere was used. Wavelength ranges of 290-410nm and 400-790nm were scanned on each specimen and charts of percentage transmission obtained. Values at 10nm intervals were read manually and tabulated. Average percentage light transmission values were calculated by averaging the tabulated values over the specific wavelength range for each sample. Percentage remaining light transmission values were then calculated for each sample at each exposure by comparing average values with those obtained for the unweathered control sample.

A7: Impact Testing

All tests were carried out in a constant temperature room set at 23°C. A falling weight impact tester was used with a hemispherically headed dart of diameter 12.5mm and a supporting ring of diameter 25mm. The dart of weight 10kg was dropped from a fixed height of 0.431m with an impact velocity of 3ms^{-1} and a total energy of 45J. Samples 40x65mm were cut from 2mm thick sheets of control and weathered specimens. Weathered samples were placed face down on the support ring so as to put the weathered face in tension. Samples were impacted one at a time and data displayed initially on an oscilloscope screen, the signal then being transferred to a data processor which allowed a graph and numerical values of the impact event to be plotted and transferred to a computer. A computer programme was then run to calculate force, energy and displacement values. Three replicates of each sample were tested and average values calculated.

In testing the effect of abrasion on impact resistance, the samples were first abraded using the BRE abrasive impact pendulum device (see reference 131 for details of how to set up the equipment). Samples were abraded with either Grade Zero (G0) or Grade Two (G2) emery paper. Samples of size 200x65mm, 2mm and 3mm thick, were abraded and then three pieces 50x65mm were cut from this avoiding the ends. These three samples were then impact tested using the procedure described above, the abraded side being placed face down on the support ring to put this face in tension. Average values of force, energy and displacement were then calculated for each material in the unscratched and scratched state.

To test reproducibility of the results three materials were chosen on which nine samples were impact tested.

APPENDIX B : CHARACTERISATION OF REFERENCE MATERIALS

APPENDIX B1 : FUNCTIONAL GROUP ANALYSIS
INFRARED SPECTRA (PAS)

PMMA-1 REFERENCE

PMMA-2 REFERENCE

200
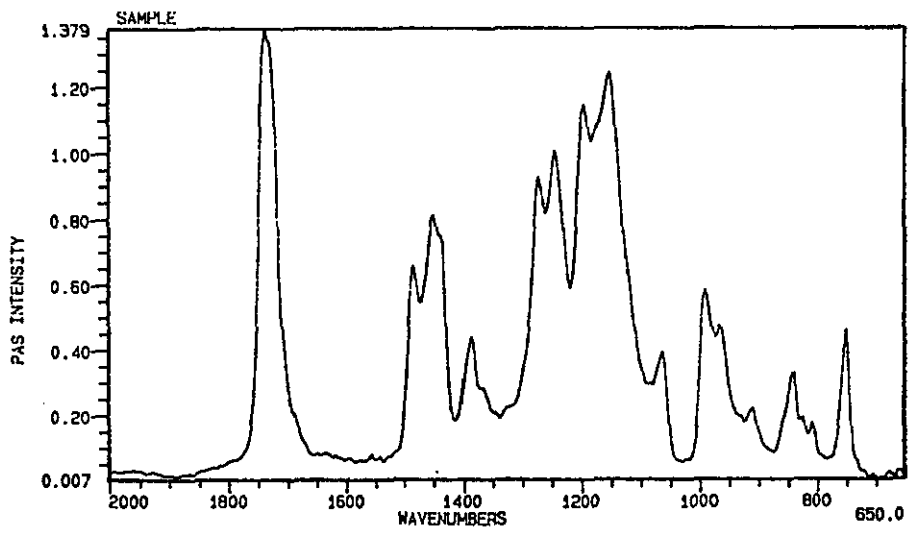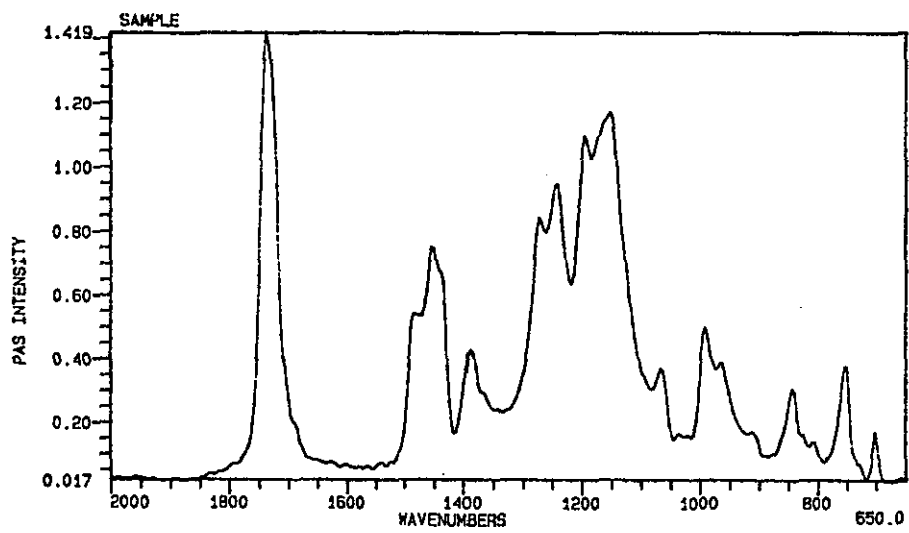
PVC-1 REFERENCE

PVC-2 REFERENCE

201
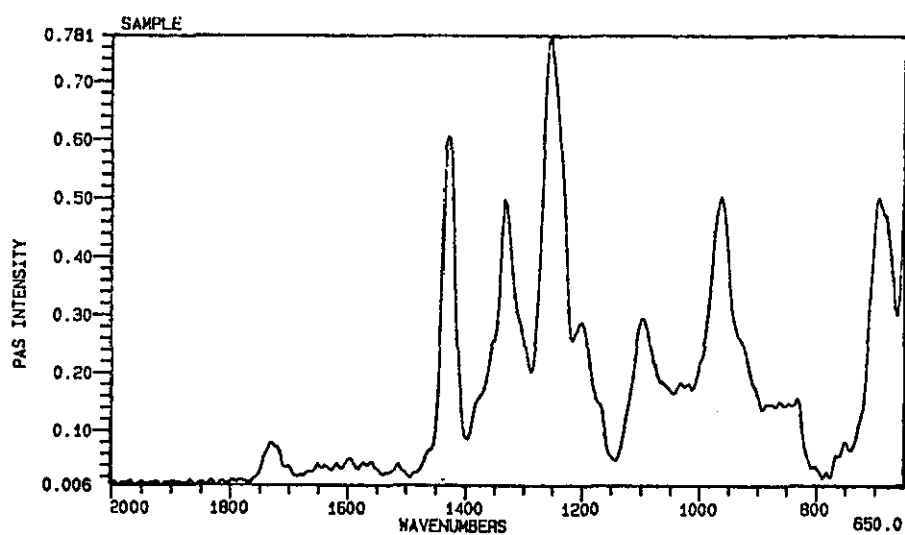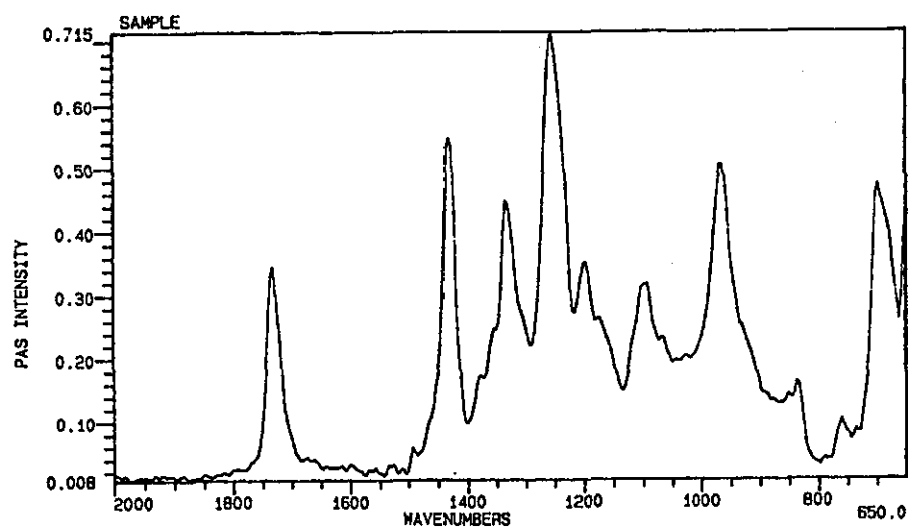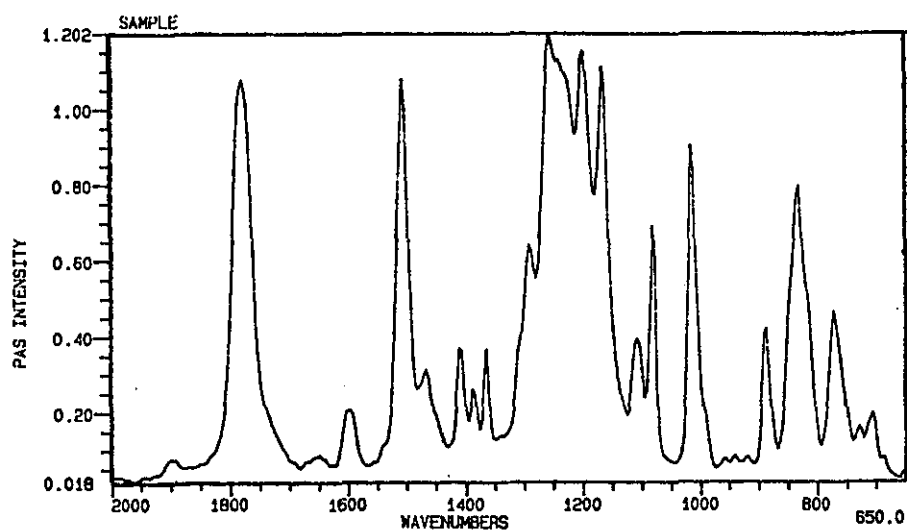
PC-1 REFERENCE

PC-2 REFERENCE
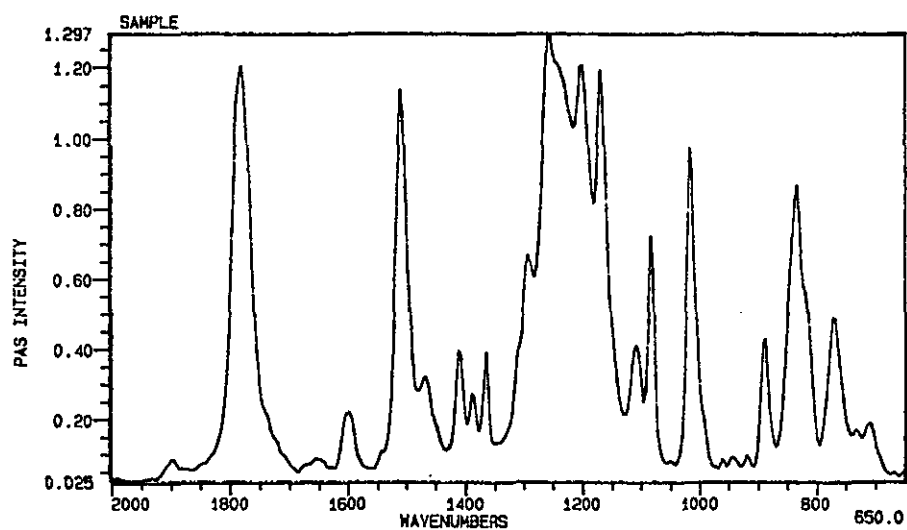
LIBRARY SPECTRA OF POSSIBLE PMMA ADDITIVES
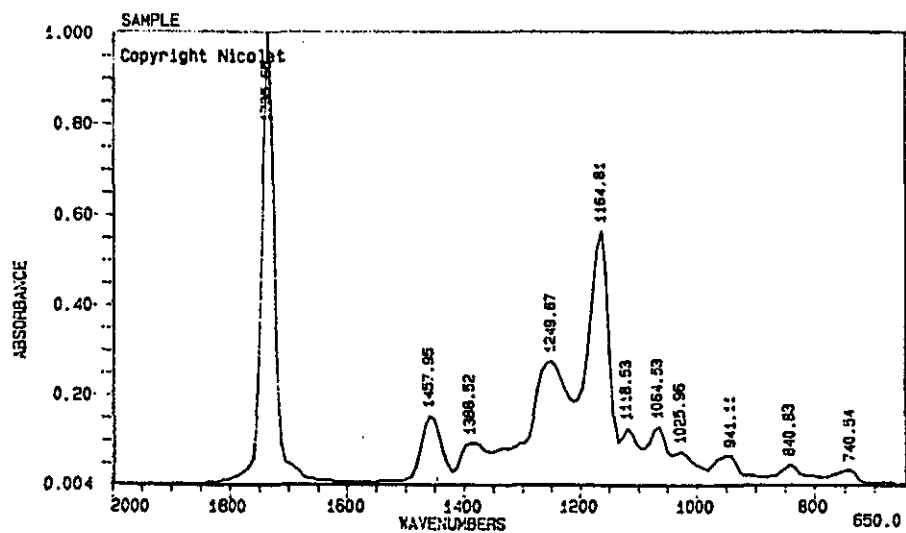
BUILDING RESEARCH
ESTABLISHMENT

Poly(butyl acrylate)
Library: SEA006   Spec#: 874

203

SUBTRACTION SPECTRA FOR PVC-1 AND PVC-2 TO SHOW ADDITIVES

PVC-1

PVC-2

204
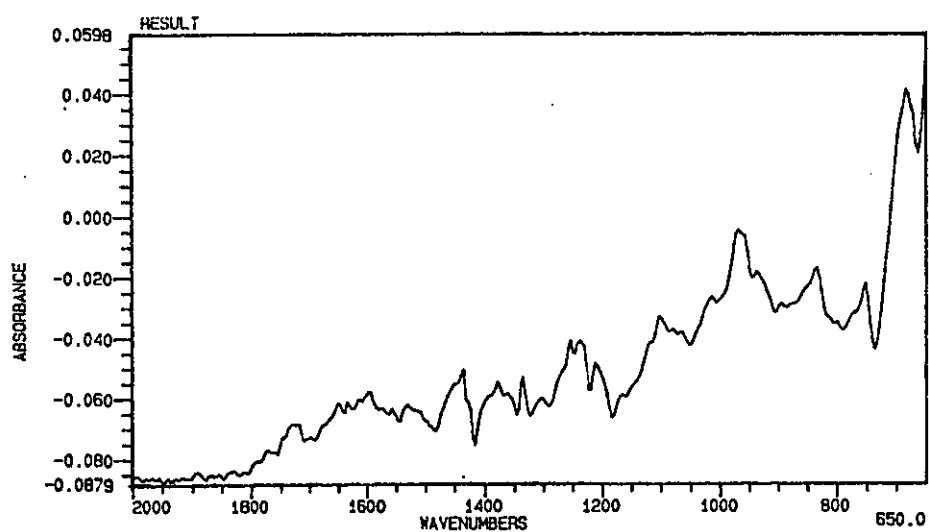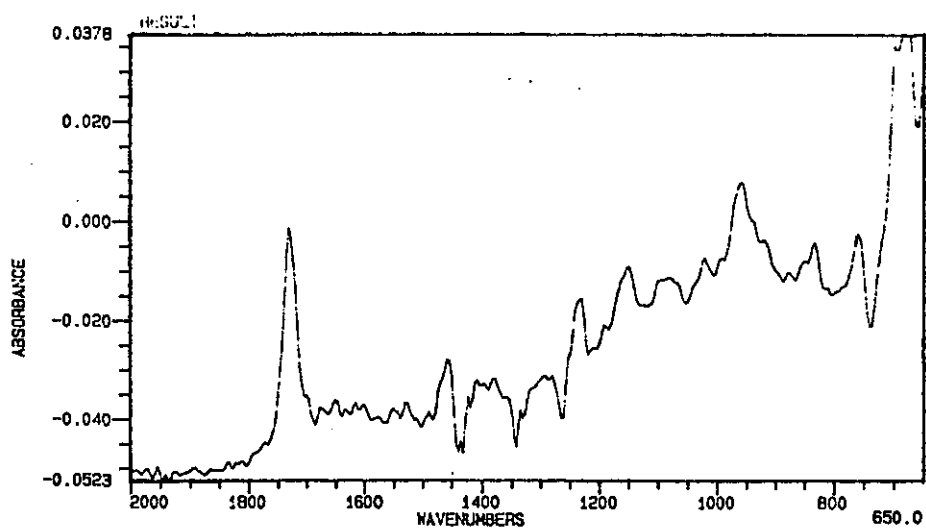
LIBRARY SPECTRA OF POSSIBLE PVC ADDITIVES
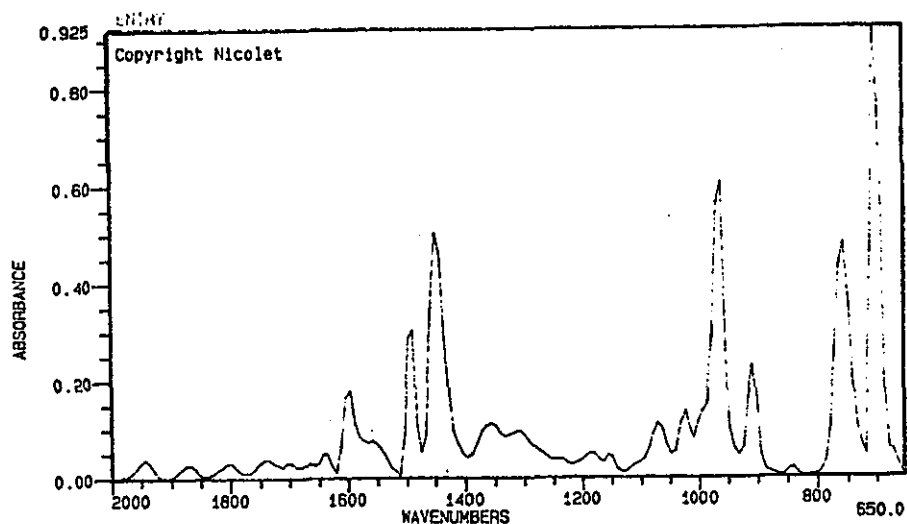
BUILDING RESEARCH
ESTABLISHMENT

Poly (styrene: butadiene)
Library: SEA006   Spec#: 208
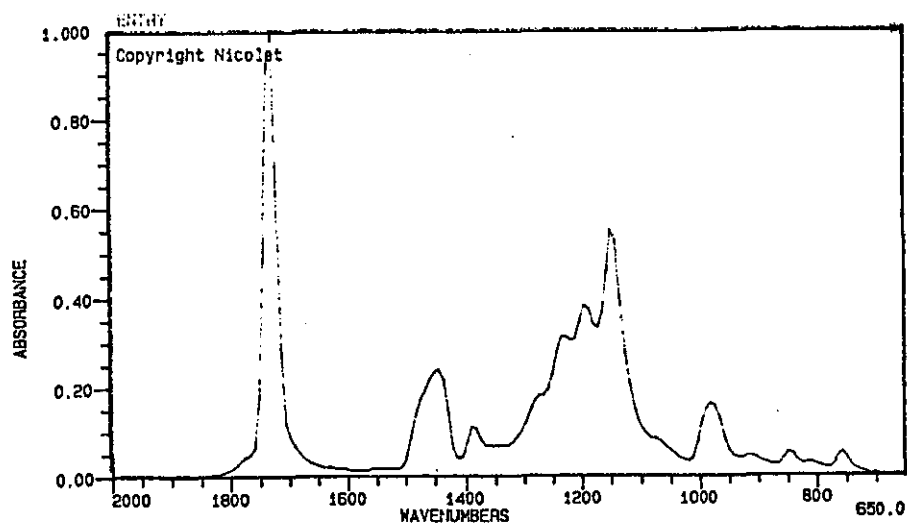
BUILDING RESEARCH
ESTABLISHMENT

Poly (methyl methacrylate: butadiene), 27mol%BD
Library: SEA006   Spec#: 172

205

APPENDIX B2: MOLECULAR WEIGHT DETERMINATION
GEL PERMEATION CHROMATOGRAPHY

CALIBRATION

Calibration File - CALP
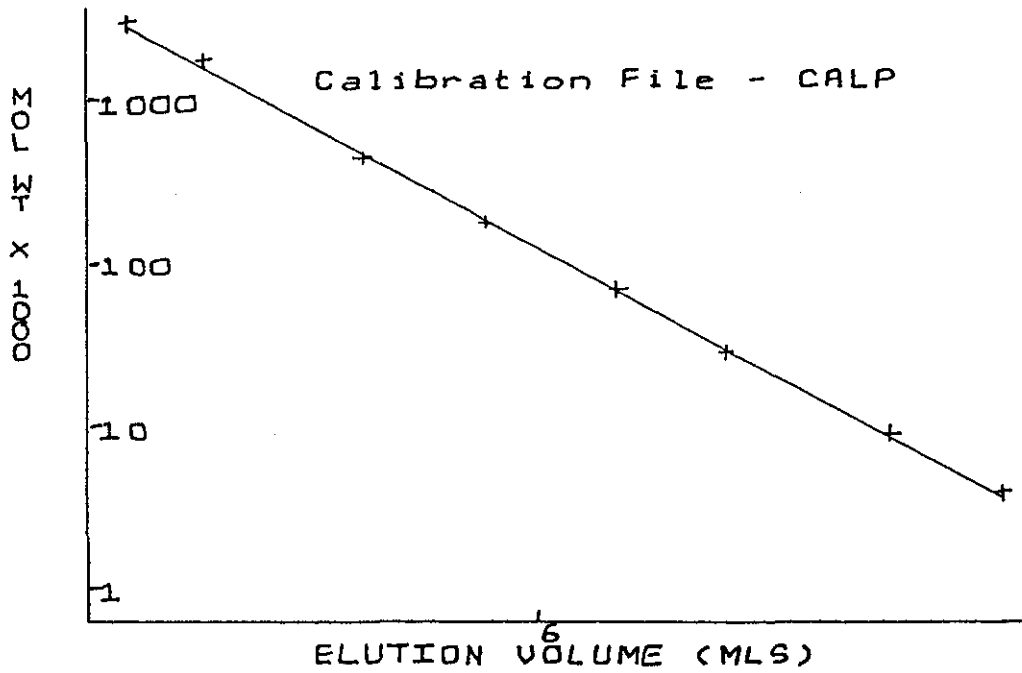
| Vol (ml) | Standards | Molecular Weight | | | |
| | | Cubic Fit | | Linear Fit | |
		Calc	Ratio	Calc	Ratio
7.22	3770	3841	0.98	3668	1.03
6.93	9000	8659	1.04	8466	1.06
6.50	28000	28752	0.97	29258	0.96
6..20	68000	66750	1.02	69502	0.98
5.86	173000	175812	0.98	185289	0.93
5.53	450000	460241	0.98	479926	0.94
5.11	1750000	1638544	1.07	1611470	1.09
4.91	2950000	3067073	0.96	2868939	1.03

207

PMMA-1 GPC TRACE


```
Mw= 2280000      Mn= 694000
Mz= 5010000      Mw/Mn= 3.29
```
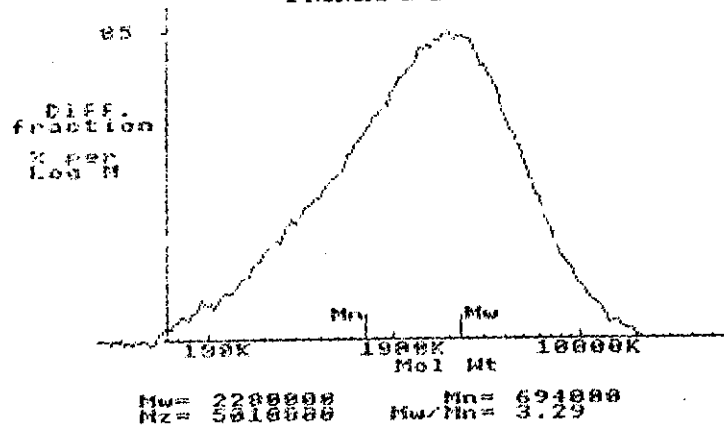
Identification- -
Data File - - -
Date - - - - - 30.01.95
Flow rate (ml/min) 1
Solvent - - - - THF
Internal standard- None
Columns : -
  MIXED GEL

Calibration file : CALP (Cubic fit)

Peak :-			Mark-Houwink constants		
	Eluted mls	Mol.Wt.		K	a
Start	4.47	21600000	Polymer	1.28E-5	6.90E-1
Stop	6.62	3660	Standard	1.60E-5	7.10E-1
Max.	5.12	196000			

Baseline from 4.47 mls to 6.62 mls

PMMA-2 GPC TRACE
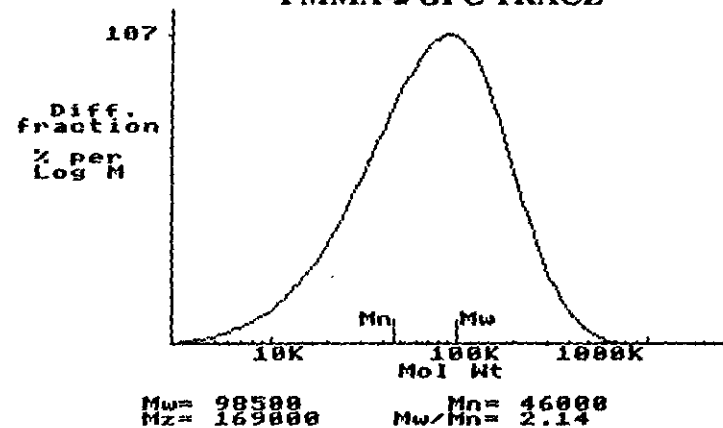

```
Mw= 98500       Mn= 46000
Mz= 169000      Mw/Mn= 2.14
```

Identification- -.
Data File - - -
Date - - - - - 30.09.92
Flow rate (ml/min) 1
Solvent - - - - THF
Internal standard- None
Columns : -
  MIXED GEL

Calibration file : CALSUE (Cubic fit)

Peak :-			Mark-Houwink constants		
	Eluted mls	Mol.Wt.		K	a
Start	5.98	851000	Polymer	1.28E-5	6.90E-1
Stop	8.13	3140	Standard	1.60E-5	7.10E-1
Max.	6.85	94100			

Baseline from 5.98 mls to 8.13 mls

PVC-1 GPC TRACE
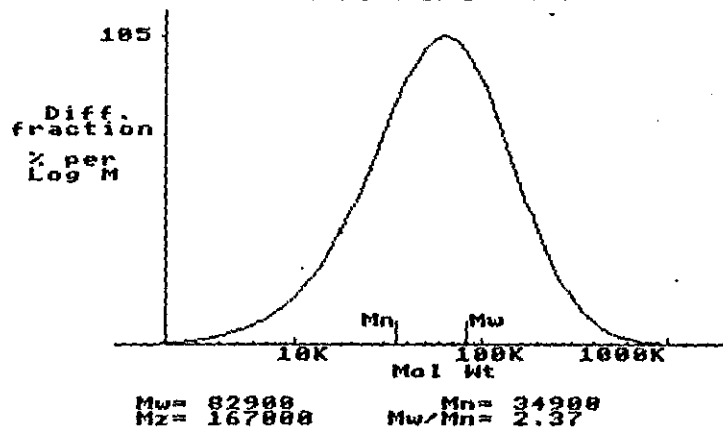

```
Mw= 82900          Mn= 34900
Mz= 167000         Mw/Mn= 2.37
```

Identification- ·-
Data File - - -
Date - - - - - 30.09.92
Flow rate (ml/min) 1
Solvent - - - - THF
Internal standard- None
Columns : -
  MIXED GEL

Calibration file : CALSUE (Cubic fit)

Peak :-			Mark-Houwink constants		
	Eluted mls	Mol.Wt.		K	a
Start	5.55	1330000	Polymer	1.50E-5	7.70E-1
Stop	8.32	1140	Standard	1.60E-5	7.10E-1
Max.	6.75	64400			

Baseline from   5.55 mls to   8.32 mls

PVC-2 GPC TRACE
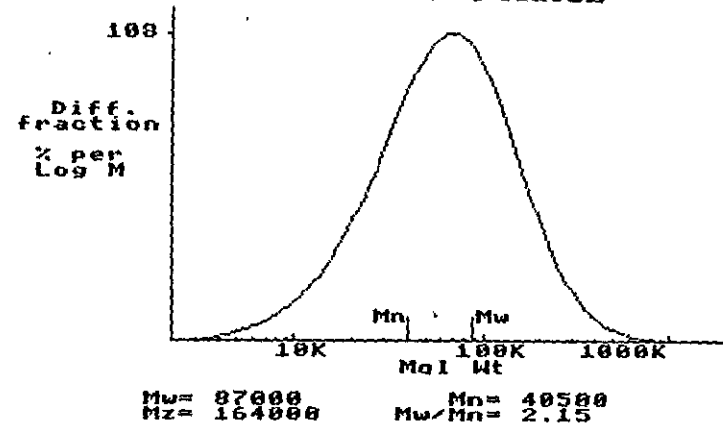

```
Mw= 87000          Mn= 40500
Mz= 164000         Mw/Mn= 2.15
```

Identification- ·-
Data File - - -
Date - - - - - 30.09.92
Flow rate (ml/min) 1
Solvent - - - - THF
Internal standard- None
Columns : -
  MIXED GEL

Calibration file : CALSUE (Cubic fit)

Peak :-			Mark-Houwink constants		
	Eluted mls	Mol.Wt.		K	a
Start	5.61	1120000	Polymer	1.50E-5	7.70E-1
Stop	8.02	2690	Standard	1.60E-5	7.10E-1
Max.	6.71	70200			

Baseline from   5.61 mls to   8.02 mls

PC-1 GPC TRACE
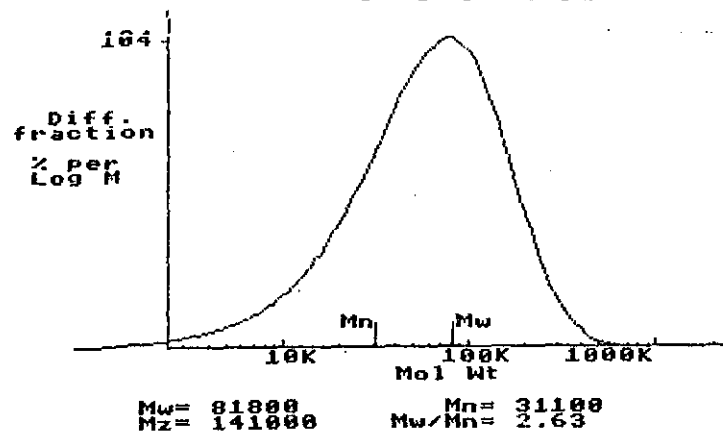
Mw= 81800   Mn= 31100
Mz= 141000   Mw/Mn= 2.63

Identification- -
Data File - -'-
Date - - - - 30.09.92
Flow rate (ml/min) 1
Solvent - - - - THF
Internal standard- None
Columns : -
 MIXED GEL

Calibration file : CALSUE (Cubic fit)

Peak :-	Eluted mls	Mol.Wt.	Mark-Houwink constants	K	a
Start	6.10	662000	Polymer	1.04E-5	6.97E-1
Stop	8.59	822	Standard	1.60E-5	7.10E-1
Max.	6.95	77600			

Baseline from   6.10 mls to   8.59 mls

PC-2 GPC TRACE
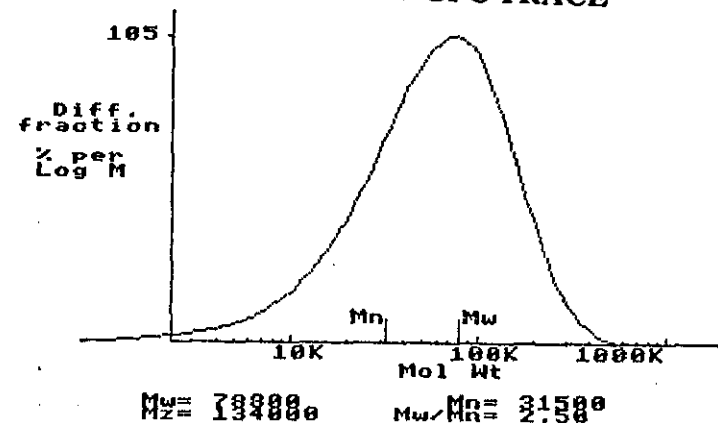
Mw= 78800   Mn= 31500
Mz= 134000   Mw/Mn= 2.50

Identification- -
Data File - - -
Date - - - - 30.09.92
Flow rate (ml/min) 1
Solvent - - - - THF
Internal standard- None
Columns : -
 MIXED GEL

Calibration file : CALSUE (Cubic fit)

Peak :-	Eluted mls	Mol.Wt.	Mark-Houwink constants	K	a
Start	6.11	642000	Polymer	1.04E-5	6.97E-1
Stop	8.60	790	Standard	1.60E-5	7.10E-1
Max.	6.98	73100			

Baseline from   6.11 mls to   8.60 mls

APPENDIX B3: DETERMINATION OF Tg AND OTHER TRANSITIONS
DIFFERENTIAL SCANNING CALORIMETRY (DSC)
DYNAMIC MECHANICAL ANALYSIS (DMA)

DETERMINATION OF Tg FOR PMMA REFERENCE SAMPLES

Sample: PMMA-1
Size: 5.0000 mg
Method: GLASS TRANSITION
Comment: UNAGED MATERIAL

DSC

File: C:GLAZ.005
Operator: SUE
Run Date: 20-May-93 14:47
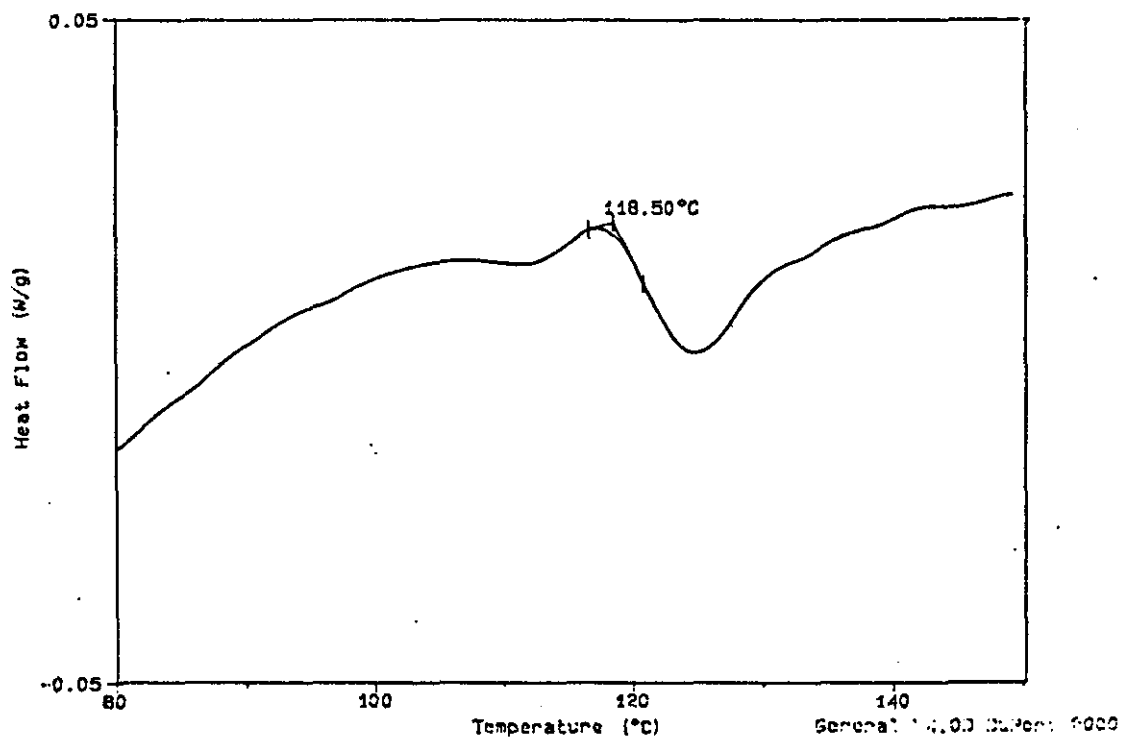
Sample: PMMA-2
Size: 5.0000 mg
Method: GLASS TRANSITION
Comment: UNAGED MATERIAL

DSC

File: C:GLAZ.007
Operator: SUE
Run Date: 20-May-93 15:03

212
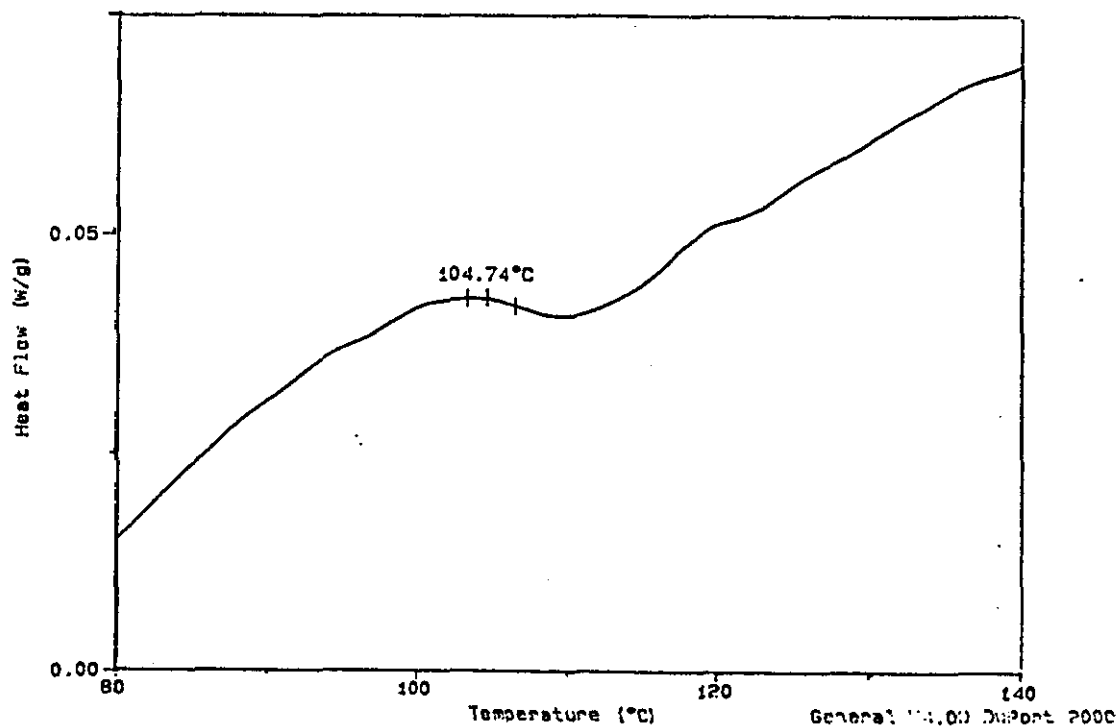
DETERMINATION OF Tg FOR PVC REFERENCE SAMPLES

Sample: PVC-1
Size: 5.0000 mg
Method: GLASS TRANSITION
Comment: UNAGED MATERIAL

DSC

File: C:GLAZ.001
Operator: SUE
Run Date: 20-May-93 12:00
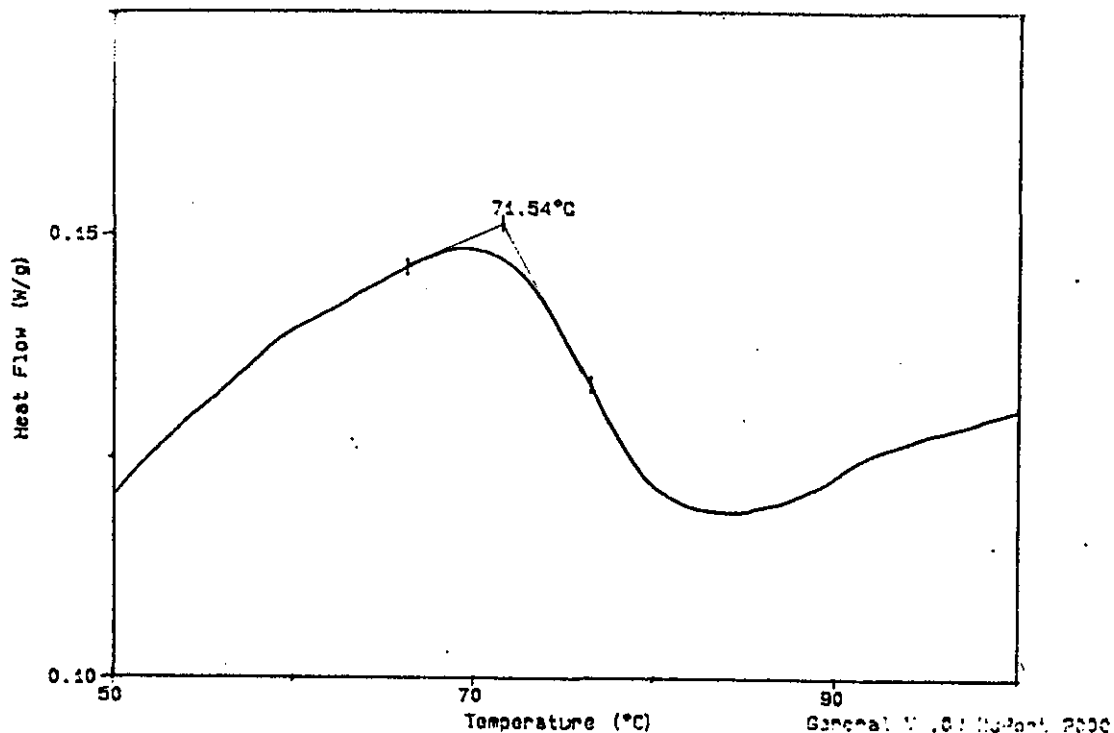
Sample: PVC-2
Size: 5.0000 mg
Method: GLASS TRANSITION
Comment: UNAGED MATERIAL

DSC

File: C:GLAZ.002
Operator: SUE
Run Date: 20-May-93 12:21

213
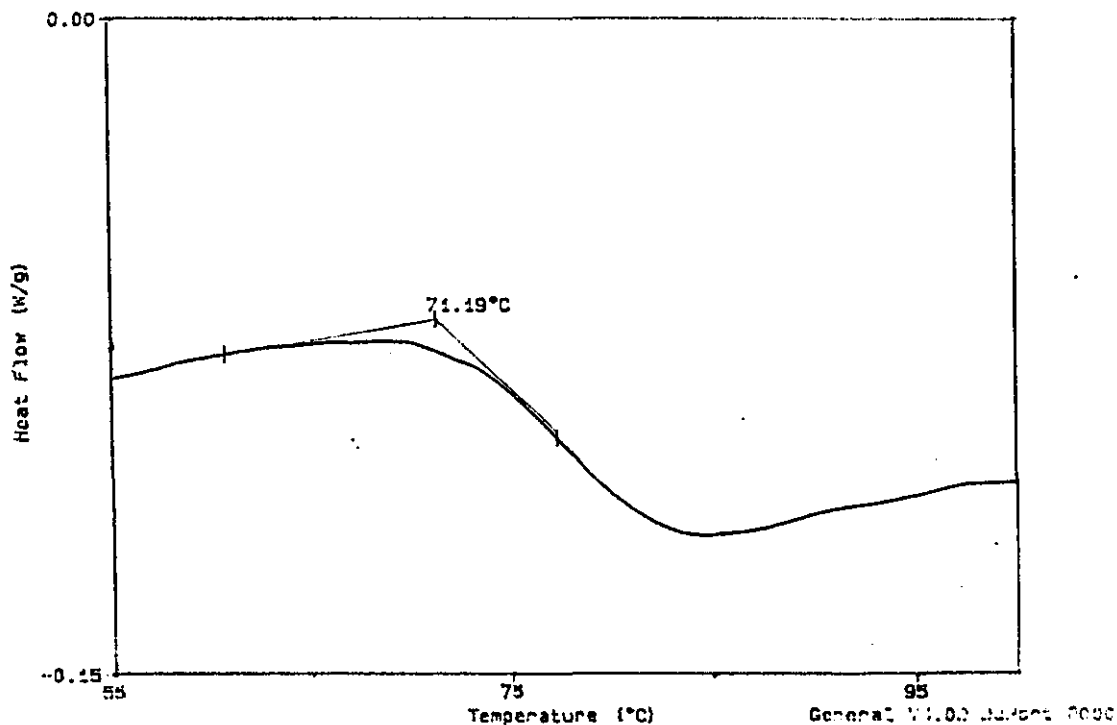
DETERMINATION OF Tg FOR PC REFERENCE SAMPLES

214
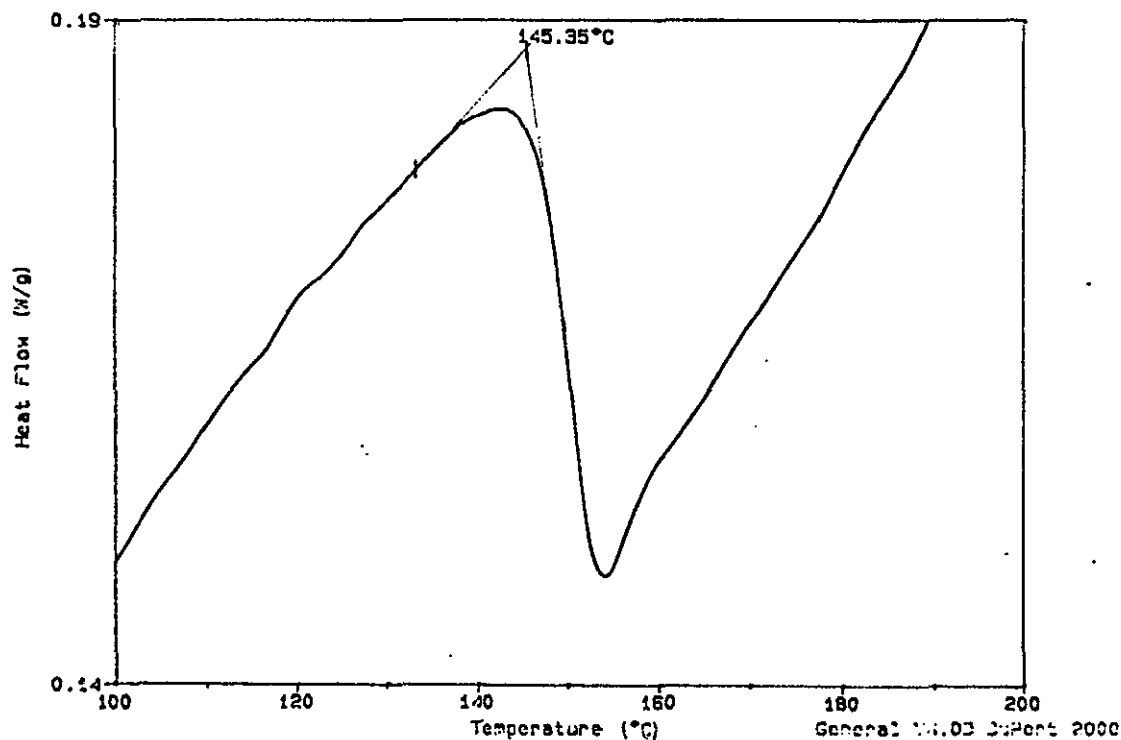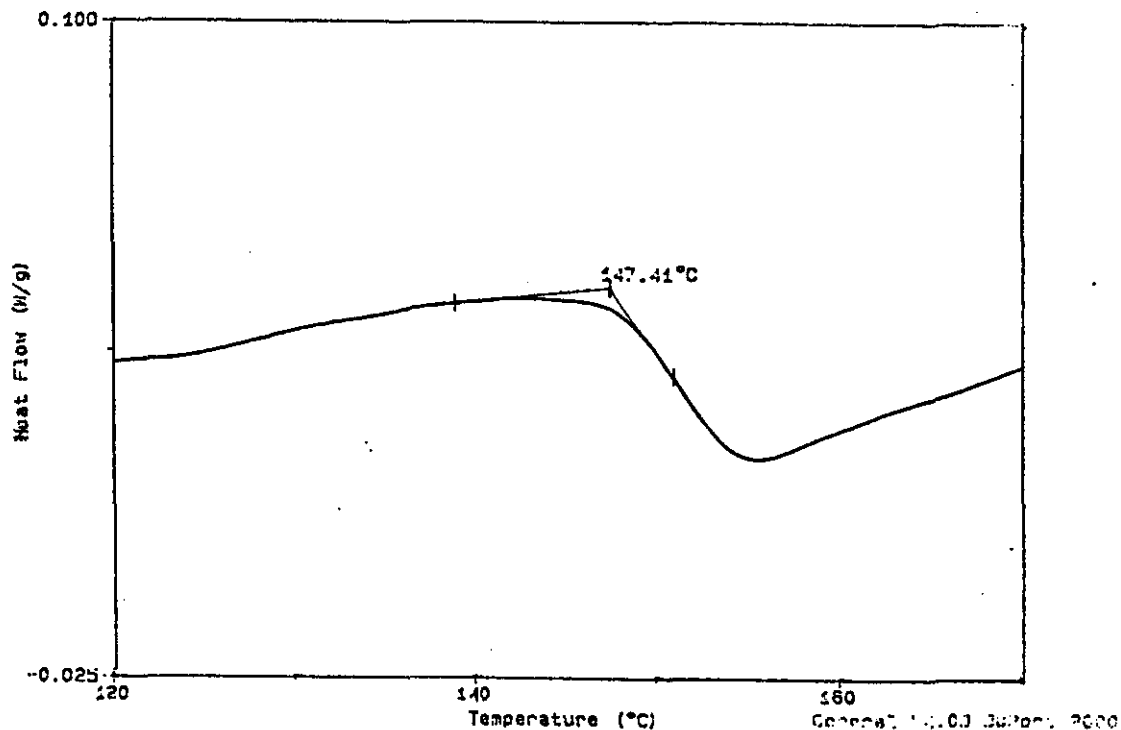
DETERMINATION OF HEAT OF FUSION FOR PVC SAMPLES

Sample: PVC
Size: 17.9000 mg
Method: PVC
Comment: PVC 1 (REFERENCE)

DSC

File: C:SUE.001
Operator: SUE
Run Date: 30-Jan-95 11:30

115.91°C
2.594J/g

182.41°C

139.36°C

189.55°C

Heat Flow (W/g)

Temperature (°C)

General V4.0D DuPont 2000
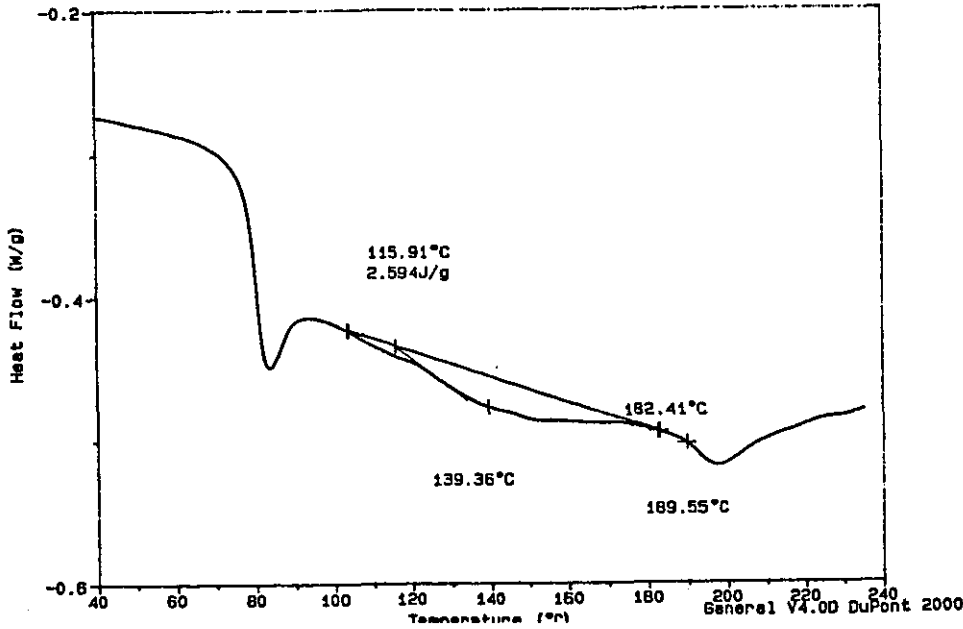
Sample: PVC
Size: 12.1000 mg
Method: PVC
Comment: PVC 2 (REFERENCE)

DSC

File: C:SUE.002
Operator: SUE
Run Date: 30-Jan-95 11:55

110.44°C
2.382J/g

177.95°C

135.33°C

Heat Flow (W/g)

Temperature (°C)

General V4.0D DuPont 2000
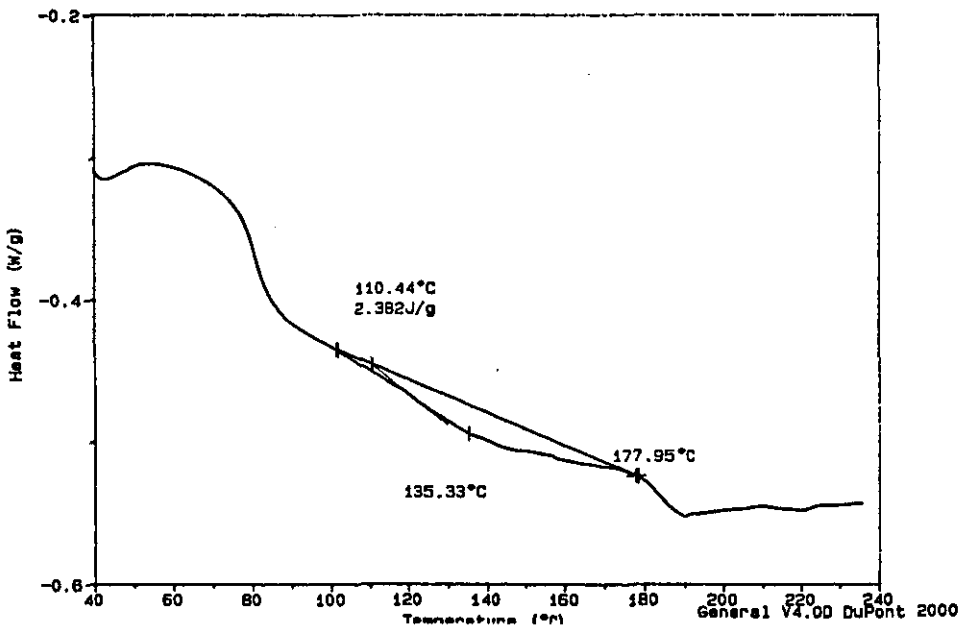
DMA TRACES

PMMA-1

PMMA-2

216

PVC-1

PVC-2

217

PC-1

PC-2

218
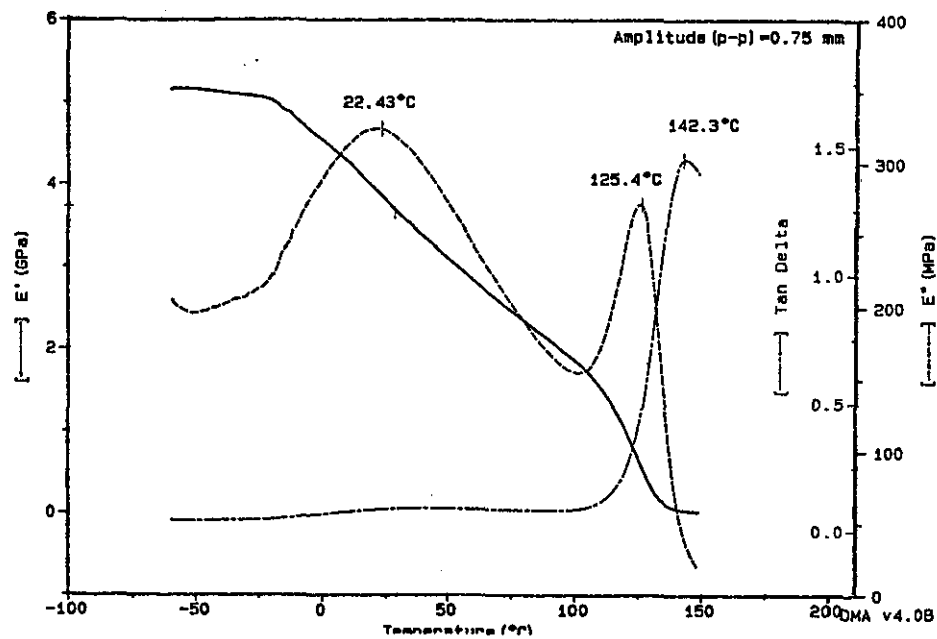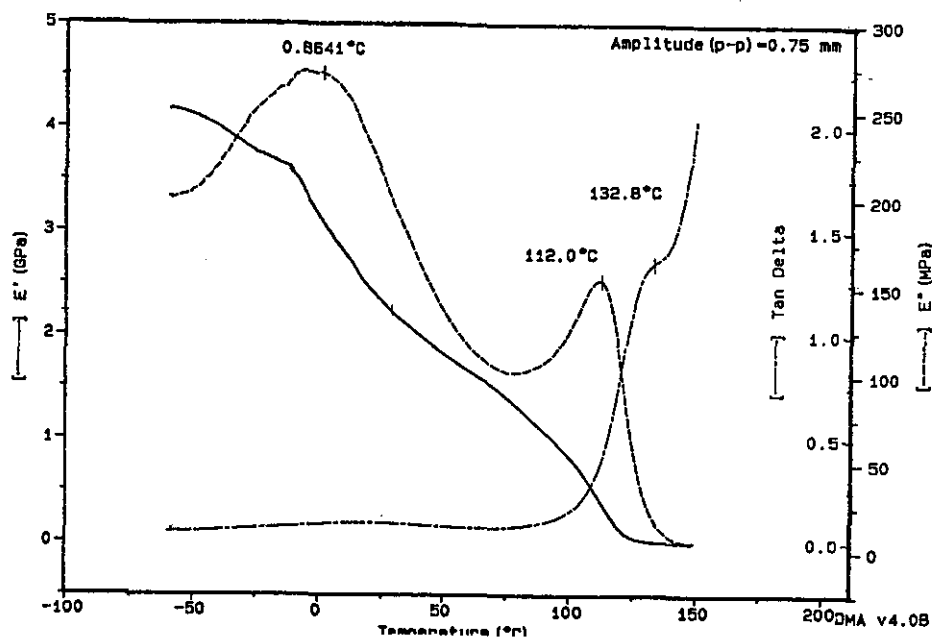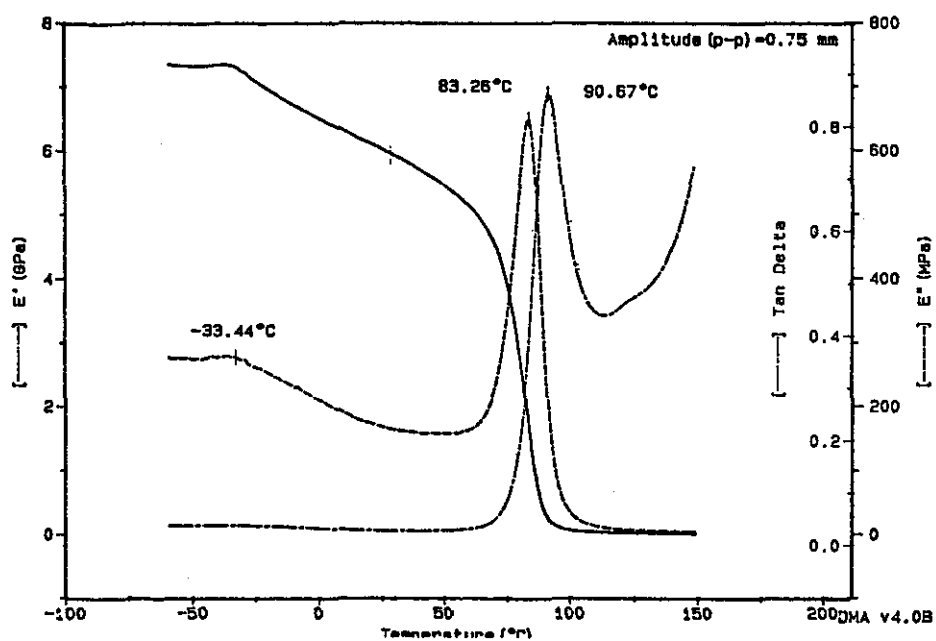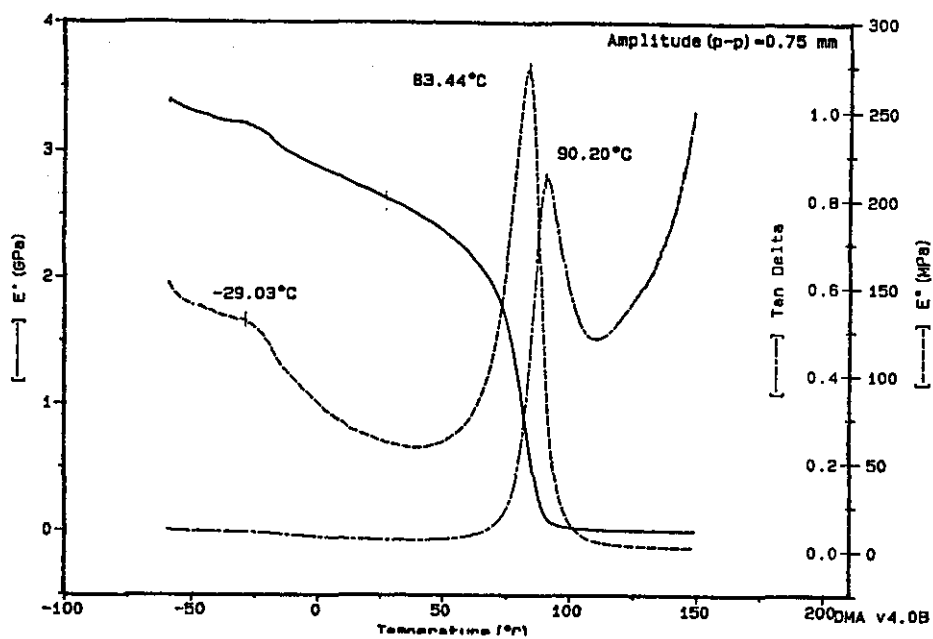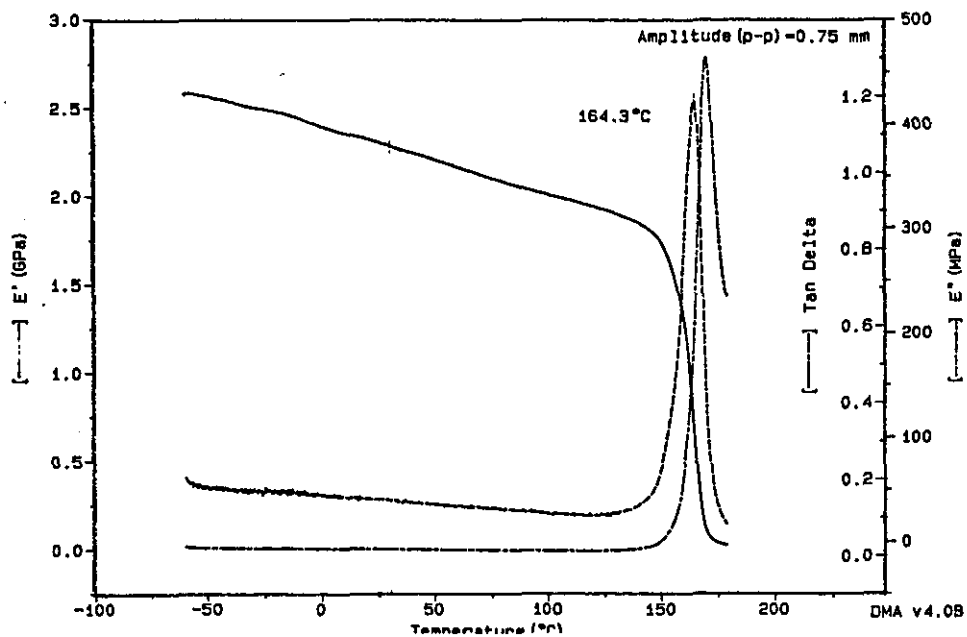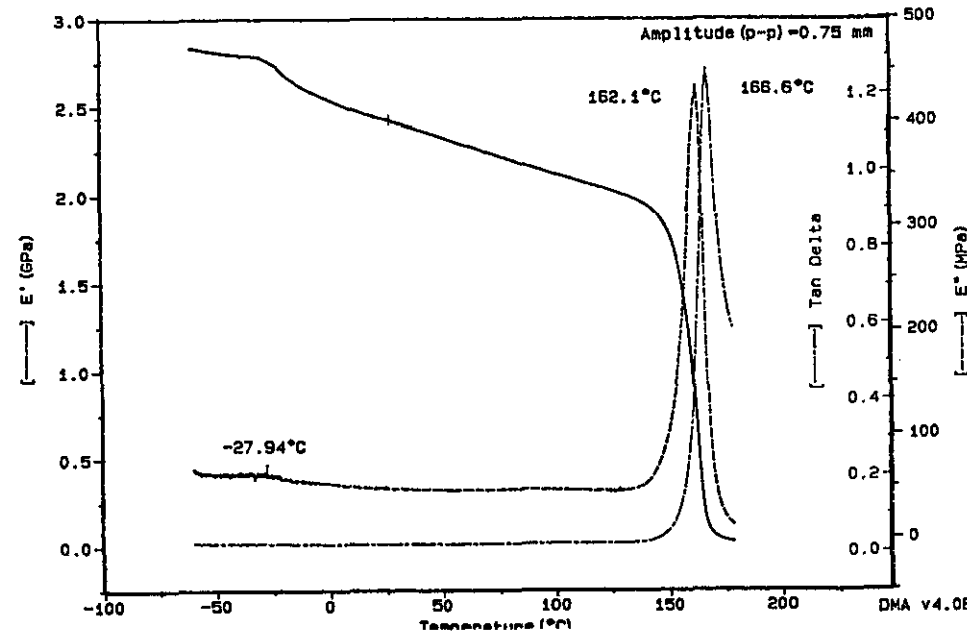
APPENDIX C: CHARACTERISATION OF CHANGES ON WEATHERING

APPENDIX C1: FUNCTIONAL GROUP ANALYSIS
INFRARED SPECTRA (PAS)

All spectra are measured using PAS, those given as % transmission have not been converted to PAS Intensity units.

PMMA-1 14500 hours in Xenotest-1200
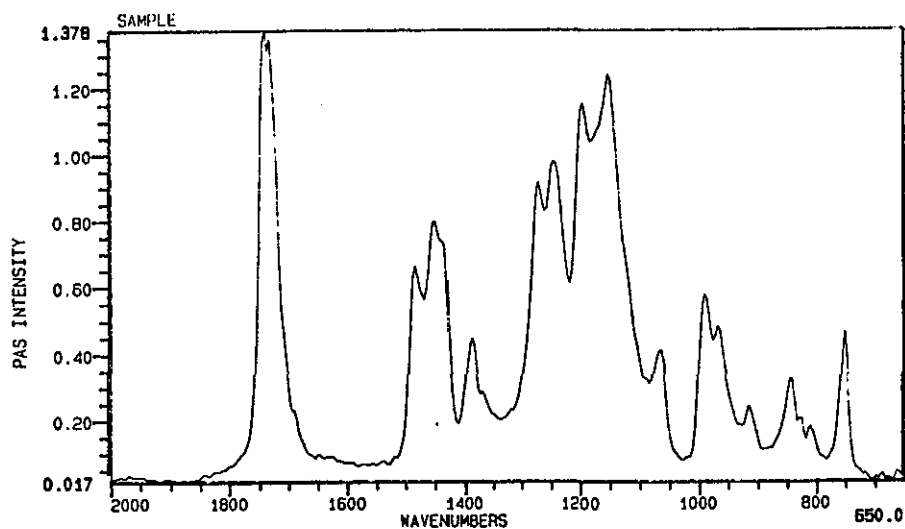
PMMA-1 2000 hours in Q-UV, UV-A Lamps
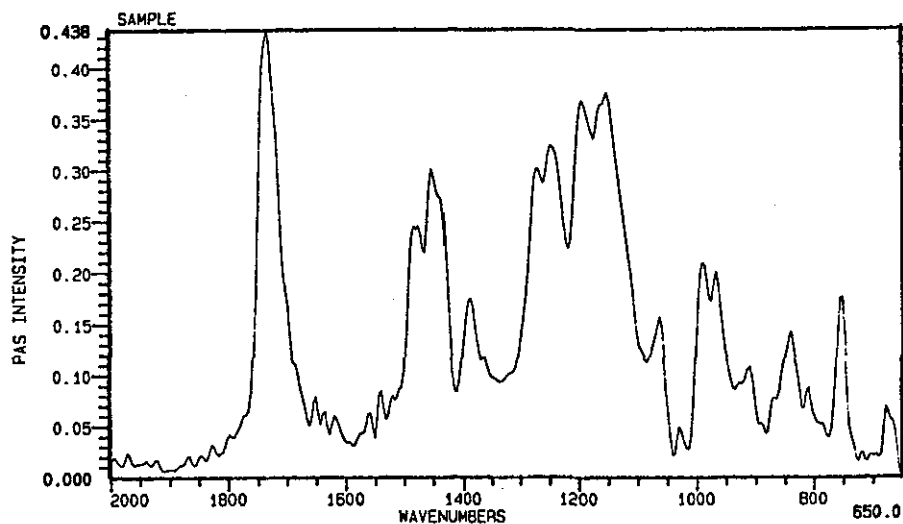
PMMA-1 2000 hours in Q-UV, UV-B Lamps
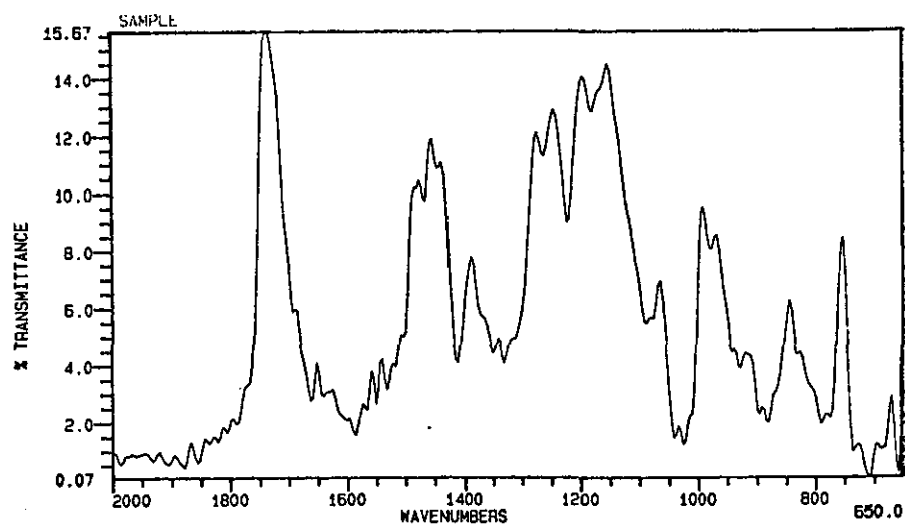
PMMA-2 6750 hours in Xenotest-1200
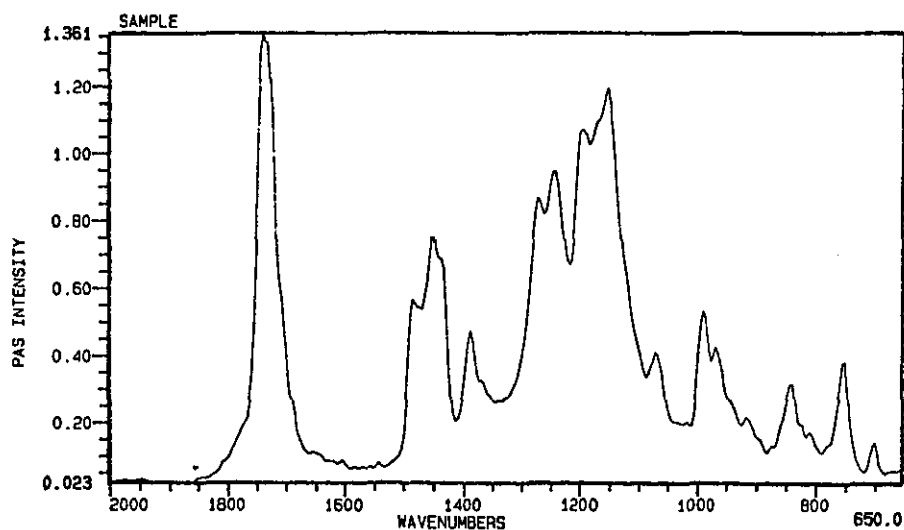
PMMA-2 2000 hours in Q-UV, UV-A Lamps

PMMA-2 2000 hours in Q-UV, UV-B Lamps

222
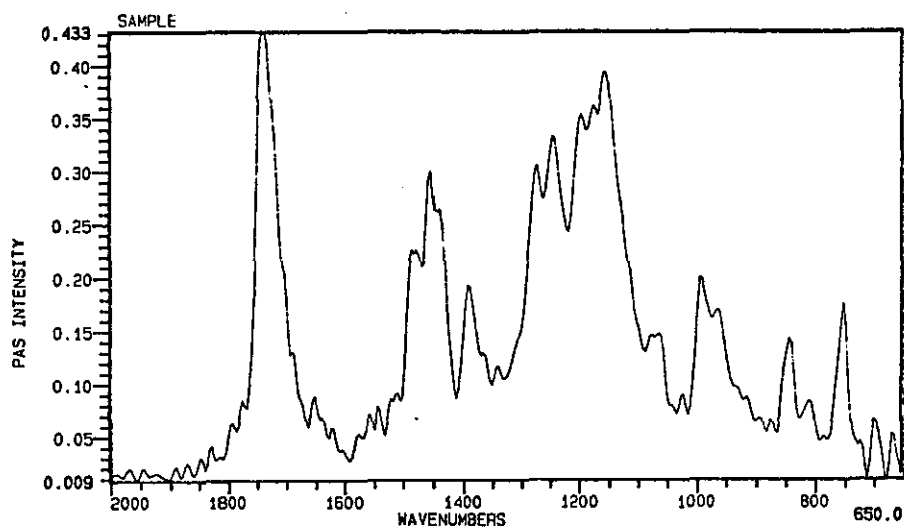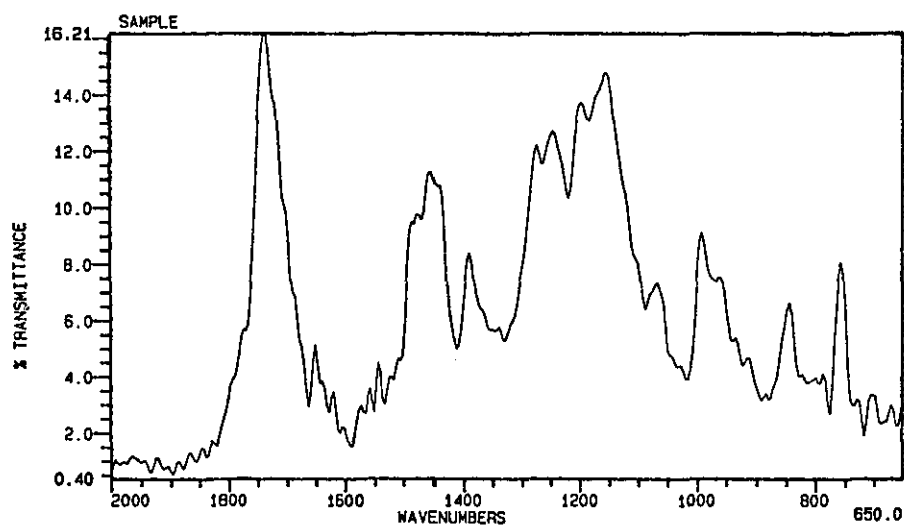
PVC-1 8000 hours in Xenotest-1200
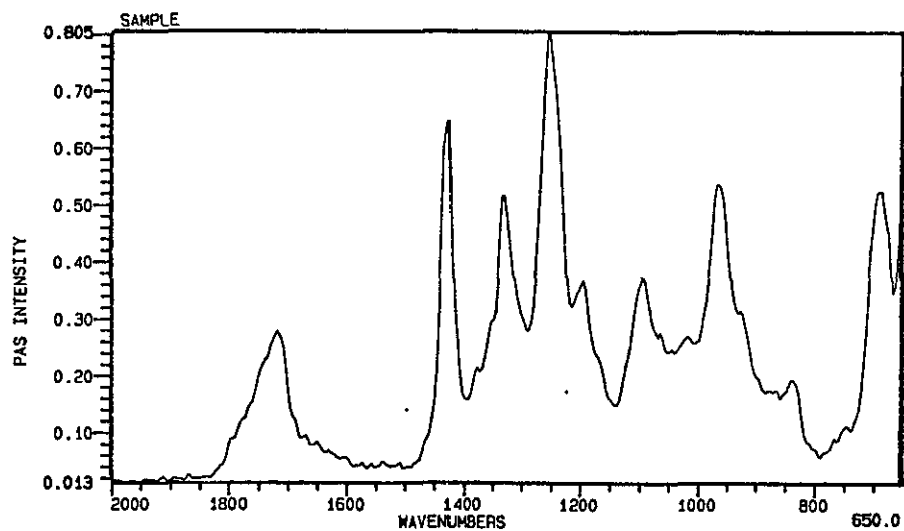
PVC-1 2000 hours in Q-UV, UV-A Lamps

PVC-1 2000 hours in Q-UV, UV-B Lamps

223
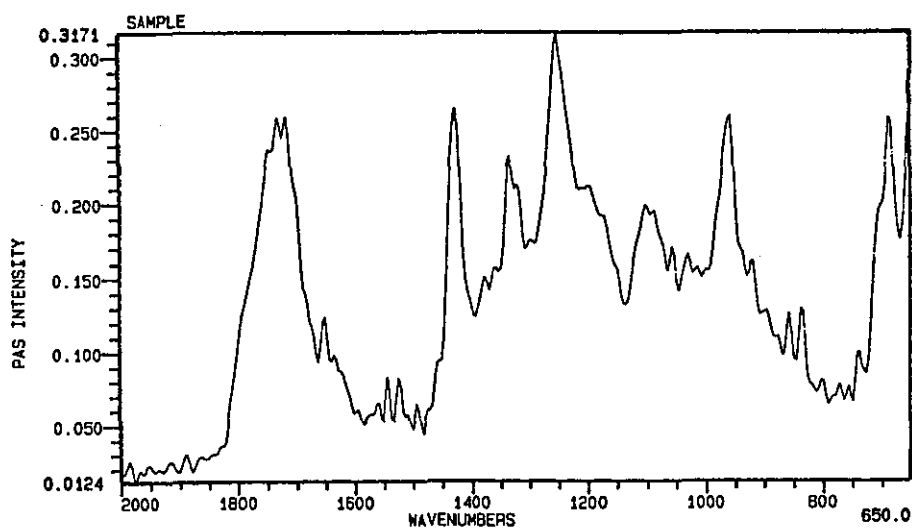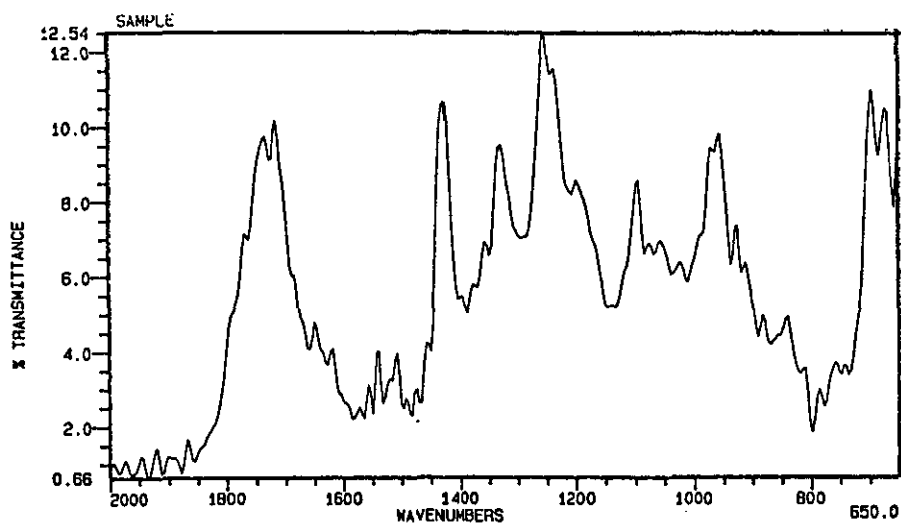
PVC-2 1500 hours in Xenotest-1200
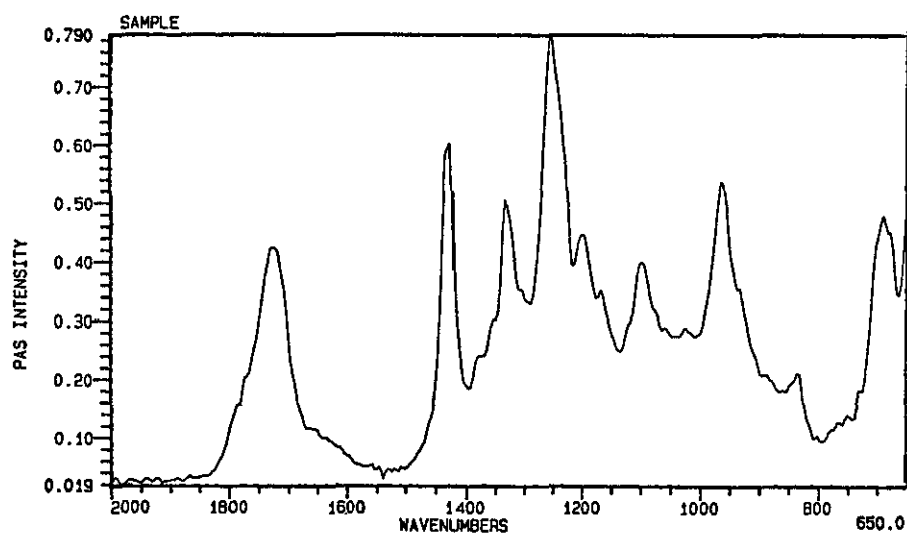
PVC-2 2000 hours in Q-UV, UV-A Lamps

PVC-2 2000 hours in Q-UV, UV-B Lamps

224
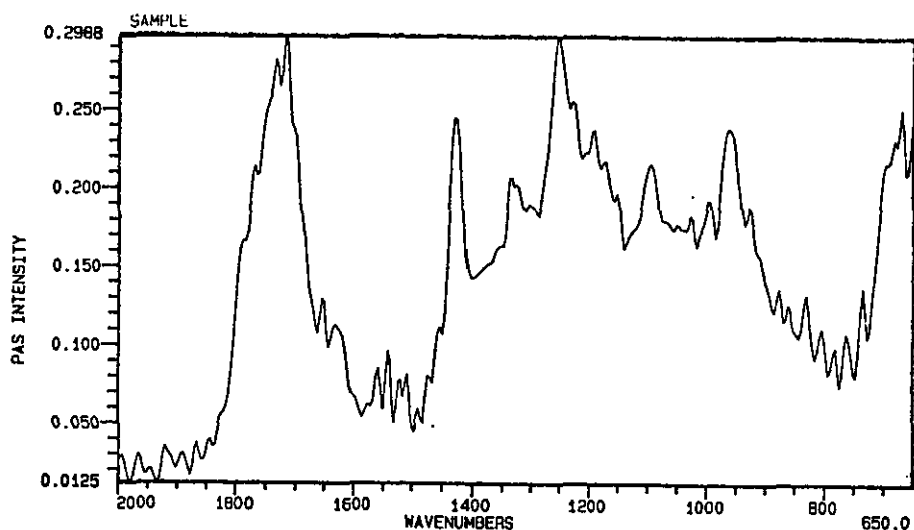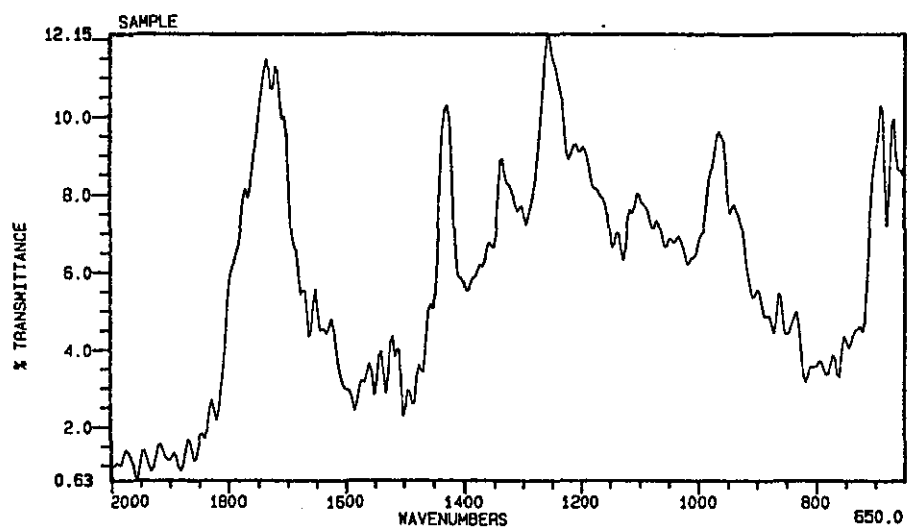
PC-1 2000 hours in Xenotest-1200
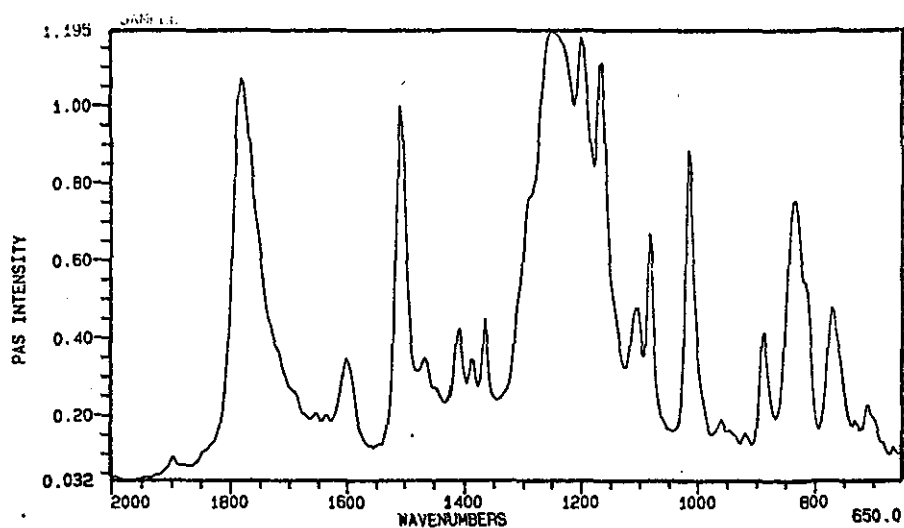
PC-1 2000 hours in Q-UV, UV-A Lamps
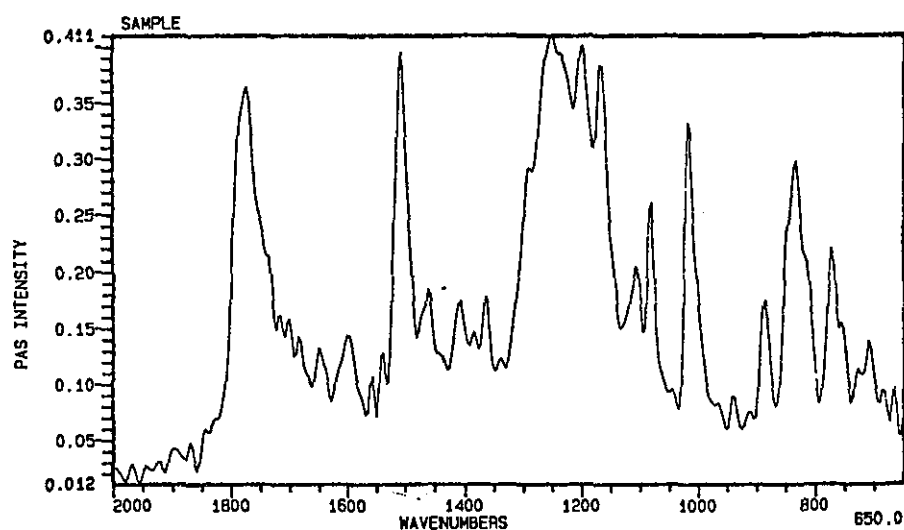
PC-1 2000 hours in Q-UV, UV-B Lamps
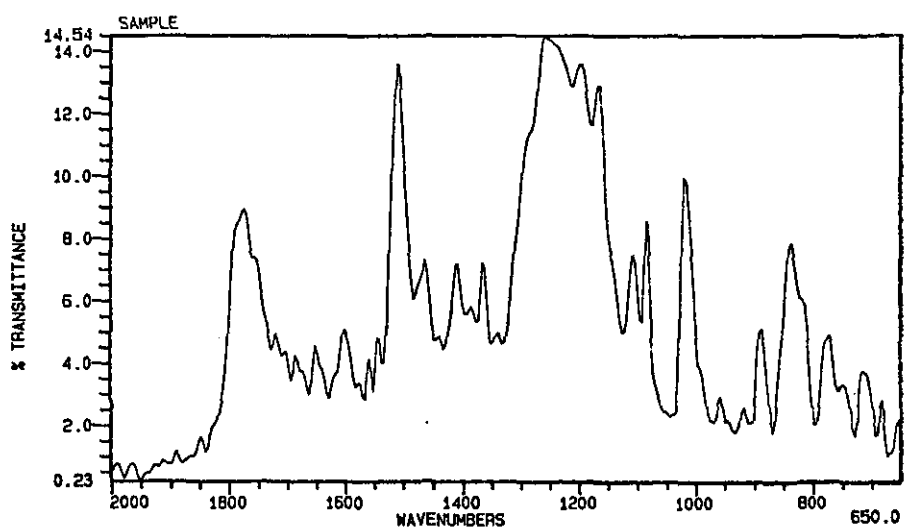
PC-2 2000 hours in Xenotest-1200
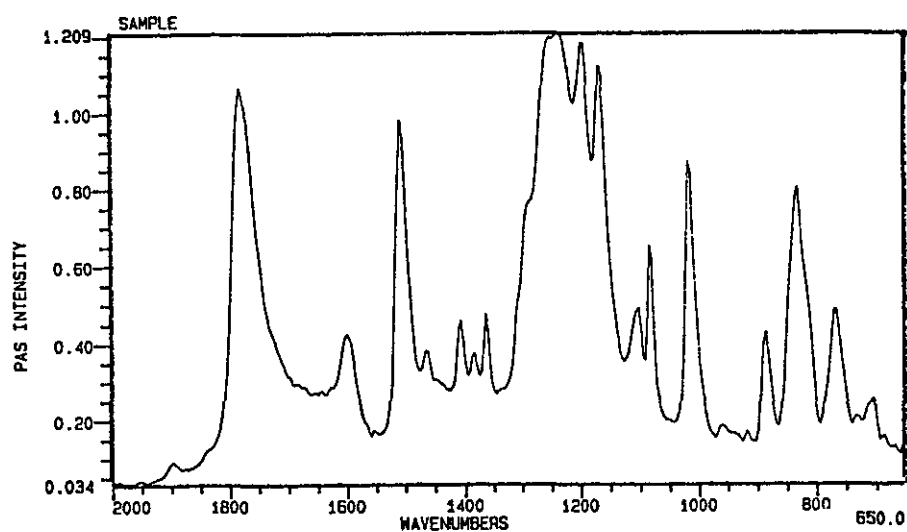
PC-2 2000 hours in Q-UV, UV-A Lamps

PC-2 2000 hours in Q-UV, UV-B Lamps

226
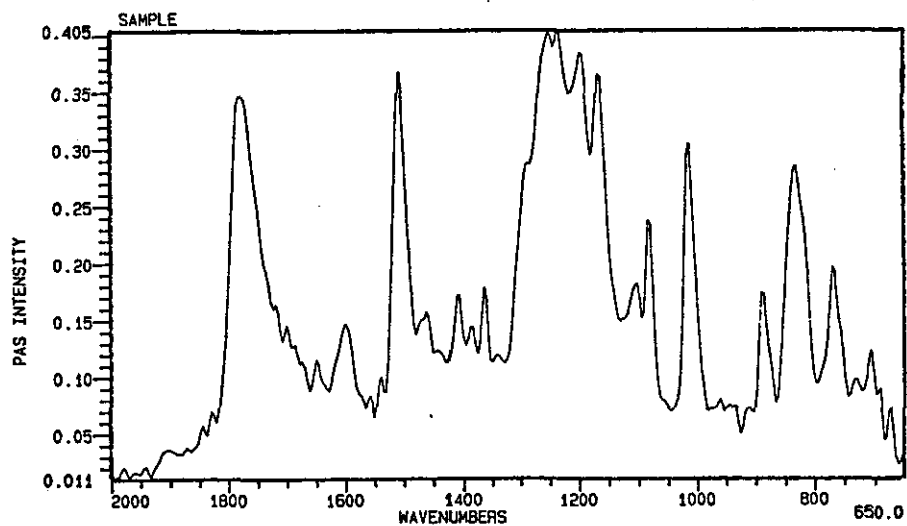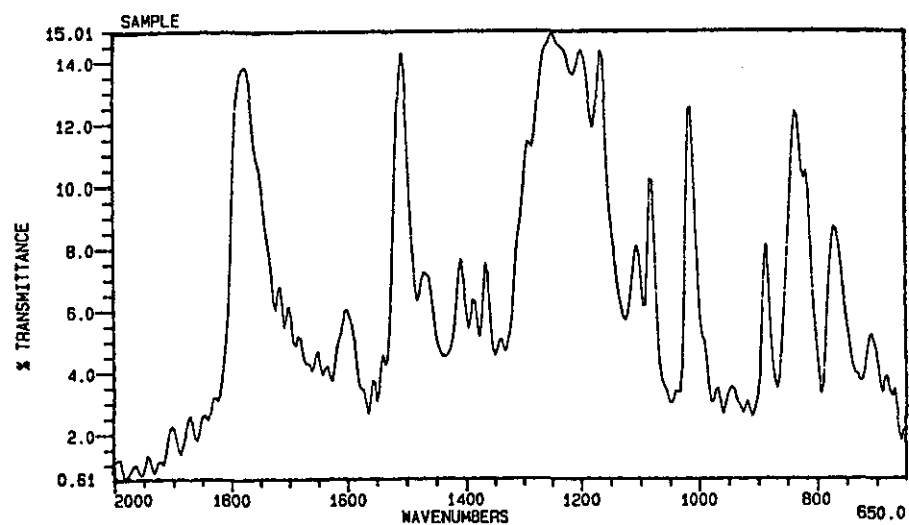
Peak Intensity Tables

PVC-1 Q-UV, UV-B Exposure (Figure 4.4)

Peak cm⁻¹	Relative PAS Value			
	Exposure (hours)			
	0	500	1000	2000
1785	0.11	0.19	0.18	0.35
1750	0.24	0.40	0.42	0.78
1730	0.28	0.39	0.5	0.83
1715	0.29	0.57	0.57	0.88
1650	0.28	0.28	0.43	0.46

PVC-2 Q-UV, UV-B Exposure (Figure 4.5)

Peak cm⁻¹	Relative PAS Value				
	Exposure (hours)				
	0	250	500	1000	2000
1780	0.23	0.44	0.61	0.64	0.78
1750	0.32	0.65	0.79	0.85	1.05
1734	0.75	0.85	1.06	0.95	1.23
1715	0.69	0.88	0.97	1.23	1.26
1650	0.42	0.49	0.57	0.64	0.65

227

PC-1 Xenotest-1200 Exposure (Figure 4.3)

Relative PAS Value							
Peak cm^{-1}	Exposure (hours)						
	0	250	500	750	1000	1250	1500
1825	0.03	0.05	0.09	0.14	0.15	0.19	0.08
1780	1.21	1.17	1.21	1.09	0.99	0.95	1.05
1750				0.85	0.72	0.77	0.74
1720		0.23	0.41	0.70	0.62	0.71	0.62
1700		0.17	0.33	0.20	0.63	0.81	0.64

228

APPENDIX C2: MOLECULAR WEIGHT DETERMINATION

PMMA-1 1000 hours in Xenotest-1200

Mw= 765000   Mn= 340000
Mz= 1380000   Mw/Mn= 2.25

PMMA-1 2000 hours in Xenotest-1200

Mw= 510000   Mn= 167000
Mz= 1110000   Mw/Mn= 3.05
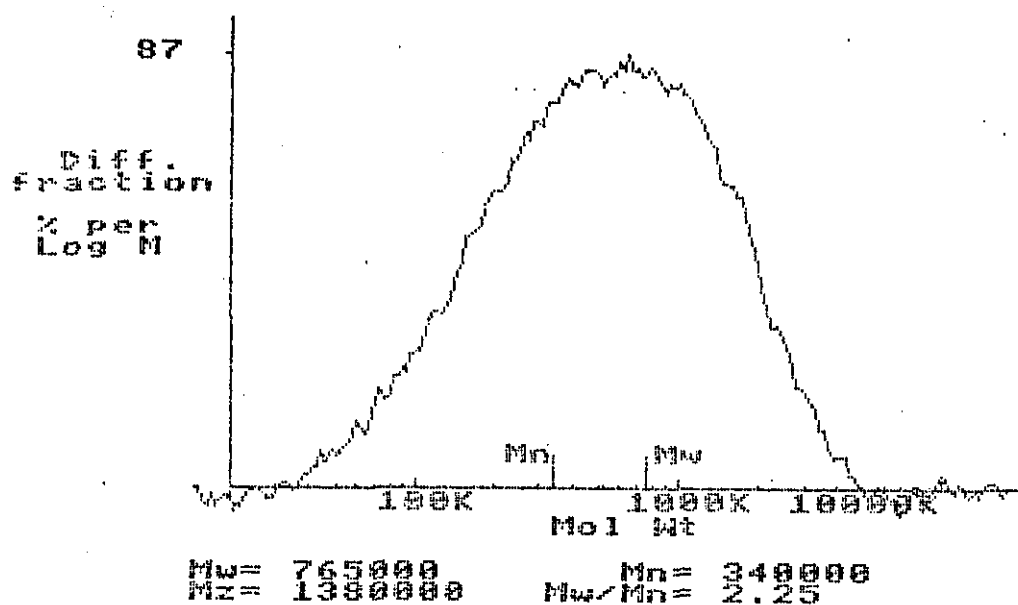
PMMA-1 4000 hours in Xenotest-1200

Mw= 399000 Mn= 159000
Mz= 833000 Mw/Mn= 2.50
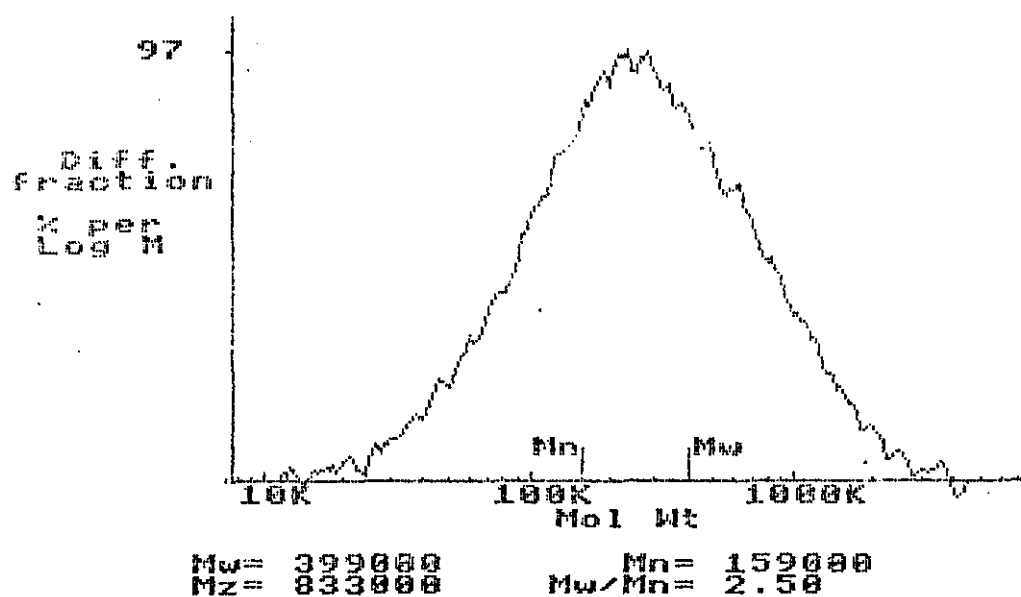
PMMA-1 6000 hours in Xenotest-1200
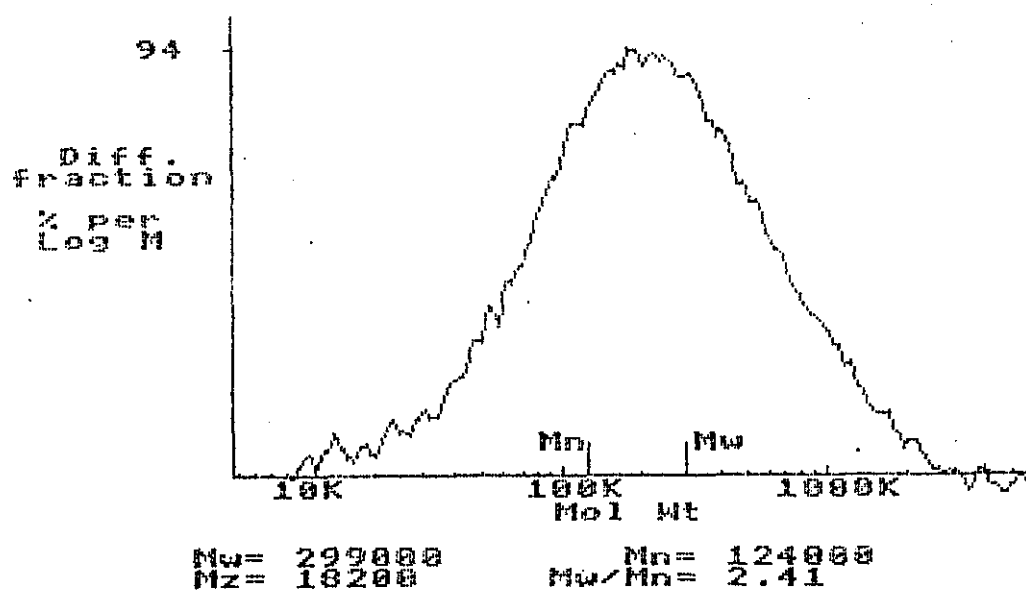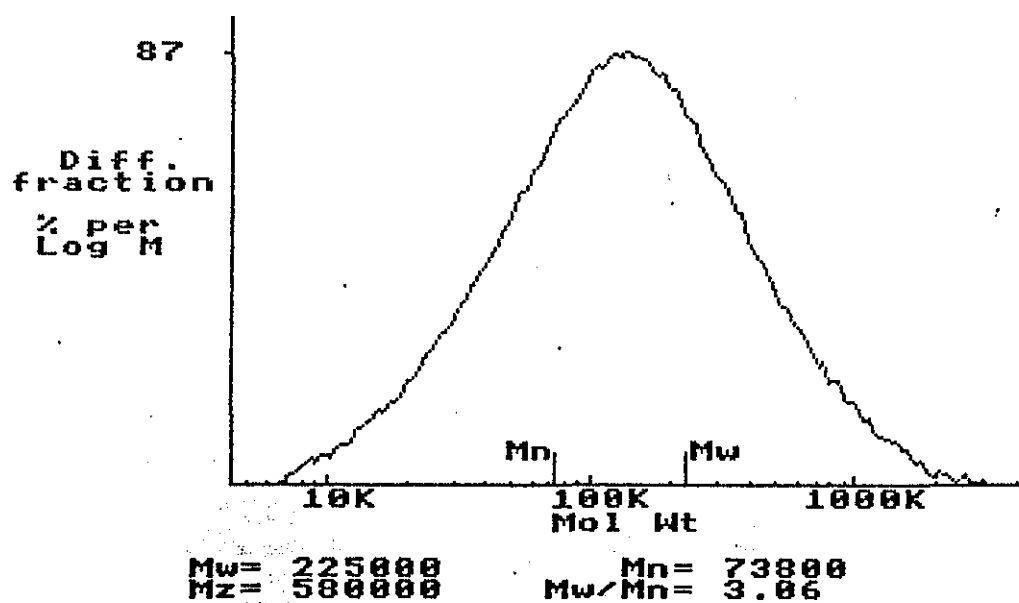
Mw= 299000 Mn= 124000
Mz= 18200 Mw/Mn= 2.41

231

PMMA-1 12000 hours in Xenotest-1200

Mw= 225000   Mn= 73800
Mz= 580000   Mw/Mn= 3.06

PMMA-1 2000 hours in Q-UV, UV-A Lamps

Mw= 357000   Mn= 132000
Mz= 1030000   Mw/Mn= 2.70

PMMA-1 2000 hours in Q-UV, UV-B Lamps


```
99  ┤
        Diff.
      fraction
       % per
       Log M


                         Mn|      |Mw
        ├────────┬─────────┬──────────┬──
           10K      100K      1000K
                      Mol Wt
```

        Mw= 257000   Mn= 101000
        Mz= 865000   Mw/Mn= 2.54

PMMA-2 6750 hours in Xenotest-1200


```
119 ┤
        Diff.
      fraction
       % per
       Log M


                       Mn|    |Mw
        ├───────┬──────────┬──────────┬──
           10K      100K      1000K
                     Mol Wt
```

        Mw= 81700   Mn= 42000
        Mz= 138000   Mw/Mn= 1.94

233

PVC-1 8000 hours in Xenotest-1200

Mw= 74000 Mn= 28700
Mz= 151000 Mw/Mn= 2.58

PVC-2 1500 hours in Xenotest-1200

Mw= 82400 Mn= 33500
Mz= 188000 Mw/Mn= 2.46

PC-1 1750 hours in Xenotest-1200


```
Mw=  72100        Mn=  24000
Mz=  134000    Mw/Mn=  3.00
```

PC-2 1500 hours in Xenotest-1200


```
Mw=  75700        Mn=  25700
Mz=  140000    Mw/Mn=  2.94
```

APPENDIX C3: THERMAL ANALYSIS

Determination of Tg for PMMA-1 Weathered Samples
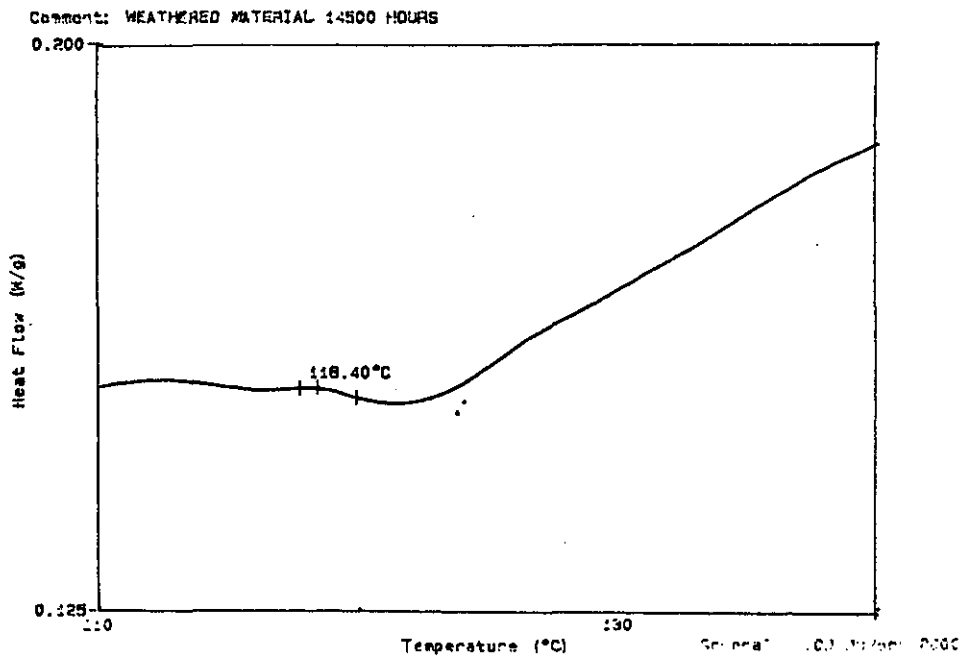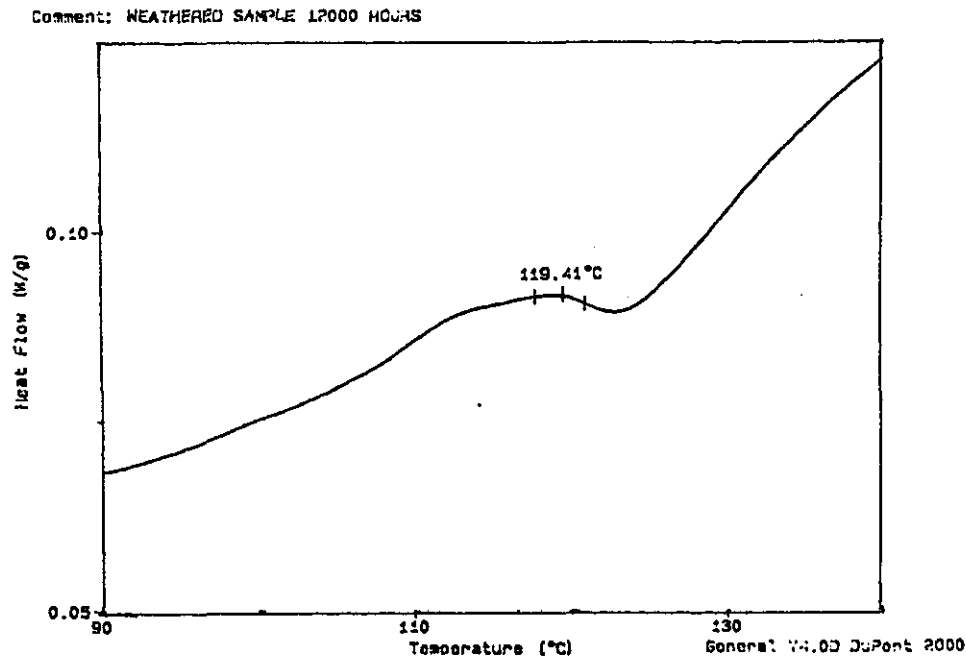
Determination of Tg for PMMA-2 Weathered Sample

238
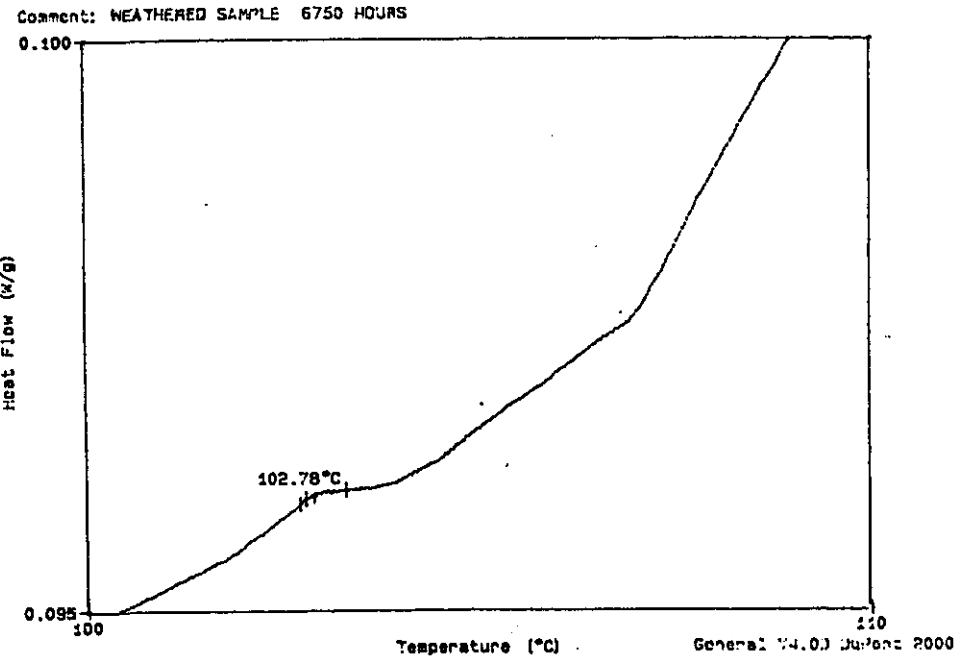
Determination of Tg for PVC-1 Weathered Sample

Comment: WEATHERED MATERIAL 8000 HOURS
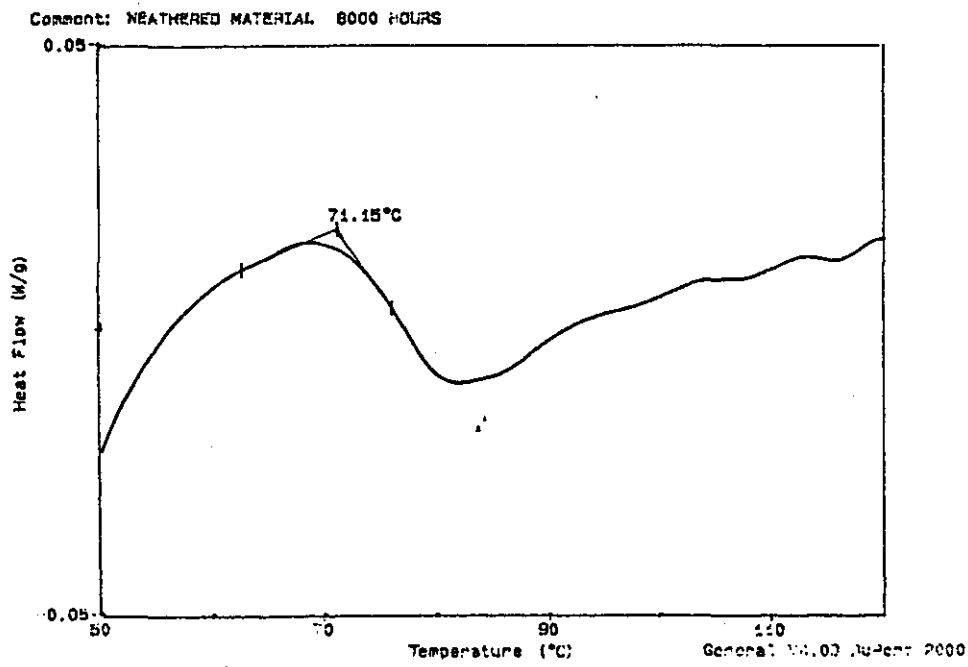
Determination of Tg for PVC-2 Weathered Sample

Comment: WEATHERED MATERIAL 1750 HOURS

239
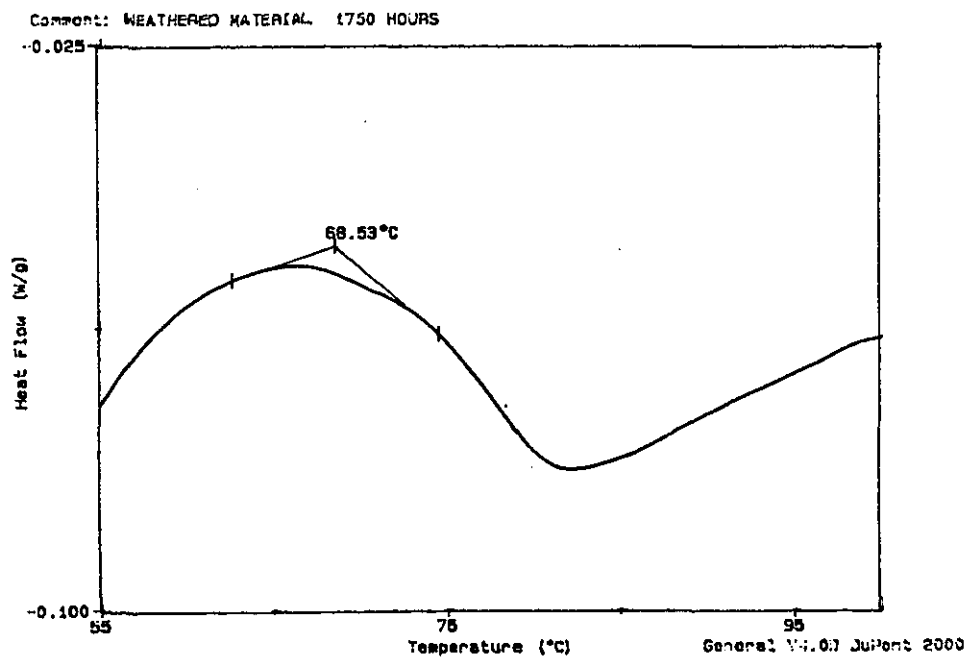
Determination of Tg for PC-1 Weathered Sample
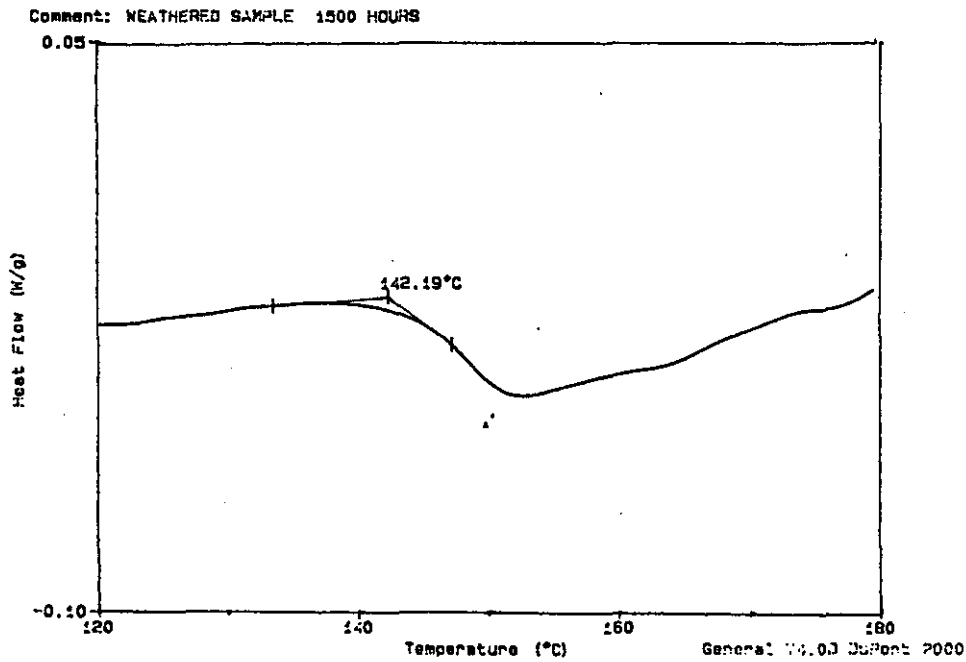
Determination of Tg for PC-2 Weathered Sample
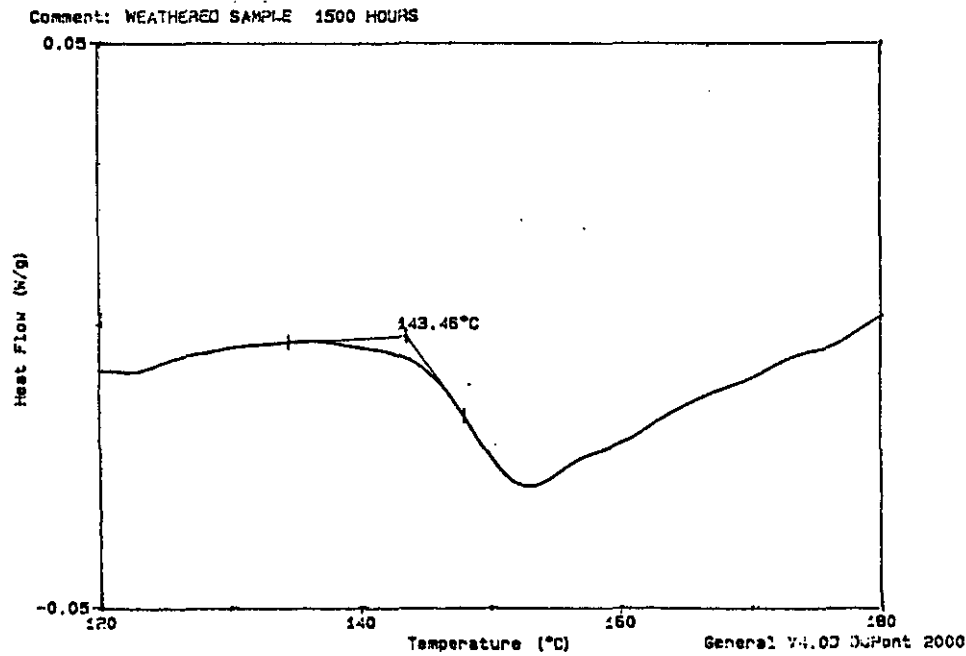
APPENDIX C4: CHANGES IN OPTICAL PROPERTIES

COLOUR AND GLOSS DATA

Results of Samples Exposed in QUV-UVB Lamps (45°/50°)

Sample	EXP	L*	a*	b*	DL*	Da*	Db*	DE*	Gloss
PMMA-1	0	96.26	-1.15	3.46					153.5
	500	94.96	-2.74	9.17	-1.00	-1.60	5.71	6.07	149.6
	1000	95.01	-2.71	9.44	-1.25	-1.56	5.98	6.31	149.0
	1500	94.99	-2.87	9.37	-1.27	-1.72	5.91	6.29	149.7
	2000	95.25	-2.46	8.13	-1.01	-1.31	4.67	4.96	150.0
PMMA-2	0	94.67	-1.75	4.03					145.1
	500	94.23	-1.79	5.34	-0.45	0.04	1.31	1.39	137.6
	1000	93.51	-1.72	6.15	-1.17	0.03	2.12	2.42	129.5
	1500	92.83	-1.82	6.84	-1.85	-0.07	2.81	3.37	124.9
	2000	91.99	-1.78	7.31	-2.68	-0.03	3.28	4.26	116.5
PVC-1	0	87.12	-0.61	1.53					139.7
	500	84.06	-1.02	8.59	-3.06	-0.41	7.06	7.71	120.0
	1000	71.03	-0.77	15.27	-16.09	-0.16	13.74	21.16	7.3
	1500	72.83	-0.59	13.86	-14.29	0.03	12.33	18.88	5.8
	2000	72.62	-0.24	14.06	-14.50	0.38	12.54	19.18	5.7
PVC-2	0	89.07	-2.04	2.72					143.2
	500	71.08	0.46	34.74	-17.99	2.50	32.02	35.77	56.8
	1000	64.66	3.21	36.67	-24.42	5.26	34.95	42.96	5.3
	1500	57.62	7.13	40.69	-31.46	9.17	37.97	50.16	3.4
	2000	57.01	8.67	41.76	-32.06	10.71	39.04	51.64	2.7
PC-1	0	94.84	-1.35	3.55					169.4
	500	93.80	-3.72	11.94	-1.04	-2.37	8.39	8.78	161.5
	1000	93.05	-4.00	14.53	-1.79	-2.66	10.98	11.45	142.5
	1500	92.68	-3.96	14.13	-2.17	-2.62	10.58	11.12	98.8
	2000	92.04	-3.90	14.53	-2.80	-2.55	10.98	11.62	65.5
PC-2	0	94.45	-0.51	2.83					169.5
	500	93.80	-3.72	11.94	-1.04	-2.37	12.41	12.98	138.5
	1000	91.77	-3.80	16.55	-2.68	-3.29	13.72	14.36	78.3
	1500	91.19	-4.81	19.83	-3.26	-4.30	17.00	17.83	56.9
	2000	90.63	-4.63	19.85	-3.82	-4.12	17.03	17.93	35.1

242

Results of Samples Exposed in QUV-UVA Lamps (45°/50°)

Sample	EXP	L*	a*	b*	DL*	Da*	Db*	DE*	Gloss
PMMA-1	0	96.25	-1.14	3.48					153.3
	500	95.33	-2.00	7.01	-0.91	-0.86	3.53	3.75	150.5
	1000	94.07	-2.33	8.37	-1.18	-1.19	4.90	5.13	149.2
	1500	95.11	-2.47	8.31	-1.13	-1.33	4.83	5.14	149.9
	2000	95.42	-2.00	6.76	-0.83	-0.86	3.28	3.49	150.2
PMMA-2	0	94.66	-1.67	3.82					145.2
	500	94.66	-1.68	4.53	0.00	0.02	0.71	0.72	143.0
	1000	94.27	-1.51	4.87	-0.39	0.17	1.05	1.13	140.0
	1500	94.15	-1.55	4.88	-0.51	0.12	1.06	1.19	137.7
	2000	93.88	-1.48	4.83	-0.78	0.20	1.01	1.29	136.2
PVC-1	0	87.15	0.53	1.37					140.0
	500	86.93	0.21	0.97	-0.22	0.74	-0.41	0.88	143.4
	1000	86.07	0.05	3.22	-1.08	0.58	1.85	2.25	137.9
	1500	84.31	-0.35	6.43	-2.84	0.18	5.06	5.81	101.1
	2000	78.25	-0.39	8.72	-8.90	0.14	7.35	11.63	39.0
PVC-2	0	89.03	-2.03	2.68					141.3
	500	85.37	-3.30	18.16	-3.66	-1.28	15.49	15.96	126.9
	1000	82.19	-2.72	24.15	-6.85	-0.69	21.47	22.56	107.1
	1500	71.57	-0.55	30.34	-17.46	1.48	27.67	32.78	27.7
	2000	66.85	1.80	36.40	-22.18	3.83	33.73	40.56	6.6
PC-1	0	94.81	-1.35	3.45					170.0
	500	94.16	-2.55	8.14	-0.65	-1.19	4.68	4.88	165.5
	1000	92.59	-3.21	12.33	-2.22	-1.85	8.88	9.34	146.7
	1500	92.05	-3.42	13.07	-2.76	-2.07	9.62	10.22	136.0
	2000	91.18	-3.34	14.08	-3.64	-1.98	10.63	11.41	120.4
PC-2	0	94.32	-0.49	2.90					170.3
	500	93.61	-2.16	9.01	-0.71	-1.67	6.12	6.39	163.9
	1000	91.99	-3.06	14.18	-2.34	-2.57	11.28	11.81	144.1
	1500	91.42	-3.24	15.07	-2.91	-2.75	12.17	12.81	130.7
	2000	90.47	-3.20	15.52	-3.85	-2.71	12.63	13.48	110.8

243

Results of Samples Exposed in QUV-UVB (60°/50°)

Sample	EXP	L*	a*	b*	DL*	Da*	Db*	DE*	Gloss
PMMA-1	0	96.05	-0.89	3.78					150.8
	500	94.49	-2.77	10.00	-1.56	-1.88	6.22	6.68	147.1
	1000	94.37	-2.80	10.01	-1.68	-1.91	6.23	6.73	144.3
	1500	94.08	-2.87	10.70	-1.97	-1.98	6.92	7.46	143.6
	2000	93.73	-2.66	10.01	-2.32	-1.77	6.23	6.88	143.2
PMMA-2	0	94.49	-1.68	4.57					144.8
	500	93.04	-1.85	6.69	-1.45	-0.17	2.12	2.57	127.1
	1000	91.72	-1.82	8.08	-2.77	-0.14	3.51	4.47	117.7
	1500	90.68	-2.06	10.28	-3.81	-0.38	5.71	6.87	103.9
	2000	-	-	-	-	-	-	-	-
PVC-1	0	86.86	-0.54	2.41					146.9
	500	77.12	-0.81	16.88	-9.74	-0.27	14.47	17.44	85.0
	1000	72.50	1.07	20.45	-14.36	1.61	18.04	23.11	17.9
	1500	70.93	3.34	22.09	-15.93	3.88	19.68	25.61	13.3
	2000	68.72	4.36	22.88	-18.14	4.90	20.47	27.79	11.0
PVC-2	0	88.99	-1.82	2.83					141.0
	500	63.93	5.84	38.92	-25.06	7.66	36.09	44.60	45.2
	1000	57.93	10.25	39.13	-31.06	12.07	36.30	49.28	17.5
	1500	49.67	15.78	33.78	-39.32	17.60	30.95	53.04	7.5
	2000	47.37	17.41	32.63	-41.62	19.23	29.80	54.68	8.4
PC-1	0	94.73	-1.27	3.93					168.8
	500	92.61	-4.07	14.85	-2.12	-2.80	10.92	11.47	154.2
	1000	91.89	-3.93	15.61	-2.84	-2.66	11.68	12.31	143.2
	1500	91.76	-3.89	15.74	-2.97	-2.62	11.81	12.46	127.7
	2000	91.24	-3.93	15.87	-3.49	-2.66	11.94	12.72	118.4
PC-2	0	94.23	-0.48	3.17					168.5
	500	92.24	-3.87	16.16	-1.99	-3.39	12.99	13.57	154.8
	1000	91.77	-3.90	17.23	-2.46	-3.42	14.06	14.68	145.0
	1500	91.49	-3.89	17.69	-2.74	-3.41	14.50	15.15	129.4
	2000	90.79	-3.86	18.09	-3.44	-3.38	14.92	15.68	122.3

Results of Samples Exposed in QUV-UVA (60°/50°)

Sample	EXP	L*	a*	b*	DL*	Da*	Db*	DE*	Gloss
PMMA-1	0	96.04	-0.91	3.81					150.8
	500	94.75	-2.29	8.19	-1.29	-1.38	4.38	4.77	147.1
	1000	95.10	-2.44	8.37	-0.94	-1.53	4.56	4.90	146.6
	1500	94.55	-2.23	8.29	-1.49	-1.32	4.48	4.90	145.0
	2000	94.20	-1.92	7.36	-1.84	-1.01	3.55	4.12	144.8
PMMA-2	0	94.57	-1.67	4.62					144.7
	500	93.67	-1.61	5.55	-0.90	0.06	0.93	1.30	138.3
	1000	92.90	-1.51	6.19	-1.67	0.16	1.57	2.29	115.3
	1500	92.12	-1.36	6.88	-2.45	0.31	2.26	3.35	111.9
	2000	91.53	-1.49	7.34	-3.04	0.18	2.72	4.08	110.1
PVC-1	0	86.98	-0.31	1.61					153.4
	500	85.51	0.03	4.11	-1.47	0.34	2.50	2.92	149.1
	1000	75.67	0.09	16.48	-11.31	0.40	14.87	18.69	51.6
	1500	68.87	1.93	20.76	-18.11	2.24	12.15	26.45	8.9
	2000	65.96	3.95	24.10	-21.02	4.26	22.49	31.08	5.1
PVC-2	0	88.91	-1.71	2.58					139.8
	500	79.21	-1.20	29.80	-9.70	0.51	27.22	28.90	112.0
	1000	59.31	6.44	38.83	-29.60	8.15	36.25	47.50	11.2
	1500	54.92	9.72	39.96	-33.99	11.43	37.38	51.80	3.1
	2000	53.47	11.49	38.10	-35.44	13.20	35.52	51.88	3.2
PC-1	0	94.72	-1.23	3.97					167.8
	500	93.07	-2.89	10.70	-1.65	-1.66	6.73	7.13	154.9
	1000	91.96	-3.52	14.61	-2.76	-2.29	10.64	11.23	135.7
	1500	91.42	-3.44	14.96	-3.30	-2.21	10.99	11.69	130.5
	2000	90.84	-3.49	15.28	-3.88	-2.26	11.31	12.17	124.9
PC-2	0	94.36	-0.39	3.16					168.6
	500	92.54	-2.58	11.91	-1.82	-2.19	8.75	9.20	158.1
	1000	91.30	-3.32	17.69	-3.04	-2.93	13.83	14.46	135.0
	1500	90.35	-3.24	17.69	-4.01	-2.85	14.53	15.34	125.9
	2000	89.61	-3.32	18.34	-4.75	-2.93	15.18	16.17	118.7

Results of Samples Exposed in X-1200 on black backing

Sample	EXP	L*	a*	b*	DL*	Da*	Db*	DE*	Gloss
PMMA-1	0	96.24	-1.26	3.85					149.9
	500	95.86	-1.27	4.32	-0.38	-0.01	0.47	0.60	148.9
	1000	95.85	-1.47	5.21	-0.39	-0.21	1.36	1.43	149.5
	1500	95.80	-1.49	5.34	-0.44	-0.23	1.49	1.57	149.4
	2000	95.60	-1.56	5.30	-0.64	-0.30	1.45	1.61	149.1
	13750	88.96	-1.46	9.01	-7.28	-0.20	5.16	8.93	77.9
PMMA-2	0	94.64	-2.08	4.78					141.4
	500	94.09	-1.38	3.67	-0.55	0.70	-1.11	1.42	138.2
	1000	94.94	-1.34	3.63	0.30	0.74	-1.15	1.40	140.7
	1500	94.84	-1.41	4.39	0.20	0.67	-0.39	0.80	137.3
	2000	94.58	-1.38	4.26	-0.06	0.70	-0.52	0.87	135.3
	6500	86.49	-1.27	10.01	-8.15	0.81	5.23	9.72	80.3
PVC-1	0	87.03	-0.69	1.83					138.6
	500	86.15	0.66	-0.21	-0.88	1.35	-2.04	2.60	132.0
	1000	86.58	0.96	-0.07	-0.45	1.65	-1.90	2.56	136.0
	1500	86.64	0.78	0.02	-0.39	1.47	-1.81	2.36	136.6
	2000	84.26	0.43	0.54	-0.54	1.12	-1.29	1.79	130.8
	3250	84.26	-0.57	6.77	-2.77	0.12	4.94	5.66	103.7
PVC-2	0	89.48	-2.21	3.93					143.5
	500	81.78	-2.41	24.55	-7.68	-0.20	20.62	22.00	119.9
	1000	60.95	4.89	37.20	-28.51	7.10	33.27	44.29	49.9
	1250	60.78	5.58	38.06	-28.68	7.79	34.13	45.26	3.2
PC-1	0	94.34	-1.30	3.77					167.9
	500	93.02	-2.57	7.96	-1.32	-1.27	4.19	4.57	130.8
	1000	90.99	-2.73	9.71	-3.35	-1.43	5.94	6.97	95.5
	1500	88.85	-2.79	11.51	-5.49	-1.49	7.74	9.61	48.6
	2000	89.67	-2.73	11.56	-4.67	-1.43	7.79	9.19	44.8
PC-2	0	94.62	-0.38	2.62					176.5
	500	93.78	-2.24	8.51	-0.84	-1.86	5.89	6.23	168.8
	1000	81.13	-2.63	20.00	-13.49	-2.25	17.38	22.12	15.4
	1500	81.42	-2.60	19.62	-13.20	-2.22	17.00	21.64	5.4
	2000	83.03	-2.96	17.04	-11.59	-2.58	14.42	18.68	7.0

Results of Samples Exposed on X-1200 on open-back holders

Sample	EXP	L*	a*	b*	DL*	Da*	Db*	DE*	Gloss
PMMA-1	0	96.36	-1.23	3.98					149.5
	500	96.20	-1.29	4.22	-0.16	-0.06	0.24	0.30	148.0
	1000	96.09	-1.31	4.29	-0.27	-0.08	0.31	0.42	149.2
	1500	95.93	-1.43	4.70	-0.43	-0.20	0.72	0.86	149.3
	2000	95.92	-1.45	4.83	-0.44	-0.22	0.85	0.98	148.2
	21000	91.27	-1.00	5.70	-4.04	-0.01	2.09	4.55	94.8
PMMA-2	0	94.88	-1.75	4.34					141.7
	500	94.89	-1.57	3.86	0.01	0.18	-0.48	0.51	139.0
	1000	94.97	-1.56	3.89	0.09	0.19	-0.45	0.50	141.7
	1500	94.79	-1.51	3.89	-0.09	0.24	-0.45	0.52	142.0
	2000	94.96	-1.40	3.99	0.08	0.35	-0.35	0.50	140.4
	12000	89.37	-1.21	9.38	-5.04	0.30	5.19	7.24	93.1
PVC-1	0	87.06	-0.25	0.99					135.3
	500	87.04	0.29	-0.15	-0.02	0.54	-1.14	1.26	135.4
	1000	87.03	0.27	-0.23	-0.03	0.52	-1.22	1.33	136.5
	1500	87.09	0.13	-0.14	0.03	0.38	-1.13	1.19	136.4
	2000	87.14	0.27	-0.23	0.08	0.52	-1.22	1.33	136.4
	3250	85.99	-0.53	3.02	-0.68	-0.70	3.02	3.17	104.2
PVC-2	0	89.67	-2.42	4.32					139.3
	500	85.21	-2.35	11.38	-4.46	0.07	7.06	8.35	131.5
	1000	84.86	-2.49	12.77	-4.81	-0.07	8.45	9.72	127.2
	1500	84.08	-2.20	12.77	-5.59	-0.22	8.45	10.13	121.3
	2000	82.57	-2.13	16.20	-7.10	-0.29	11.88	13.84	117.7
PC-1	0	95.26	-1.55	4.12					164.8
	500	95.01	-2.15	5.73	-0.25	-0.60	1.61	1.74	165.6
	1000	94.03	-3.04	9.78	-1.23	-1.49	5.66	5.98	160.2
	1500	92.28	-3.58	13.61	-2.98	-2.03	9.49	10.15	138.4
	2000	91.87	-3.54	13.08	-3.39	-1.99	8.96	9.78	123.4
PC-2	0	95.42	-1.10	3.65					167.1
	500	95.14	-2.08	6.30	-0.31	-0.98	2.65	2.84	165.1
	1000	93.81	-3.22	11.46	-1.61	-2.12	7.81	8.25	162.0
	1500	92.50	-3.58	13.76	-2.92	-2.48	10.11	10.81	148.6
	2000	92.04	-3.74	14.54	-3.38	-2.64	10.89	11.70	143.7

Mean Light Transmission Values 290-400nm

Sample	Exposure Type	% Transmission after exposure in Xenotest-1200 (openback)					
		0hrs	250hrs	500hrs	1000hrs	1500hrs	2000hrs
PMMA-1	X-1200	53.3			53.9		54.3
	UV-A	53.6		52.9	54.4	56.2	43.8
	UV-B	55.3	51.6	49.5	54.2		45.6
PMMA-2	X-1200	14.0			13.6		13.3
	UV-A	14.0		13.8	13.8	13.7	10.2
	UV-B	15.5	13.9	13.8	13.7		9.6
PVC-1	X-1200	4.4			4.3		4.3
	UV-A	4.6		4.5	4.3	3.5	2.6
	UV-B	4.7	4.3	3.8	2.8		1.8
PVC-2	X-1200	6.9		3.7	2.8	2.0	1.6
	UV-A	7.2		4.6	3.1	2.2	1.4
	UV-B	7.5	3.6	2.5	1.3		1.0
PC-1	X-1200	3.7		3.5	3.2	2.6	2.5
	UV-A	3.7		3.5	3.2	2.7	2.5
	UV-B	3.7	2.5	2.5	2.4		2.3
PC-2	X-1200	4.5		3.8	3.4	3.2	2.9
	UV-A	4.8		4.3	3.3	3.0	2.0
	UV-B	4.4	2.7	2.7	2.7		1.6

% Remaining Light Transmission (290-400nm)

Sample	Exposure Type	\% Remaining after exposure in Xenotest-1200 (openback)					
		0hrs	250hrs	500hrs	1000hrs	1500hrs	2000hrs
PMMA-1	X-1200	100			101.1		101.9
	UV-A	100		98.7	101.5	104.9	81.7
	UV-B	100	93.3	89.5	98.0		82.5
PMMA-2	X-1200	100			97.1		95.0
	UV-A	100		98.6	98.6	97.9	72.9
	UV-B	100	89.7	89.0	84.4		61.9
PVC-1	X-1200	100			97.7		97.7
	UV-A	100		97.8	93.5	76.1	56.5
	UV-B	100	91.5	80.9	59.6		38.3
PVC-2	X-1200	100		53.6	40.6	29.0	23.2
	UV-A	100		63.9	43.1	30.6	19.4
	UV-B	100	48.0	33.3	17.3		13.3
PC-1	X-1200	100		94.6	86.5	70.3	67.6
	UV-A	100		94.6	86.5	73.0	67.6
	UV-B	100	67.6	67.6	64.9		62.1
PC-2	X-1200	100		84.4	75.6	71.1	64.4
	UV-A	100		89.6	68.8	62.5	41.7
	UV-B	100	61.4	61.4	61.4		36.4

Mean Light Transmission Values 410-790nm

Sample	Exposure Type	% Transmission after exposure in Xenotest-1200 (openback)					
		0hr	250hrs	500hrs	1000hrs	1500hrs	2000hrs
PMMA-1	X-1200	92.9			91.5		90.4
	UV-A	92.7		92.6	92.4	92.2	92.1
	UV-B	95.2	95.0	94.8	94.8		94.4
PMMA-2	X-1200	91.1			90.4		89.3
	UV-A	91.2		91.0	90.9	90.4	90.0
	UV-B	93.7	93.4	92.6	92.1		90.4
PVC-1	X-1200	84.9			84.2		81.7
	UV-A	84.9		85.1	82.2	78.5	65.1
	UV-B	87.0	85.8	82.3	69.3		55.1
PVC-2	X-1200	82.7		68.9	63.1	56.8	51.7
	UV-A	82.8		75.4	66.5	62.6	41.2
	UV-B	85.0	73.8	66.4	46.1		41.6
PC-1	X-1200	88.4		87.0	84.4	83.6	82.5
	UV-A	88.5		87.2	85.2	83.5	82.3
	UV-B	90.5	87.0	86.8	86.9		84.0
PC-2	X-1200	88.6		87.4	85.2	83.9	80.3
	UV-A	88.7		87.9	83.5	79.9	79.4
	UV-B	91.1	87.2	86.5	85.8		78.8

% Remaining Light Transmission (410-790nm)

Sample	Exposure Type	% Remaining after exposure in Xenotest-1200 (openback)					
		0hrs	250hrs	500hrs	1000hrs	1500hrs	2000hrs
PMMA-1	X-1200	100			98.5		97.3
	UV-A	100		99.9	99.7	99.5	99.4
	UV-B	100	99.8	99.6	99.6		99.2
PMMA-2	X-1200	100			99.2		98.0
	UV-A	100		99.8	99.7	99.1	98.7
	UV-B	100	99.7	98.8	98.3		96.5
PVC-1	X-1200	100			94.2		96.2
	UV-A	100		100.2	96.8	92.5	76.7
	UV-B	100	98.6	94.6	79.7		63.3
PVC-2	X-1200	100		83.3	76.3	68.7	62.5
	UV-A	100		91.1	80.3	75.6	49.8
	UV-B	100	86.8	78.1	54.2		48.9
PC-1	X-1200	100		98.4	95.5	94.6	93.3
	UV-A	100		98.5	96.3	94.4	93.0
	UV-B	100	96.1	95.9	96.0		92.8
PC-2	X-1200	100		98.6	96.2	94.7	90.6
	UV-A	100		99.1	94.1	90.1	89.5
	UV-B	100	95.7	95.0	94.2		86.5

MICROGRAPHS

PVC-1 Xenotest-1200 4000 hours
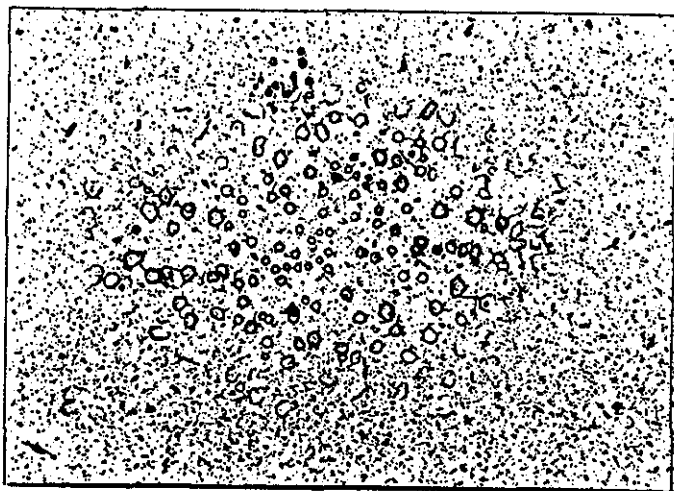
PVC-1 UV-A 1000 hours
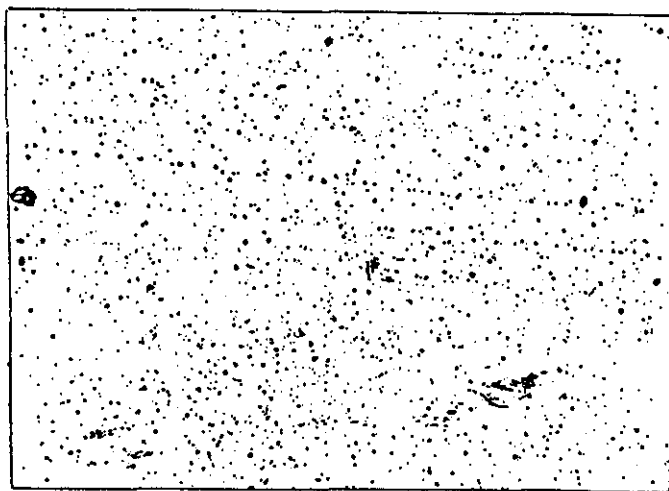
PVC-1 UV-B 500 hours
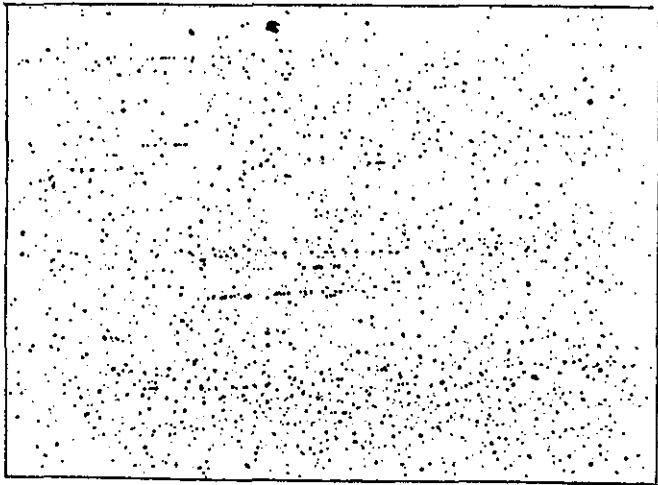
PVC-1 UV-B 1000 hours
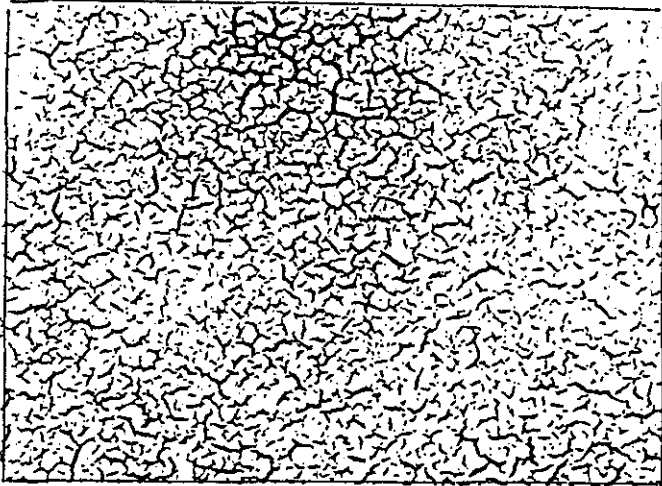
PVC-2 Xenotest-1200 2000 hours

253

PVC-2 UV-A 1000 hours
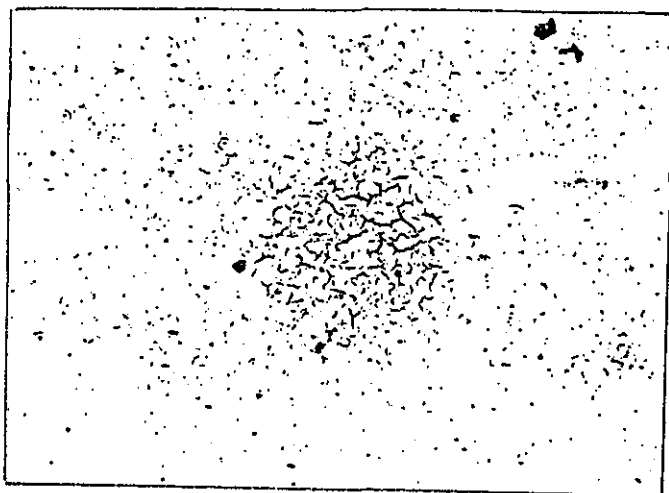
PVC-2 UV-A 1500 hours
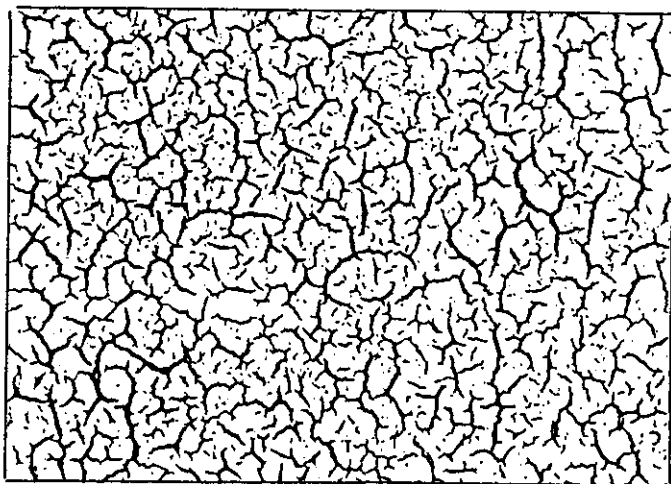
PVC-2 UV-A 2000 hours
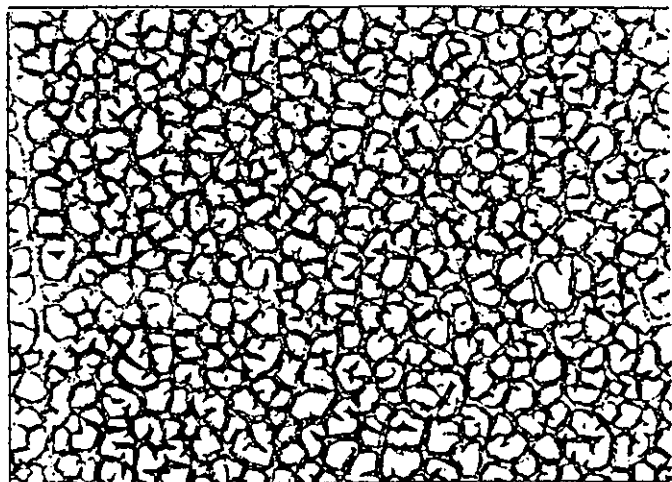
PC-1 Xenotest-1200 1000 hours
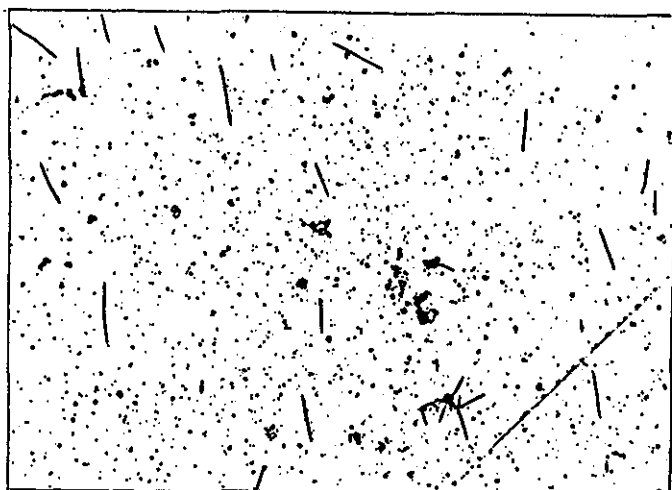
PC-1 UV-A 1000 hours

PC-1 UV-B 2000 hours

255
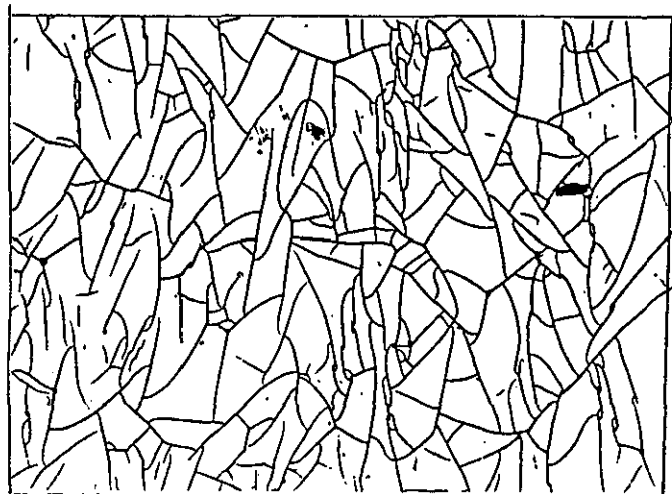
PC-2 Xenotest-1200 1000 hours
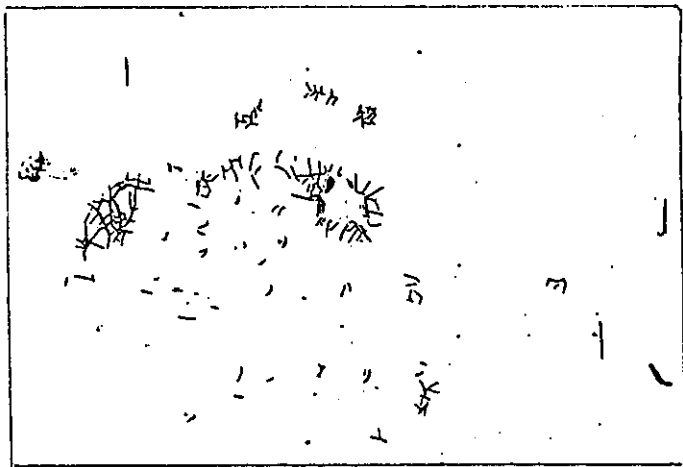
PC-2 Xenotest-1200 3500 hours

PC-2 UV-A 1000 hours

256
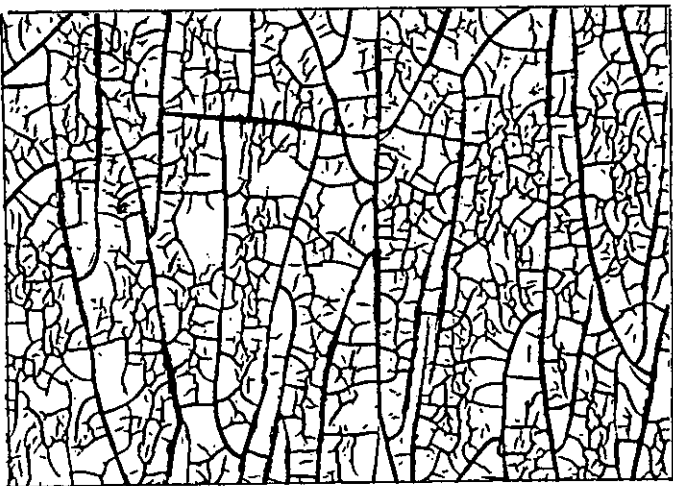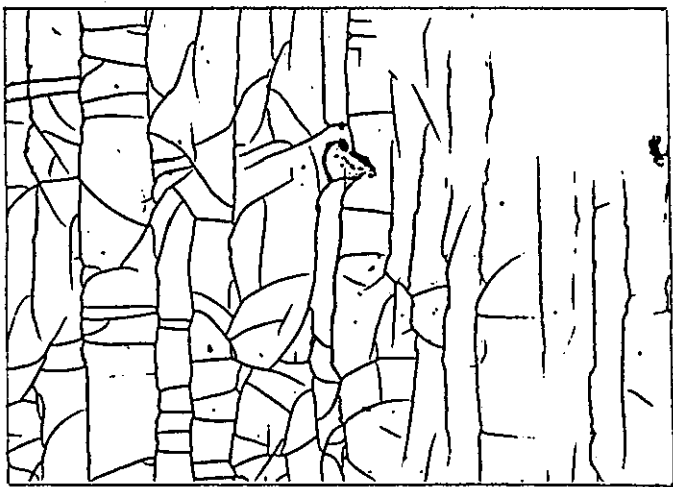
APPENDIX C5: CHANGES IN IMPACT PROPERTIES

PMMA-1 Impact Test Data

Exposure (hours)	Force at Failure (N)	Displacement to Failure (mm)	Energy at Failure (Nm)	Mode of Failure
Reference	289 285 274	0.82 0.82 0.79	0.10 0.10 0.10	Brittle brittle brittle
14500 X-1200	316 279 248	0.94 0.94 0.88	0.12 0.11 0.09	Brittle brittle brittle
500 UV-A	380 340	2.37 1.29	0.52 0.20	Brittle brittle
1000 UV-A	284 278	1.06 1.03	0.12 0.13	Brittle brittle
1500 UV-A	244 262	1.14 1.06	0.12 0.13	Brittle brittle
250 UV-B	269 245	1.11 1.11	0.13 0.12	Brittle brittle
500 UV-B	302 304	0.97 0.99	0.12 0.13	Brittle brittle
1000 UV-B	291 348	1.38 1.61	0.20 0.29	Brittle brittle

PMMA-2 Impact Test Data

Exposure (hours)	Force at Failure (N)	Displacement to Failure (mm)	Energy at Failure (Nm)	Mode of Failure
Reference	2523 2458 1945	5.30 5.14 5.09	5.65 5.08 4.57	Brittle brittle brittle
1250 X-1200	925 1027 600	2.48 2.78 2.20	1.14 1.31 0.70	Brittle brittle brittle
4250 X-1200	567 582 589	1.82 1.76 1.79	0.46 0.45 0.50	Brittle brittle brittle
8000 X-1200	117 164 155	1.58 1.49 1.03	0.16 0.15 0.08	Brittle brittle brittle
500 UV-A	2402	5.18	4.78	Brittle
1000 UV-A	1591 1807	3.64 4.05	2.30 2.81	Brittle brittle
1500 UV-A	723 1278	2.31 3.38	0.79 1.76	Brittle brittle
250 UV-B	2598 2147	5.03 4.99	5.02 3.98	Brittle brittle
500 UV-B	693 674	2.63 3.07	0.88 0.98	Brittle brittle
1000 UV-B	371 469	1.52 4.94	0.26 1.39	Brittle brittle

PVC-1 Impact Test Data

Exposure (hours)	Force at Failure (N)	Displacement to Failure (mm)	Energy at Failure (Nm)	Mode of Failure
Reference	2778 2392 2951	4.84 4.95 5.13	5.45 4.47 6.01	Ductile ductile ductile
500 X-1200	3346 3399 3431	4.63 4.92 4.86	6.23 6.40 6.43	Ductile ductile ductile
750 X-1200	3647 3503	4.38 4.39	6.86 6.68	Ductile ductile
1000 X-1200	3558 3686 980	4.84 4.52 1.81	7.23 7.15 0.94	Ductile ductile brittle
1250 X-1200	833.33 1002.61 813.07	1.61 1.99 1.64	0.60 0.93 0.59	Brittle brittle brittle
2500 X-1200	284 208	2.87 2.63	0.46 0.26	Brittle brittle
8000 X-1200	228 280 256	2.14 2.17 2.64	0.30 0.32 0.43	Brittle brittle brittle
500 UV-A	3265	4.69	6.02	ductile
1000 UV-A	314 140	1.20 1.23	0.18 0.11	Brittle brittle
1500 UV-A	189 197	1.17 1.06	0.11 0.09	Brittle brittle
250 UV-B	558 520	1.44 1.61	0.35 0.31	Brittle brittle
500 UV-B	214 176	1.14 0.97	0.12 0.08	Brittle brittle
1000 UV-B	413	1.46	0.24	Brittle

PVC-2 Impact Test Data

Exposure (hours)	Force at Failure (N)	Displacement to Failure (mm)	Energy at Failure (Nm)	Failure Mode
Reference	2627	5.21	5.66	ductile
	2637	5.24	5.68	ductile
	2676	5.36	5.83	ductile
110 X-1200	2774	4.85	5.46	Ductile
	2852	4.78	5.63	ductile
	2859	5.08	5.66	ductile
250 X-1200	2833	5.43	5.73	Ductile
	2837	5.83	5.96	ductile
	369	1.99	0.45	brittle
	278	1.20	0.17	brittle
	366	1.44	0.25	brittle
390 X-1200	487	2.19	0.58	Brittle
	395	1.55	0.32	brittle
	457	1.99	0.50	brittle
500 X-1200	373	1.32	0.23	Brittle
	489	2.22	0.59	brittle
	462	2.11	0.54	brittle
3500 X-1200	302	1.52	0.22	Brittle
	392	2.11	0.46	brittle
	374	2.46	0.54	brittle
500 UV-A	823	5.36	2.24	Brittle
	366	2.20	0.43	brittle
1000 UV-A	589	3.04	0.88	Brittle
	481	3.10	0.88	brittle
1500 UV-A	319	1.76	0.28	Brittle
	361	2.14	0.40	brittle
250 UV-B	480	3.45	0.82	Brittle
	368	1.70	0.30	brittle
500 UV-B	530	2.52	0.73	Brittle
	507	2.52	0.70	brittle
1000 UV-B	575	3.10	0.92	Brittle

PC-1 Impact Test Data

Exposure (hours)	Force at Failure (N)	Displacement to Failure (mm)	Energy at Failure (Nm)	Failure Mode
Reference	2350 2275 2471	5.31 4.71 6.06	5.11 4.62 5.67	Ductile ductile ductile
3750 X-1200	2640 2640 2437	4.53 4.59 4.56	4.97 4.99 4.69	Ductile ductile ductile
5750 X-1200	2594 2660	4.82 4.85	5.01 5.14	Ductile ductile
500 UV-A	2817 2784	4.61 4.91	5.53 5.36	Ductile ductile
1000 UV-A	2823 2849	4.81 4.73	5.50 5.49	Ductile ductile
1500 UV-A	2634 2718	4.73 4.64	5.09 5.26	Ductile ductile
250 UV-B	2797 2640	4.82 4.73	5.41 5.12	Ductile ductile
500 UV-B	2725 2712	4.94 4.70	5.35 5.32	Ductile ductile
1000 UV-B	2673 2771	4.82 4.78	5.06 5.44	Ductile ductile

PC-2 Impact Test Data

Exposure (hours)	Force at Failure (N)	Displacement to failure (mm)	Energy at Failure (Nm)	Failure Mode
Reference	2758 2562 2608	5.64 5.19 5.22	6.26 5.57 5.59	Ductile ductile ductile
3750 X-1200	2568 2614 2640	4.68 4.79 4.65	5.03 5.09 5.15	Ductile ductile ductile
5750 X-1200	2856 2849	4.90 5.02	5.62 5.57	Ductile ductile
500 UV-A	2882 2980	4.96 4.99	5.60 5.83	Ductile ductile
1000 UV-A	2987 2673	4.89 4.67	5.99 5.16	Ductile ductile
1500 UV-A	1209	4.19	2.28	Ductile
250 UV-B	2778 2816	5.07 4.67	5.58 5.57	Ductile ductile
500 UV-B	2823 2849	4.72 4.81	5.60 5.71	Ductile ductile
1000 UV-B	2843 2797	4.96 4.76	5.55 5.48	Ductile ductile

APPENDIX D: EFFECT OF ABRASION ON IMPACT RESISTANCE

Impact Test Data for 2mm Thick Samples, Grade 0 Scratch

Sample	Force at Failure (N)	Displacement to Failure (mm)	Energy at Failure	Failure Mode
PMMA-1	261 239 228	0.76 0.94 0.88	0.09 0.13 0.10	Brittle brittle brittle
PMMA-2	356 353 361	1.32 1.32 1.44	0.23 0.24 0.27	Brittle brittle brittle
PVC-1	282 377 281	0.92 1.26 1.03	0.12 0.21 0.12	Brittle brittle brittle
PVC-2	282 360 383	1.00 1.23 3.34	0.13 0.19 0.66	Brittle brittle brittle
PC-1	2569 2346 2536	5.54 4.97 5.45	5.64 4.85 5.50	Ductile ductile ductile
PC-2	2294 2631 2673	5.53 5.56 5.38	6.06 5.87 5.91	Ductile ductile ductile

Impact Data for 2mm Thick Samples, Grade 2 Scratch

Sample	Force at failure (N)	Displacement to Failure (mm)	Energy at failure (Nm)	Failure Mode
PMMA-1	322 327 305	1.08 1.20 0.82	0.23 0.22 0.12	Brittle brittle brittle
PMMA-2	329 301 282	1.23 1.26 1.29	0.19 0.20 0.21	Brittle brittle brittle
PVC-1	338 264 246	0.88 0.79 0.82	0.12 0.09 0.08	Brittle brittle brittle
PVC-2	281 304 333	1.06 1.49 1.85	0.13 0.23 0.31	Brittle brittle brittle
PC-1	2408 2431 2575	5.31 5.11 5.51	5.10 5.15 5.67	Ductile ductile ductile
PC-2	2686 2627 2686	5.53 5.56 5.38	6.06 5.87 5.91	Ductile ductile ductile

266

Impact Data for 3mm Thick Samples, References

Sample	Force at Failure (N)	Displacement to Failure (mm)	Energy at failure (Nm)	Failure Mode
PMMA-1	784 651 643	1.17 0.70 0.70	0.50 0.22 0.22	Brittle brittle brittle
PMMA-2	3134 3431 3212	4.39 4.71 4.40	6.30 7.36 6.74	Brittle brittle brittle
PVC-1	5824 5823 5627	5.47 5.46 5.97	16.21 16.21 15.82	ductile ductile ductile
PC-2	3673 3941 4131	5.55 5.89 6.42	9.45 10.72 11.37	Ductile ductile ductile

Impact data for 3mm Thick Samples, Grade 0 Scratch

Sample	Force at failure (N)	Displacement to Failure (mm)	Energy at Failure (Nm)	Failure Mode
PMMA-1	668 656 588	1.23 0.91 0.82	0.46 0.34 0.28	Brittle brittle brittle
PMMA-2	899 804 842	1.17 1.05 1.38	0.49 0.45 0.56	Brittle brittle brittle
PVC-1	991 1275 1205	0.88 1.11 1.05	0.38 0.62 0.57	Brittle brittle brittle
PC-2	3902 4098 4281	5.84 6.02 6.10	10.55 11.28 11.67	Ductile ductile ductile

Impact Test Data for 3mm Thick Samples, Grade 2 Scratch

Sample	Force at Failure (N)	Displacement to Failure (mm)	Energy at Failure (Nm)	Failure Mode
PMMA-1	672 663 693	1.14 1.11 1.20	0.46 0.46 0.46	Brittle brittle brittle
PMMA-2	686 686 682	1.61 1.11 1.17	0.71 0.43 0.43	Brittle brittle brittle
PVC-1	573 558 834	0.76 0.73 0.91	0.19 0.19 0.31	Brittle brittle brittle
PC-2	4033 4085 4314	5.94 5.97 6.03	11.02 11.10 11.88	Ductile ductile ductile

Reproducibility Data for Impact Test, 2mm thick samples

Sample	Measurement Number	Force at failure (N)	Displacement to Failure (mm)	Energy at failure (Nm)
PMMA-1 Reference	1	306	0.79	0.10
	2	305	0.88	0.12
	3	301	0.85	0.10
	4	330	0.91	0.12
	5	304	0.94	0.12
	6	286	0.85	0.11
	7	289	0.82	0.10
	8	285	0.82	0.10
	9	274	0.79	0.10
	Mean	298	0.85	0.11
	±S.d.	16	0.05	0.01
PMMA-1 Grade 0 Scratch	1	319	0.91	0.13
	2	294	0.91	0.12
	3	296	0.91	0.12
	4	270	0.94	0.11
	5	266	0.91	0.11
	6	275	0.94	0.11
	7	261	0.76	0.09
	8	239	0.94	0.13
	9	228	0.88	0.10
	Mean	272	0.90	0.11
	±s.d.	28	0.06	0.01
PVC-1 Reference	1	3029	5.15	6.20
	2	3069	5.15	6.31
	3	2422	4.98	4.49
	4	3049	5.21	6.27
	5	3036	5.18	6.21
	6	2971	5.13	5.98
	7	2778	4.84	5.45
	8	2392	4.95	4.47
	9	2951	5.13	6.01
	Mean	2855	5.08	5.71
	±s.d.	269	0.13	0.70

PVC-1 Grade 0 Scratch	1	285	1.06	0.12
	2	350	1.41	0.19
	3	497	1.67	0.32
	4	348	1.35	0.18
	5	455	1.67	0.27
	6	335	1.17	0.24
	7	282	0.94	0.12
	8	377	1.26	0.21
	9	281	1.03	0.12
	Mean	357	1.28	0.20
	±s.d.	76	0.26	0.07
PC-2 Reference	1	2647	5.53	5.77
	2	2660	5.87	6.10
	3	2667	5.30	5.86
	4	2673	5.65	5.99
	5	2660	5.79	6.02
	6	2594	5.36	5.62
	7	2758	5.64	6.26
	8	2562	5.19	5.57
	9	2608	5.22	5.59
	Mean	2648	5.51	5.86
	±s.d.	56	0.25	0.25
PC-2 Grade 0 Scratch	1	2581	5.42	5.53
	2	2745	5.61	6.22
	3	2725	5.41	6.06
	4	2660	5.33	5.77
	5	2634	5.39	5.77
	6	2634	5.33	5.76
	7	2294	5.17	4.94
	8	2631	5.56	5.84
	9	2673	5.30	5.87
	Mean	2620	5.39	5.75
	±s.d.	132	0.13	0.36

APPENDIX E: PUBLICATIONS

TESTING PVC-U BUILDING COMPONENTS FOR DURABILITY USING ARTIFICIAL WEATHERING

by D Gardiner BSc, PhD and S M Halliwell BSc

SUMMARY

This paper provides a summary of current progress in the revision of the basic International Standards relating to artificial weathering of plastics. These provide improvements in the control over light sources, duration of exposure and temperature. Applications to European Standards being developed for window profiles and rooflights are discussed, along with methods of assessing the effects of weathering on colourfastness.

TESTING PVC-U BUILDING COMPONENTS FOR DURABILITY USING ARTIFICIAL WEATHERING

D.Gardiner and S.M.Halliwell*

This paper provides a summary of current
progress in the revision of the basic
International Standards relating to artificial
weathering of plastics. These provide
improvements in the control over light sources,
duration of exposure and temperature.
Applications to European Standards being·
developed for window profiles and rooflights are
discussed, along with methods of assessing the
effects of weathering on colourfastness.

INTRODUCTION

Artificial weathering tests are used increasingly to set
performance requirements for durability of plastics building
components used externally. Whilst natural weathering in use is
the ultimate test, for approvals purposes much shorter timescales
and greater consistency of conditions are needed. Modern
artificial weathering procedures offer this in principle, but it
is essential to identify and control the relevant variables. This
is the objective of the current revision in ISO/TC61, Plastics, of
ISO 4892(1). It is intended that this should correspond with
methods being prepared for paints and rubbers.

In anticipation of publication of the revision of ISO 4892,
the new technical principles are being incorporated in the draft
European Standards for PVC-U windowframe profiles being developed
in CEN/TC33/WG1/TG5. The result should be a more tightly defined
procedure than current practice, represented by BS 7413(2), and is
being supported by extensive interlaboratory tests. Other
applications in hand include specifications for plastics
rooflights in CEN/TC128 and Part 3 of the comparable data standard
for plastics, a UK initiative being developed in ISO/TC61. This
will form an addition to BS 7008(3) and relate to time dependant
properties.

*Building Research Establishment, Garston, Watford, UK.

REVISION OF ISO 4892

The revision would exclude enclosed carbon arc light sources and bring fluorescent lamp devices within the formal scope. A 4-part structure is proposed:-

Part 1: General Guidance
Part 2: Xenon Arc Sources
Part 3: Fluorescent Lamps
Part 4: Open-flame carbon arc lamps.

Improved Temperature Control. The use of black panel thermometers has caused uncertainty because of the variety of designs and a specification for a black standard thermometer has been introduced. This will generally indicate higher temperatures and be both more consistent and better related to surface temperatures reached by plastics components. A white standard thermometer is also specified and may be more relevant to white or transparent test pieces.

Xenon Arc Devices. Two spectral distributions for filtered xenon arcs are defined; Method A, to simulate direct sunlight and Method B to simulate sunlight through windowglass. A simplified set of preferred operating parameters includes: black standard temperature = 65±3°C; water spray cycle 18 min. ON, 102 min. OFF; relative humidity in dry period, 50±5% or 65±5%. Account is taken of more recent instrument design which permits control of irradiance by monitoring lamp output at a fixed wavelength or bandpass, for example at 340 nm in the UV using method A. Descriptions of the typical features of aircooled and water-cooled designs are included. The use of the blue wool scales is dropped, certainly for Method A. Instead it is proposed to define exposure duration in terms of integrated irradiance over a defined wavelength bandpass (eg. 290-800 nm) to a defined total dose (eg. x GJm^{-2}). This requires an adequate knowledge of radiation incident on the samples and its variation with time, strictly speaking through continuous measurement.

Proposed applications to PVC-U product standards. The proposed EN for white PVC-U window profiles includes an artificial weathering test using xenon arc lamps, as above:- Method A; maximum black standard temperature 65±3°C; water spray 18 minutes ON, 102 minutes OFF with R.H. 65±5%. The target irradiances over the bandpass 290-800 nm, i.e. UV + visible radiation, are 8 and 12 GJm^{-2}. These values are considered to correspond approximately to 5 years exposure in northern and southern Europe, respectively.

Interlaboratory tests are in hand in support of these proposals and to help define methods to assess the effects of weathering. Some 20 weathering devices are included and, whilst firm conclusions cannot yet be drawn, the main sources of variability are expected to include:- light intensity; cabinet air temperature needed to achieve a common black standard temperature; lamp output in the short wavelength ("UV-B") region. The latter is being measured using polysulphone films(4). Changes in colour are to be assessed relative to the, near white, staining grey scale and the corresponding method for instrumental assessment, developed for textiles(5). A maximum contrast rating of 4 is proposed. Three distinct methods for assessing changes in impact

strength are being compared, reflecting current practices within Europe and being variants on the Charpy and tensile impact methods.

Proposed applications to rooflights

Standards development in CEN TC128 includes plastics rooflights, both of the profiled type, eg. ref (6), and formed rooflights fitted to upstands. The particular challenge here is to define an artificial weathering procedure which can fairly be applied to a wide range of materials, PVC-U, acrylic, polycarbonate and GRP. The effects of surface coatings and of vacuum forming need to be taken into account. It is hoped that the same basic procedure proposed for PVC-U profiles can be employed here. Temperature control of samples is again critical, especially for PVC, and is strongly influenced by the method of mounting. Samples mounted open at the back will achieve much lower temperatures than if backed by radiation absorbing materials with poor ventilation. This can be used to control test piece temperature. It is noted that significant failures have occurred in practice with PVC rooflights mounted in ways which tend to raise operational temperatures, for example; tinted lights, shapes which trap heated air but lack ventilation, double glazed units and the like. There is a need to be able to simulate such effects in artificial weathering procedures.

Fluorescent Lamps. It has proved difficult in drafting Part 3 of ISO 4892 as revised to accommodate the rather different approaches incorporated in American and German practice. The former in the form of the well known UV-condensation cycle devices is the more widely used, but the latter offers more precise control over exposure conditions, with direct water spray being used. The preferred test cycle of 4 hours UV exposure at 60°C, followed by 4 hours of condensation at 50°C, following American practice (7), is recommended, utilizing "UV-A" lamps with peak output at 340 nm. However this may be an excessive temperature for PVC products. It needs to be kept in mind that fluorescent lamps will not produce the range of temperature differentiation with sample colour characteristic of sunlight or xenon arc lamps. Plastics materials may also give uneven condensation behaviour in some conditions because of the low thermal conduction. More work is needed before we can suggest recommended procedures for PVC components with confidence.

METHODS FOR MEASUREMENT OF OPTICAL PROPERTIES

At present there is no appropriate method for the instrumental measurement of colour of plastics as such. It is suggested that the method for paints be used (8), being based on the CIELAB procedure. However this is not without problems and is being revised in ISO/TC35. It is hoped to adopt the same procedure for plastics in due course. At the present time proposals are being studied in ISO/TC61 to develop methods for the measurement of light transmission and haze of transparent plastics and also of specular reflectance. Such methods are needed, inter alia, to feed into the much needed revision of ISO 4582 which deals with assessment of changes produced by weathering(9).

Colour measurement is also of value for quality control in manufacture. A working party of the British Plastics Federation Windows Group has been studying the application of a British Standard procedure (10) for determining small colour differences and will publish their findings shortly.

CEN/TC33/WG1/TG5 are attempting to define what is a white PVC windowframe profile. The phrase "white or near white" is used in BS 7413(2), but something more precise is needed. Using the CIELAB system (8), the following proposal has been tabled:-

$L* \geq 82$ (chromaticity co-ordinate $Y \geq 60$)
$-2.5 \leq a* \leq 5$; $-5 \leq b* \leq 15$

If accepted, this would bring pale grey and cream colours within the scope. Darker colours will be dealt with separately, since new issues are raised relating to durability and thermal movement. Proposals for woodgrain finishes are in hand in BSI committee B538/1/1.

REFERENCES

1. ISO 4892: 1981 $\equiv$ BS 2782: Part 5: Method 540B: 1982 Methods of exposure to laboratory light sources.

2. BS 7413: 1991 Specification for white PVC-U extruded hollow profiles with heat welded corner joints for plastics windows: materials type A.

3. BS 7008:- Acquisition and presentation of comparable data for basic properties of plastics.

4. BS 2782: Part 5: Method 540C: 1988 Determination of ultraviolet light intensity using polysulphone film.

5. ISO 105 $\equiv$ BS 1006: 1990: Colour fastness of textiles and leather: Part A03: Grey scale for assessing staining, and Part A04: Method for the instrumental assessment of the degree of staining of adjacent fabrics.

6. BS 4203: Extruded rigid PVC corrugated sheeting: Part 1: 1980. Specification for performance requirements.

7. ASTM G53-88 Standard Practice for Operating Light- and Water-Exposure Apparatus (Fluorescent UV-Condensation Type) for Exposure of Nonmetallic Materials.

8. ISO 7724/1/2/3 $\equiv$ BS 3900: Parts D8, D9, D10: 1986. Paints: Determination of colour and colour difference: principles: measurement: calculation.

9. ISO 4582 $\equiv$ BS 2782: Part 5: Method 552A: 1981 Determination of changes in colour and variations in properties after exposure to daylight under glass, natural weathering, or artificial light.

10. BS 6923: 1988 Method for calculation of small colour differences.

THE CONDUCT AND ASSESSMENT OF ARTIFICIAL WEATHERING PROCEDURES FOR PLASTICS
GLAZING MATERIALS USED EXTERNALLY

by S M Halliwell BSc and D Gardiner BSc, PhD.

SUMMARY

Transparent or translucent plastics glazing materials have been widely used in
external building applications. Examples of unacceptable durability have,
however, been seen in practise, particularly when high operating temperatures in
sunlight occur. Hence the need for reliable artificial weathering tests to
assess proposed combinations of plastics glazing materials in a reasonably short·
time. The procedures described in this paper take account of the revision
currently proposed in ISO/TC61 for ISO 4892 : Plastics - Methods of Exposure to
Laboratory Light Sources including Part 2 : Xenon Arc and Part 3 : Fluorescent
Lamps.·

Test procedures are assessed for their degradative effects on commercial glazing
materials of polyvinylchloride, acrylic and polycarbonate, including examples of
surface coated sheet. At this stage, procedures based on xenon arc sources
appear to be most generally applicable. The full solar wavelength range is
needed to promote the effects observed in practice.

THE CONDUCT AND ASSESSMENT OF ARTIFICIAL WEATHERING PROCEDURES FOR PLASTICS GLAZING MATERIALS USED EXTERNALLY

S M HALLIWELL AND D GARDINER
Building Research Establishment, Watford, England

Abstract
Transparent or translucent plastics glazing materials offer a useful combination of light weight, toughness, ease of forming to complex shapes and excellent light transmission. Hence their widespread use for example as rooflights. However the plastics used are more susceptible than is glass to the combined effects of degradation by weathering, notably ultraviolet light, heat and moisture.

Examples of unacceptable durability have been seen in practice, particularly when high operating temperatures in sunlight occur. Hence the need for reliable artificial weathering tests to assess proposed combinations of plastics glazing materials in a reasonably short time. The procedures described in this paper take account of the revisions currently proposed in ISO/TC61 for ISO 4892 : Plastics – Methods of Exposure to Laboratory Light Sources including Part 2 : Xenon arc sources and Part 3 : Fluorescent Lamps.

In conducting these tests particular consideration is given to the control and effects of sample temperature. Test procedures are assessed for their degradative effects on commercial glazing materials of polyvinylchloride, acrylic and polycarbonate, including examples of surface coated sheets. At this stage, procedures based on xenon arc sources appear to be most generally applicable. The full solar wavelength range is needed to promote the effects observed in practice. The method of mounting strongly influences the temperature of transparent test pieces and thus the test results.
Keywords: Xenon, Fluorescent, Plastics, Poly(methylmethacrylate), Poly(vinylchloride), Polycarbonate, Weathering

1 Introduction

Certain plastics are attractive materials for use in glazing applications because of their light weight, ease of handling and installation, high light transmission and, in some cases, better shatter resistance than glass. Greater freedom of design is another advantage that plastics have over glass. Loss of surface quality can be caused by scratching during service or by surface deterioration caused by exposure to the environment. The effects of weathering consist of a complex set of processes in which the combined action of

ultraviolet light and oxygen are predominant. Deterioration of most plastics materials starts at the outer surface and may take the form of discoloration, pitting, erosion and microcracking. Mechanical properties, such as tensile strength and impact resistance, of many plastics deteriorate when subjected to prolonged outdoor exposure.

Polymethylmethacrylate (PMMA) is claimed to be one of the most weather resistant polymers and there are many instances of its successful use in building applications, particularly as a replacement for glass. The advantages of PMMA are its outstanding light transmission, good impact resistance and its excellent weatherability and durability. However, because of their flammability, fire resistance is always a major factor when considering the use of acrylics in buildings.

Polyvinylchloride (PVC) is probably the most adaptable of the synthetic polymers and more than any other polymer it has benefitted from the use of additives such as processing aids, plasticisers, stabilisers, comonomers and fillers. PVC can thus be compounded at reasonable cost over a range of applications, despite its inherent instability to sunlight.

Polycarbonate began to replace glass and acrylic in vandalised areas, e.g. subways, during the 1960's. The 1980's saw a growth in its use, a main reason for this being conservational factors since its fire performance is relatively good. However, limited resistance to chemicals and UV light is a disadvantage for use of polycarbonates; satisfactory weathering resistance is usually only achieved by surface coating to enhance UV stability.

The effects of weather on such materials are of considerable technical and commercial importance, and this has lead to the need for methods of assessing the durability of a polymer and of finished products. Natural exposure trials are often used but these require a long duration and in a constantly developing market manufacturers and customers need durability results in as short a time as possible. Hence the use of accelerated devices using artificial light sources. It is particularly important that such tests should identify materials or products not suitable for permanent outdoor use whilst not unfairly distorting the comparative performance of disparate types.

2 Artificial Weathering Procedures

Historically, several distinct types of light source have been developed for artificial weathering purposes and applied in product performance requirements. The main types are included in the 1981 version of ISO 4892. This international standard is now being revised and will take the following form so as to distinguish more clearly between the different approaches:-

   ISO 4892 : Methods of exposure to laboratory light sources.

   Part 1: General Guidance
   Part 2: Xenon Arc Sources
   Part 3: Fluorescent UV Lamps
   Part 4: Open Flame Carbon Arc Lamps

At the same time, substantial efforts have been made to reduce the number of optional variations and the intrinsic variability of the recommended procedures. The aim is to provide basic methods which will be more reproducible from time to time and between laboratories and so usable with greater confidence as the basis of product performance specifications and for product development. The main aspects dealt with are:-

- radiation spectral distribution, intensity and exposure duration;
- control of temperature through use of black standard thermometers;
- simplification of recommended values for operating temperatures, relative humidities, water-spray cycles and the like.

Two preferred radiation distributions are now defined for xenon arc light sources, Method A to simulate direct sunlight and Method B to simulate daylight through windowglass with much reduced "UV-B" levels. A radiation intensity in the wavelength range 290-800 nm of 550 ± 50 Wm^{-2} is suggested, though other levels may be used. To control the total radiation dose and allow for such variations, it is proposed to express the exposure in terms of total irradiance, integrated over the wavelength range 290-800 nm for example, in the sample plane. Test piece temperature is dependant, amongst other things, on the intensity of radiation and the light absorption characteristics of the test piece. Control is by means of a black standard thermometer, which is intended to replace the variety of black panel thermometers available previously. A black standard temperature of $65 \pm 3°C$ is being proposed for normal purposes and may be controlled by means of cabinet air temperature. A water spray cycle of 102 minutes OFF/18 minutes ON is preferred. This gives time for samples to dry off and for a well defined maximum operating temperature for test pieces to be established. Preferred relative humidities in the dry period are $50 \pm 5\%$ or $65 \pm 5\%$ for normal test purposes.

Fluorescent lamps are brought within the formal structure as Part 3 of the revised standard. This is intended to accommodate both American (ASTM G53) and German (DIN 53384) practice. Considering the former UV-Condensation type, the preferred lamp type is the "UV-A" with peak emission at 340 nm, though of course the more aggressive "UV-B" type with peak emission at 313 nm may also be used. The preferred test cycle for normal purposes is proposed to be:-

- 4 hours UV exposure at 60°C, followed by
- 4 hours condensation at 50°C.

Other cycles may be used, but a certain minimum excess of condensation temperature over room temperature is essential if efficient condensation is to result on plastics test pieces which may have rather low thermal conductivity.

A major purpose of the work reported here was to investigate the application of the principles and

recommendations of the revised version of ISO 4892 on glazing materials. It is intended to apply this experience to defining performance requirements for plastics glazing product standards.

3 Experimental

3.1 Artificial weathering equipment

Xenon arc exposures were conducted in a Xenotest 1200 U using borosilicate filters to provide a light distribution as close as available to ISO 4892 : Part 1 : Method A and with a light intensity in the wavelength range 290-800 nm of approximately 800 Wm^{-2} in the sample plane. Cabinet air was controlled at 28 $\pm$ 1°C, 65% $\pm$ 5% RH using a recirculatory cooling unit which provided a maximum black standard temperature of 65°C in the dry period. The water spray cycle was 18 minutes ON:102 minutes OFF. Sample size was 200 x 65 mm mounted so as to face the lamps continuously and both with no backing at all ("open-backed") and with a black backing allowing a 3 mm air gap ventilated top and bottom ("black-backed"). The former method provided a test piece surface temperature of appropriately 30°C, whilst the latter was in the range 55 $\pm$ 5°C at maximum, with highest temperatures developed towards the centre of each test piece.

Ultraviolet-condensation cycle exposures were conducted using a Q-UV apparatus with 2 types of fluorescent lamp on either side separated by a divider:-

- "UV-A" lamps with maximum emission at 340 nm; and
- "UV-B" lamps with maximum emission at 313 nm.

The effects of a lower and a higher temperature test cycle were also compared, namely:-

- 4 hours UV exposure at 50°C; 4 hours condensation at 45°C; and
- 4 hours UV exposure at 60°C; 4 hours condensation at 50°C.

The latter is proposed as being preferred in ISO 4892 : Part 3: fluorescent lamps. Sample size was 265 x 75 mm, mounted so as to fully occupy the normal aluminium sample holders.

3.2 Methods of assessment

3.2.1 Surface temperature

Surface temperatures of test pieces were measured using a non-contact infrared thermometer. Readings were taken towards the end of a dry period by removing test pieces from the Xenotest 1200 and taking readings as quickly as possible. In general different test polymer surfaces gave similar readings.

3.2.2 Measurement of colour changes

Colour differences produced by weathering were measured using a Macbeth 1010S colorimeter with diffuse illumination and viewing 8° to the normal, using CIE Standard Illuminant C, simulating north daylight. Results are expressed in terms of

CIE 1976 L^* a^* b^* units. The transparent test pieces were assessed in reflectance mode by backing with a white ceramic tile so that light passed twice through the material. The colour differences between exposed and unexposed materials were determined in each case.

3.2.3 Measurement of changes in gloss

Changes in specular reflectance (gloss) produced by weathering were determined using an instrument with 60° geometry complying with BS 3900 : Part D5 : 1986. It is necessary to use an instrument capable of reading up to 200 gloss units since there is reflectance from both upper and lower surfaces of transparent test pieces. Results are expressed as a percentage of the gloss of the unweathered materials.

3.2.4 Test materials

The results presented here are for a range of plastics glazing materials representative of current practice in the UK and intended to illustrate the range of performance which may be encountered in practice. All were untinted and 3 mm thick.

Material 1:	Cast acrylic sheet with no UV-absorber;
Material 2:	Exterior grade pressed polyvinylchloride (PVC) sheet;
Material 3:	Interior grade pressed PVC sheet with impact modifier;
Material 4:	Exterior grade pressed PVC sheet with UV absorbing surface coating;
Material 5:	Extruded plain polycarbonate sheet;
Material 6:	Extruded polycarbonate with a UV-absorbing surface coating.

4 Results and discussion

The observed changes in gloss are summarised in Table 1 for the six test materials. The initial 60° gloss measurements were high because specular reflection from both upper (weathered) and lower surfaces were detected. If the transparent materials darken in colour during weathering this will reduce the intensity of the light from the lower face of the test piece and so may register as a small loss of gloss. Where substantial losses of gloss are recorded this is due to erosion of the upper, weathered surface.

The corresponding observed changes in colour are recorded in Tables 2 and 3. The principle changes in colour in all cases was in yellowness; thus a positive value of Δb^* in Table 2 denotes an increase in yellowness. The total colour differences, in Table 3, are affected mainly by yellowing (Δb^*) and darkening (- ve ΔL^*). Changes in colour of these transparent materials were measured using a reflectance technique with a white tile as backing. This method is very sensitive for comparative purposes, but exaggerates the absorption that would be experienced by light passing once through the material. It is expected that substantial loss of gloss in the weathered surface would affect the measured colour change to some extent, although the optical arrangement

of the colorimeter should minimise such effects.

Transparent samples exposed to a xenon arc lamp will transmit much of the incident energy causing any backing to heat up, which in turn may heat the test piece. For the Xenotest 1200, transparent samples in the "open backed" mode show surface temperature of ca 30°C, little above cabinet air. Introduction of a black backing with limited air circulation between raises the maximum temperature of the outer test piece surface to 50-60°C, much closer to the maximum black standard temperature of 65°C. The effects of the more severe operating conditions on optical properties depends strongly on polymer type. The unstabilised PVC-U sheet (3) is most adversely affected by the higher temperature whereas uncoated polycarbonate (5) is apparently little affected, showing very similar loss of gloss and small colour changes under these two conditions. The very stable acrylic sheet (1) shows only slight signs of differentiation after 10,000 lamp hours. The stabilised (2) and surface-coated PVC (4) and polycarbonate (6) sheets are all seen to perform well even under forcing, higher temperature conditions.

In the case of the UV-Condensation (Q-UV) apparatus there is limited potential for radiation heating. Most samples will absorb all the incident radiation and surface temperatures are close to air temperature which is either 50°C or 60°C in the 2 test cycles used here. Comparison of results at these two temperatures again show a strong dependency on polymer type. The uncoated PVC sheets (2,3) are strongly affected, even by the UV-A lamp. It is considered that the very rapid loss of gloss and discolouration shown by the stabilised sheet (2) is unrepresentative of the practical performance of the product which one might be lead to conclude is only marginally better than the interior grade product (3) in its durability. The precise reasons for this are not clear, but the following differences between xenon and fluorescent lamp exposures may contribute:-

- Prolonged high temperature of exposure in the Q-UV;
- Presence of short wavelength ultraviolet light in output from UV-B lamps;
- Absence of longer wavelengths from the fluorescent lamps which may have a bleaching action on the yellow chromophores produced;
- Differences in leaching of hydrogen chloride by water spray as compared to condensation cycles. Hydrogen chloride is a biproduct of PVC degradation on which it has an autocatalytic effect.

The polycarbonate sheet (5) also develops more and earlier discolouration in the Q-UV than in the Xenotest 1200, the effect being most marked with the UV-B lamps and little affected by increased temperature. Curiously, however, loss of gloss appears to be reduced in the Q-UV with more loss of gloss under the UV-B lamp at the lower of the two test temperatures. Again, the reasons for this apparently anomalous behaviour are not clear and are the subject of further investigation. As with PVC-U, the behaviour in the Xenotest 1200 seems to accord more closely with performance

Table 1. Comparison of changes in 60° gloss as percentage of initial values

Device	Xenotest 1200		Q-UV (UV/Condensation cycle)			
Type	Xenon arc		UV-A lamps		UV-B lamps	
Exposure (hours)	Open-backed	Black-backed	50°/45° cycle	60/50° cycle	50°/45° cycle	60/50° cycle
1:- Pressed acrylic sheet						
250	99.7	99.3	98.9	97.9	97.7	97.9
500	99.0	99.3	98.2	97.5	97.5	95.5
1,000	99.8	99.7	97.3	97.2	97.1	95.8
1,500	99.9	99.7	97.8	95.4	97.4	95.0
2,000	99.1	99.5	98.0		97.7	
10,000	89.8	66.0				
2:- Pressed polyvinyl chloride sheet: external grade						
250	99.9	97.4	102.7	98.1	100.6	96.1
500	100.1	95.2	102.4	97.2	85.9	58.1
1,000	100.9	98.6	98.5	33.6	5.2	9.7
1,500	100.8	98.6	72.2	5.8	4.2	9.0
2,000	100.8	94.4	27.9		4.1	
4,000	101.0					
8,000	77.0					
3:- Pressed polyvinyl chloride sheet: interior grade						
250	91.1	85.9	94.0	87.5	81.9	78.8
500	85.2	83.6	89.8	80.1	39.7	32.1
1,000	80.9	34.8	75.8	8.0	3.7	12.1
1,500			19.6	2.1	2.4	5.3
2,000			4.7		1.9	
4:- Extruded polyvinyl chloride sheet: surface coated						
250	95.2	98.3	98.9		97.5	
500	97.3	96.9	98.4		94.0	
1,000	94.5	92.3	95.5		91.2	
1,500	88.9	92.0	94.9		89.4	
2,000	90.5	91.9	93.6		91.8	
4,000	84.6					
5:- Polycarbonate sheet without surface coating						
250	98.6	100.9	96.0	97.2	91.8	95.2
500	96.0	93.6	96.2	93.8	81.8	91.9
1,000	51.7	39.3	84.6	80.1	46.2	83.4
1,500	32.0	37.9	76.7	74.2	33.6	76.8
2,000			65.1	20.7		
6:- Polycarbonate sheet with surface coating						
250	98.7	100.1	97.9	97.7	101.6	
500	97.3	99.6	96.8	94.1	97.0	
1,000	94.2	97.3	97.0	80.9	86.6	
1,500	92.1	105.6	93.6	67.6	48.0	
2,000	90.6	104.4	86.4	52.8		
4,000	59.7	77.2				

Table 2. Comparison of changes in yellowness (Δb*)

Device	Xenotest 1200		Q-UV (UV/Condensation cycle)			
Type	Xenon arc		UV-A lamps		UV-B lamps	
Exposure (hours)	Open-backed	Black-backed	50°/45° cycle	60/50° cycle	50°/45° cycle	60/50° cycle
1:- Pressed acrylic sheet						
250	0.2	0.5	1.5	2.9	4.5	5.4
500	0.2	0.5	3.5	4.4	5.7	6.2
1,000	0.3	1.4	4.9	4.6	6.0	6.4
1,500	0.7	1.5	4.8	4.9	5.9	7.4
2,000	0.9	1.5	3.3		4.7	
10,000	1.5	3.4				
2:- Pressed polyvinyl chloride sheet: external grade						
250	-1.0	-2.0	-0.9	0.2	1.5	2.9
500	-1.1	-2.0	-0.4	2.5	7.1	14.5
1,000	-1.2	-1.9	1.9	14.9	13.7	18.1
1,500	-1.1	-1.8	5.1	21.6	12.3	20.7
2,000	-1.2	-1.3	7.4		12.5	
4,000	0.7					
8,000	3.0					
3:- Pressed polyvinyl chloride sheet: interior grade						
250	6.7	14.4	12.1	18.9	25.7	31.8
500	10.4	20.6	15.5	27.2	32.0	36.1
1,000	12.4	33.3	21.5	36.3	35.0	35.2
1,500			27.7	34.5	38.0	31.9
2,000			33.7		39.0	
4:- Extruded polyvinyl chloride sheet: surface coated						
250	0.3	0.4	0.5		0.6	
500	0.4	0.8	0.8		0.9	
1,000	1.0	2.1	1.5		1.5	
1,500	2.0	3.0	2.3		2.0	
2,000	2.2	4.0	3.1		2.6	
4,000	4.6					
5:- Polycarbonate sheet without surface coating						
250	1.9	2.5	2.8	2.6	11.6	11.9
500	4.1	5.8	6.1	8.8	12.4	13.0
1,000	6.5	8.6	11.3	13.8	13.7	14.4
1,500	8.2	8.3	12.2	14.4	17.0	14.6
2,000			12.6		17.0	
6:- Polycarbonate sheet with surface coating						
250	-0.3	-0.2	0.3		0.6	0.4
500	-0.1	-0.1	0.7		2.7	1.5
1,000	0.0	0.4	1.0		2.4	3.2
1,500	0.3	1.9	2.8		3.1	4.0
2,000	1.1	2.0	2.9		6.8	
4,000	2.5	7.6				

Table 3. Comparison of total colour difference (ΔE*)

Device	Xenotest 1200		Q-UV (UV/Condensation cycle)			
Type	Xenon arc		UV-A lamps		UV-B lamps	
Exposure (hours)	Open-backed	Black-backed	50°/45° cycle	60/50° cycle	50°/45° cycle	60/50° cycle
1:- Pressed acrylic sheet						
250	0.2	0.6	1.6	3.1	4.8	5.8
500	0.3	0.6	3.8	4.8	6.1	6.7
1,000	0.4	1.4	5.1	4.9	6.3	6.8
1,500	0.9	1.6	5.1	5.3	6.3	7.9
2,000	1.0	1.6	3.5	5.0		
10,000	1.6	4.8				
2:- Pressed polyvinyl chloride sheet: external grade						
250	1.1	2.5	1.2	0.9	1.8	3.4
500	1.3	2.6	0.9	2.9	7.7	17.4
1,000	1.3	2.6	2.3	18.7	21.2	23.1
1,500	1.2	2.4	5.8	29.3	18.9	27.3
2,000	1.3	1.8	11.6		19.2	
4,000	0.9					
8,000	3.2					
3:- Pressed polyvinyl chloride sheet: interior grade						
250	7.9	15.3	12.4	19.7	27.1	34.7
500	12.2	22.0	16.0	28.9	35.8	44.6
1,000	13.9	44.4	22.6	47.5	43.0	51.3
1,500			32.8	50.5	50.2	53.3
2,000			40.6		51.6	
4:- Extruded polyvinyl chloride sheet: surface coated						
250	0.7	0.8	0.5		0.6	
500	0.7	1.1	0.8		1.0	
1,000	1.4	2.3	1.5		1.5	
1,500	2.3	3.3	2.4		2.1	
2,000	2.5	4.3	3.2		2.8	
4,000	5.0					
5 :- Polycarbonate sheet without surface coating						
250	2.0	2.7	3.0	2.8	12.2	12.5
500	4.3	6.2	6.4	9.2	13.0	13.6
1,000	8.4	10.6	11.8	14.5	14.4	15.0
1,500	10.3	9.7	12.8	15.1	17.8	15.2
2,000			13.5		18.0	
6:- Polycarbonate sheet with surface coating						
250	0.3	0.3	0.7		0.9	0.7
500	0.2	0.3	1.1		2.9	1.8
1,000	0.4	0.7	1.3		2.8	3.5
1,500	0.5	2.1	3.2		3.6	5.3
2,000	1.3	2.2	3.1		7.4	
4,000	2.8	8.2				

observed in practice.

As regards the pressed acrylic sheet this, like the polycarbonate, shows somewhat more yellowing in the Q-UV and especially under the UV-B lamp than in the Xenotest 1200. Gloss retention has so far been good throughout. The coated PVC sheet is indicated to have good colour and gloss retention in all three weathering devices. However the behaviour of the surface coated (6), as compared to the uncoated (5) polycarbonate appears to be anomalous in the QUV, especially with the UV-B lamp at the higher temperature.

5 Conclusions

The work described in this paper is still in progress and it is planned to produce a more complete picture in due course. At this stage it is considered that artificial weathering using suitably filtered xenon arc lamps offers the most suitable approach to comparative weathering tests which involve direct comparison of a wide range of polymer types. This includes the situation where the relative performance of coatings of dissimilar polymers applied to a given base polymer are to be compared.

In testing transparent materials in xenon arc weathering devices it is particularly important to specify and control the method of mounting since this strongly influences the temperature of the test pieces. Those methods reported here, "open-backed" and "black-backed" represent the extremes of temperature which can result from such variations. PVC is affected much more than polycarbonate by weathering at higher temperatures.

The use of fluorescent lamps remains attractive because of lower operational costs, but may tend to distort the relative performance of dissimilar polymers, making interpretation of results more difficult. The preferred test cycle given in the revision of ISO 4892 : Part 3; namely; UV exposure to UV-A lamps (340 nm peak emission) for 4 hours at 60°C/condensation for 4 hours at 50°C appeared excessively aggressive towards an established grade of UV-stabilised PVC. This approach nevertheless has considerable value for the comparative testing of similar compounds, e.g. for development work, and for repeat testing for quality control purposes where the main purpose is to demonstrate consistency of production. A significant measure of acceleration could well be advantageous for the latter purpose.

6 References

CIE Publication No 85 : 1989; Technical Report - Solar
    Spectral Irradiance.
ISO 2813 = BS 3900:Part D5:1980; Measurement of Specular
    Gloss of Non-metallic Paint Films.
ISO 4892:1981 = BS 2872:Part 5:Method 540B:1982; Plastics:
    Methods of exposure to Laboratory Light Sources.
ISO 7724/-1/-2/-3 = BS 3900:Parts D8, D9, D10:1986;
    Paints: Determination of Colour and Colour Difference:
    Principles; Measurement; Calculation.

Artificial weathering procedures for plastics glazing materials

S. M. Halliwell* and D. Gardiner

Building Research Establishment, Garston, Watford WD2 7JR, UK

Transparent or translucent plastics glazing materials are of light weight, tough, easily formed into complex shapes and transmit light well. This useful combination of properties allows widespread use in construction, for example as rooflights. However, the plastics used are more susceptible to degradation by weathering than the traditionally used glass, notably the combined effects of ultraviolet light, heat and moisture. Complete inhibition of degradation is not possible but the general world trend to an increase in the use of plastics in external applications has led to the development of many new products which improve stability and increase component service life. However, examples of unacceptable durability have been seen in practice, particularly when high operating temperatures in sunlight occur. Hence the need for reliable artificial weathering tests to assess proposed combinations of plastics glazing materials in a reasonably short time. The procedures described in this paper take account of the revisions currently proposed in ISO/TC61 for ISO 4892: Plastics – Methods of Exposure to Laboratory Light Sources, including Part 2: Xenon Arc Sources and Part 3: Fluorescent UV Lamps. In conducting these tests particular consideration is given to the control and effects of sample temperature. Test procedures are assessed for their degradative effects on commercial glazing materials of polyvinylchloride, acrylic and polycarbonate, including examples of surface-coated and thermoformed sheets. Procedures based on xenon arc sources appear to be most generally applicable because the full solar wavelength range is needed to promote the effects observed in practice. The method of mounting strongly influences the temperature of transparent test pieces and thus the test results, enabling the temperature sensitivity of materials and products to be investigated.

Keywords: *artificial weathering; plastics glazing materials; test procedures*

Certain plastics are attractive materials for use in glazing applications because of their light weight, ease of handling and installation, extensive light transmission and, in some cases, better shatter resistance than glass. Greater freedom of design is another advantage that plastics have over glass. Loss of surface quality can be due to scratching during service or by surface deterioration caused by exposure to the outdoor environment. The effects of weathering consist of a complex set of processes in which the combined action of ultraviolet light and oxygen are predominant. Deterioration of most plastics materials starts at the outer surface and may take the form of discoloration, pitting, erosion and microcracking. Mechanical properties, such as tensile strength and impact resistance, of many plastics deteriorate when subjected to prolonged outdoor exposure.

Polymers currently used on a large scale may be divided into three groups depending on their resistance to photodegradation:

1 highly photostable polymers that are commonly used without photostabilizer added, e.g. acrylics;
2 moderately photostable polymers that can be used without photostabilizer, e.g. polycarbonates;

3 poorly photostable polymers which require extensive stabilization for outdoor uses, e.g. polyvinylchloride.

Poly(methylmethacrylate) (PMMA) is claimed to be one of the most weather-resistant polymers. However, because of their flammability, fire resistance is always a major factor when considering the use of acrylics in buildings. Polycarbonate began to replace glass and acrylic in vandalized areas, e.g. subways, during the 1960s. The 1980s saw a growth in its use, but limited resistance to chemicals and UV light is a disadvantage for its use. Polyvinylchloride (PVC) is probably the most adaptable of the synthetic polymers and more than any other polymer has benefited from the use of additives such as processing aids, plasticizers, comonomers and fillers. PVC can thus be compounded at reasonable cost over a range of applications.

The effects of weather on such materials are of considerable technical and commercial importance, and this has led to the need for methods of assessing the durability of a polymer and of finished products. Natural exposure trials are often used but these require a long duration and in a constantly developing market manufacturers and customers need durability results in as short a time as possible. Hence the use of accelerated devices using artificial light sources. Such devices incorporate as many of the outdoor weather factors

*Correspondence to Mrs S. M. Halliwell

as possible but allow these factors to be controlled more uniformly so that standard test conditions can be set up. Artificial test methods are used for three main reasons:

1 To accelerate but reproduce the effects of exposure to weather, in particular exposure to natural daylight. The effects of this are followed throughout exposure.
2 For quality control purposes to check variations between different batches of material.
3 To evaluate a product using prescribed procedures.

It is particularly important that such tests should identify materials or products not suitable for permanent outdoor use whilst not unfairly distorting the comparative performance of disparate types.

Modern artificial weathering procedures in principle allow consistency of conditions but it is essential to identify and control the relevant variables. This is the objective of the revised standard ISO 4892: Methods of Exposure to Laboratory Light Sources. It is intended that this should correspond with methods being prepared for paints and rubbers.

Applications to rooflights pose the particular challenge of defining an artificial weathering procedure which can fairly be applied to a wide range of materials, e.g. PVC, acrylic and polycarbonate. The effects of surface coatings and of vacuum forming need to be taken into account. Standards development in CEN/TC128 is moving towards European Standards for light-transmitting plastics rooflights materials. Temperature control of samples is critical, especially for PVC; significant failures have occurred in practice with PVC rooflights mounted in ways which tend to raise operational temperatures, e.g. double-glazed units[1] and shapes which trap heated air but lack ventilation. There is a need to be able to simulate such effects in artificial weathering procedures.

Artificial weathering procedures

Historically, several distinct types of light source have been developed for artificial weathering purposes and applied in product performance requirements. The main types are included in the 1981 version of ISO 4892[2]. This international standard has been revised in ISO/TC61 to distinguish more clearly between the different approaches. The revision excludes enclosed carbon arc light sources and brings fluorescent lamp devices within the formal scope. The standard has a four-part structure:

ISO 4892: Methods of Exposure to Laboratory Light Sources
  Part 1: General Guidance
  Part 2: Xenon Arc Sources
  Part 3: Fluorescent UV Lamps
  Part 4: Open Flame Carbon Arc Lamps

Substantial efforts have been made to reduce the number of optional variations and the intrinsic variability of the recommended procedures. The aim is to provide basic methods which will be more reproducible from time to time and between laboratories and so usable with greater confidence as the basis of product performance specifications and for product development. The main aspects dealt with are:

● radiation spectral distribution, intensity and exposure duration;
● control of temperature through use of black standard thermometers;
● simplification of recommended values for operating conditions.

Two radiation distributions are now defined for xenon arc light sources; Method A to simulate direct sunlight, and Method B to simulate daylight through window glass with much reduced UV-B levels[3]. A radiation intensity in the wavelength range 300–800 nm of 550 ± 50 W m^{-2} is suggested, though other levels may be used. To control the total radiation dose and allow for such variations, it is proposed to express the exposure in terms of total irradiance, integrated over the wavelength range (e.g. 300–800 nm) to a defined total dose (e.g. X GJ m^{-2}) in the sample plane. This requires an adequate knowledge of radiation incident on the samples and its variations with time, strictly speaking through continuous measurement. The use of blue wool scales is dropped, certainly for Method A, and account is taken of more recent instrument design permitting the use of one of two methods of controlling the UV irradiance[4]. The more common, known as narrow-band control, maintains a constant irradiance level at a specific wavelength, typically 340 nm, throughout the life of the lamp. The other, broad-band control, keeps the integral of irradiance, 340 to 400 nm, constant.

Test piece temperature is dependent, amongst other things, on the intensity of radiation and the light absorption characteristics of the test piece. Measurement is by means of a black standard thermometer, which is intended to replace the variety of black panel temperatures available previously. This will be better related to surface temperatures reached by plastics components and will provide a more consistent means of controlling the temperature of the weathering device. A white standard thermometer is also specified and may be more relevant to white or transparent test pieces. A black standard temperature of 65 ± 3 °C is proposed for normal purposes, being influenced by radiation intensity, and controlled by cabinet air temperature and rate of circulation.

Historically, a range of water spray cycles has been used. The revised version of ISO 4892 attempts to simplify this to a single preferred choice of 18 min on/102 min off. This cycle was selected because it gives time for samples to dry off and for well-defined maximum operating temperatures for test pieces to be established. Clearly other cycles may continue to be used for particular purposes. Relative humidities in the

dry period are to be 50 ± 5% or 65 ± 5% for normal test purposes.

In anticipation of publication of the revision of ISO 4892, the new technical principles are being incorporated in the draft European Standards for plastics materials. The proposed EN for white PVC-U window profiles includes an artificial weathering procedure using xenon arc, as above. The target irradiances over the bandpass 290–800 nm, i.e. UV and visible radiation, are 8 and 12 GJ m^{-2}. These values are considered to correspond approximately to 5 years exposure in northern and southern Europe respectively. The proposed EN for transparent plastics sheets[5] also recommends artificial weathering by xenon arc using filtering to keep the spectral distribution as close as possible to that detailed in ISO 4892: Part 2.

Temperature control is critical, especially for PVC. The surface temperature reached by transparent test pieces in particular is strongly influenced by the method of mounting. Samples mounted open at the back will achieve much lower temperatures than if backed by radiation-absorbing materials with poor ventilation. This can be used to influence test piece temperature. It is noted that significant failures have occurred in practice with PVC rooflights mounted in ways which tend to raise operational temperatures, e.g. tinted lights, shapes which trap heated air but lack ventilation, double-glazed units and the like[1]. There is a need to be able to simulate such effects in artificial weathering procedures.

Fluorescent lamps are brought within the formal structures of ISO 4892 as Part 3 of the revised standard. This is intended to accommodate both American (ASTM G53) and German (DIN 53384) practice. The former in the form of the UV-condensation cycle devices is the more widely used, but the latter offers more precise control over exposure conditions, with direct water spray being used. The test cycle of 4 hours UV exposure at 60 °C, followed by 4 hours of condensation at 50 °C, following American practice, is recommended, using UV-A lamps with peak output at 340 nm. However, this may be an excessive temperature for PVC products. Fluorescent lamps will not produce the range of temperature differentiation with sample colour characteristic of sunlight or xenon arc lamps. Plastics materials may also give uneven condensation behaviour in some conditions because of the low thermal conduction. More work is needed before we can suggest recommended procedures with confidence.

A major purpose of the work reported here was to investigate the application of the principles and recommendation of the revised version of ISO 4892 on glazing materials. It is intended to apply this experience to defining performance requirements for plastics glazing product standards.

Experimental

Artificial weathering equipment

Xenon arc exposures were conducted in a Xenotest 1200 U using borosilicate filters to provide a light distri-bution as close as possible to ISO 4892: Part 2: Method A and with a light intensity in the wavelength range 290–800 nm of approximately 800 W m^{-2} in the sample plane. Cabinet air was controlled at 28 ± 1 °C, 65 ± 5% RH using a recirculatory cooling unit, which provided a maximum black standard temperature of 65 °C in the dry period. The water spray cycle was 18 minutes on/102 minutes off. The sample size was 200 × 65 mm mounted so as to face the lamps continuously and both with no backing at all (open backed) and with a black backing allowing a 3 mm air gap ventilated top and bottom (black backed). The former method provided a test piece surface temperature of approximately 30 °C, whilst the latter was in the range 55 ± 5 °C, with the highest temperatures developed towards the centre of each test piece. Samples were exposed for a minimum of 1500–2000 lamp hours (4.4–5.8 GJ m^{-2}) with exposure periods extended if necessary.

Ultraviolet-condensation cycle exposures were conducted using a Q-UV apparatus with two types of fluorescent lamp, one type either side separated by a divider: UV-A lamps with maximum emission at 340 nm; and UV-B lamps with maximum emission at 313 nm. The effects of test cycles at two different temperatures were also compared, namely 4 hours UV exposure at 45 °C/4 hours condensation at 50 °C; and 4 hours UV exposure at 60 °C/4 hours condensation at 50 °C. The latter is proposed as being preferred in ISO 4892: Part 3: Fluorescent UV Lamps. The sample size was 265 × 75 mm, mounted so as to occupy fully the normal aluminium sample holders. Samples were exposed for up to 2000 lamp hours.

Methods of assessment

Surface temperature. Surface temperatures of test pieces were measured using a non-contact infrared thermometer. Readings were taken towards the end of a dry period by removing test pieces from the Xenotest 1200 and taking readings as quickly as possible. In general different test polymer surfaces gave similar readings.

Measurement of colour changes. At present there is no International Standard method for the instrumented measurement of colour of plastics as such. It is suggested that the method for paints be used using the CIELAB procedure[6] based on the CIE 1976 L^*, a^*, b^* colour space. However, this is not without problems and is being revised in ISO/TC35. It is hoped to adopt the same procedure for plastics in due course. Colour differences produced by weathering were measured using a Macbeth 1010S colorimeter with diffuse illumination and viewing 8° to the normal, using CIE Standard Illuminant C, simulating north daylight. For comparative purposes and in the absence of transmission measurement facilities the transparent test pieces were assessed in reflectance mode by backing with a white tile so that light passed twice through the material. The colour differences between exposed and unexposed materials were determined in each case.

At the present time proposals are being studied in ISO TC61/SC5 to develop methods for the measure-

ment of light transmission and haze of transparent plastics and also of specular reflectance. Such methods are needed to feed into the much needed revision of ISO 4582 which deals with the assessment of changes produced by weathering[7].

Measurement of changes in gloss. Changes in specular reflectance (gloss) produced by weathering were determined using an instrument with 60° geometry complying with ISO 3813[8]. It is necessary to use an instrument capable of reading up to 200 gloss units since there is reflectance from both the upper and lower surfaces of transparent test pieces. Results are expressed as a percentage of the gloss of the unweathered materials.

Test materials. The results presented here are for a range of plastics glazing materials representative of current practice in the UK and intended to illustrate the range of performance which may be encountered in practice. All were untinted and 3 mm thick.

PMMA-1 Cast acrylic sheet, no UV absorber
PVC-1 Pressed PVC sheet, exterior grade, bulk stabilized
PVC-2 Extruded PVC sheet, interior grade, impact modified

PVC-3 Extruded PVC sheet, acrylic surface coating
PVC-4 Extruded PVC sheet, acrylic surface coating, thermoformed
PC-1 Extruded PC sheet, indoor glazing grade
PC-2 Extruded PC sheet, exterior grade, bulk stabilized
PC-3 Extruded PC sheet, acrylic surface coating
PC-4 Extruded PC sheet, acrylic surface coating, thermoformed

Results

Results for PMMA-1, PVC-1–3 and PC1–3 are given in *Tables 1–3*. The filter used for the Xenotest 1200 is borosilicate, UV-A lamps have peak emission at 340 nm and UV-B lamps at 313 nm. Results for PVC-4 and PC-4 are given in *Table 4*. Exposure is actual lamp exposure in hours; this is quoted rather than irradiance levels to give an indication of the time required for each test. For the samples exposed in the Xenotest 1200, the light intensity in the 300–800 nm bandpass is about 800 W m^{-2} on average, corresponding to an irradiance of approximately 2.9 GJ per 1000 hours exposure. However, corresponding figures for the fluorescent lamp

Table 1 Comparison of changes in 60° gloss as a percentage of initial values

Device		Xenotest 1200		Q-UV (UV-condensation cycle)			
Type		Xenon arc		UV-A lamps		UV-B lamps	
Sample	Exposure (h)	Open-back	Black-back	45°/50°	60°/50°	45°/50°	60°/50°
PMMA-1	500	99.0	99.3	98.3	97.5	97.5	95.5
	1000	99.8	99.7	97.3	97.2	97.1	95.8
	1500	99.9	99.7	97.8	96.2	97.4	95.2
	2000	99.1	99.5	98.0	96.0	97.7	95.0
	10 000	89.8	66.0				
PVC-1	500	100.1	95.2	102.4	97.2	85.9	58.1
	1000	100.9	98.6	98.5	33.6	5.2	9.7
	1500	100.8	98.6	72.2	5.8	4.2	9.0
	2000	100.8	94.4	27.9	3.3	4.1	7.5
	8000	77.0	(3250 74.8)				
PVC-2	500	94.4	83.6	89.9	80.1	39.7	32.1
	1000	91.3	34.8	75.8	8.0	3.7	12.2
	1500	87.1	2.2	19.6	2.1	2.4	5.3
	2000	84.5	–	4.7	2.3	1.9	6.0
PVC-3	500	97.3	87.6	98.4		94.0	
	1000	94.5	84.3	95.5		91.2	
	1500	88.9	(1250 55.7)	94.9		89.4	
	2000	91.2		93.6		91.8	
	3750	84.6					
PC-1	500	100.5	77.9	97.4	92.3	95.3	91.4
	1000	97.2	56.9	86.3	80.9	84.1	84.8
	1500	84.0	23.0	80.0	77.8	58.3	75.7
	2000	74.9	26.7	70.8	74.4	38.7	70.1
	3750	17.8					
PC-2	500	98.8	95.6	96.2	93.8	81.8	91.9
	1000	96.9	8.7	84.6	80.1	46.2	86.1
	1500	88.9	3.1	76.7	74.7	33.6	76.8
	2000	86.0	3.9	65.1	70.4	20.7	72.6
	3750	16.8	4.5				
PC-3	500	97.3	100.8	96.8		94.1	97.0
	1000	94.2	98.5	97.0		80.9	86.6
	1500	92.1	106.9	93.6		67.6	48.0
	2000	90.6	105.6	86.4		52.8	
	4000	59.7	77.2				

Table 2 Comparison of changes in yellowness (Δb^*)

Device		Xenotest 1200		Q-UV (UV-condensation cycle)			
Type		Xenon arc		UV-A lamps		UV-B lamps	
Sample	Exposure (h)	Open-back	Black-back	45°/50°	60°/50°	45°/50°	60°/50°
PMMA-1	500	0.2	0.5	3.5	4.4	5.7	6.2
	1000	0.3	1.4	4.9	4.6	6.0	6.4
	1500	0.7	1.5	4.8	4.9	5.9	6.9
	2000	0.9	1.5	3.3	3.6	4.7	6.2
	10 000	1.5	3.4				
PVC-1	500	−1.1	−2.0	−0.4	2.5	7.1	14.5
	1000	−1.2	−1.9	1.9	14.9	13.7	18.1
	1500	−1.1	−1.8	5.1	19.2	12.3	19.7
	2000	−1.2	−1.3	7.4	22.5	12.5	20.5
	8000	3.0	(3250 4.9)				
PVC-2	500	7.1	20.6	15.5	27.2	32.0	36.1
	1000	8.5	33.3	21.5	36.3	35.0	35.2
	1500	8.5·	34.1	27.7	34.4	38.0	30.9
	2000	11.9		33.7	35.5	39.0	29.8
PVC-3	500	0.4	6.5	0.8		0.9	
	1000	1.0	7.1	1.5		1.5	
	1500	2.0	(1250 2.3)	2.3		2.0	
	2000	2.1		3.1		2.6	
	3750	4.6					
PC-1	500	1.6	4.2	4.7	6.7	8.4	10.9
	1000	5.7	5.2	8.9	10.6	11.0	11.7
	1500	9.5	7.7	9.6	11.0	10.6	11.8
	2000	9.0	7.8	10.6	11.3	11.0	11.9
	3750	18.2					
PC-2	500	5.7	5.9	6.1	8.8	12.4	13.0
	1000	7.8	17.4	11.3	13.8	13.7	14.4
	1500	10.2	17.0	12.2	14.4	17.0	14.6
	2000	10.9	14.4	12.6	15.2	17.0	14.9
	3000	11.3	11.4				
PC-3	500	−0.1	−0.1	0.7		2.7	1.5
	1000	0.0	0.4	1.0		2.4	3.2
	1500	0.3	1.9	2.8		3.1	4.0
	2000	1.1	2.0	2.9		6.8	
	4000	2.5	7.6				

exposures are not easily defined because of the very different spectral distributions.

In order to assess the validity of each test it is useful to rank the materials according to their exposure behaviour. Colour change and changes in gloss are used to evaluate the procedures. The materials are ranked in order of decreasing durability, 1 being the most durable material (*Tables 4* and *5*).

Discussion

Optical measurements

The initial 60° gloss measurements were high because specular reflection from both upper (weathered) and lower surfaces was detected; changes from the initial values are shown in *Table 1*. If the transparent materials darken in colour during weathering this will reduce the intensity of the light from the lower face of the test piece and so may register as a small loss of gloss. Where substantial losses of gloss are recorded this is due to erosion of the upper, weathered face.

Comparison of *Tables 2* and *3* shows that the principal contributor to changes in total colour (ΔE^*) was generally in yellowness; thus a positive value of Δb^* in

Table 2 denotes an increase in yellowness. The negative Δb^* for PVC-1 exposed to xenon arc radiation is due to long-wavelength UV bleaching of the yellow-coloured species produced during processing. Changes in colour of these transparent materials were measured using a reflectance technique with a white tile as backing. This method is very sensitive for comparative purposes, but exaggerates the absorption that would be experienced by light passing once through the material. It is expected that substantial loss of gloss in the weathered surface would affect the measured colour change to some extent, although the optical arrangement of the colorimeter should minimize such effects. The colorimeter utilizes diffuse illumination and viewing at 8° to normal. In this case inclusion of diffuse reflection reduces the sensitivity of the colour difference measured to changes in gloss; see ISO 7724[6].

Temperature effects

Transparent samples exposed to a xenon arc lamp will transmit much of the incident energy, causing any backing to heat up, which in turn may heat the test piece. In the Xenotest 1200, transparent samples in the open-backed mode achieve surface temperatures of

Table 3 Comparison of total colour difference (ΔE^*)

Device		Xenotest 1200		Q-UV (UV-condensation cycle)			
Type		Xenon arc		UV-A lamps		UV-B lamps	
Sample	Exposure (h)	Open-back	Black-back	45°/50°	60°/50°	45°/50°	60°/50°
PMMA-1	500	0.3	0.6	3.8	4.8	6.1	6.7
	1000	0.4	1.4	5.1	4.9	6.3	6.8
	1500	0.9	1.6	5.1	4.9	6.3	7.5
	2000	1.0	1.6	3.5	4.1	5.0	6.9
	10 000	1.6	4.8				
PVC-1	500	1.3	2.6	0.9	2.9	7.7	17.4
	1000	1.3	2.6	2.3	18.7	21.2	23.1
	1500	1.2	2.4	5.8	16.5	18.9	25.6
	2000	1.3	1.8	11.6	31.1	19.2	27.8
	8000	3.2	(3250 5.7)				
PVC-2	500	8.4	22.0	16.0	28.9	35.8	44.6
	1000	9.7	44.4	22.6	47.5	43.0	49.3
	1500	10.1	45.3	32.8	51.8	50.2	53.0
	2000	13.8		40.6	51.9	51.6	54.7
PVC-3	500	0.7	7.6	0.8		1.0	
	1000	1.4	8.5	1.5		1.5	
	1500	2.3	(1250 64.1)	2.4		2.1	
	2000	2.4		3.2		2.8	
	3750	5.0					
PC-1	500	1.7	4.6	4.9	7.1	8.8	11.5
	1000	6.0	5.7	9.3	11.2	11.5	12.3
	1500	10.2	9.6	10.2	11.7	11.1	12.5
	2000	9.8	9.2	11.4	12.2	11.6	12.7
	3750	20.9					
PC-2	500	2.9	6.2	6.4	9.2	13.0	13.6
	1000	8.3	22.1	11.8	14.5	14.4	15.0
	1500	10.8	21.6	12.8	15.1	17.8	15.2
	2000	11.7	18.7	13.5	16.2	18.0	15.7
	3000	14.1	14.5				
PC-3	500	0.2	0.3	1.1		2.9	1.8
	1000	0.4	0.7	1.3		2.8	3.5
	1500	0.5	2.1	3.2		3.6	5.3
	2000	1.3	2.2	3.1		7.4	
	4000	2.8	8.2				

about 30 °C, little above cabinet air. Introduction of a black backing with limited air circulation raises the temperature of the outer test piece surface to 50–60 °C, much closer to the maximum black standard temperature of 65 °C. Sample surface temperatures were estimated using a non-contact infrared thermometer. It was necessary to remove mounted test pieces on their sample holders from the weathering chamber to make the measurements because the thermometer could be affected by stray radiation from the lamps. Temperatures were measured within 5 seconds thus minimizing underestimation due to cooling.

In the case of the UV condensation (Q-UV apparatus) there is limited potential for radiation heating since the radiant intensity is much lower. Most samples will absorb all the incident radiation, and their surface temperatures are close to air temperature which is either 45 °C or 60 °C in the two test cycles used here. A common condensation temperature of 50 °C was used for both cycles.

Comparative effects of the artificial weathering regimes

Pressed acrylic sheet (PMMA-1). This material contains no added UV absorber but at 3 mm thickness exhibits measurable absorption towards the shorter UV end of the solar spectrum. It has a long history of use in the UK and normally shows good gloss and colour retention in practice. The performance in the xenon arc device is in line with this expectation, there being only slight loss of gloss and yellowing even at the higher temperature of test.

Whilst the fluorescent lamp exposures also indicate good gloss retention, an appreciable level of yellowing was observed. This was most evident with the UV-B lamps and at the higher exposure temperature.

PVC sheets (PVC-1–3). PVC-1 is a pressed PVC-U sheet, thought to contain efficient stabilizers. Again it has a long history of use in the UK and was expected to perform well under test, at least at operating temperatures below about 45 °C. As with PMMA-1, it showed good colour and gloss retention even at the higher surface temperature in the xenon arc device. However, it proved very prone to loss of gloss and yellowing on exposure to the fluorescent lamps. These effects were much more noticeable at 60° than 45° in the UV cycle and with the UV-B lamps.

PVC-2 was an interior grade and, as might be expected, showed significant and rapid discoloration

under all six test conditions. In this case the higher-temperature xenon arc condition caused early discoloration and loss of gloss. There is a history in the UK of similar early failures, within 4 to 6 years, of inadequately stabilized PVC-U rooflights which are constructed so as to promote high operating temperatures in sunlight[9]. This effect is highly dependent on aspect to the sun. It is important that a test cycle be available which will give early warning of susceptibility to high operating temperatures. The effects of exposure to UV lamps are similar to that of PVC-1. It seems that none of the fluorescent lamp cycles used adequately differentiates between these two materials.

By contrast, PVC-3 performed well except under the higher-temperature xenon arc condition, when it blackened rapidly between 1000 and 1250 hours. This extruded product possessed a surface coating with a UV absorber. The results suggest that this is effective at protecting the underlying polymer from yellowing at low temperatures and in the Q-UV where little long-wavelength radiation is present. Being a relatively new product its long-term practical performance is not yet established. However, there is a risk that the relative performance of this product, compared with PVC-1, may not be as good as indicated by the fluorescent lamp test.

Polycarbonate sheets (PC-1-3). According to the respective manufacturers' literature, PC-1 is an indoor glazing grade, whilst PC-2 is a bulk stabilized grade suitable for external use. Their relative performance on exposure to the xenon arc cycles was not consistent with this, especially at the higher operating temperature. Thus PC-2 showed greater and more rapid loss of gloss and discoloration than PC-1, particularly when mounted over black backing. The reasons for this are not clear and would bear further examination. Exposure to UV-A lamps caused comparable yellowing of the two with limited loss of gloss, even at the higher UV exposure temperature. Exposure to UV-B lamps caused similar

results to UV-A except that, curiously, there was more rapid loss of gloss at the lower UV exposure temperature (45 °C). We have no convincing explanation for this anomaly at this stage.

The surface-coated grade, PC-3, contained a protective UV absorber and showed improved resistance to yellowing under all the conditions tested and substantially improved gloss retention under the higher-temperature xenon arc test, compared with the uncoated versions tested. As with the surface-coated PVC-3, the fluorescent lamps caused only small changes in colour and gloss at the durations tested.

Intercomparison of polymer types and test cycles
Tables 4 and *5* show the relative rankings for gloss and colour retention for the seven materials tested based on performance up to 2000 hours in the six test regimes. It is important that, in trying to define a test procedure capable of application to the wide variety of polymer types and surfaces used for glazing purposes, no disproportionate bias should be introduced for or against any particular type. At the same time, it will be helpful to be able to investigate the effects of design variables, such as surface temperature, which are likely to be encountered in practice.

Considering the two xenon arc cycles first, these were designed to simulate two extremes of operating conditions: firstly, that of free ventilation in which sample temperature is close to external air temperature; and secondly, that in which the surface temperature of the material is raised by virtue of hot air trapped behind. The latter condition can be encountered in practice in structures such as poorly ventilated barrel vault roofs, for example. Comparison of the yellowing induced by the xenon arc exposure, *Table 5*, shows the same ranking order for both low-temperature (open-backed) and higher-temperature (black-backed) exposure modes. However, the extreme discoloration of PVC-2

Table 4 Materials ranked by loss of gloss

| Rank | Xenon arc | | UV-A | | UV-B | |
	Open-back	Black-back	45°/50°	60°/50°	45°/50°	60°/50°
1	PVC-1	PC-3	PMMA-1	PMMA-1	PMMA-1	PMMA-1
2	PMMA-1	PMMA-1	PVC-3	PC-1	PVC-3	PC-2
3	PVC-3	PVC-1	PC-3	PC-2	PC-3	PC-1
4	PC-3	PVC-3	PC-1	PVC-1	PC-1	PC-3
5	PC-2	PC-1	PC-2	PVC-2	PC-2	PVC-1
6	PVC-2	PC-2	PVC-1		PVC-1	PVC-2
7	PC-1	PVC-2	PVC-2		PVC-2	

Table 5 Materials ranked by Δb^* value

| Rank | Xenon arc | | UV-A | | UV-B | |
	Open-back	Black-back	45°/50°	60°/50°	45°/50°	60°/50°
1	PVC-1	PVC-1	PC-3	PMMA-1	PVC-3	PC-3
2	PMMA-1	PMMA-1	PVC-3	PC-1	PMMA-1	PMMA-1
3	PC-3	PC-3	PMMA-1	PC-2	PC-3	PC-1
4	PVC-3	PVC-3	PVC-1	PVC-1	PC-1	PC-2
5	PC-1	PC-1	PC-1	PVC-2	PVC-1	PVC-1
6	PC-2	PC-2	PC-2		PC-2	PVC-2
7	PVC-2	PVC-2	PVC-2		PVC-2	

Table 6 Comparison of virgin and thermoformed material exposed in Xenotest 1200

Mounting		Open-back			Black-back		
Sample	Exposure (h)	% gloss	Δb^*	ΔE^*	% gloss	Δb^*	ΔE^*
PVC-4	500	101.2	−0.8	1.1	101.8	−0.9	1.0
virgin	1000	96.5	−0.7	1.0	98.9	−0.5	0.7
sheet	1500	91.2	−0.7	0.9	95.8	2.0	2.5
	2000	94.1	−0.6	0.9	97.3	1.3	1.4
	2250				65.4	12.2	51.6
	4500	93.1	−0.1	0.7			
PVC-4	500	100.6	−0.8	1.0	101.1	−0.9	0.9
thermo-	1000	98.8	−0.9	1.0	98.5	−0.4	0.7
formed	1500	97.3	−0.8	1.0	91.8	1.6	2.3
	2000	96.5	−0.8	0.9	92.2	1.1	2.1
	2250				73.2	18.7	40.2
	4500	74.7	0.9	2.3			
PC-4	500				99.4	0.2	0.5
virgin	1000				97.3	1.2	1.4
sheet	1500				100.4	1.5	1.8
	2000				98.3	1.7	2.2
	7000				32.3	10.4	11.8
PC-4	500				99.5	−0.2	0.5
thermo-	1000				92.2	1.4	1.7
formed	1500				94.5	1.7	2.0
	2000				89.8	1.7	2.0
	7000				64.9	4.1	4.6

and PVC-3 under the higher-temperature xenon arc condition does not necessarily register as yellowing. Much the same order is seen for gloss retention, bearing in mind that the better samples show little change in gloss. However, the use of the higher test temperature significantly affects the gloss retention of PVC-2 and PC-2 relative to PC-1. Account of this needs to be taken in defining xenon arc exposure conditions for transparent materials of this kind. By comparison, the main effects on ranking order of using fluorescent lamps is by down-rating the performance of the exterior grade PVC-1 and upgrading both PVC-3 and PC-2. These effects are most noticeable with the UV-B lamp and at 60 °C. However, even with the UV-A lamp at 45 °C PVC-1 rates poorly on gloss retention. A UV exposure temperature of 45 °C is about as low as can consistently be maintained using Q-UV equipment in a normal laboratory. This temperature may be more appropriate than 60 °C for the present purpose. In general the use of UV-A lamps, which is the preferred option in ISO 4892: Part 3, as revised, and especially at the lower operating temperature, comes closest to giving the same ranking order as seen with xenon arc equipment but tends to be more severe on PVC relative to polycarbonate. The tendency of PMMA-1 to yellowing may also be exaggerated.

Effects of thermoforming

Plastics glazing materials are frequently thermoformed into pyramids, domes and the like from flat sheet. This process may be deleterious to durability to weathering because of the reheating involved. In addition, not all forms of surface coating will withstand the biaxial stretching involved in thermoforming without some loss of protective function. As can be seen from *Table 6*, material PVC-4, both virgin and thermoformed, had changed little after 2000 hours exposure to the xenon arc lamps in the black-backed mode, but then darkened

very rapidly by 2250 hours. The protective coating seems to be more effective than for PVC-3. In all cases, the apparent loss of gloss is mainly associated with loss of specular reflection from the unexposed face caused by darkening. This effect was not seen in the lower-temperature, open-backed mode after twice the exposure time, but some genuine loss of gloss was detectable with the thermoformed material in the open-backed mode. It was evident that the material had withstood thermoforming without undue ill-effects for its durability. In either condition it would need to be used with caution in situations likely to be associated with high operating temperatures in sunlight. The coated polycarbonate, by contrast, withstood prolonged exposure to the high-temperature condition quite well. Interestingly, the thermoformed test piece appeared the more stable in this case.

It is considered that these findings tend to confirm the need to specify carefully the method of mounting transparent samples exposed to broad-band light sources, such as xenon arc lamps. Furthermore, utilizing different methods of mounting opens up the possibility of simulating different circumstances of use in practice, whilst employing constant operating conditions in other respects.

One potential source of variation between models of artificial weathering devices of the xenon arc type is that, in order to operate at a given black standard temperature, 65 ± 3 °C, it may be necessary to operate at significantly different cabinet air temperatures. In the present context this could mean that transparent samples mounted in the black-backed mode might have reasonably comparable maximum surface temperatures. However, the same samples mounted in the open-backed mode might vary considerably in their surface temperatures, being largely governed by cabinet air temperature in this case.

Conclusions

It is considered that artificial weathering using suitably filtered xenon arc lamps, as defined in Method A of ISO 4892: Part 2, offers the most suitable approach to comparative weathering tests which involve direct comparison of a wide range of polymer types. This includes the situation where the relative performance of coatings of dissimilar polymers to a given base polymer are to be compared.

In testing transparent materials in xenon arc weathering devices it is important to specify the method of mounting since this strongly influences the temperature of the test pieces. The methods reported here, open back and black back, simulate the extremes of temperatures which can result from such variations. The light transmission of PVC can be affected much more than polycarbonate by weathering at higher temperatures. This accords with observations on rooflights in practice in the UK[9].

One point requiring further consideration is that different xenon arc weathering devices operating at the same black standard temperature may need to be set at significantly different cabinet air temperatures. It follows that the surface temperatures reached by transparent materials in the open-backed mode are likely to vary correspondingly. This would need to be the subject of further investigation more broadly based than was possible in the work reported here.

The preferred options cited in ISO 4892: Part 3: Fluorescent UV Lamps are the use of UV-A (340 nm) lamps and a test cycle of 4 hours UV exposure at 60 °C and then 4 hours condensation at 50 °C. The present work suggests that the use of UV-A lamps should lead to fewer apparently anomalous results for glazing materials than UV-B lamps. The latter tended to exaggerate the yellowing of polycarbonates in particular, in a way not seen in UK climates[10]. In addition, we conclude that it is reasonable to use a lower UV exposure temperature than 60 °C, 45 °C having been used in this case. In general, this lower temperature did not exaggerate yellowing so much and also, with the UV-A lamp, gave a less distorted impression of the relative performance of well-proven PVC glazing. None of the fluorescent lamp conditions tested reproduce the type of behaviour seen with PVC-2 and PVC-3 in the black-backed mounted xenon arc mode. This type of behaviour, typically involving rapid and severe discoloration following a more or less prolonged period of little change, has been seen in practice in the UK, where PVC-U rooflights are widely used, and is associated with high surface temperatures of the glazing units, usually rooflights, in sunlight[9]. Considerable care is needed in interpreting the results of fluorescent lamp exposures, especially when a range of polymer types is being compared.

References

1 Anon. *Building* 1975, 28 February, 53
2 ISO 4892: 1981 = BS 2782: Part 5: Method 540B: 1982: Plastics: Methods of Exposure to Laboratory Light Sources
3 CIE Publication No. 85. Technical Report – Solar Spectral Irradiance, 1989
4 Scott, K.P. *1st Int. Symp. on Weatherability, Materials Life Society, Japan, May 1992*
5 prEN 1013: Light Transmitting Profiled Plastics Sheets for Single Skin Roofing. General Requirements and Methods of Testing
6 ISO 7724/1/2/3 = BS 3900: Parts D8, D9, D10: 1986. Paints: Determination of Colour and Colour Differences: Principles: Measurement: Calculation
7 ISO 4582 = BS 2782: Part 5: Method 552A: 1981: Determination of Changes in Colour and Variations in Properties after Exposure to Daylight under Glass, Natural Weathering, or Artificial Light
8 ISO 2813 = BS 3900: Part D5: 1980: Measurement of Specular Gloss of Non-metallic Paint Films at 20°, 60° and 85°
9 Decker, C. and Balandier, M. *Environ. Polym. J.* 1982, 18, 1085
10 Brown, H. *Archit. J.* 1991, November