EFFECTS OF BLENDING AND SUBSEQUENT PROCESSING ON MORPHOLOGY OF PVC POWDER PARTICLES

by

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A Doctoral Thesis submitted in partial
fulfilment of the requirements
for the award of

Doctor of Philosophy of the
Loughborough University of Technology

March 1979

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ACKNOWLEDGEMENTS

I wish to thank Mr. D. A. Hemsley for his guidance, help and invaluable suggestions throughout this research project.

I am grateful to the Federal Government of Nigeria for the bursary and to Institute of Management and Technology, Enugu, Nigeria, for the study leave which enabled me to complete this research.

Finally my sincere thanks to my wife and children for their patience, understanding, encouragement and prayerful support during my absence from home in course of this work.

I acknowledge that the ion-etching and the scanning transmission electron microscopy (STEM) including X-ray analysis were carried out on my behalf by Institut für Kunststoffverabeitung, Aachen, West Germany and by JEOL respectively.

I hereby state that neither this thesis nor the work contained herein has been submitted to this or any other institution for a degree.

Emesi Katchy

SUMMARY

Changes in powder morphology and additive distribution of mass and suspension PVC blends have been investigated. The techniques used to characterise and assess the processing behaviour of the powder blends have included microscopy, density, particle size analysis, torque and capillary rheometry.

It was found that PVC particles are largely unchanged in character by blending. Only small changes in particle shape, size and surface texture were observed. However, significant changes of bulk density were observed. The particulate structure of PVC remained intact and there were no pronounced differences in the processability of blends discharged at different temperatures. These results suggest that shear is necessary if changes are to be made to PVC powder structure. It was also found that solid additives unlike liquid additives, are not absorbed into the resin particles but coat the surfaces.

The powder blends were then processed by compression moulding and properties such as tensile behaviour, fracture surface morphology, microstructure and refractive index were examined.

The tensile behaviour was found to be determined by the microstructure of the moulding. At low moulding temperatures the particulate structure of PVC was largely retained and the moulding failed in a brittle manner. But as the particulate structure was obliterated at higher moulding temperatures, ductile behaviour occurred, with necking rupture or cold-drawing. Similar breaking or yield stress could be obtained from both polymers provided appropriate moulding temperatures were employed. The appearance of the fracture surfaces and yield or breaking stress were in substantial agreement irrespective of polymer type.

Refractive index was found to decrease with increasing moulding temperature, suggesting crystallinity was being destroyed.

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CHAPTER 1

INTRODUCTION

1.1 Aim of Research Project

This work forms part of a large programme designed to study the relationships between PVC powder morphology, processing conditions, structure and properties of mouldings.

PVC powder Morphology $\longleftrightarrow$ Processing Conditions $\longleftrightarrow$ Structure $\longleftrightarrow$ Properties

The use of direct powder processing has now become so wide-spread that the granule stage is virtually eliminated. The usual method is that the PVC powder and additives are mixed in a high speed mixer. After the mix has reached a certain temperature it is then discharged into a cooler where it is cooled to temperatures at which it can be handled.

This study is divided into two parts. The first part is concerned with dry blending and the changes that take place in the morphology of the PVC powder particles as a result of the blending. For clearly, if there is a gross modification of the PVC morphology as a consequence of blending, then subsequent processing will yield products of varied properties.

More simple systems have been chosen in order to fully understand the behaviour in terms of any changes to both the surface and internal structure of the PVC powder itself and the location, dispersion and distribution of individual additives.

Mass and suspension polymerised PVC were used. Apart from the fact that these two constitute the majority of PVC consumption, it would enable us to find out if morphological changes are dependent on polymer type.

It is also aimed to establish relevant criteria for the characterisation of the blends produced. Therefore factors like particle size and size distribution, particle shape, nature of particle surface, bulk density and ease of processing were investigated.

The second part of the research project involves the subsequent processing of the blends. The microstructure and mechanical properties of the mouldings were to be studied with a view to contributing to the correlation of structure, processing conditions and properties.

The processing method to be employed was compression moulding. Since compression moulding involves minimal shear, 1-10 sec^{-1}, it would afford us the opportunity to observe the early stages of any structure modification thus separating the contribution of shear and temperature to structural changes.

The mechanical properties of the mouldings to be investigated were tensile properties and the associated fracture surface morphology. Fracture surface studies would throw light on the mechanisms taking place during fracture.

Finally the refractive index of the mouldings was to be studied. For processed material, refractive index can provide significant information on the variables involved in the processing.

The primary techniques involved in these investigations would be optical and electron microscopy.

1.2 Background

Several studies, mostly on crystalline or semicrystalline polymers have been made on the effect of processing conditions on the properties and morphology of polymers[1-6]These studies indicate a correlation between processing conditions, properties and morphology. It seems possible therefore, that if we can control the morphology by choosing the right processing variables we can then produce mouldings of specific or desired properties. Alternatively, if we know the morphology we can predict the properties and design products accordingly.

Polyvinyl chloride, PVC, was first reported a little over hundred years ago. Today, it is the most widely used thermoplastic material. Total world consumption in 1977 was about 14 million tonnes. In the United Kingdom alone consumption was about 0.5 million tonnes.

The rapid growth in PVC is due mainly to its versatility and low-material price. Rigid PVC can be extruded into pipe, conduit, sheet or profiles, while plasticised (flexible) PVC finds use in cable-insulation, laminations, floor coverings, films and foils. Indeed, the use of PVC is legion. Almost every facet of our daily lives from packaging to building construction or transport, involves one application of PVC or another.

PVC powder processing is fast outstripping the use of pellets or granules. Moritz[7] estimates that 95% of all pipes, 85% of blow mouldings, 95% of injection mouldings and 75% of Venitian blinds made from PVC are processed directly from powder blends. Many reasons are given for the upsurge of powder processing but the main one is economics[7-14]. In the first instance PVC is produced as a powder. Therefore any process that involves the use of the material in the powder form obviously means savings in material and compounding costs. The number of processing stages involved between the polymer and finished product

is reduced.

As the PVC is heated only once the thermal treatment is reduced. Less stabiliser and lubricant are therefore needed thereby improving properties like impact resistance, weathering and light resistance of the products.

Granules or pellets may not always be produced to the same degree of gelation. Thus overgelled granules will be difficult to melt thereby yielding products of different quality.

1.3 Manufacture of PVC

PVC is manufactured by three main polymerisation methods, namely Mass (or Bulk), Suspension and Emulsion. A fourth method, Solution polymerisation is used to produce limited amounts of speciality polymers. The breakdown by process of PVC production is given in Table 1.

TABLE 1[15]

Year	Nameplate capacity (thousand tonnes)			
	Suspension	Emulsion	Mass	Total
1960	1430	360	12	1800
1965	2900	660	140	3700
1970	6200	1160	340	7700
1975	9800	1700	1000	12500

In emulsion polymerisation the vinyl chloride monomer is dispersed by agitation in water containing an emulsifying agent or soap and a water soluble catalyst (initiator). The PVC resin is formed as discrete spherical particles protected by the emulsifying agent. Since water is the medium there are no expensive solvent recovery problems. However, a serious drawback is contamination by emulsifiers and catalysts. These additives used in the polymerisation process are retained in the polymer after drying and can affect electrical properties, initial colour, clarity and the lubrication and stabilisation of the final formulation. Emulsion polymers therefore, are not usually used where crystal clarity and excellent initial colour are demanded.

Mass polymerisation generally requires simpler equipments and the yield is 75-85% and pure as it is free from emulsifiers, suspension agents, solvents, buffers and surface active agents. The reaction is strongly

exothermic and therefore batch temperature control can be a problem. Because one-stage mass polymerisation of PVC yielded low apparent density material with a large particle size distribution, the two-stage process developed by Pechiney-Saint-Gobain has become popular. A description of the two-stage process is given by Chatelain[16], and Thomas[17].

In the two-stage process two phases are involved. First there is a liquid phase in which the seed polymer particles are formed in a vertical prepolymeriser reactor. The degree of conversion is limited to 10% and there are no temperature control problems. The second phase is a solid powdery phase. The seed particles are transfered to a horizontal reactor specially designed to stir powdery material and where reaction proceeds to a high degree of conversion. No drying step is required as there is no water or solvent in the reaction mass.

Suspension polymerisation is by far the most common method of manufacturing PVC. Here the monomer is suspended as liquid droplets in an aqueous medium by means of a suspending agent. Because suspending agents have large effect on type of particles produced their nature is jealously guarded in industry.

Conventional suspending agents like PVA or gelatine yield regular polymer particles with relatively rough or smooth surface, [illegible] Secondary suspending agents like ethylene oxide condensation products with polyols, used together with the conventional or primary ones, give porous, irregular polymer particles.

Suspension polymerisation is initiated by monomer-soluble catalyst, Lauroylperoxide being [illegible] widely used. Each monomer droplet is the precursor of one particle of the end-product. These droplets have a natural tendency to coalesce. This is prevented by stirring and the

use of a colloid dissolved in the aqueous phase. In fact the nature and amount of colloid, type of agitation and temperature employed affect the size and appearance of the resin.

A low colloid content and moderate agitation yields spherical and fairly large, 100 - 200 μm, resins. Each resin particle has a 'skin' or membrane ∿ 100 Å thick over the surface. Tregan[18] has called this type of PVC particles 'Unicellular' particle powders as they consist of a single cell.

In contrast, higher colloid content and rapid agitation result in particles of several cells - 'Multicellular' particles. If they have a small number of large cells, they are multimacrocellular and multimicrocellular if they have a large number of small cells.

Bologna[19] has made a fairly full description of industrial suspension polymerisation.

1.4 Morphology and Particulate Structure of PVC

Emulsion PVC particles are generally fine, dusty and spherical. The bulk density is low and the particles break easily.

Mass PVC particles have a narrower size distribution and show a regularity in shape and porosity. Suspension PVC particles are irregularly shaped and their overall porosity shows a greater degree of variation between and within the particles. This can easily be illustrated by adding some DOP to PVC particles. When viewed by transmitted light under the microscope it is observed that the mass PVC particles lighten more evenly as they absorb the DOP. But the suspension particles absorb the DOP much more slowly overall, and have a greater variation of light and dark portions.

Transmission electron microscopy examination of ultrathin sections of mass and suspension polymerised particles shows they have analogous morphology. For example, similar particulate and inter-granular spaces are seen. However, a basic difference between the two is the presence of 'skin' or membrane over the surface of the suspension type particles. While the edge of the ultrathin section of mass PVC is free from all surface barriers that of suspension has a colloidal membrane. Fig. 1 shows the 'skin' on suspension PVC.

Tregan and Bonnemayre[18] report that from a closer examination of the skin it appears to consist of two films of comparable thickness - an outer film based on the colloid and an inner film based on PVC.

In general, suspension PVC is cheaper and has better powder flow characteristics than emulsion PVC. Mass PVC gives better clarity and has faster plasticiser absorption than suspension PVC because of the absence of 'skin', emulsifying agents, etc. Emulsion PVC is extremely easy to soften and flux when processed in rigid or plasticised formulations. This makes it preferable in processes demanding rapid fluxing.

Fig. 1: Transmission electron micrograph of ultrathin section of Suspension PVC particle showing 'skin'.

Magnification: x13,000

An excellent description of different types of PVC grains can be found in reference 18 (see Fig. 2).

Bort et al[20] were the first to report the particulate character of PVC. Since then several papers[21-36] have appeared on the particulate nature of PVC.

Berens and Folt[22] studied the melt flow of uncompounded suspension and emulsion polymerised PVC in a capillary rheometer. They subjected PVC resins to various heat and shear treatment and observed marked differences in their melt flow properties. These differences still occurred even where the molecular weight and molecular weight distribution, intrinsic viscosity and chemical constitution of the polymer are unchanged. They therefore postulated that at low processing temperatures PVC particles were involved in melt flow by slipping past one another while at higher temperatures molecular deformation and particle merging occurred. To prove this they carried out an electron microscopy examination of PVC fracture surfaces and found that particle identity was retained or obliterated depending on the degree of thermo-mechanical treatment the PVC has received.

On a closer electron microscopy examination of a microtomed section of suspension polymerised PVC,Berens and Folt[24] found the resin has an open aggregate of roughly round particles 0.5 - 1.5 μm in size. They called these primary particles and are the melt flow units. Vidyaikina et al[21] investigated the effect of shear and temperature on PVC resin by electron microscopy using the technique of fracture surface replication. They concluded that the original macroglobular structure of PVC resin is first broken down during processing to reveal what they called 'microglobular' structures 0.1 μm size. On further processing these microglobules disappear leaving stretched 'cape-like' formations. Under certain conditions, for example increased milling in one direction,

Fig. 2: Different types of PVC grains as described by Tregan and Bonnemayre[18].

THE DIFFERENT TYPES OF PVC PARTICLES

Microstructure and transparence of particles immersed to equilibrium in DOP

CELLULAR PARTICLES (SUSPENSION)

Unicellular

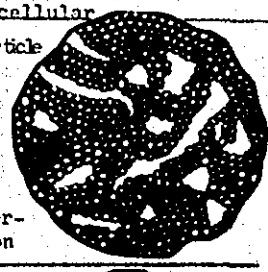
Closed pore opaque particle

Two media with very different indices

air ▭

solid ■

Pronounced light dispersion



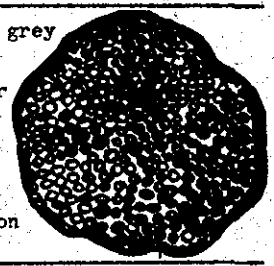
Open pore semi-opaque grey particle

Two media with similar liquid index

liquid ▭

solid ■

Slight light dispersion

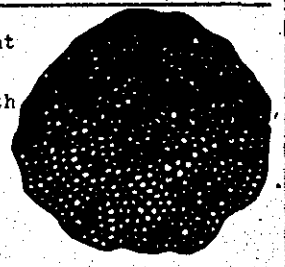


Non-porous transparent particle

Spherical diopter with homogeneous index (compact granules)

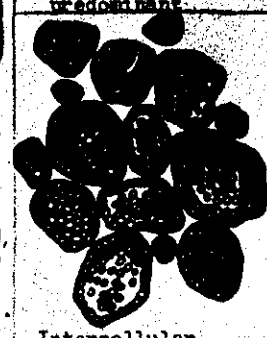
solid ■

No light dispersion



Multicellular

Intracellular porosity predominant

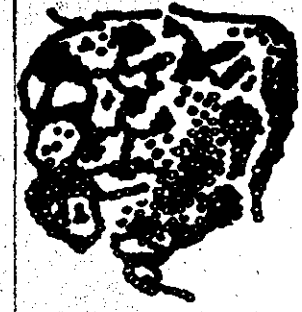


Intercellular porosity predominant

Paracellular

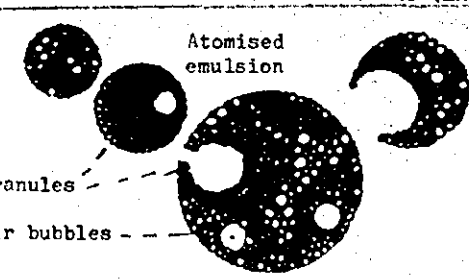
Discontinuous pericellular membrane

Pericellular membrane not detectable

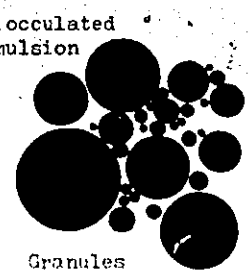


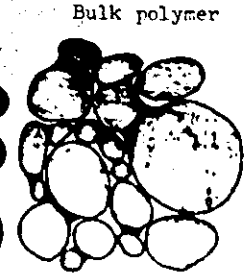
NON-CELLULAR PARTICLES (EMULSION-BULK)

Spherical



Undefined





anisotropic fibrillar structures 0.01 μm thick are ultimately seen. Incorporation of additives did not affect these structural changes though their appearances may be finer. Geil[30] states that additives, especially plasticisers tend to exude to the surface and obstruct any structure which was present.

Gezovich and Geil[28] working on the morphology of both rigid and plasticised PVC used cold-stage and ion-etching techniques of electron microscopy sample preparation. In the former method, the samples were fractured in vacuo on a liquid nitrogen cold stage, while in the latter case they were etched with argon ions. Each was followed up immediately with C-Pt shadowing and replicated in the usual manner.

They found PVC contains aggregates on three sizes: 0.1 - 0.5 μm, 1 - 10 μm and 100 - 200 Å nodules As the resin particles they used were ∿ 100 μm in size and porous, the 0.1 - 0.5 μm and 1 - 10 μm particles are, they presumed sub-structures in PVC.

Other co-workers of Geil[33] using other commercial type suspension and mass polymerised PVC carried out similar studies and showed PVC to contain particles of three different sizes: 100 - 200 Å, 0.1 - 0.5μm and 1 μm and larger. Further, they tried to correlate the relationship between processing, morphology and property of PVC.

Hattori et al[31] using the technique of PMMA embedding and ultrathin sections instead of fracture surface replication, examined the structure of PVC powders and mouldings by electron microscopy. They showed PVC resin particles to be made up of 0.5 - 1.5 μm particles bonded together in a three-dimensional sponge-like lattice. During processing, the original resin particles break-down to 0.5 - 1.5 μm particles and as the processing conditions become more severe, fibrils ∿ 300 Å thick appear. These fibrils are practically indestructible. Hattori presented a structural arrangement of PVC shown in Fig. 3.

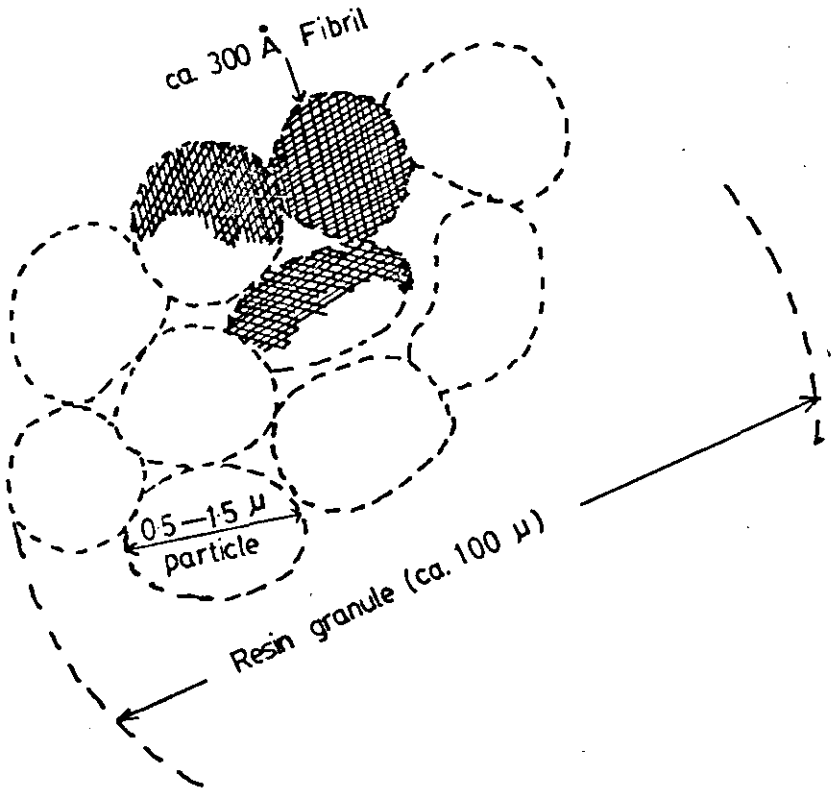


Fig. 3: Schematic illustration of PVC Structure[31]

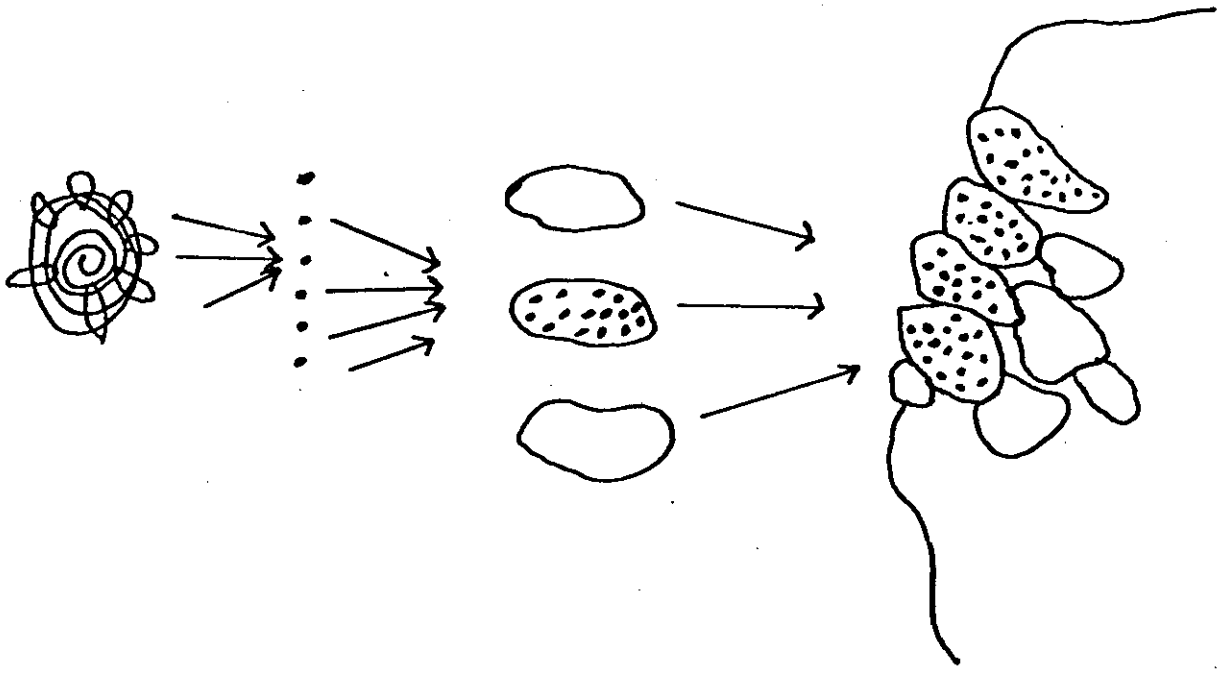


Fig. 4: Microstructure of PVC[32]

Shinagawa[32] in his own study of microstructure of PVC and its mouldings used suspension, emulsion and mass polymerised PVC of various degree of polymerisation and some modified PVC. He identified 1 - 2 μm size particles which he called secondary particles and their substructures of 200 - 500 Å he called primary particles. His illustration of PVC microstructure is shown in Fig. 4. During polymerisation one molecular chain grows, curling itself into a particle of 20 - 30 Å in diameter. These particles cluster together to form the primary particles 200 - 300 Å in diameter. They in turn build up the secondary particles 1 - 2 μm diameter. Shinagawa[32] estimates about 100 million primary particles are contained in a secondary particle. Finally the secondary particles agglomerate into the resin particle ∿ 100 μm in diameter.

Robinson et al[184], from studies on the kinetics of polymerisation of Vinylchloride by Cotman et al[185] have built up a similar picture. During polymerisation PVC chain begins to precipitate from the monomer when it attains a length of ∿ 20 monomer units. The chains bundle together into what they called 'basic particles' which eventually reach ∿ 200 Å in diameter. These basic particles cluster to form primary particles 1000 - 2000 Å in diameter. The polymer now grows in a different way. The primary particles increase in size, not by forming bigger clusters but by surface growth of successive polymer layers until polymerisation terminates when the monomer is exhausted.

Shinagawa also observed secondary particles are wrapped with membranes in suspension PVC but not in mass polymerised type. Emulsion PVC is the aggregate of spherical secondary particles. During processing the resin particle is broken down to the secondary particles and finally into the primary particles.

Following the suggestion of Gonze[29], Faulkner[34] investigated the

temperature-torque profile of a PVC compound in a Brabender Plastograph, starting from room temperature to the temperature at which degradation occurs. He observed three characteristic peaks in the curve and explained them as the breakdown of PVC powder particles, microgranules and primary particles respectively. He called them Stage III, Stage II and Stage I particles, their respective sizes being 100 - 150 μm, 0.5 - 2 μm and 10 nm. His arrangement of these particles, based on Hori[27] is similar to the one of Hattori[31].

Tsou and Geil[30], and Lyngane-Jorgensen[37] have suggested that the subprimaries contain a crystalline core. Recently, Geil[38] has raised some questions about the internal structure of the 0.1 μm particles. He suggested a direct examination of them by the newer technique of scanning transmission electron microscope (STEM) since PVC like most synthetic polymers is sensitive to electron beam damage. Furthermore STEM can operate on samples 0.1 μm thick. He also mentioned other techniques like dark-field microscopy could be tried. It is important to know precisely where the crystals, if any are, and their size and perfection.

As can be seen in the above discussion, various terms have been employed to describe the morphology of PVC. In order to allow a common understanding of terms, the terminology given in Table 2 is being recommended for use[(39)].

Processing of PVC, from the foregoing review, involves the progressive break down of the particulate structure of the resin under the influence of shear and or heat. The processability of PVC can therefore be assessed by the extent to which this particulate structure is destroyed or broken down. That is, the degree of fusion or gelation of the resin. In view of the fact that PVC must be processed with additives, most of the studies have been based on the effect of

additives on the fusion or melt flow of PVC. Both rigid and plasticised formulations have been extensively investigated by the use of the Brabender Plastograph[43-55] and capillary rheometers[56-64].

The studies with the Brabender Plastograph involve measuring the fusion time, that is, time from start to maximum torque, fusion torque and in some cases melt viscosity. The results obtained are very dependent on the test conditions - sample size, rotor speed, mixer temperature and of course, on the nature and concentration of the additives. However, the general conclusion is that lubricants retard fusion[71], while fusion rate increases with plasticiser concentration, resin particle size or with plasticisers which are good solvents for PVC.

In capillary rheometry, the viscosity, given in terms of shear stress against shear rate is measured.

The study of the rheology of PVC has shown some anomalous effects.[194-196] For instance, a decrease in the apparent viscosity has been observed. Also the post extrusion die swell of PVC increases with increasing temperature at constant shear rate contrary to other polymers. Others include higher viscosity for a given molecular weight than expected when compared to other common polymers like polyethylene and polystyrene and anomalous elastic behaviour which are attributed to association and/or the effect of micro-crystallinity.

Particulate flow mechanism has been used to account satisfactorily for these anomalous flow behaviour and physical property observed in PVC[40,41]. Two flow mechanisms have therefore been proposed for PVC: a particle flow, favoured by high molecular weight, low temperature and large resin particle size, and a molecular flow. Collins and Krier[42] have provided additional evidence of two flow mechanisms by obtaining two different activation energies from a plot of viscosity against

reciprocal temperature. Collins and Metzger[65] interpreted the presence of two flow activation energies as resulting from morphological changes.

Table 2 - Terminology for PVC Morphology[39]

Term	Approximate size in typical PVC	Origin of Description
Grain	100 µm	Free flowing at room temperature
Agglomerate	10 µm	Formed during polymerisation by merging of primary particles
Primary particle	1 µm	Formed from single polymerisation site at conversions of 10 - 50%
Domain	100 nm	Presence not clearly proven, possibly formed by mechanical working within or from primary particles
Microdomains	10 nm	Crystallite or nodule?

1.5 Additives for PVC

PVC in an unmodified form is a hard, horny material, which cannot readily be processed. It easily degrades at the temperatures required to process it. However, with the addition of a bewildering array of additives, PVC can be fabricated into a host of products ranging from soft and flexible to tough and rigid. These additives can be broadly classified into two: (a) those that eliminate undesirable properties by chemical reactions e.g. Heat stabiliser, UV absorbers, flame retardants, anti oxidants; (b) those that modify, improve or enhance polymer properties or even reduce formulation costs, by physical means e.g. plasticisers, lubricants, impact modifiers, processing aids and fillers.

Plasticisers are added to PVC resin to promote softness and flexibility in the finished article. They are usually colourless, odourless, non-volatile, polar, high-boiling organic liquids or solids with high molecular weight and good heat stability. They can be classified as primary or secondary plasticisers depending on their solvating power and compatibility with PVC. They can also be classified according to their molecular weight into monomeric and polymeric plasticisers.

Commercially plasticisers are divided into five groups: (1) General purpose plasticisers e.g. esters of phthalic acids of which butyl, dibutyl and octyl phthalates (DBP, DiBP, DOP) are the most common. (2) Flame retardant plasticisers e.g. aromatic phosphates. (3) Low temperature plasticisers. (4) Non-migrating plasticisers. (5) Extenders.

Before a plasticiser is selected for a given application it must meet a number of criteria. The most important are compatibility, volatility, migration resistant, chemical inertness, non-toxicity, efficiency and cost.

The degradation of PVC by heat is well documented in literature.

Excellent reviews have been made by Baum[66], Geddes[67], Braun[68] and Ayrey et al[69]. Thermal degradation starts off with hydrogen chloride being ripped out of the molecule resulting in conjugated double bonds and discoloration being formed.

The essential requirements of a stabiliser are:

(1) to react with hydrogen chloride - HCl acceptor

(2) disruption of conjugated double bonds by e.g. Diels-Alder type reaction.

(3) replacement of highly reactive allylic chlorine atoms by more stable group, e.g. ester group

(4) interference with the radical chain reaction; this includes interference with oxidation reactions, chain-scission and cross-linking reactions.

To achieve this one may have to combine more than one additive.

Stabilisers may be classified according to their chemical nature:

(a) Lead compounds

(b) Other metal compounds

(c) Organotin compounds

(d) Organic compounds

(e) Mixed stabilisers.

Lead compounds apart from being the oldest are the largest used group of stabilisers because of their low cost and extremely good heat stability. They also have good electrical properties and low water absorption. But they are toxic and therefore excluded from use in food packaging, toys and medical equipment.

Organotin compounds are tin organic derivatives mainly based on dibutyl or dioctyl carboxylic acids and mercapto compounds. They are the most effective group of stabilisers for PVC especially where excellent clarity and surface finish are required in rigid PVC. They possess

excellent heat stability, good light stability, crystal clarity, excellent compatibility, non-plate-out, non-staining and non-toxic (octyls) properties. Though their unit cost is relatively high, they are usually used at lower levels and consequently on a cost performance basis they are cheaper.

A PVC article for outdoor use should possess good light stability and weatherability besides having good heat stability. None of the heat stabilisers can of its own provide sufficient light stability to PVC. UV stabilisers are therefore added to PVC formulations. They are usually substituted benzophenones, or azoles, or organophosphorus compounds.

Lubricants[70] are added to PVC formulations to prevent the polymer melt from sticking to the hot metal surfaces of the processing equipment, thus stopping decomposition of the material and subsequent production shut down. Lubricants also reduce frictional heat between the resin particles during fusion and between the resin molecules after fusion. Therefore they affect fusion rate and lower melt viscosity[71] and hence flow characteristics of the melt during processing. The end result then of adding lubricants, is to facilitate fabrication of the finished product without detriment to its physical properties.

Lubricants can be classified in several ways: (a) according to chemical structure[72], (b) effect on glass transition temperature[73], (c) mode of action as 'external' and 'internal' lubricants[74], (d) polarity[75], (e) compatibility[76].

Many compounds have been proposed as lubricants for PVC, though several of them have little or no advantage over other products available. In general they consist of the following types of product:

fatty acids

fatty acid amides

fatty acid esters

metal soaps

fatty alcohols

hydrocarbons

Fillers are used mainly to reduce overall costs and bring about other desirable properties for specific applications. The main drawback in using fillers is that they may detract from the tensile strength of the finished products. Depending on the type of filler used, fillers can exert a marked effect on the processing characteristics of the PVC compound. The most common fillers for PVC are calcium carbonate, clay, silica and carbon black. Sometimes asbestos is included as a filler.

Other miscellaneous additives encountered in PVCprocessing include pigments/colourants, impact modifiers, processing aids.

Pigments/colourants impart colour and provide resistance to radiation. The most common pigment used for PVC is titanium dioxide noted for its white colour and resistance to UV radiation. Impact modifiers increase the resistance ofthe PVC product to fracture. Common types used are ABS (acrylonitrile-butadiene-styrene), MBS (methacrylate-butadiene-styrene), CPE (chlorinated polyethylene) and grafted PVC polymers. Processing aids are used to improve the processing behaviour of PVC resulting in greater elasticity and strength behaviour of PVC resulting in greater elasticity and strength of the melt. They are polymeric materials, the most important being the acrylic processing aids.

1.6 Compounding of PVC

As already mentioned in Section 1.5 PVC is rarely used in its pure form. It has to be mixed or compounded with additives to achieve good material and processing properties.

In the early days the practice was to premix PVC and the additives and then homogenize them in a compounding machine[77].

The most common types of premixers are Ribbon blenders, Air mixers, Tumble mixers, Sigma-blade mixers and Paddle mixers[78,79].

In these premixers, little or no frictional heat is developed therefore for plasticised blends jacket heating and cooling facilities are necessary. But because of poor heat transfer blending cycles are rather long. With rigid formulations not more than mere dispersion of the ingredients is involved and it is not surprising such blends exhibit a tendency to separate out on handling.

The advent of high speed mixers[77,80] in the mid 50's has dramatically changed this practice. High speed mixers can be operated over a wide range of conditions so that powder blends can be extruded or moulded directly without the need for granulation. The basic principle is that all the ingredients are mixed in a single operation to obtain a "dry", free-flowing powder.

In general, a high speed mixer consists of a mixing chamber with a rotor or mixing impeller at the bottom. An adjustable baffle blade deflects slow moving material from the top of the vortex down into the correct working area. The blend temperature is measured by an Iron/Constantan thermocouple either protruding through the baffle or through the wall of the mixing bowl. Fig. 5 is a diagrammatic representation of a high speed mixer.

As the impeller rotates at high speed it creates a vortex mixing action. This results in air being sucked into the blend thus fluidising

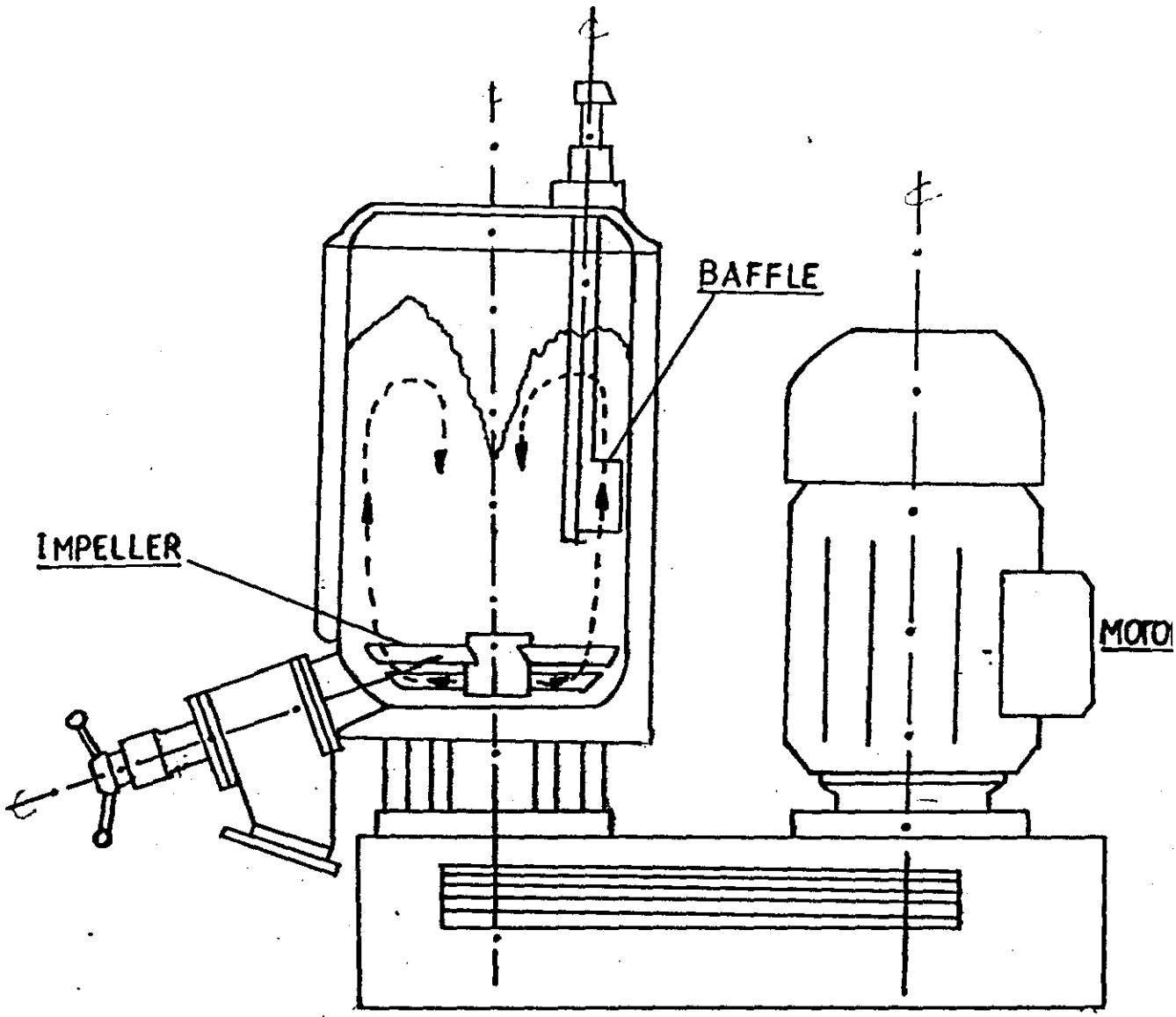


Fig. 5: Diagrammatic Representation of a high-speed mixer

the system. Collisions occur between the particles themselves and with the walls of the mixer and the impeller. These collisions result in the generation of frictional heat raising the temperature of the blend.

When the required temperature is reached, the blend is discharged usually through a pneumatic valve into an associated low-speed cooler mixer. The cooler mixer generally has a large surface/volume ratio and it is here that the hot blend is cooled to a temperature at which it can be handled.

The main compounding machines for PVC are Roll mills, Internal mixers and compounding extruders.

Roll mills usually consist of two cylindrical highly polished rolls, rotating in opposite direction and at different speeds - "friction ratio" $\sim$ 1:4. This creates the required shearing action and a temperature difference of 10°C between therolls is normally sufficient.

Internal mixers[77] are commonly referred to as Banbury mixers after the original designer. They are quite intensive in their action and can be operated at relatively high speeds (20 - 100 r.p.m.) and under pressure.

Compounding extruders[77] have the advantage of operating continuously and can give very high outputs. Important commercial types are Buss-Ko-Kneader, Werner and Pfleiderer Kombi-Platt, Twin-screw extruders. Fig. 6 shows the various routes for converting PVC resins into finished products[81].

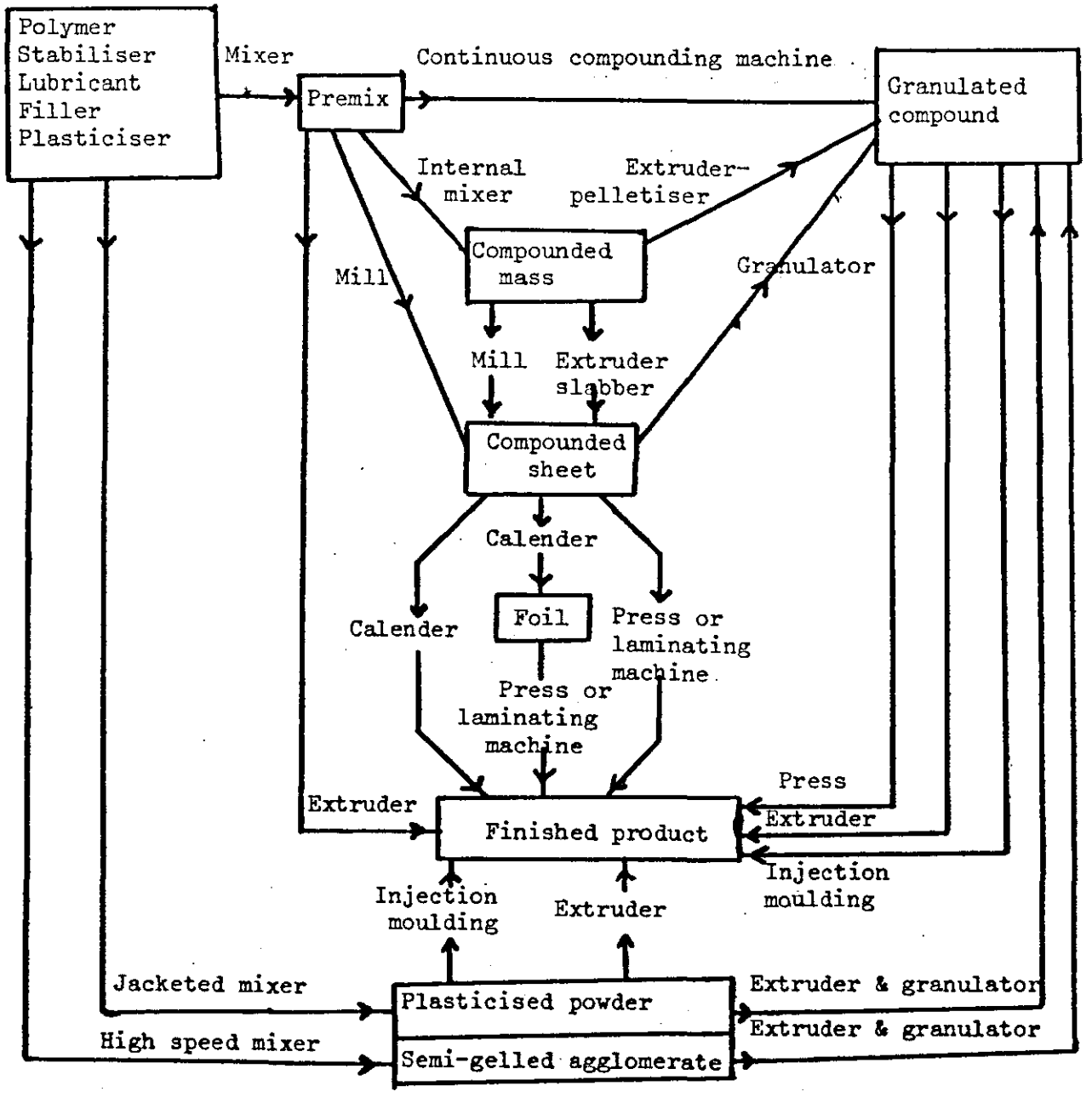


Fig. 6: Routes for conversion of PVC resins to finished products[81]

CHAPTER II

FORMULATION AND PREPARATION OF BLENDS

The materials and formulations used in the research project are described in this chapter. Their typical properties taken from technical data sheets are given. Also described here is the preparation of blends.

2.1 Materials

Two commercial grade PVC resins were used for this work: Breon M80/50 mass PVC made by BP and Corvic D55/09 suspension PVC made by ICI. They will be referred to as PVC-M and PVC-S respectively throughout this work.

These two grades were specifically chosen for two main reasons. First, the manufacturers have indicated these grades would be commercially available for a long time. Therefore any findings or conclusions resulting from the research programme here could be of immediate use to the industry.

In order to discount variations in test results being due to changes from one batch of polymer resin to another, a large quantity - about a tonne - of each grade from one batch number and recipe was acquired initially.

The second reason for choosing these grades of resin is that they have a low to medium molecular weight. Therefore they are easier to process because of easier gelation and lower melt viscosity characteristics.

Both grades are suitable for applications requiring excellent crystal clarity, especially where absence of "fish-eyes" is absolutely essential as in thin film, foil and bottles.

Typical applications for the PVC-S are for extrusion of complex sections and clear sheets in the case of rigid formulations. Plasticised formulations are used for calendering of sheets especially vinyl floorings. The PVC-M is particularly suitable for blow-moulding, injection moulding and calendered sheet and film application.

Technical data of the two grades of polymer are given in Tables 3 and 4.

2.2 Formulation

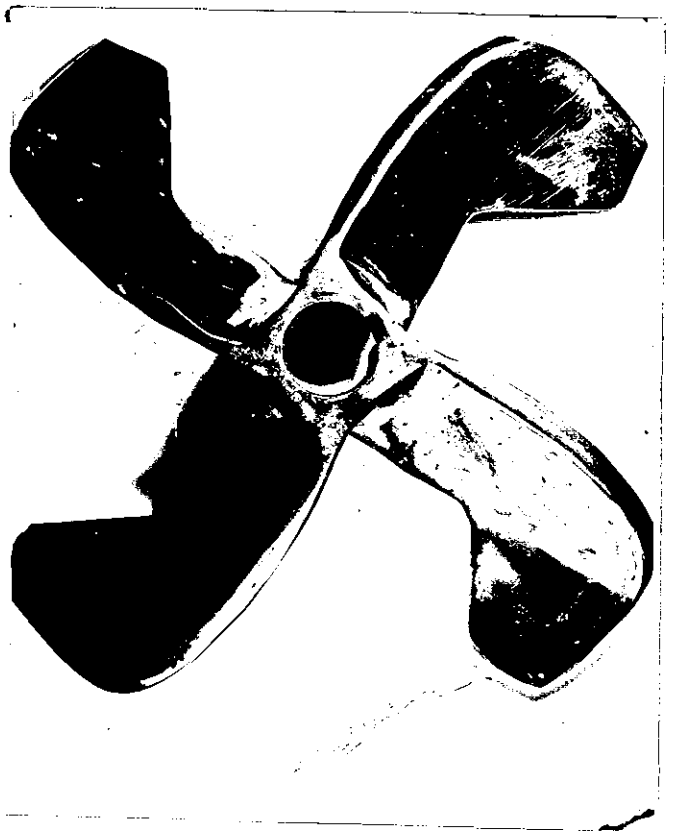
PVC easily degrades at the temperatures required to process it. It therefore has to be mixed with certain additives before processing (see 1.5). A typical commercial PVC formulation would contain stabilisers, lubricants, processing aids, impact modifiers etc. However, in order to readily identify the ingredients in the blend a simple system consisting of PVC resin, solid tribasic lead sulphate stabiliser (TBLS) or liquid thiotin stabiliser (Stanclere T135) and calcium stearate lubricant, has been employed. These additives were supplied by Akzo Chemie U.K. Ltd., Interstab Division. They have been added at levels normally used in commercial productions.

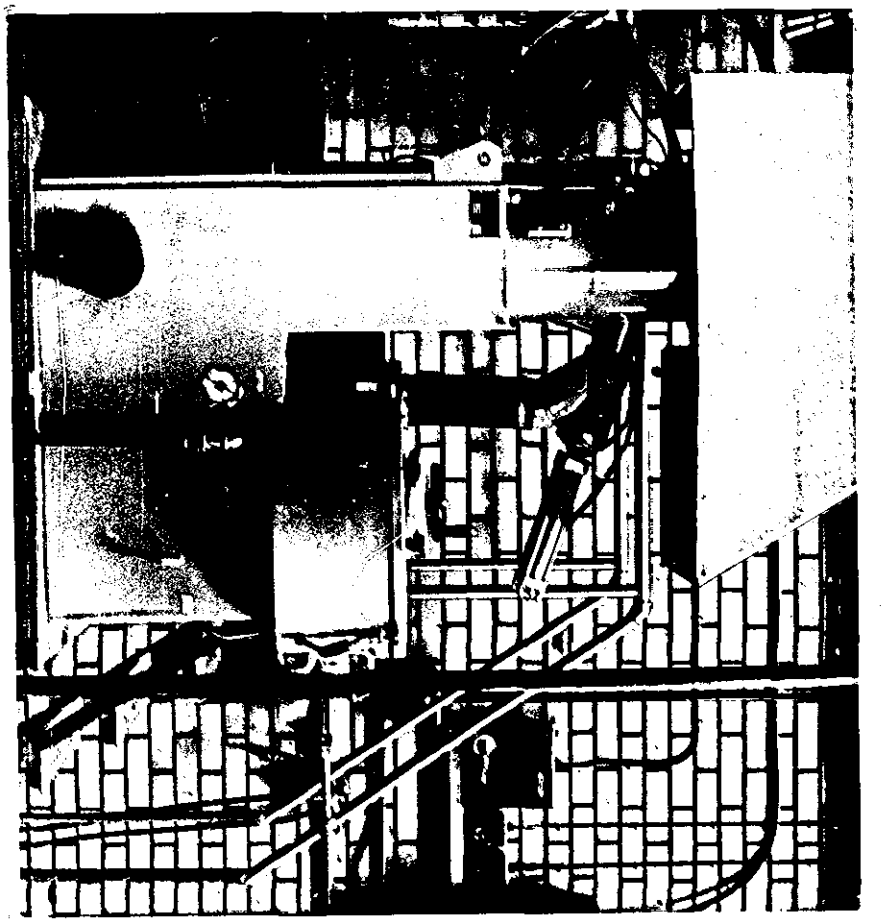
Typical properties of these additives are given in Tables 5 and 6. Tables 7 and 8 show the details of the formulations.

2.3 Preparation of Blends

Blends of formulations described in 2.2 were prepared in an 8 litre T. K. Fielder Laboratory Mixer. The mixer is fitted with stock temperature measurement facilities, jacket temperature control and a separate cooling chamber or cooler unit. (See Fig. 7) The general construction and principle of a high speed mixer have already been described in Section 1.6.

Fig. 7: T. K. Fielder Laboratory Mixer/Cooler Unit.
Lower picture shows the impeller.





The Fielder has a working capacity of 3-6 litres (or 2-3 kg) and with impeller speeds ranging from 500-4000 r.p.m. it can be operated over a wide choice of conditions, for example, from gentle blending as in ribbon-blender to high speed mixing. An iron/constantan thermocouple protruding through the baffle measures the product temperature. The mixing bowl is made of highly polished stainless steel. This permits easy cleaning and eliminates cross contamination between materials to give consistent results. It also reduces wall friction.

At the end of the mixing cycle the blend was discharged through a pneumatic valve into a low speed cooler mixer which has cold water circulating in the inner jacket.

While the principal aim of blending is a proper mixing of polymer resin with additives to yield a dry, free-flowing powder, experience from processors, especially extruders, point out that a prerequisite for successful powder operation is consistency of blends. With this in mind one object in this part of the programme was to establish conditions under which one obtains a product whose characteristics like particle size and size distribution, particle shape, bulk density, powder flow and moisture content showed minimal batch-to-batch variations.

Some of the disadvantages mentioned against powder processing include poor extruder output because of low powder density and lack of devolatilisation of the material which cause defects such as voids or bubbles in extruded profiles. However, by choosing the right mixing conditions increased bulk density, elimination of moisture and volatiles and improved flow properties of the powder blends could be obtained. This requires blending to high temperatures consistent with thermal stability of the mix.

According to Guimon[128] factors which affect powder blend properties like bulk density,homogeneity or state of gelification are mixing time, blend discharge temperature, condition of vessel, shape and speed of rotor blades, weight of charge to the mixer and manner of cooling the hot blend. In establishing blending conditions therefore, high charge and rotor speeds were sought. These would increase the frictional heat generated (see 1.6) and thus shorten the mixing time. An extended time cycle will reduce overall output and could affect the economics of direct powder processing.

Finally, it was also intended to find a set of operation variables which gave rise to blends which were spatially homogeneous and whose powder particles were significantly modified in shape, size and topographical features.

The optimum conditions used for the preparation of blends are given in Table 9.

Consideration was given to the order of addition of additives to find out the effect of each on the blending cycle. Attempts to commence blending with only PVC and add TBLS or calcium stearate later were unsuccessful. After the initial rapid temperature rise the PVC in the mixer turned into one solid mass and stopped the motion of the impellers. Consequently the power consumption increased and the motor tripped off. This clearly indicates the need for additives.

In (A) either or all the additives were added at the start of the blending operation. Variations included adding the lubricant 20°C before the final discharge temperature.

In (B) steam heating of the mixer was used as enough frictional heat could not be generated to raise the blend temperature over 100°C. The lubricant was added at the start of blending and the stabiliser added when the mix temperature was 70°C.

It must be pointed out that the thermocouple gives an average temperature of the bulk material in the mixing vessel. It does not indicate the surface temperature of the individual particles. The reliability and accuracy of the reading depends on the thermocouple being incontinuous contact with the mix and the mix itself being in a fluidised state, maintaining a vortex action. If not, the thermocouple would only give the temperature of the material in contact with it and this may be a very small fraction of the entire mix. Because of the frictional heat generated on the powder particles their surfaces should be at much higher temperatures than the thermocouple would indicate. As a means of ascertaining the true temperatures of the particles a series of wax of different melting points was added to the mix before blending. These waxes change colour on melting.

Unfortunately this was unsuccessful. If added in pulverised form they became finely dispersed into the blend. On the other hand if added in lumps or crumbs signs of melting could not be detected. Other materials that could be smeared on the rotor blades or baffle or walls of the mixer should be explored. Then definite points would be examined during or after blending.

Table 3 - Technical Data of M80/50

Specific viscosity (0.5% solution in cyclohexanone)		0.39 - 0.41
K value		56 - 58
Viscosity No. (ISO method R174:1961)		78 - 82
Bulk density (BS 2782, part 5 Method 501A) kg/m^3		640 - 680
Particle size µm	99.9% min	<250
	90% min	>100
	6% max	< 63

Table 4 - Technical Data of D55/09

K value	62	Note 1
Viscosity No. (ISO-R174)	95	
Packing density (g/ml)	0.64	Note 2
Apparent density (ISO-R60) g/ml	0.59	
Relative density (Archimedes method)	1.40	
Weight Passing 60 mesh (250 µm) %	99.9	Note 3
Weight Passing 200 mesh (75 µm) %	5.0	Note 3
Volatiles content	0.2	Note 4

Note 1: Calculated from relative viscosity data obtained bymethod ISO-R174

Note 2: From volume of 20 g of polymer in cylinder dropped 30 times from a height of 51 mm (2 ins.)

Note 3: Weight % passing 60 mesh sieve (BS 410:1969) by sieving dry polymer for 30 minutes in humid air

Note 4: Weight loss after one hour at 135°C (295°F)

Table 5 - Typical Properties of Lead Stabiliser

Compound	Tribasic Lead Sulphate
Formula	$3PbO.PbSO_4.H_2O$
Form	Powder
Colour	White
Bulk density g/l	1200
Specific gravity	7.2
Lead content %	83.4

Table 6 - Typical Properties of Stanclere T135

Type	Thiotin
Colour (Gardner)	1
Density g/ml at 20°C	1.11
Refractive Index n_D^{20}	1.508
Viscosity Poise at 20°C	<0.5

Table 7 - Lead-formulation (A)

PVC resin	100	phr	by	weight
TBLS	4	"	"	"
Calcium Stearate	1.5	"	"	"

Table 8 - Tin-formulation (B)

PVC resin	100	phr	by	weight
Stanclere T135	3	"	"	"
Calcium Stearate	0.5	"	"	"

Table 9 - Blending Conditions

	(A)	(B)
Weight of charge (Kg of PVC resin)	3	2
Rotor speed r.p.m.	4,000	3,500
Jacket temperature °C	-	70
Temperature of Stabiliser addition °C	-	50
Cooler unit rotor speed r.p.m.	1,000	1,000
Cooling period min.	2 - 3	2 - 3

PART 1

EVALUATION OF PROPERTIES OF PVC POWDER BLENDS

This part deals exclusively with the work on powder blends. It contains the description of experimental techniques used to assess or characterise the blends, the results obtained and a discussion of these results.

CHAPTER III

EXPERIMENTAL TECHNIQUES

In direct powder processing the granulation stage is completely omitted thus providing enormous savings in equipment costs and materials handling. If these benefits are to be achieved consistency of powder blends must be ensured to avoid erratic or pulsating productions. There is therefore a need to understand the behaviour of the PVC particles during blending and the effect that the blending has on subsequent properties.

The experimental techniques used to study powder morphology, characterise and assess the processability of the various blends (see 2.3) are given in this chapter. They include microscopy, differential thermal analysis, bulk and apparent density[82], size distribution[83,84], jet milling[104-106] and the use of a capillary and torque rheometer.

3.1 Microscopy

In 1.4 evidence of the existence of particulate structure in PVC was reported[20-36]. The structures are of the order of ∿ 10 nm to ∿ 100 μm. The limits of resolution in optical microscopy are ∿ 2000 Å (0.2 μm), ∿ 50 - 100 Å in scanning electron microscopy (SEM) and ∿ 10 Å in

transmission electron microscopy (TEM) (manufacturers' claim vary from 2 - 4 Å; 10 Å is working limit for polymers). Both optical and electron microscopy have therefore been employed in this study. Optical microscopy and TEM were used to study the internal structure of the powder particles while SEM was used to study the shape and topographical features.

3.1.1 Microtomy

The use of sectioning techniques (microtomy) to study the internal structure of powder particles was chosen since it is generally accepted as the primary method of polymer specimen preparation. Compared with other methods such as ion beam etching the chanves of producing 'artefacts' are minimal. In fact 'artefacts' are almost always due to poor quality sections - sections full of marks resulting from knife edge imperfections (longitudinal marks), judder (transverse marks) or excessive residual strain.

To hold the PVC powder particles with sufficient rigidity, they were embedded in an epoxy resin, Araldite, contained in a gelatin capsule. Methacrylates were avoided as the embedding material because of their swelling action on PVC, although used by some workers, e.g. Hattori et al[31].

Araldite is the trade name for epoxy resins made by Ciba Ltd., Basle. They harden uniformly with only ∿ 2% shrinkage. They are stable under electron bombardment and are recommended for high resolution studies of sections. The embedding mixture was made up as follows[86]:

Araldite CY212 - epoxy resin	:	10.0 ml
HY964 (dodecenyl succinic anhydride) - hardener	:	10.0 ml
DY064 (tridimethylaminomethyl phenol) - accelerator	:	0.5 ml
DBP (dibutyl phthalate) - plasticiser	:	1.0 ml

It was then allowed to set overnight at 60°C.

Depending on the section thickness required the embedded powder resins were then sectioned with freshly made glass knives either using Leitz base sledge microtome (5 μm) or an LKB Ultratome (800 - 900 Å). A freshly made glass knife is significantly sharper than one a day or two old. The sectioning was done at room temperature (20±2°C) as the PVC resin and the blends had glass transition temperatures of 83°C and 75-83°C respectively (see 4.4) and hence were sufficiently hard and rigid.

3.1.2 Optical Microscopy

Stanclere T135 being a liquid stabiliser (see 2.2), it was thought necessary to observe its interaction with PVC particles. Unblended PVC resin particles were dispersed in excess stabiliser (T135) and heated on a Mettler hot stage at the rate of 3°C per minute until they became completely transparent. They were photographed at various temperatures. This test has been used by Bigg[87], Lotmentsev et al[88], Anagnostopoulos et al[89] as a method for studying polymer-plasticiser interaction.

The 5 μm thick sections were mounted in Cedar Wood oil or Clove oil and examined with a Reichert Zetopan Microscope set up for phase-contrast or differential interference contrast (DIC) microscopy. These two modes of microscope observation were chosen because as will be explained later, they enable us add contrast to the specimen and hence make it more visible or see more details.

In order to fully evaluate and interpret the images formed it is necessary to understand how the phase contrast or DIC microscope works. The optical principles of individual instruments are always fully described in their instruction manuals. The theory and details of

these methods can be found in textbooks on microscopy and in literature[90-95]. However, the broad principles involved will be briefly described here.

A colourless transparent or almost colourless transparent material may under ordinary microscope illumination be practically invisible. This is due to the fact that there is no 'contrast' between the surrounding medium andthe material. Contrast is produced if the refractive index difference between the material and its surroundings is altered. The material may then be seen as almost a homogeneous structure even though it may be composed of minute structures having slight differences in refractive index.

The phase contrast microscope converts these slight differences in refractive index or phase difference into changes of amplitude (or brightness), and produces an image that is easily seen. In simple terms then, the refractive index differences in a specimen are changed into bright-dark differences with the phase contrast method and it thus becomes visible.

Consider three light waves from a point source (Fig. 8). B passes through a non-absorbing specimen and is slowed down or retarded with respect to A which does not pass through the specimen. A and B are therefore out of phase. Unfortunately the human eye is not sensitive to phase differences and as a result the image of the specimen can scarcely be seen. If C passes through an absorbing medium M, the amplitude is reduced and this change is visible to the eye as intensity or brightness.

When two coherent light waves strike a screen at the same point the resultant wave is the sum of the amplitudes of the two waves. If the waves are in phase we get an increased light. On the other hand, if one of these light waves has been retarded in some way by half a wave-length, then instead of getting increased light on the screen there will be no light. This is because coherent light waves can interfere with one another. Therefore depending on the relative

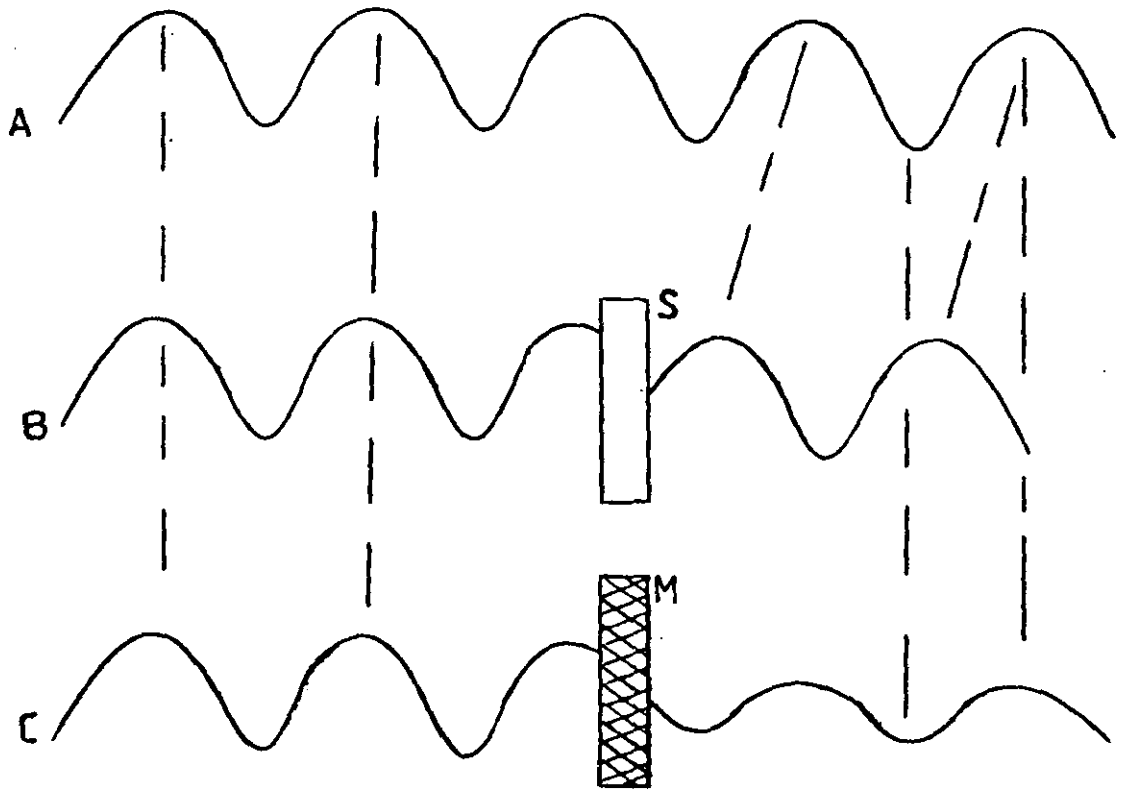


Fig. 8

amplitudes of the waves involved this interference may result in complete extinction or reduction of intensity of light. In other words, combinations of amplitude and phase produce dark, lighter or darker grey contrast.

Phase contrast relies on enhancing the retardation of light refracted or diffracted by the specimen so that it can destructively interfere with the light passing directly through the specimen, thereby producing easily visible difference in amplitude. The basic requirements of a phase contrast microscope are an annulus or ring and a phase-retardation plate. The annulus which is fitted on the condenser restricts the illumination of the pupil and ensures the specimen is illuminated with a hollow cone of light. The phase-retardation plate, fitted on the objective, is semi-transparent in order to render the diffracted and undiffracted portions of the light energy roughly equal, thereby achieving maximum contrast in the image formed.

Phase contrast microscopy is however, not without some disadvantages. The image is characterised by a 'halo' around the boundaries because some of the diffracted light inevitably passes through the ring-shaped area of the phase retardation plate and adds itself to the directly transmitted light which has been confined to this area.

Another limitation of the phase contrast method is that the relationship between the phase change given by a specimen and the relative brightness of its image is not a linear one - an object does not automatically appear darker the greater the phase change it produces. Indeed a given contrast in the image does not uniquely define a path difference.

Finally, transmitted light phase contrast work requires superior 'quality' and thinner sections, that is sections that are strain free and free from deep knife marks. This can multiply the usual thin sectioning problems. For instance 1 μm thick sections could not be

obtained with the Leitz microtome on every cutting stroke. Even when obtained they were either curled up or looked 'shredded'. This was in spite of using freshly made glass knives.

The Nomarski differential interference contrast method(DIC), like phase contrast, produces an image based on converting the phase changes in the light passing through the specimen into changes of wave amplitude. In this method the phase changes are between $\lambda/10$ and a full wavelength and unlike phase contrast method, this is not achieved by causing a single beam of directly transmitted light and the light diffracted by the specimen itself to produce a destructive or additive interference. Instead, a beam of plane polarised light is sheared into two by a modified Wollaston prism (Nomarski prism). The distance between the two rays is very small so that both beams pass through the specimen which will give rise to path differences. The two beams are then recombined by another Nomarski prism in such a manner that an analyser prepares them to interfere and produce the final image with relief contrast.

The DIC image is free from the 'halo' of phase contrast and has a three-dimensional appearance. This is entirely an artefact of the contrasting system which arises when the optical path is 'biased' by adjustment of the equipment so that the background colour is dark grey. Because the contrast developed in the DIC image arises from a lateral shearing of the beam passing through the microscope condenser, the contrast is directional.

3.1.3 Electron Microscopy

For scanning electron microscopy (SEM) a few grains of PVC powder particles were mounted on a stub with 'Durofix' glue and vacuum coated with carbon (∿ 200 Å thickness) in an Edwards E12E4 Vacuum Coating Unit. The stub was placed on the base plate and the carbon source suspended approximately 6 in. above it. The carbon source consisted of two 1/4" rods having different faces. One had a reduced diameter of 3/32" with a length of 1/4" and the other had a flat surface across the 1/4" diameter.

A shield was placed below the carbon rods to shield the heat away from the specimen after evaporation. After evacuating the chamber to 1×10^{-4} torr., the 10V 90 amp. circuit was switched on until the carbon rods began to evaporate at the centre. When the thin end of the evaporating rod disappeared the current was switched off and the chamber closed off before admitting air into it.

The stub was then placed in the Edwards S150 Sputter Coater and sputter coated with gold under the following settings:

Cooling Water flow	:	0.5 litre/min
HT Voltage Control	:	5
Current meter	:	15 mA
Gas Admit	:	15
Pressure gauge	:	2×10^{-1} torr
Time	:	2 min

While, for reasons to be explained later, it is necessary to coat the particles with gold, prolonged sputter coating might affect their surface texture because of the attendant heating effect of the coating process. Therefore after standing the stub on the bench for ∿ 15 min. the sputter coating operation was repeated.

This procedure gave satisfactory results. It seems the carbon

pre-coating allows a continuous layer of gold deposit on the entire powder surface. The gold coating dissipates to earth the charge built up on the specimen by the electron beam and reduces beam damage to the specimen.

The powders were then examined in a 'Cambridge S2A Stereoscan' scanning electron microscope. The accelerating voltage and specimen tilt were adjusted to give adequate contrast. 2 KV was found suitable for magnifications upto x 5000 and 10 KV for x10,000 magnification. It was observed that accelerating voltages higher than these resulted in the charging of the specimen with the consequent lack or loss of resolution and specimen damage. The familiar 'burnt square' on the specimen at high magnifications easily occurred.

The basic principle of SEM is as follows: a beam of electrons is focused as a spot which is caused to move across the specimen. As the spot strikes each point on the specimen a response (or signal) is produced. These responses are collected sequentially and displayed to give an 'image'. Details of the responses can be found in such texts as Oatley[96] or Wells[97]. However, a brief account is given below.

When a beam of electrons strikes a surface, the electrons penetrate a short distance into the specimen and collide several times with the atom in it. Only if the specimen is sufficiently thin is a significant fraction of the beam transmitted. These collisions could be elastic or inelastic.

In the case of elastic collisions, the electrons suffer very little loss in energy but change direction. Some of the electrons are scattered through large angles and escape back through the surface. These are called back-scattered electrons. The amount of back scatter increases with increasing atomic number of the element and also on the energy of the incident electrons, that is on the accelerating voltage.

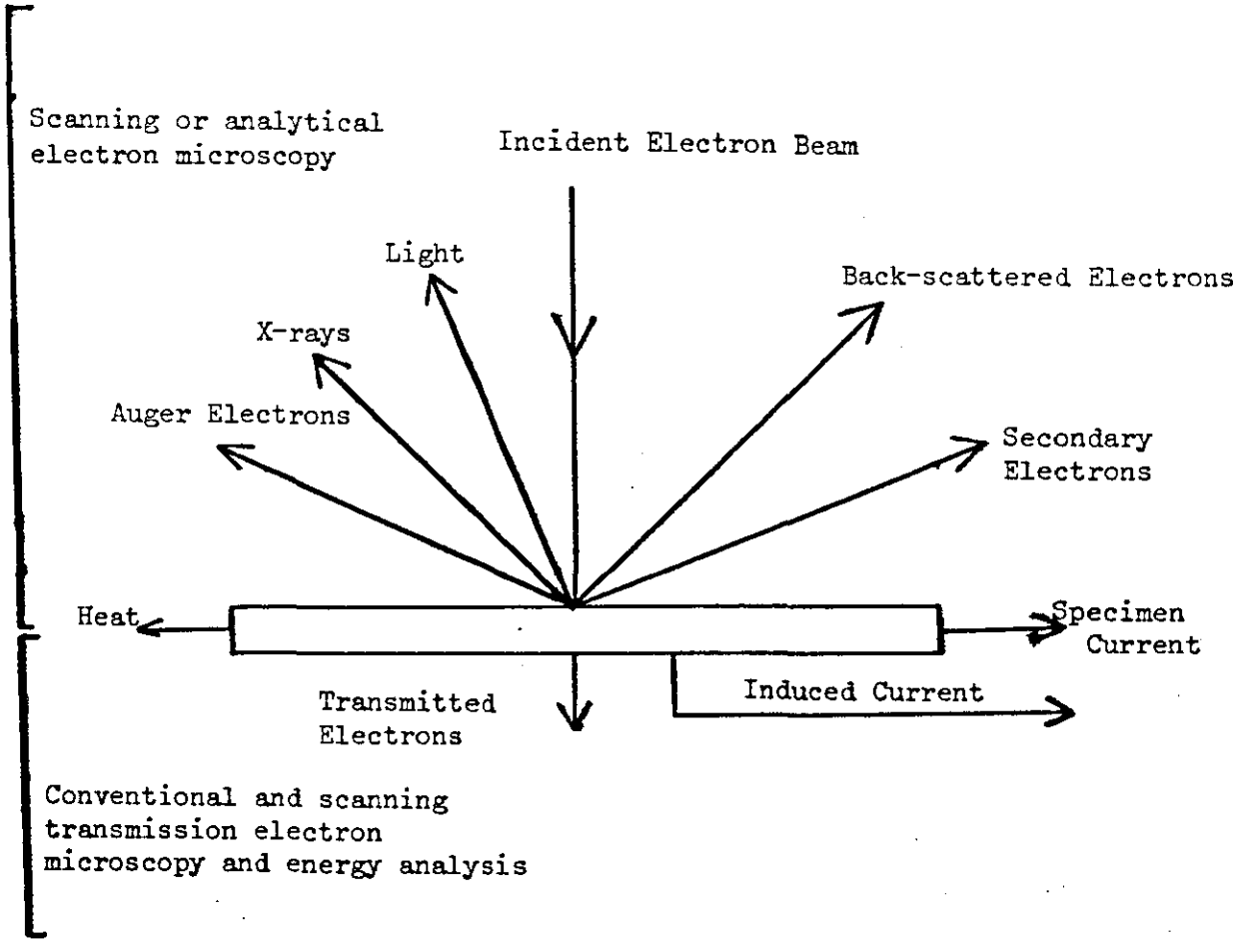


Fig. 9: Summary of various responses resulting from specimen-electron interaction

In inelastic collisions, the incident electron encounters an inner orbital electron and knocks it out from the atom entirely or into a higher unoccupied shell. The ejected electrons are called secondary electrons and generally have energies of only a few electron volts.

The vacancy is subsequently filled by an electron from a higher energy shell. In doing so it gives up an amount of energy equal to the difference in energy levels of the two shells by emitting an X-ray photon.

There may also, after the ionisation of the atom, be a subsequent rearrangement of the remaining electrons in the atom with the release of a certain amount of energy. This energy is used to eject another, Auger, electron from the atom.

Summarised in Fig. 9 is the various responses resulting when a beam of electrons strike a specimen. All these responses provide different information about the specimen. For image formation in SEM interest is centred chiefly on the back-scattered electrons and secondary electrons.

The secondary electron image is the most generally useful for studying surface topography of the specimen. In fact, unless specified in this report otherwise SEM images are of this type.

The secondary electrons are detected by a scintillator/light pipe/ photomultiplier system. The principle of this system is that the emitted secondary electrons are attracted towards a charged grid at the front of the detector. They are then accelerated into the scintillator held at a positive potential of several KV. The light generated on the impact of the electrons with the scintillator passes down the light pipe and falls on the photocathode of a photomultiplier. The photomultiplier converts the light pulses to electrical signals and multiplies them about a million times. These amplified signals

are then used to modulate the brightness of a cathode ray tube (CRT), adjusted to scan synchronously with the probing electron spot. The variations in brightness recorded produce the highly magnified 'image' of the object.

The nature of the final displayed secondary electron image depends on the intensity of secondary electrons detected during the electron probe scan of the specimen. Three main factors viz surface topography, voltage variation and elemental composition of the specimen determine this.

Elements of high atomic number give a greater yield of secondary electrons. Therefore those areas of the surface which contain higher atomic number elements would form brighter images. The surface topography at the point where the electron beam strikes the surface affects the angle of incidence. The higher the angle of incidence the more secondary electrons are produced hence the brighter the image.

As was stated earlier, if the specimen is sufficiently thin a significant fraction of the incident beam of electrons is transmitted. A lens (electromagnet) placed close to the specimen can be used to form a microscopic image of the specimen in the conventional sense. If the incident electron beam passes directly through the specimen then a 'bright-field' illumination is produced. If on the other hand a central portion of the electron beam is deflected and only diffracted electrons are used to obtain an image, then a 'dark-field' illumination results. 'Phase contrast' can be achieved on thin specimens by causing the electrons passing through immediately-adjacent areas to interact or interfere with each other.

In this study a AEI EM6G transmission electron microscope was used to examine the ultrathin sections.

PVC, like most synthetic polymers is susceptible to electron beam

damage when viewed in conventional transmission electron microscope (CTEM). Therefore, the newer technique of scanning transmission electron microscope (STEM) was also used to examine the ultrathin sections. Low et al[98] have reported the use of STEM in studying the microstructure of high density polyethylene spherulites.

STEM is the name given to the type of electron microscope developed by Crewe. This term excludes two other modes of microscopy which also provide a transmission form of scanning electron microscope. This is because they lack the high beam current density and the ultra-high vacuum system of the Crewe-type instrument[99-102] since a tungsten emitter is the electron source and a conventional oil diffusion-pumped vacuum system is used.

STEM combines the features of the two basic types of electron microscope. It consists essentially of a series of lenses for focusing an electron beam on to a specimen, a scanning system and an electron detector after the specimen. However the specimen is made thin enough to permit transmission of electrons. The electron source is a field emission gun so that a very high degree of brightness - about 10^6 times that from a comparable hot filament - can be achieved. This is essential if sufficient current is to be focused into a very small probe size thus making STEM a very high resolution scanning instrument. An additional feature of the electron detector is an electrostatic spectrometer. It is a device which enables the operator to choose if all the transmitted electrons or only those not scattered or inelastically scattered or elastically scattered through large angles are to contribute to the image.

Unlike CTEM, STEM has no lens after the specimen and therefore there are no lens distortions or further achromatism. Apart from spherical aberration which decreases with magnification, any aberrations present are independent of magnification. Because of this STEM can be used to examine thicker sections. Groves and Crewe[103] state that STEM

can be used for specimens up to five times thicker than those used in a CTEM at the same voltage. The general opinion is that beam damage in the case of the STEM mode is less than occurs when using CTEM.

The main drawback in electron microscopy of polymers is beam damage especially where high electron beam intensities have to be used to obtain high resolution information. Grubb's[192] review of works on radiation damage and electron microscopy of organic polymers indicate that three effects, namely, loss of mass or crystallinity, contrast artefacts and distortion, can lead to great changes in the image formed in the microscope. Bevis et al[193] have also examined the effects of electron beam damage on a number of polymers. They found the most important effects to be loss of material, contamination, specimen charging and degradation of diffraction patterns. It seems essential to first establish suitable operating conditions of the electron microscope when examining polymers in order to reduce these effects to tolerable levels as it is not possible to completely prevent beam damage of polymers.

3.2 Density

One of the important physical characteristics of PVC particles in establishing processing conditions is bulk/apparent density. In process equipments like extruders bulk and apparent densities affect throughputs and batch sizes. Jones and Hawkes[119] and Guimon[120] have reported increased extruder outputs with powder blends of higher bulk densities. Bulk and apparent densities also provide useful guide to handling in packaging.

Both bulk and apparent densities were measured by the usual methods. Apparent density was determined by BS 2782, Part 5, Method 501A; 1970. For bulk density assessment, 100 gm of the powder sample

was vibrated to a constant volume in a tall cylinder that fits into a Tap-pack Volumeter. The bulk density was then obtained by dividing the weight of the powder (Kg) by the volume (m^3).

3.3 Particle Size Analysis

According to ASTM D1705 particle size analysis is useful for determining batch-to-batch uniformity of PVC resins. Particle size and size distribution could determine, other things being equal, whether the resin is a dispersion resin, a dispersion-modifying resin or a general-purpose dry-blend resin.

Particle size analysis assumes greater importance in plasticised compositions. For instance, for resins of comparable porosity and molecular weight range, plasticiser absorption is largely determined by the resin surface area which is reflected by particle size and size distribution. Too many fines can cause not only dusting problems but also lead to uneven plasticiser absorption during dry blending. Oversize particles can also cause poor plasticiser absorption and subsequently can generate gels, or 'fisheyes' in the finished product.

During processing, large resin particles would require more processing to breakthem down and the time to achieve that would depend on the bulk density of the resin.

It is therefore desirable for the resin to have a narrow particle size distribution with minimum of fines or oversize.

There are a number of methods of measuring particle size and size distribution. They may be broadly classified as follows:

Method	Size Range, μm
1. Image Formation: a) Optical Microscopy	1 upwards
b) Electron microscopy	0.001 to 20
2. Light Scattering/Refraction	0.01 to 100
3. Electrical Conductivity	0.2 to 300
4. Sieves	50 upwards
5. Relative Motion between Particles and Fluid:	
a) Sedimentation	5 to 100
b) Centrifugal	0.05 to 100
c) Winnowing	5 to 100

A more detailed classification of methods of particle size analysis can be found in reference 104. The choise of a particular method depends on such factors as:

a) Size of parameter required - the size attribute that is most directly correlated with the characteristics of interest should be measured.

b) Size range of the particles to be measured - from the range indicated above it is clear that no single method is applicable to the whole range of sizes.

c) Form of specimen - specimen may be dry powder or wet emulsion etc.

d) Precision and accuracy required and time available per analysis.

In this study two methods of particle size analysis were chosen - sieve analysis[83] and an optical method[84]. The optical method involves using a Zeiss TGZ3 Particle Size Analyser. Photomicrographs at a total magnification of x100 were prepared from a representative sample of each batch of the PVC blends.

Since the size of each individual particle is measured in the optical method, it is absolutely essential that sufficient number of particles be measured or observed if the picture given by the sample

size is to be representative of the whole. Insufficient sample size or number of observations therefore becomes a source of error. At least 2,000 particles were analysed for each sample. It was found that counts above this number did not significantly affect the size analysis result.

To obtain a representative sample of the entire bulk of material for size analysis the simple technique of cone and cuttering was used. It consists of heaping the powder blend into a cone and cutting through it into two halves. Each half was then heaped into a new cone and cut again into two halves. One half was then combined with the opposite half and the process repeated until a final 20-50 gm is left from which random samples were taken to prepare the photomicrographs for the TGZ3 analysis or the 50 gm used for Sieve analysis.

Each particle on the micrograph was analysed by adjusting the area of the iris to coincide with the area of the particle. On pressing the footswitch the particle size is recorded automatically on one of the forty eight size channels on the counter.

As a much quicker alternative, a standard sieve analysis method was also employed[83]. Sample size was 50 gm, mesh sizes of sieves were 45, 53, 75, 106, 125, 150 and 180 μm, and shaking time was 15 minutes.

Some workers[85] have reported a build up of electrostatic charges on PVC particles during dry-sieve analysis. This causes the resin particles to agglomerate hence giving misleading results. Wet sieve methods are often used to overcome this problem. A wetting agent which does not swell the particles and gives a good dispersion is used to enhance complete displacement of air in porous resins. However, subsequent complete drying of the PVC powder could be difficult. An alternative method may be to spray the PVC with anti-static agent in the dry sieve method.

3.4 Milling of PVC

Jet milling or fluid energy milling[105-107] offers a quick and simple means for reducing the average particle size of powders to micron size. The basic principle is that particles are entrained by a gas stream and accelerated to high velocities. They collide with one another and with the walls of the chamber resulting in fracture and reduction in particle size.

The mill used is shown in Fig. 10 and operating variables were as follows:

Grinding fluid : Nitrogen

Pressure of Grinding fluid : 60 p.s.i.g.

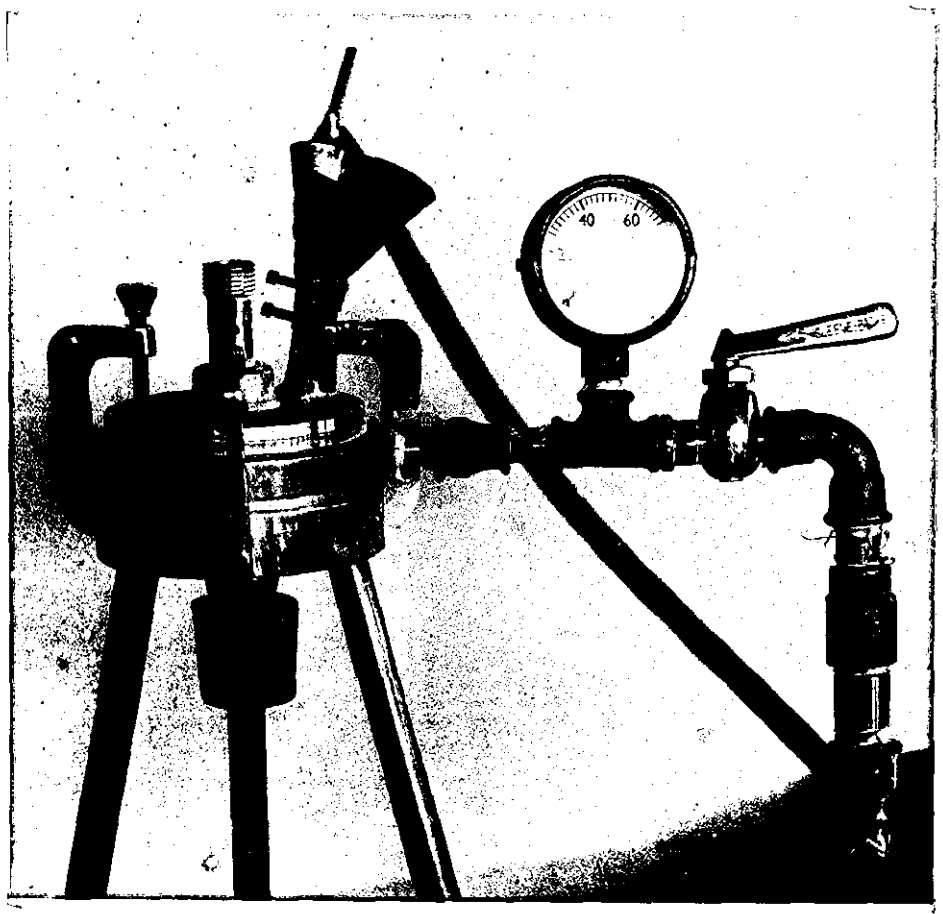
PVC feed rate : 20 - 75 gm/min

Liquid nitrogen has a boiling point of -195.8°C and therefore there is a much greater temperature gradient between it and an article immersed in it. Chilling the article should hence be much more rapid. There is also intimate contact between the exposed surface and liquid nitrogen and this should cause a more rapid chilling effect.

The glass transition temperature of PVC is about 84°C and it was therefore thought that if the material is cooled to much lower temperatures by liquid nitrogen, it would become brittle and easily shattered even by gentle grinding. Any changes in particle shape, surface characteristics and size distribution can then be studied.

A simple experiment was therefore designed as follows:
About 10 gm of PVC resin and seven steel balls (∿ 5 mm diameter) were placed in a stainless steel tube 25 mm diameter and 10 mm long. The top had a screwed cap with a long handle (160 mm long). It was then immersed in a Dewar flask filled with liquid nitrogen and the handle connected to an arm of a Griffin mechanical vibrator. See Fig. 11.

Fig. 10: Jet mill. Interior of grinding chamber is shown in the lower picture.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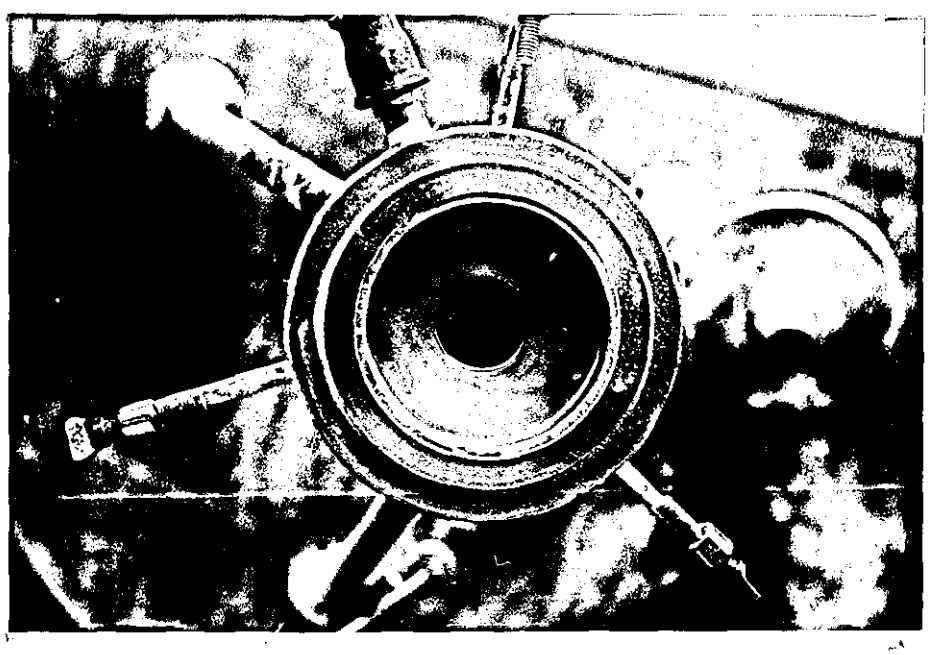


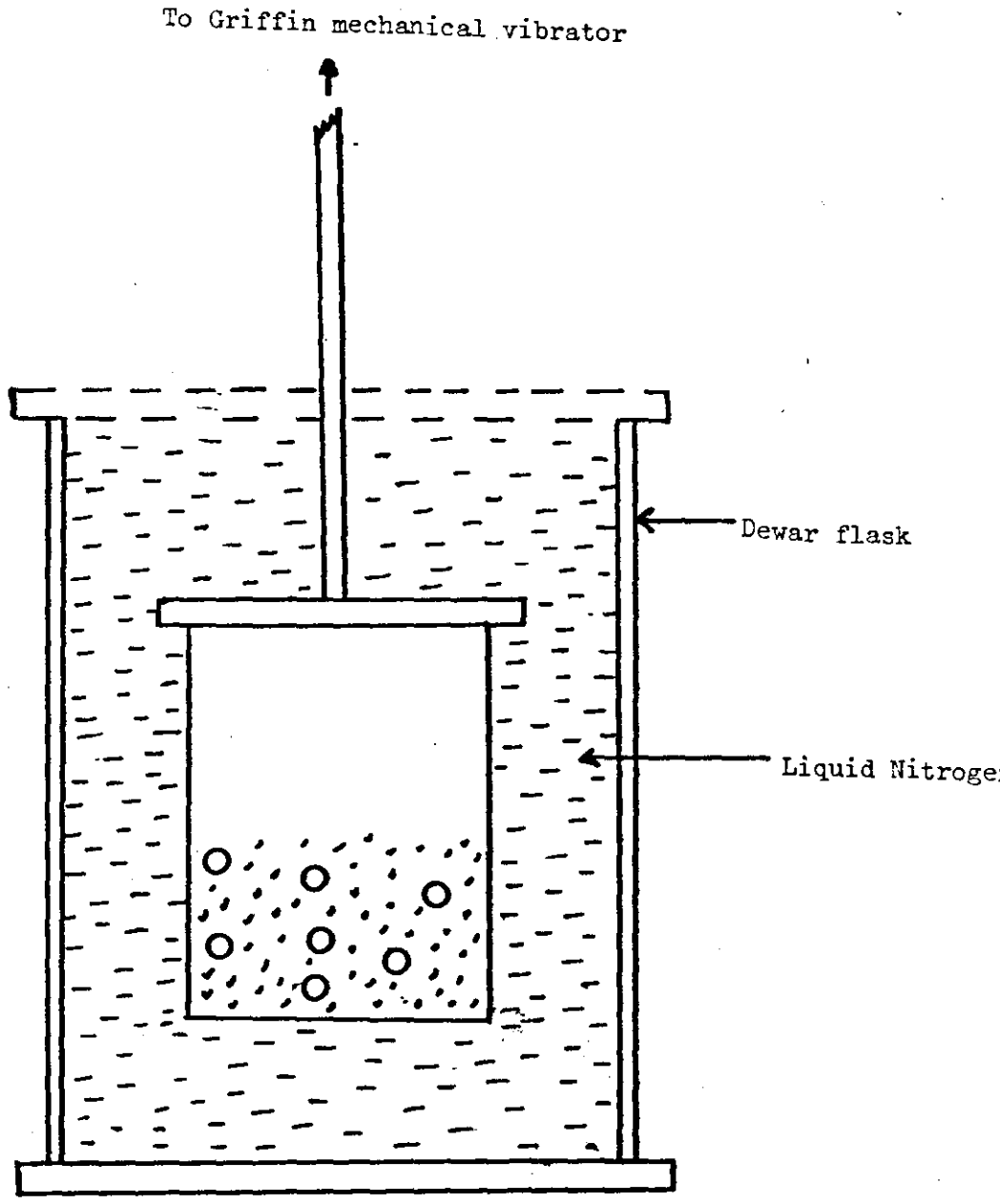

To Griffin mechanical vibrator
Dewar flask
Liquid Nitrogen

Fig. 11

After it was left standing for about half an hour to attain thermal equilibrium, it was then vibrated at the maximum speed setting for one hour.

3.5 Differential Thermal Analysis (D.T.A.)

Differential thermal analysis (D.T.A.) is a technique used to characterise a material in terms of a change in its properties with temperature. Matlack and Metzer[108] have used it to distinguish between PVC formulations and also to observe the effects of the ingredients in a rapid and reliable manner.

Most substances undergoing physical or chemical changes involve changes in heat content. These changes in heat content may be detected as differences in temperature between the material and its environment. D.T.A. measures the heat changes between the material under investigation and an inert standard. Using linear heating rate the sample and the inert reference are heated and the temperature difference between them is monitored by thermocouples placed beneath them.

The resulting curve called a thermogram or thermal spectrum, can provide information on the temperature, heat and rate of transformation and also quantitative measurements. Basically there are three types of transformations: endothermic, exothermic and second-order or glass transition. Glass transition involves motion of short-chain segments in the amorphous region and is related to the brittleness of a polymer.

The Du Pont 900 Thermal Analyser fitted with a D.S.C. cell was used. Operation of the instrument is described in the manufacturer's handbook[109]. The conditions selected are given in Table 10. Prior to each run the equipment was cooled down to -50°C in order to obtain a flat or regular baseline before the transition temperature of the blends. Immediately after each run, which was carried to 200°C, the

equipment was rapidly chilled with liquid nitrogen and the D.T.A. curve determined again.

Five determinations were made for each blend and the average reported.

Table 10

Sample weight	:	12 ± mg
Heating rate	:	20°C/min
Inert reference	:	Empty aluminium pan

3.6 Assessment of Processability of blends

The ease of processing the blends was assessed with a Davenport capillary rheometer and Brabender Plastograph. Their use and principles of operation are outlined below.

3.6.1 Capillary Rheometer

Several instruments are available for studying the flow properties of fluids. Wazer et al[110] have made a detailed study of these instruments. The most common types are capillary and rotational rheometers (or viscometers).

The basic principle of a capillary rheometer is that a sample heated to a specified temperature in a barrel is forced out through a capillary die. It is accomplished by either of two methods: a plunger is forced down into the barrel at constant speed and the required pressure measured for example, by a transducer; or a load is applied by means of weights or pressure of inert gas on the sample and the output rate measured.

The shear stress τ and shear rate $\dot{\gamma}$ are given by the expressions

$$\tau = \frac{R\Delta P}{2L} \qquad (1)$$

$$\dot{\gamma} = \frac{4Q}{\pi R^3} \qquad (2)$$

where R = radius of capillary

ΔP = pressure drop across the capillary length

L = length of capillary

Q = volumetric flow rate

Equation (1) may be corrected by using the well known Bagley end-correction[111], in which L contains a term for the entrance region. Equation (2) may be corrected for the pseudoplastic behaviour of the plastic melt using the Rabinowitch equation[112]. The corrected equations are thus

$$\tau^1 = \frac{R\Delta P}{2(L + NR)}$$

where NR is the length correction expressed as a function of the radius, and

$$\dot{\gamma}^1 = \frac{[(3n + 1)/n]Q}{\pi R^3}$$

where n is the slope of the curve of log τ versus log $\dot{\gamma}$. The factor n changes and has to be determined for each measured value of shear stress.

However, in view of the fact that only a comparison of relative values of flow properties of the PVC blends is required in this study no corrections have been applied.

In this work a Davenport capillary rheometer was used to study the melt flow characteristics of the PVC blends. The Davenport rheometer essentially consists of four parts:

(1) a heating chamber

(2) a system to control the temperature of the heating chamber

(3) a motor-driven piston

(4) a pressure measuring system.

Fig. 12 is a front view of the Davenport rheometer. The heating chamber contains a heat conducting barrel 24.13 cm long, with a nitride hardened bore. The temperature control system consists of a resistance thermometer forming one arm of an AC Bridge circuit. The output of the bridge circuit is fed into a phase sensitive amplifier controlling the energy to the heater. An electronically controlled, variable speed DC motor, drives the piston. The pressure was measured with a Pye-Ether pressure transducer mounted just above the capillary and connected to a Servoscribe millivolt recorder. Head effects are therefore negligible.

The capillary die used had a diameter of 2 mm and length of 20 mm. Barrel temperature was 180°C.

The powder blends were charged into the rheometer, compressed and held for five minutes to attain thermal equilibrium. Starting with the slowest piston speed, that is lowest shear rate, the plunger was forced down the barrel. When the extrusion pressure reached a steady value the piston speed was increased and the procedure repeated until the piston was stopped by the downward-travel limit switch.

For each required shear rate the corresponding piston speed was calculated from the equation

$$\dot{\gamma} = \frac{X}{16.5326\ R^3}$$

where X is the piston drive speed (cm/min) and R is the radius of the capillary die (cm).

Three measurements were made on each blend to ensure reliability of data and the average taken. Graphs of log extrusion pressure against log shear rate were then drawn with the results.

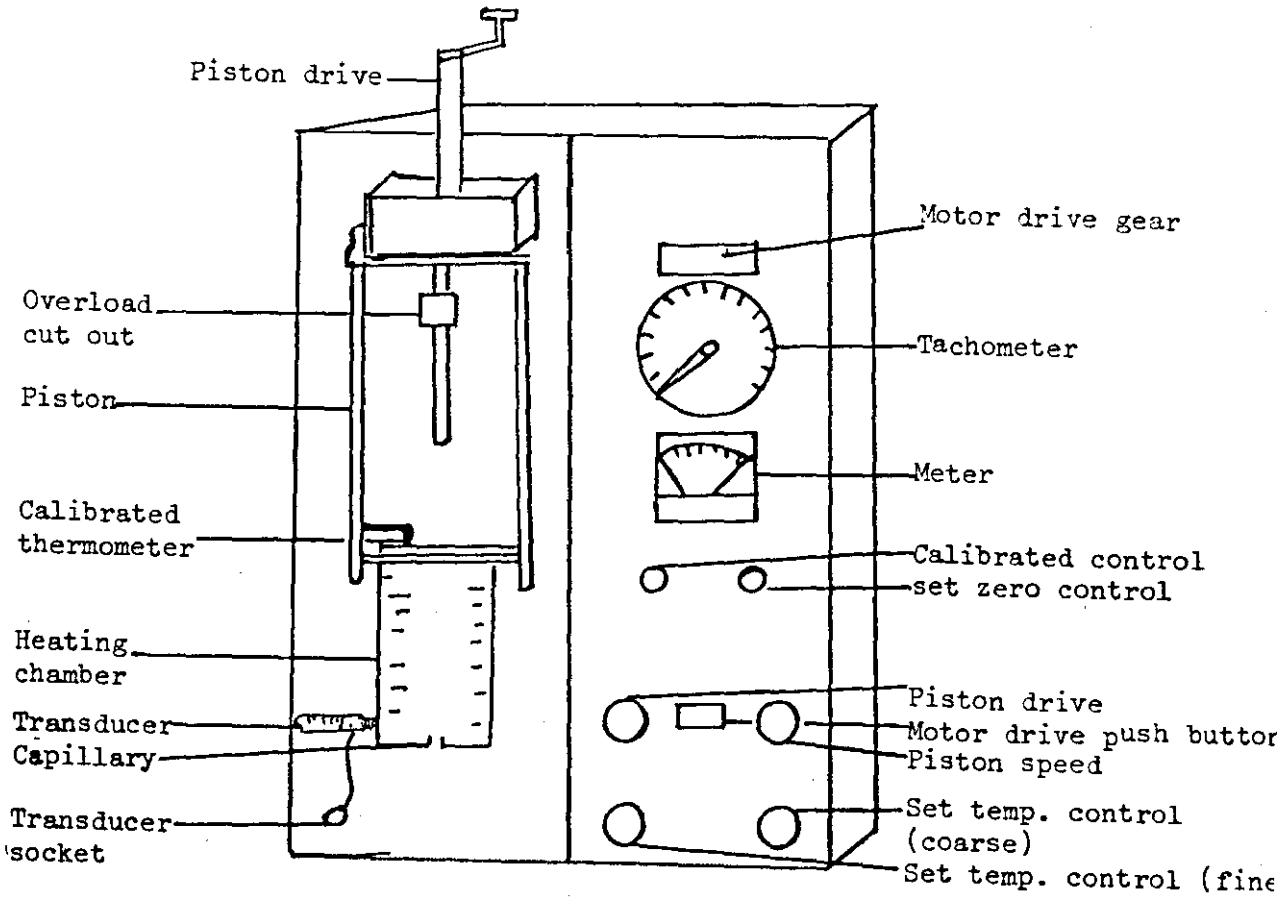


Fig. 12: Front view of Davenport Rheometer

3.6.2 Torque Rheometer

The torque rheometer used is the Brabender Plastograph made by Brabender Co. of Duisburg, West Germany. The Brabender Plastograph is a small laboratory internal mixer and simulates actual processing conditions encountered in practice. It may be used to evaluate stability and processability of PVC formulations and generally for quality control and in developing formulations.

It consists of a roller-type mixing head equipped for jacket and stock temperature measurements, and made up of a dual chamber in which there are two sigmoid counter-rotating blades driven by a dynamometer. A differential speed between the two rotors maintains interchangeable flow between the chambers. A motor drive assembly applies a torque to the test material which is confined in the chamber and worked between the blades and chamber walls.

The motor and dynamometer housing are mounted on bearings which allow them to rotate in the opposite direction to the torque applied in the mixing chamber. This rotation is restrained and balanced by a system of weights and levers so that the torque level at any instant is recorded on a graph. The movement of the levers is dampened by an oil dash pot and the degree of damping can be regulated.

A thermocouple probe inserted through the base of the mixing chamber is connected to a Smith RE511 Potentiometric Recorder to record continuously the temperature of the polymer compound. Further detailed description of the Brabender Plastograph are available in the literature[113,114].

To obtain rapid filling of the chamber especially as fusion rate was being determined, a quick loading chute was fitted on the mixing head. Sufficient polymer should be added to the mixing cavity to completely fill it after melting is complete.

A typical torque-time curve for a rigid PVC formulation is shown in Fig. 13. When the PVC blend is pressed into the mixing chamber, the torque rises rapidly to a peak as the compound fluxes (A). As it is being distributed inside the vessel the torque decreases and at the minima, mixing is completed. Gelation (or fusion) then starts (B) with the consequent increase in torque. Fusion is complete at the next peak (C) and the PVC becomes a melt. The torque then falls until a more or less constant value is attained (D). The time between the two peaks is known as fusion time and is taken as a measure of the rate of gelation. The fusion time can be used to classify efficiency or predict the processing behaviour of different formulations.

Generally the torque decreases as the fusion time increases. This may be explained in terms of lubricant effect. With little

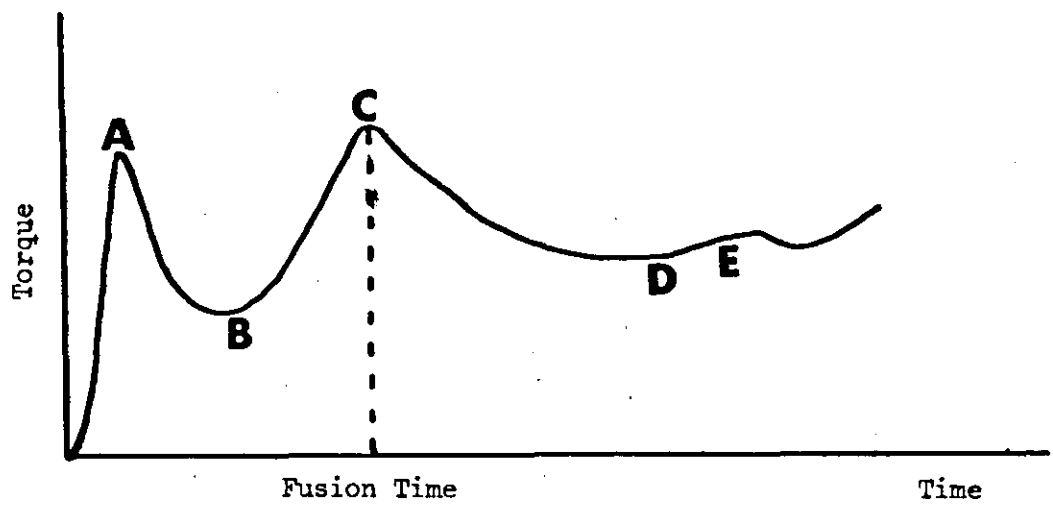


Fig. 13: Typical torque-time curve for a rigid PVC compound

lubricant we have minimal slippage giving an increase in torque whilst the work heat generated adds to readiness to gel. With high lubricant content, slippage reduces the torque and fusion time is increased as less work heat is evolved and polymer/polymer contact decreased.

After a time, which is variable depending on the test conditions for a given formulation, the torque once again rises as the resin starts to cross-link (E). This is accompanied by increased discolouration and copious evolution of hydrogen chloride. This is the degradation point and the time from the first peak is a measure of thermal stability under dynamic shear conditions. Complete degradation of the melt starts as soon as the stabiliser effect is worn off. A final rise of the torque is caused by complete charring of the melt.

A number of workers have studied the effect of experimental conditions on the Brabender curves. Mathan[115] showed that the effects of bowl temperature and rotor speed can be represented as a straight line on log log axes. He also showed that a minimum sample weight is required for the test.

The formulation, rotor speed, mixer temperature and sample weight, according to Schramm[116] affect fusion time. He emphasised that the sample weight chosen should be greater than a certain minimum value.

According to Blake[117] fusion of plasticised thermoplastics in the Brabender depends on several factors including sample weight. Hecker and Cohen[43] did not find much change in fusion rates when compounds are run at high temperatures. On using lower temperatures and a small bowl, they found that temperature increase, ram weight increase and rotor speed increase all led to increase in fusion rate. Touchette et al[44] concluded from their work on fusion rates of plasticised PVC that the results obtained are very dependent on the test conditions.

In view of all these, careful consideration had to be given to

the test conditions. Lower mixing chamber temperature and rotor speed were chosen so as to be able to more easily distinguish between the fusion time of the blends. Taking the relative density of the PVC composition to be approximately 1.39 (determined from a compression moulding of the formulation with a gradient column) the amount of resin required to fill the 28 ml chamber after melting would be 39 gm. This amount of material could not all be forced through the loading chute into the mixing chamber in a reproducible and repeatable manner. Hence the sample weight had to be reduced to a value that could be loaded very quickly and with minimum difficulties. 30 gm was found suitable. The test conditions chosen therefore were as follows:

Temperature of mixing chamber	:	140°C
Sample charge	:	30 gm
Rotor speed	:	20 r.p.m.
Load on ram	:	4 kg

In order to obtain reproducible and accurate reaults all the runs were carried out under similar conditions. For the first run of the day, the instrument was left at 140°C for at least one hour to ensure thermal equilibrium has been reached. Thereafter for each run 15 min. was found sufficient. With the motor running and the temperature recorder started, the sample was added as quickly as possible through the chute. The ram with the 4 kg load was immediately forced down on the chute and the chart drive started. The whole operation was done within 30 sec.

CHAPTER IV

RESULTS AND DISCUSSION

The results obtained by the experimental techniques employed in studying the morphology, characteristics and processability of the powder blends are reported in this chapter. For convenience the results will be discussed under the following headings: Temperature change during blending, Distribution/dispersion of additives, Effect of mixer discharge temperature on density, Effect of blending on the glass transition temperature, Effect of blending on particle shape, size distribution and internal structure and Evaluation of processing behaviour.

The discussion will then be followed by conclusions from the work on powder blending, using the equipment described.

4.1 Temperature change during blending

It was explained in section 1.6 that the high speed motion of the rotor blades leads to the generation of frictional heat which raises the temperature of the blend. Changes in temperature with mixing time for the two formulations (A) and (B) are shown in Figs. 14-16.

The shape of the curves of temperature rise with time for both polymers is similar. However, the rate of temperature rise is higher for PVC-M than PVC-S. More frictional heat is generated in the mass polymer and hence a more rapid rise in temperature occurs because the surface is rougher as there is no 'skin' or membrane on the surface and the particles have a greater regularity of shape and narrower particle size distribution.

The temperature of the blend rises very rapidly for the first five minutes, eases off for the next three or four minutes and then

begins to rise again. Above 140°C pink colouration sets in indicating degradation of the PVC powders is taking place. The effect of TBLS and calcium stearate on the temperature rise of the mix is evident from the graphs (Figs. 14 and 15 No.1 & 4). Calcium stearate retards frictional heat while TBLS promotes interparticle friction. The effect of calcium stearate is more pronounced with PVC-S than PVC-M. Similar observations have been reported by other workers[118-122] and they have also shown that the effect of each additive is specific depending on type and concentration.

When calcium stearate is added to the blend at about 20°C before the final discharge temperature, the blending cycle is shortened by 2-3 minutes. It would be reasonable to expect a higher homogeneity where the TBLS and Calcium stearate have been added at the beginning of the blending cycle. It was noted in section 2.3 that attempts to commence blending with only PVC with additives to follow later were a failure. With PVC-S the motor tripped off after about 4 minutes with the blend temperature at 60°C. For PVC-M the mixing time was 10 minutes and the temperature of the mix 80°C. This suggests that the blending must start with one of the additives present or the friction between the particles and between the particles and the walls of the vessel would be too high and may even stop the circulating movement of the powder. These temperatures of 60°C and 80°C are suspect and should be treated with a great deal of caution. The bulk of the mix had caked up and there was no longer a vortex mixing action of the powder particles. The thermocouple is simply indicating the temperature of a few particles touching it. Evidence of localised heating was obtained from traces of pink coloured particles and highly flaky material stuck on the walls of the mixer.

In formulation (B) enough frictional heat could not be generated

to raise the temperature of the mix over 100°C. Therefore the mixing vessel was heated with steam. It was observed that about 15% of PVC-M blend stuck to the walls of the mixer. This could mean a substantial loss in large commercial productions. PVC-M has no 'skin' and is more porous hence easier to densify and gell. Therefore with a preheated vessel it should be no surprise to find a layer stuck to the walls of the mixer. This suggests that the rotor blades should be redesigned to give a better sweeping action.

Table 11 summarises the time it takes the blends to reach certain temperatures.

Table 11

Type of Blend	Time (min) taken to reach:			
	80°C	100°C	110°C	120°C
PVC-S + TBLS	8	10½	11½	13
PVC-S + TBLS + Calcium Stearate	9	13	15	16
PVC-S + TBLS + Calcium Stearate*	-	-	13	15
PVC-S + Calcium Stearate	11	16½	18	19½
PVC-M + TBLS	7	10	12	14
PVC-M + TBLS + Calcium Stearate	10	13½	16	18
PVC-M + TBLS + Calcium Stearate*	-	-	13	15½
PVC-M + Calcium Stearate	8½	13½	16	18½

* Added later

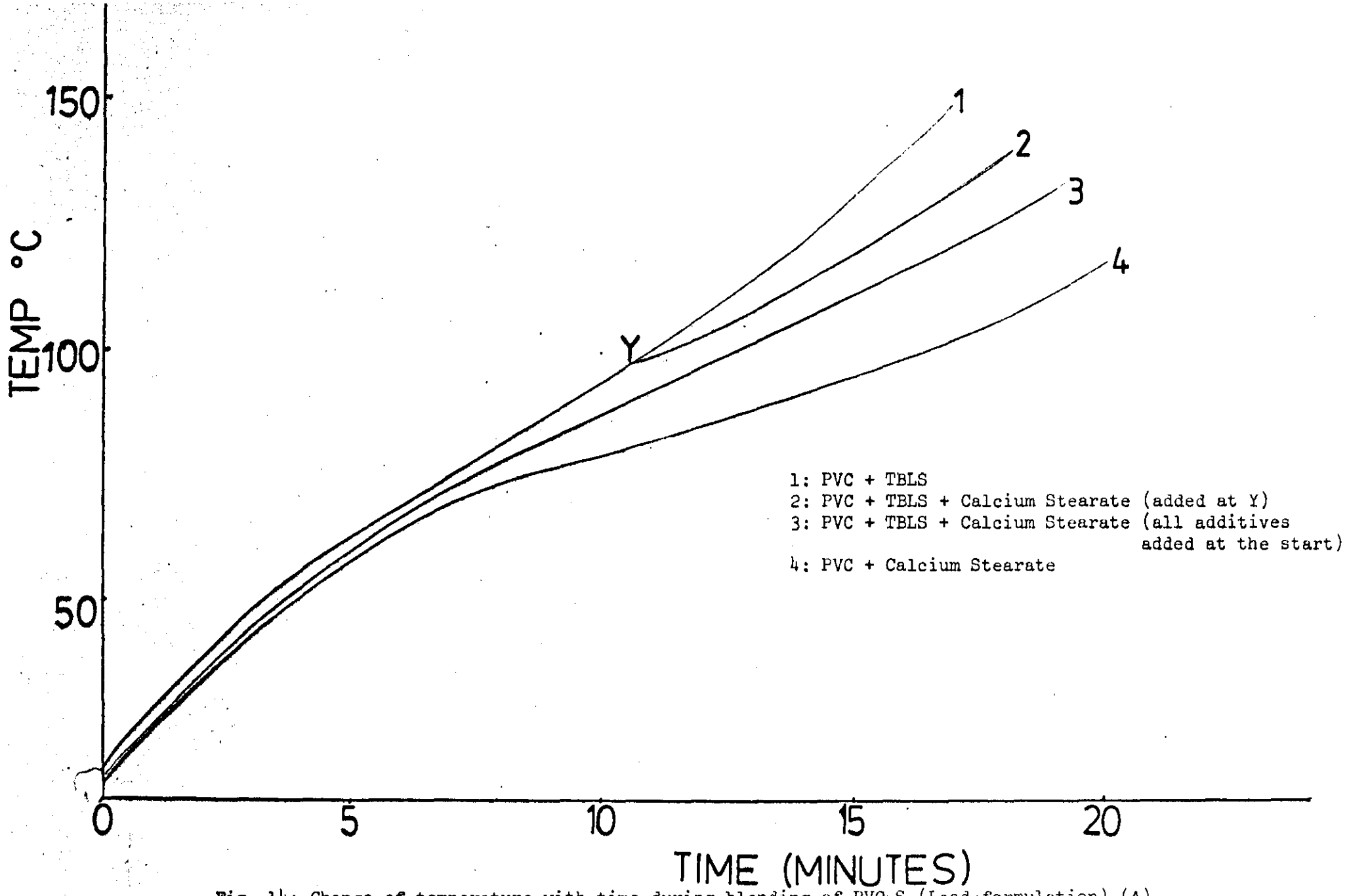


Fig. 14: Change of temperature with time during blending of PVC-S (Lead-formulation) (A)

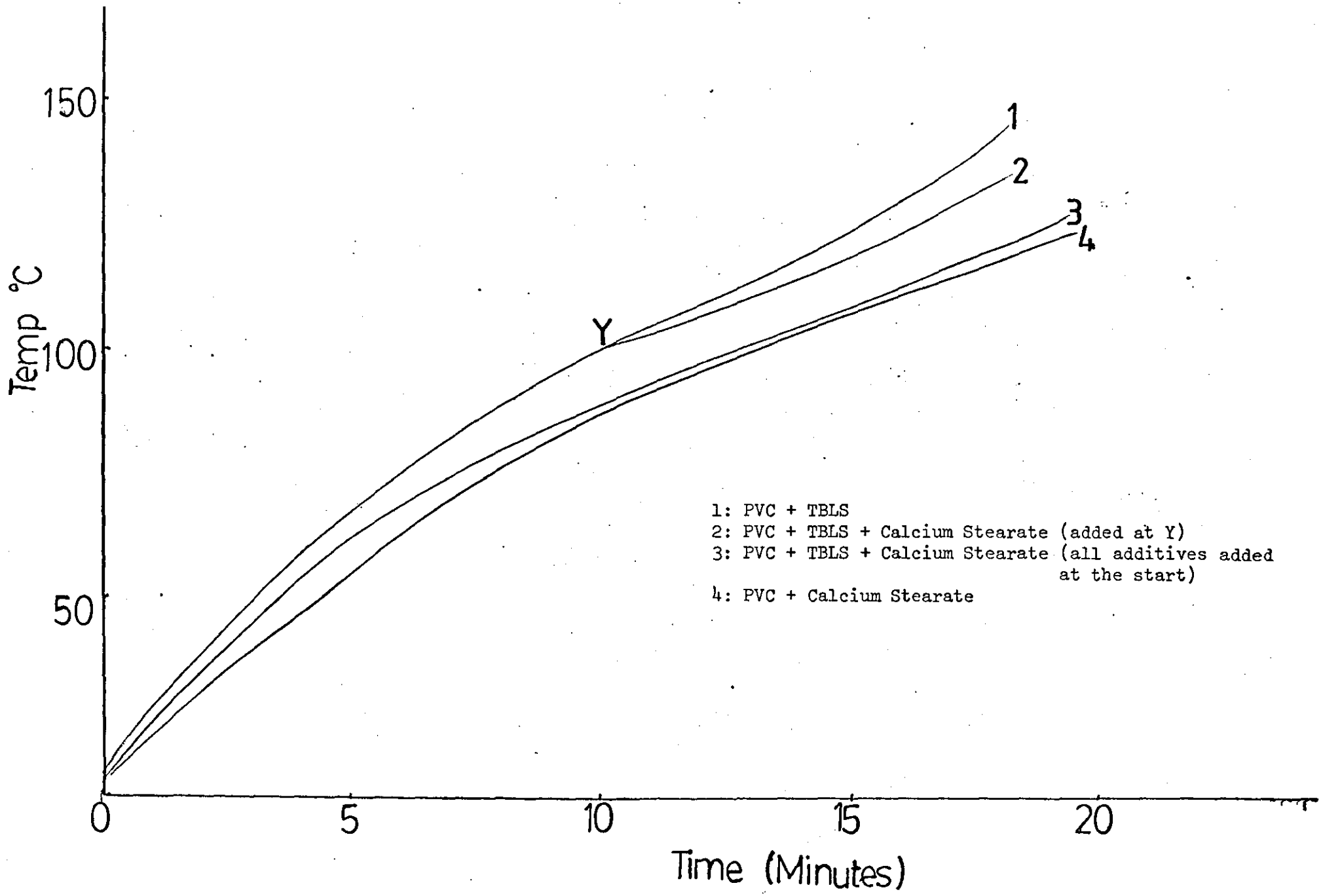


Fig. 15: Change of temperature with time during blending of PVC-M (Lead-formulation - (A))

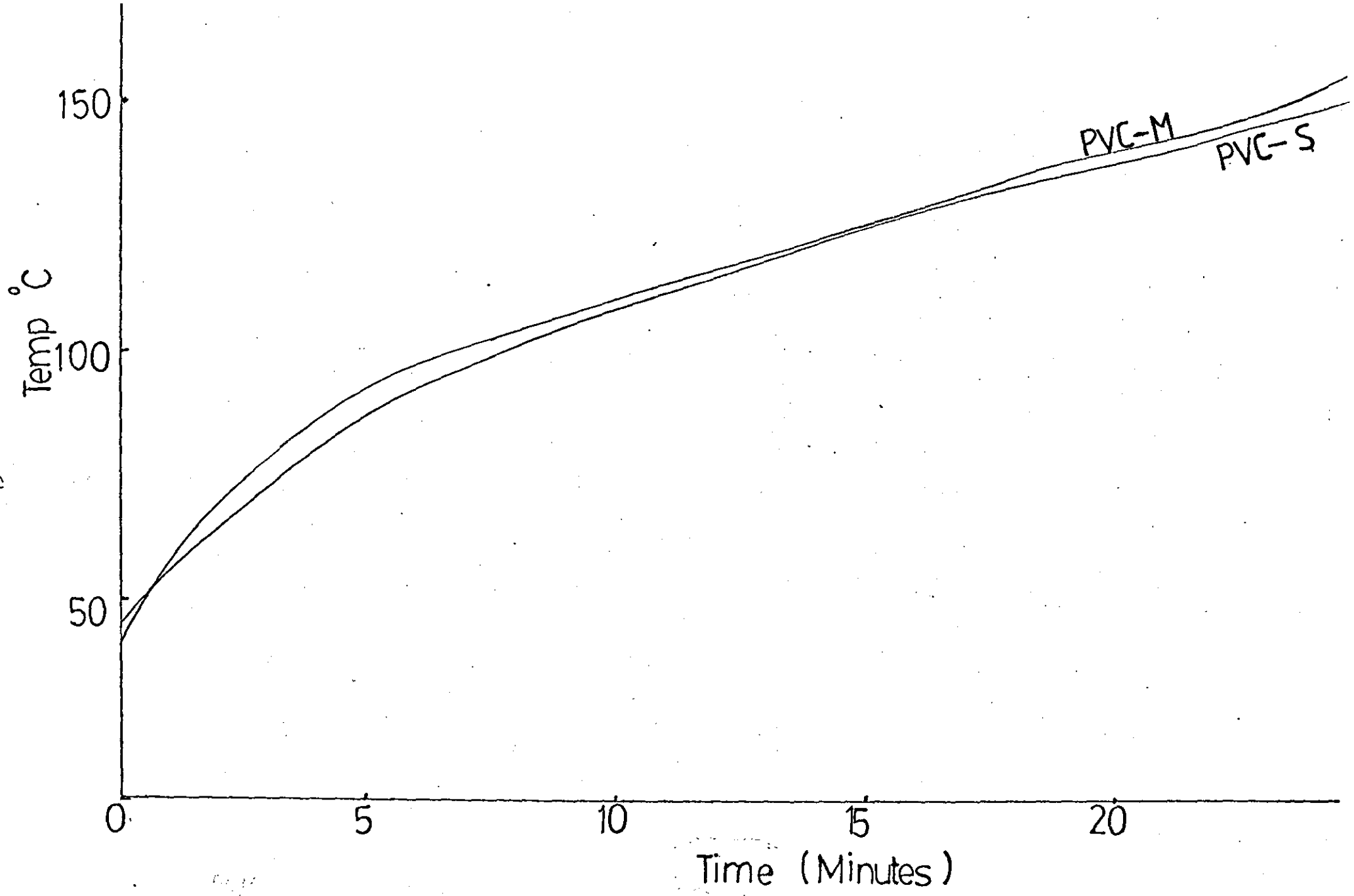


Fig. 16: Change of temperature with time during blending (Tin formulation - (B))

4.2 Distribution/Dispersion of Additives

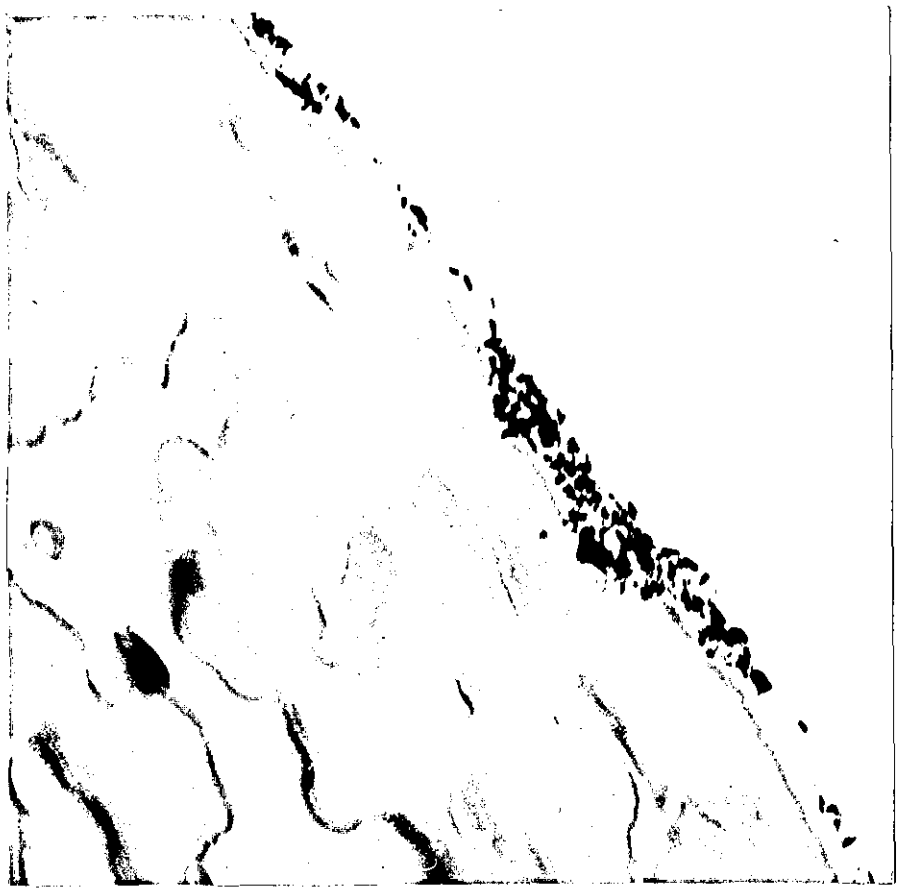
Ultramicrotomed sections of PVC powder blends discharged at 80°, 110°, 120° and 140°C were examined with a transmission electron microscope. In the lead-formulation blends there was no evidence of the solid additives being absorbed into the resin particles whether of mass or suspension type. Typical examples are shown in Figs. 17 and 18 which are respectively transmission electron micrographs of PVC-S and PVC-M powder blends discharged at 80° and 140°C. The additives are clearly seen on the surface of the particle.

With tin-formulation the situation is different. The liquid tin stabiliser is absorbed into the polymer. Figs. 19 and 20 show transmission electron micrographs of ultra-microtomed sections of tin blends discharged at 120°C. No layer of additives is seen on the surface or edge of the particles as in Figs. 17 and 18. The interaction between the tin stabiliser and PVC was further examined by thermal optical microscopy - a method that has been used for studying polymer-plasticiser interaction[87-89]. In Figs. 21 and 22 it is observed that the PVC particles become transparent as they are penetrated by the tin stabiliser. Comparing Fig. 21 and Fig. 22, the absorption of the stabiliser is faster in PVC-M than PVC-S. For instance, at 130°C PVC-M particles appear to go into solution (Fig. 22F). This can be explained by the fact that the mass polymer has no skin, is more porous and has a uniform particle size distribution and shape. Particles of approximately the same diameter and shape should have the same rate of absorption of stabiliser.

The result of a similar experiment with DOP plasticiser is shown in Figs. 23 and 24. A more detailed study of PVC-plasticiser interaction can be found in the papers by Anagnostopolous et al[89] and Khama[123].

Fig. 17: Transmission electron micrograph of ultramicrotomed sections of PVC-S powder blends (lead formulation) discharged at (a) 110°C, (b) 140°C, showing additives on surface of particles.

Magnification: x6,000



(a)

(b)

Fig. 18: Transmission electron micrograph of ultramicrotomed section of PVC-M powder blend (lead formulation) discharged at 80°C showing additives on surface of particle.

Magnification: x14,000

Fig. 19: Transmission electron micrograph of ultramicrotomed section of PVC-S powder blend (tin formulation) discharged at 120°C.

Magnification: x10,000

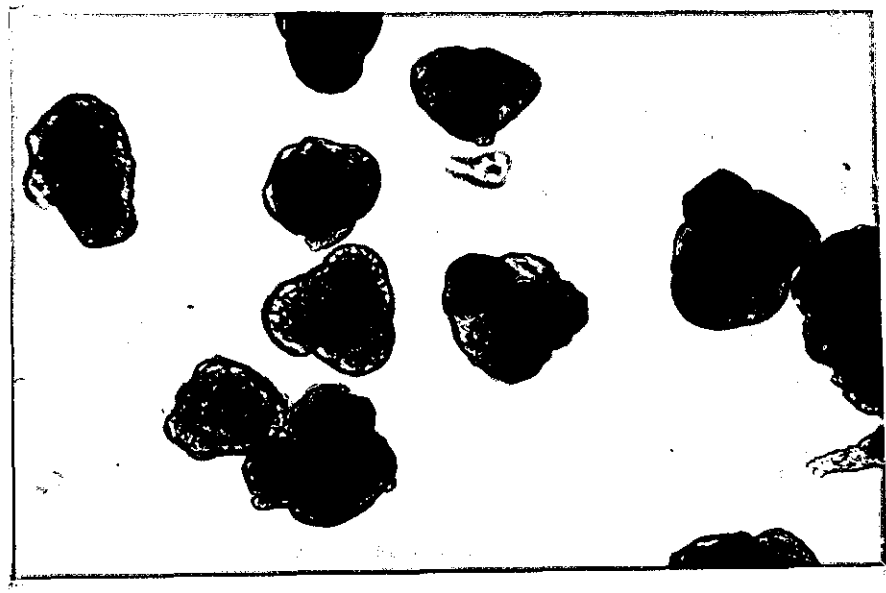
Fig. 20: Transmission electron micrograph of ultramicrotomed section of PVC-M powder blend (tin formulation) discharged at 120°C.

Magnification: x6,700

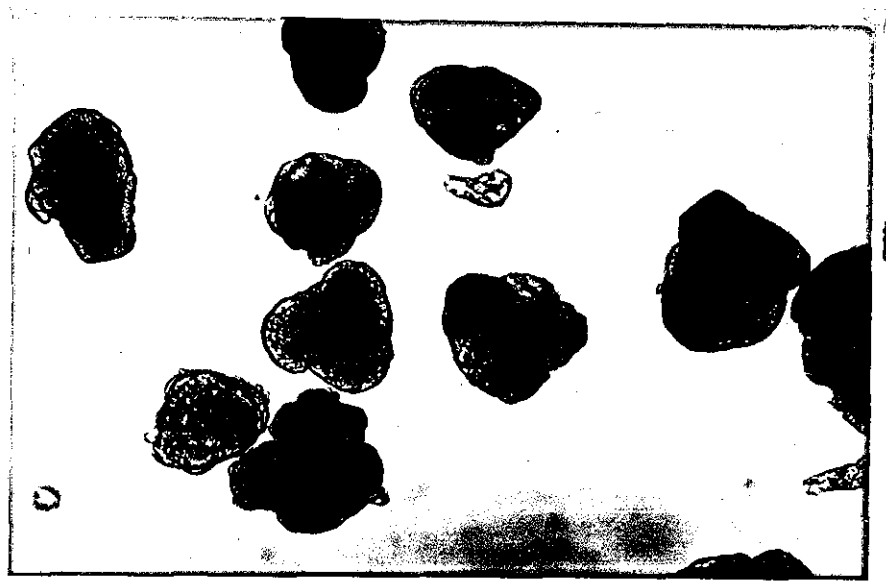
Fig. 21: Optical micrographs of PVC-S particles in tin stabiliser viewed by transmitted light at the following temperatures:

A : 50°C
B : 80°C
C : 100°C
D : 110°C
E : 120°C
F : 130°C

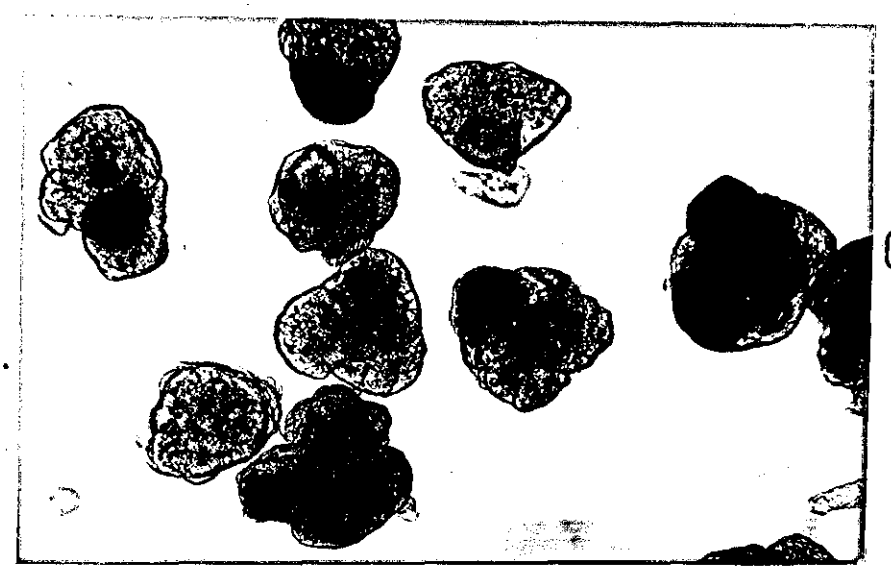
Magnification: x150



A



B



C

D

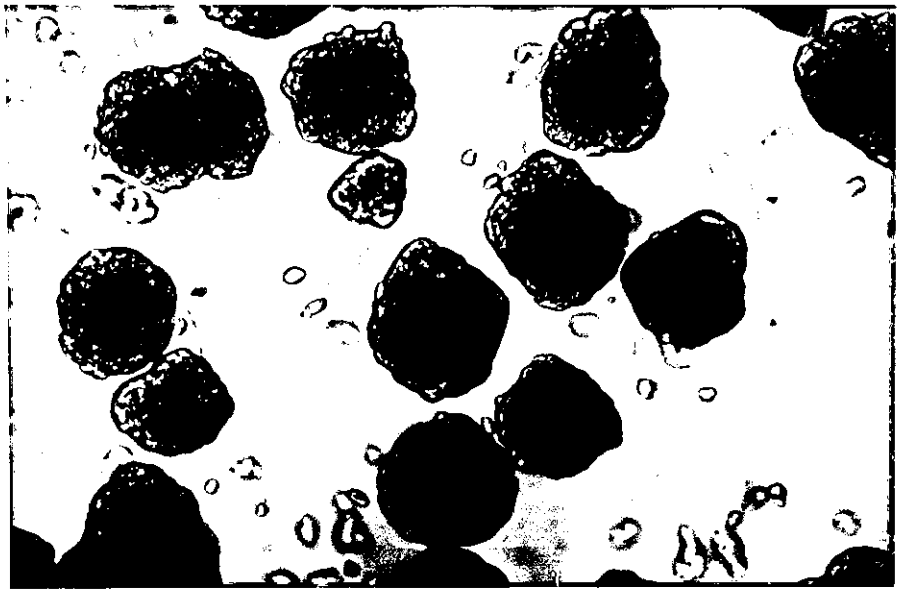
E

F

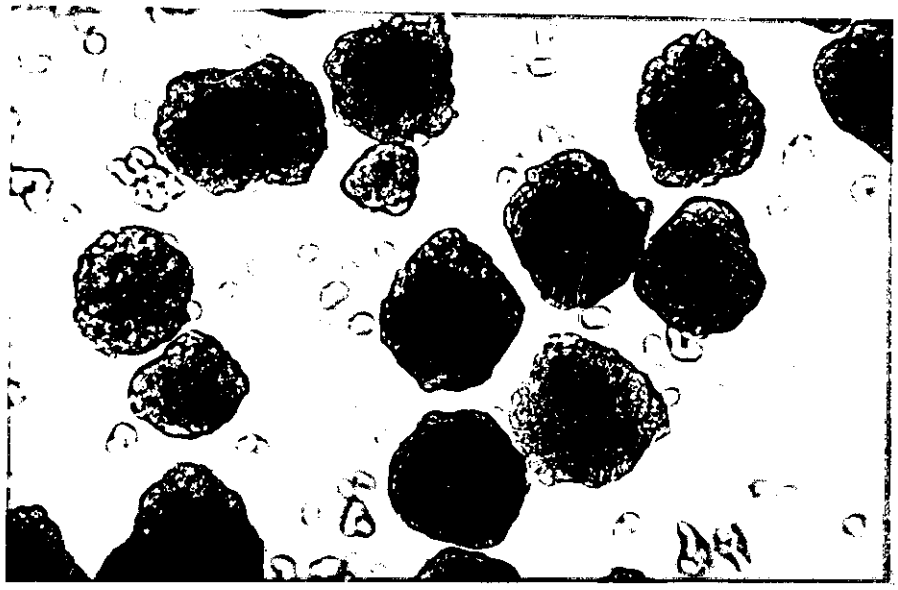
Fig. 22: Optical micrographs of PVC-M particles in tin stabiliser viewed by transmitted light at the following temperatures:-

A : 50°C
B : 80°C
C : 100°C
D : 110°C
E : 120°C
F : 130°C

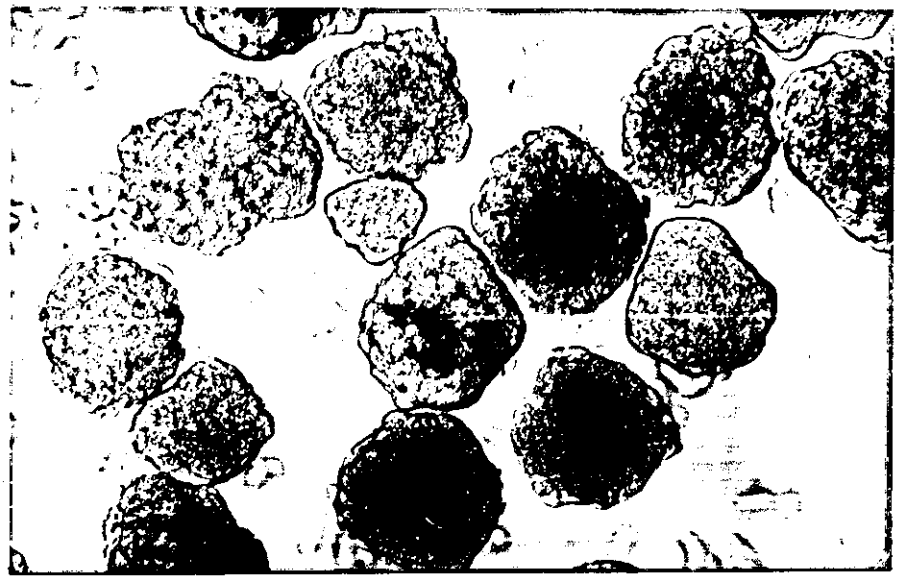
Magnification: x150



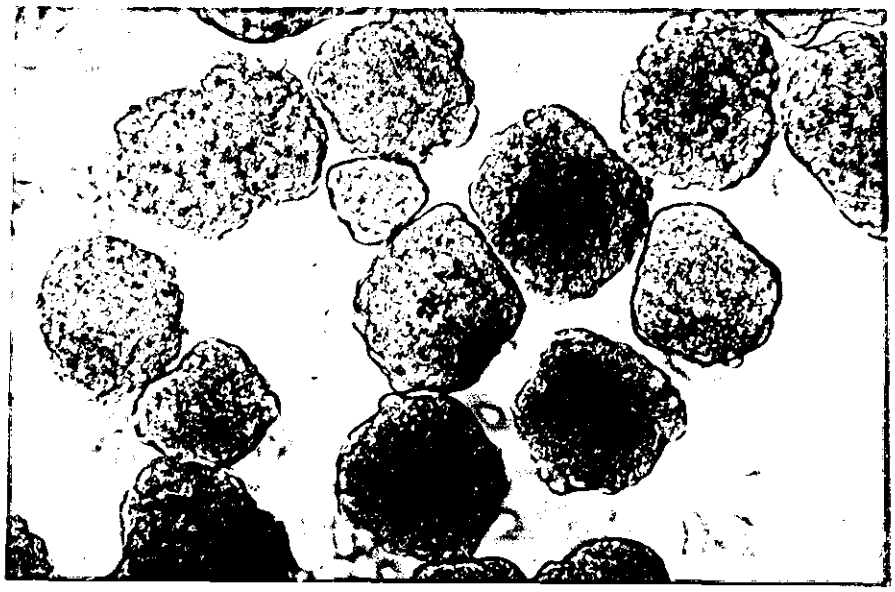
A



B



C



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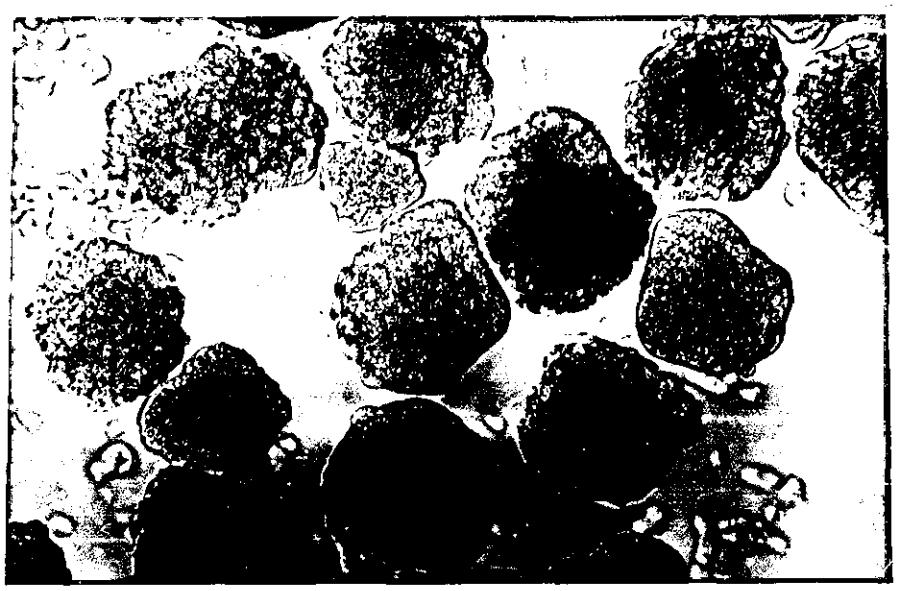


E

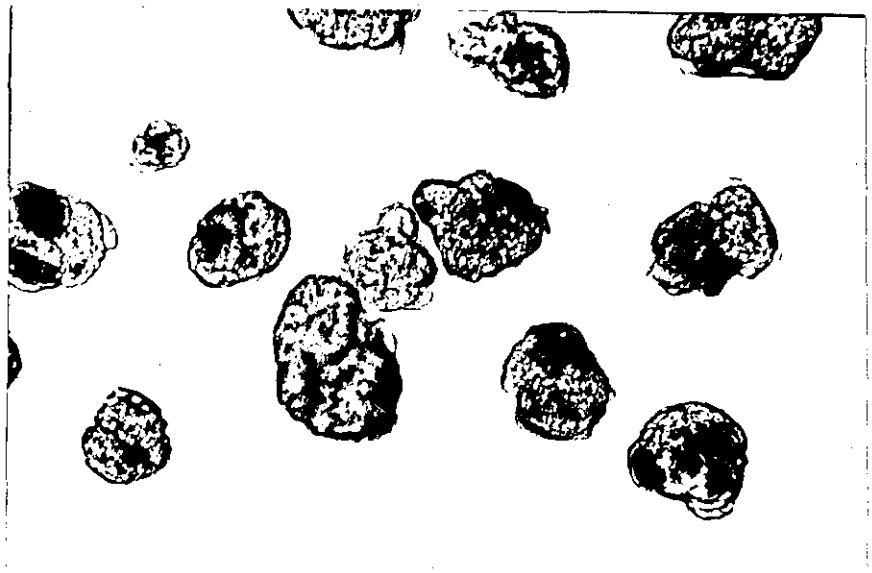
F

Fig. 23: Optical micrographs of PVC-S particles in DOP plasticiser viewed by transmitted light at the following temperatures:

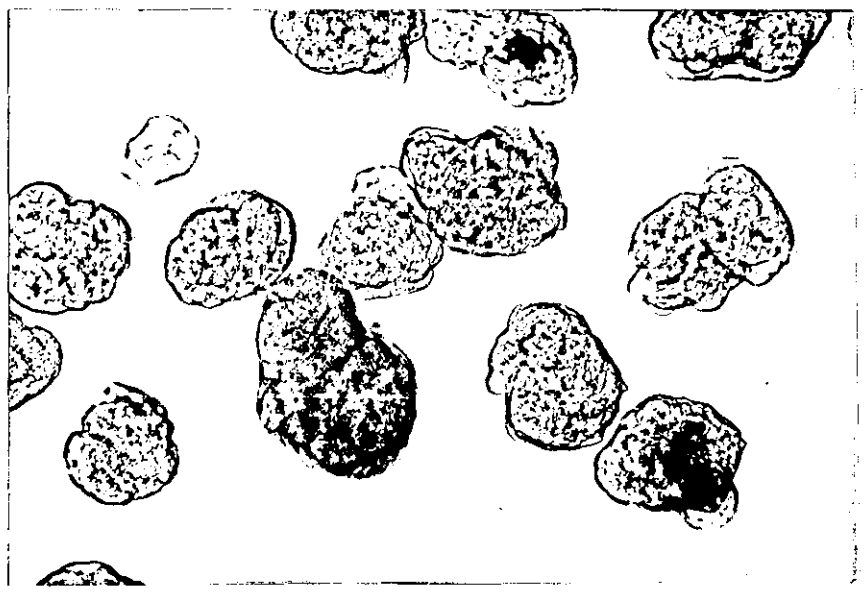
A : 50°C
B : 80°C
C : 90°C
D : 100°C
E : 110°C

Magnification: x150

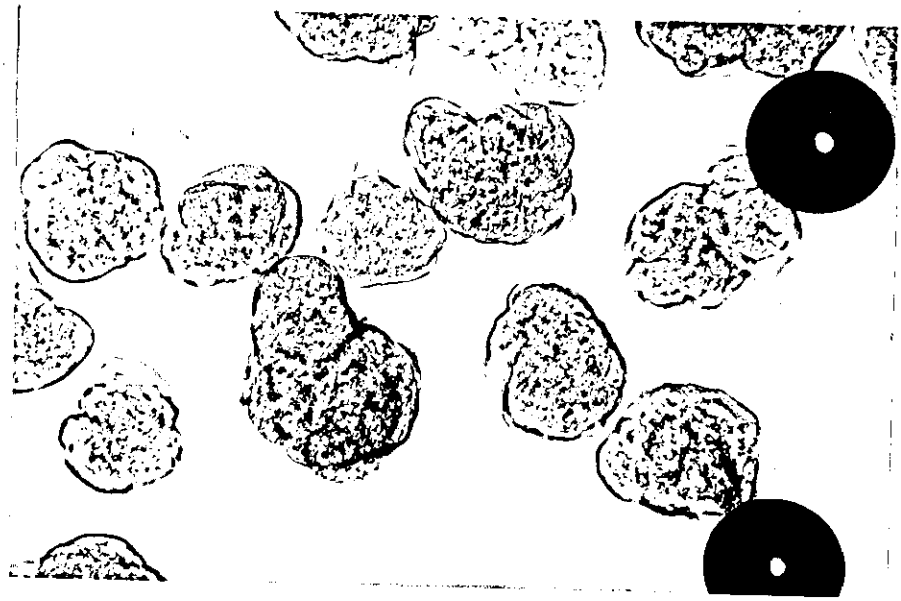
A



B



C



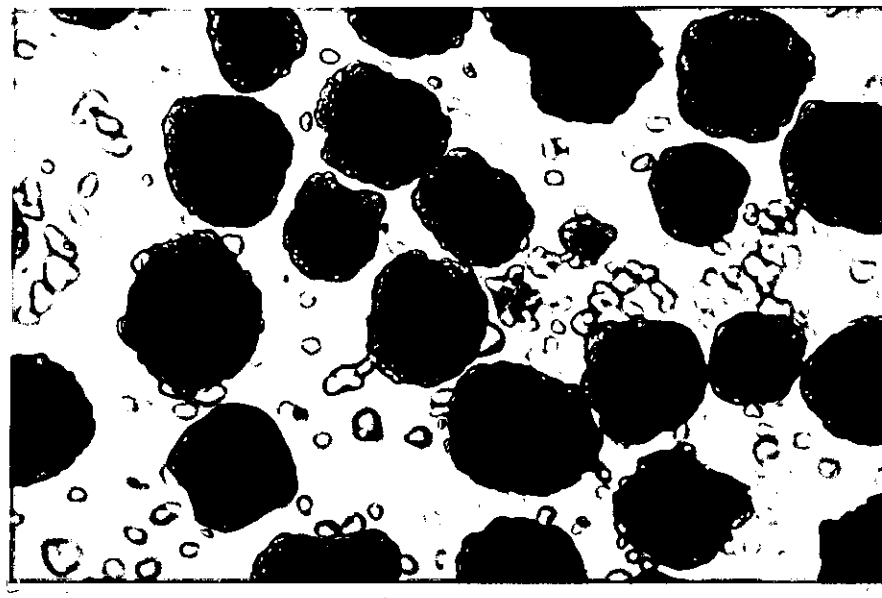
D

E

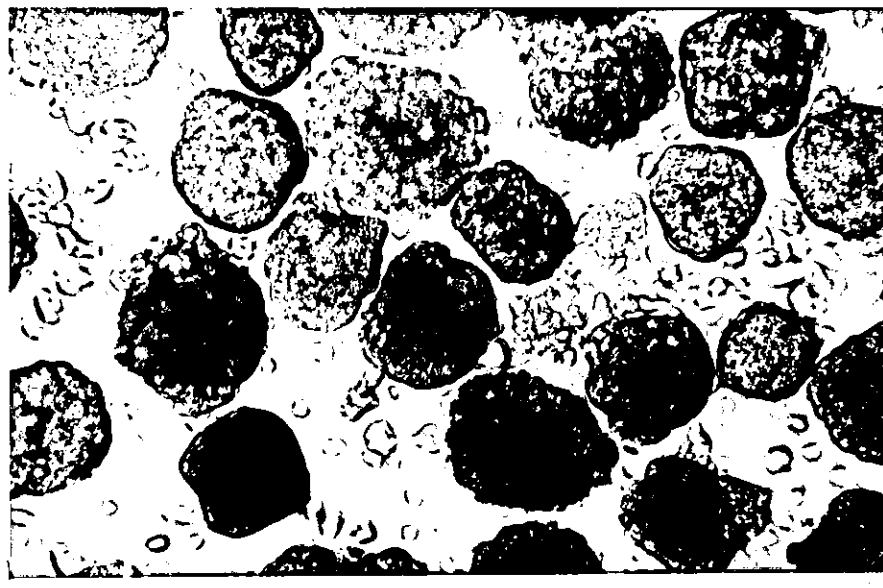
Fig. 24: Optical micrographs of PVC-M particles in DOP plasticiser viewed by transmitted light at the following temperatures:

A : 50°C
B : 80°C
C : 90°C
D : 100°C
E : 110°C

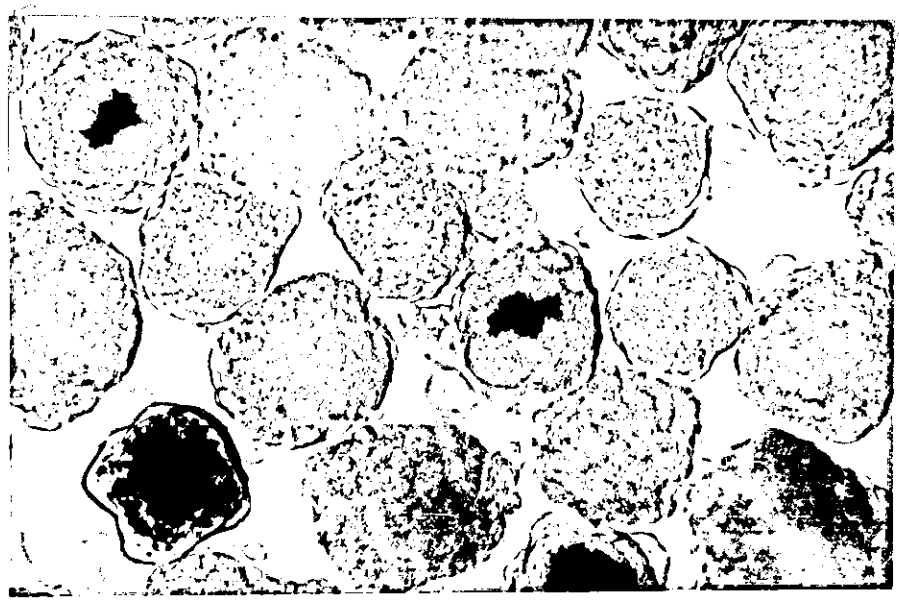
Magnification: x150



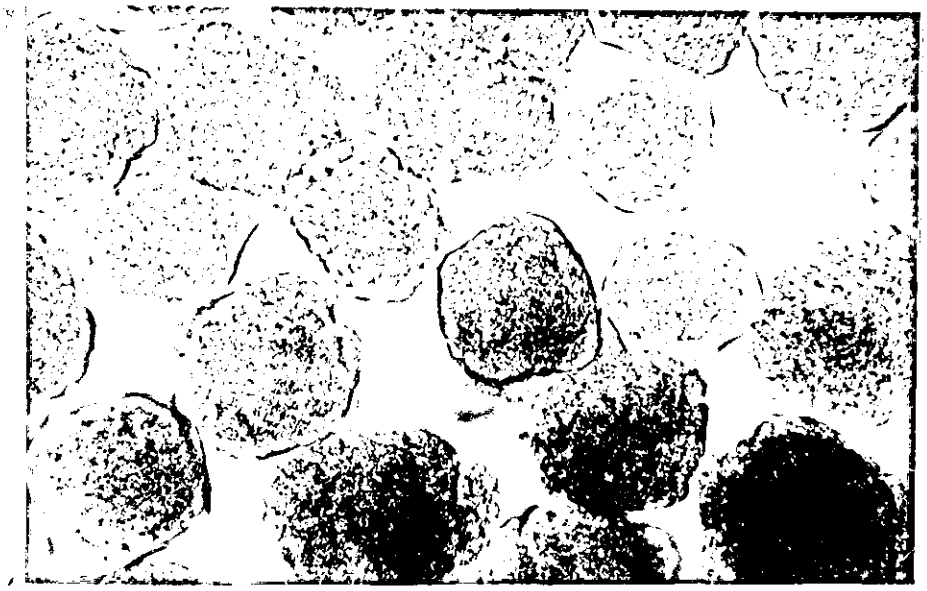
A



B



C



D

E

Swelling of the resin particles is observed in both cases though not as pronounced in that of tin stabiliser as in DOP. For example, the average increase in particle diameter of particles in the micrographs at 100°C is respectively 15% and 28% of PVC-S and PVC-M with tin stabiliser. With DOP the corresponding increase is 50% and 58%.

The calcium stearate used in this study has a melting point of 169-171°C. Because degradation was observed at temperatures above 140°C - shown by the appearance of pink colouration- the blending was not taken to such high temperatures. The lubricant therefore was not absorbed into the particles but merely coated the surface. It contrasts with the absorption of lubricant mentioned by Gale[118]. He used a fatty acid ester of low melting point, 64°C - glycerol monostearate (GMS).

4.3 Effect of Mixer Discharge Temperature on Density

Changes in density with mixer discharge temperature are shown in Fig. 25 and listed in Table 12. Higher discharge temperature yields powder blends of increased density. Bulk density increases very sharply at first, the value depending on polymer type and formulation. For example, lead formulation has a higher bulk density than tin formulation and PVC-M blend has higher density than PVC-S blend. The higher density values of PVC-M are due to the narrower particle size distribution and greater regularity of shape of the resin particles. The particle size distribution of the mass and suspension polymer are compared in Fig. 26. Figs. 27 and 28 are optical micrographs of the PVC particles viewed by reflected light.

The biggest increase in bulk density occurs between the start of the blending cycle and 80-90°C. This is because of the intense mixing action which causes the additives to be quickly dispersed in the mix.

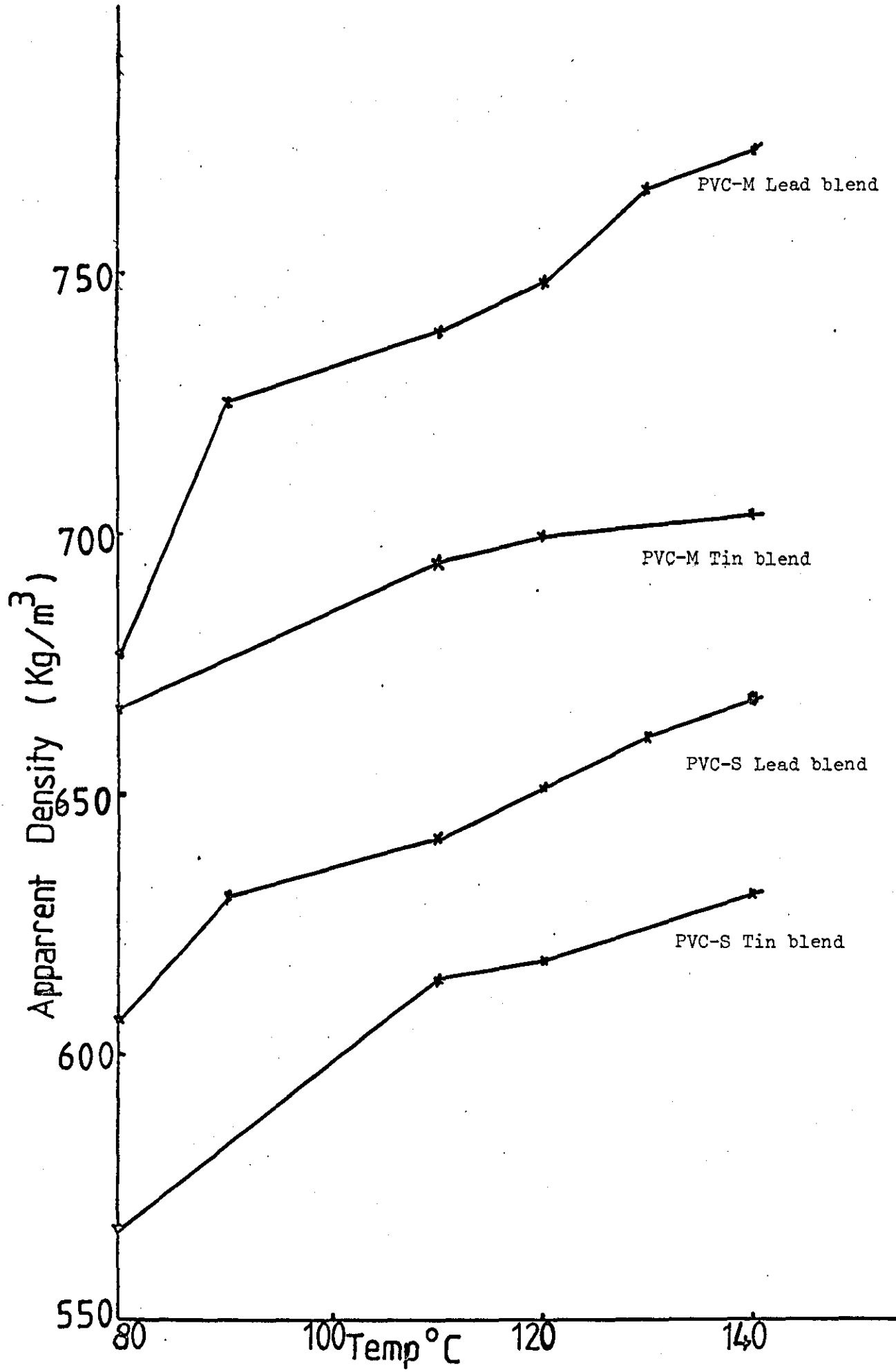


Fig. 25: Change in Apparent Density with blend discharge temperature

Table 12

Type of Blend	Discharge Temperature °C	Apparent Density Kg/m³	Bulk Density Kg/m³
Unblended PVC-S	-	551	613
Formulation (A)	80	607	674
	90	630	690
	110	641	715
	120	650	725
	130	661	736
	140	667	744
Unblended PVC-M	-	610	721
Formulation (A)	80	677	767
	90	725	780
	110	738	790
	120	747	799
	130	765	805
	140	772	815
Formulation (B)			
PVC-S	80	567	649
	110	614	675
	120	617	676
	140	630	684
Formulation (B)	80	667	752
PVC-M	110	694	757
	120	699	759
	140	702	763

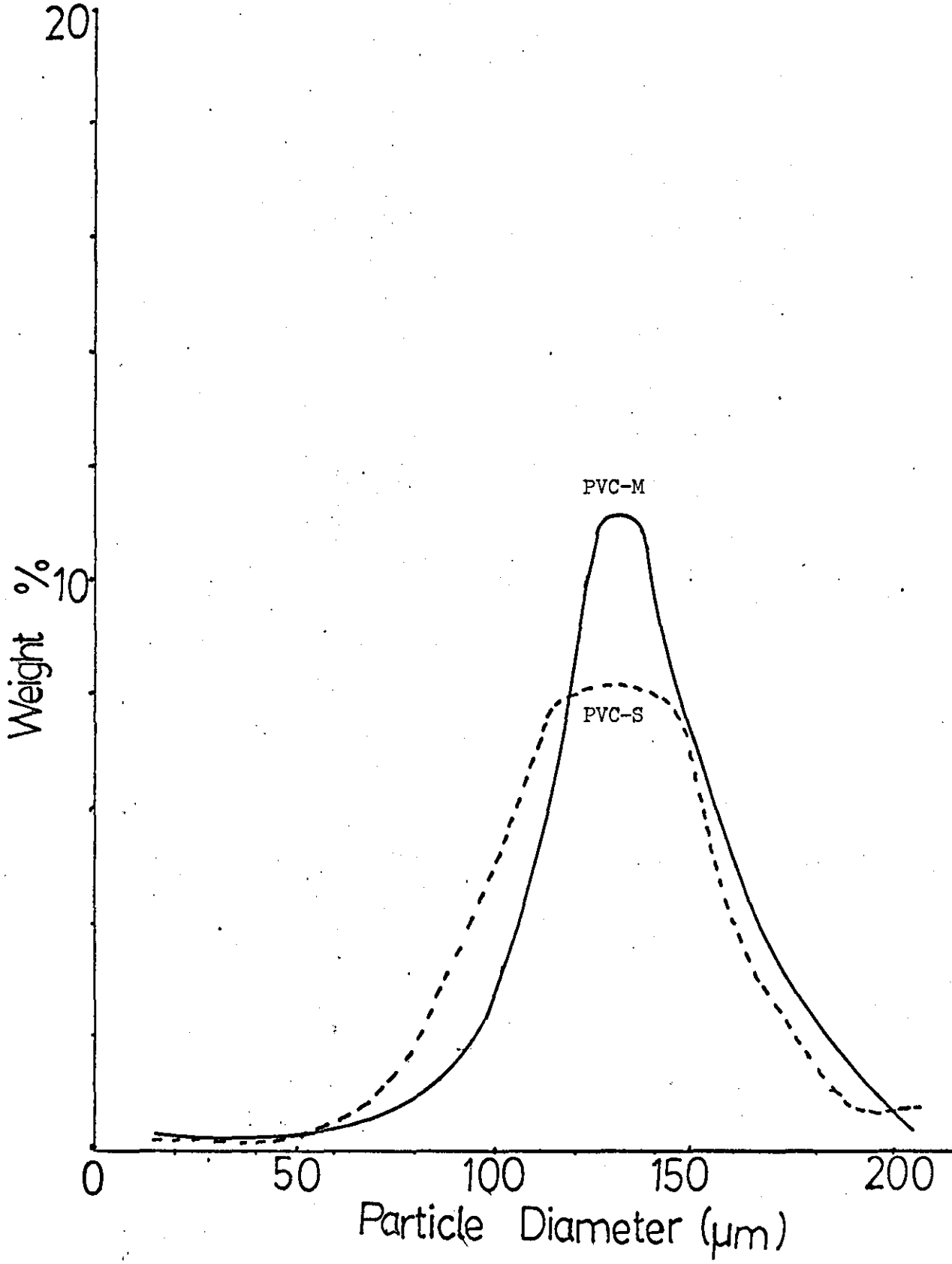


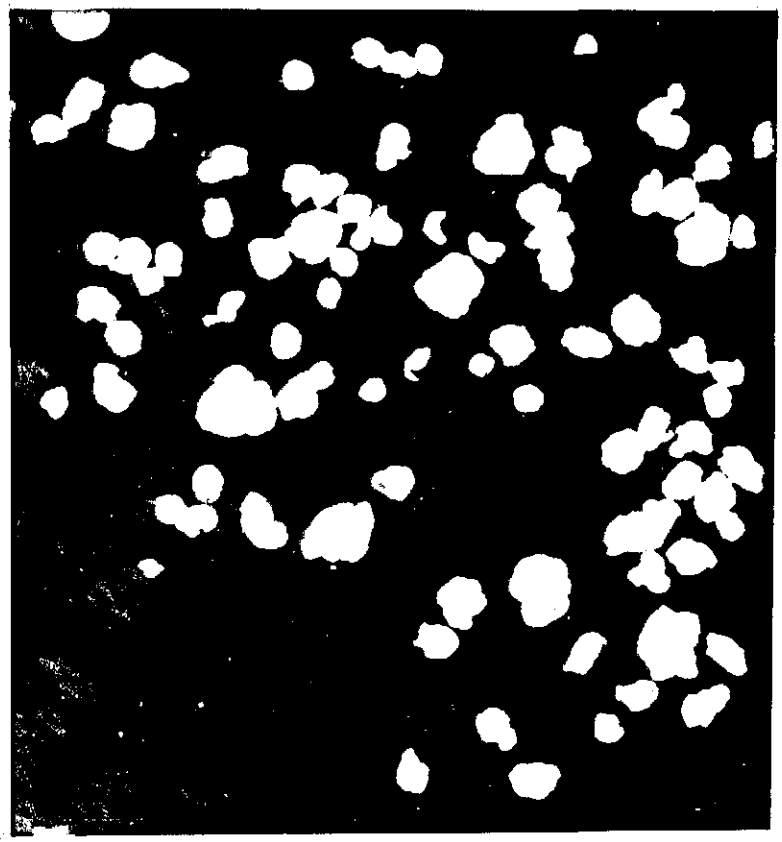
Fig. 26: Particle Size Distribution of mass and suspension polymer

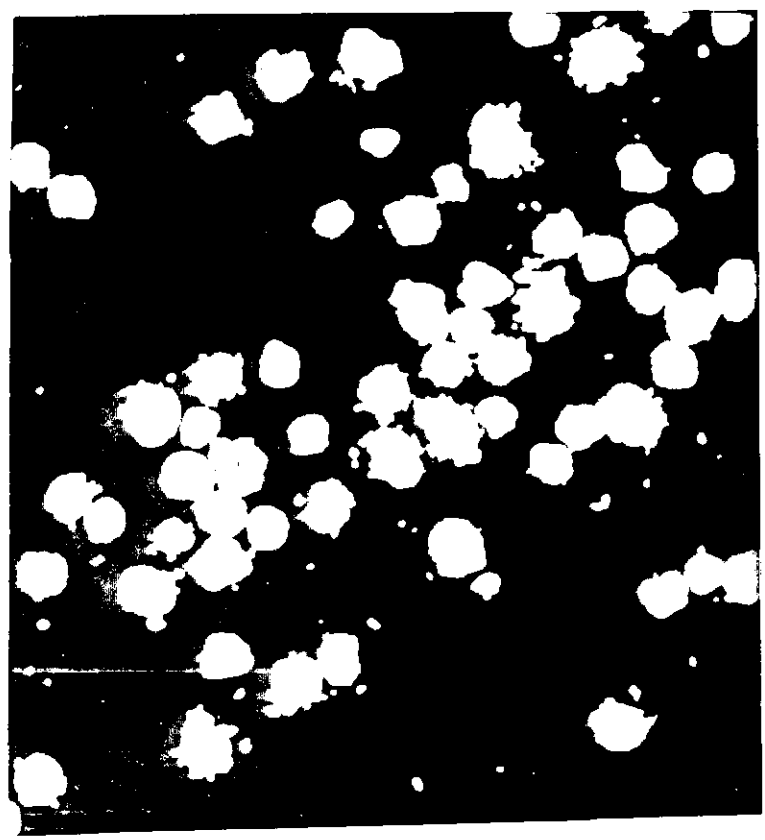
Fig. 27: Optical micrographs of PVC-S particles viewed by reflected light.

Magnification: x60

Fig. 28: Optical micrographs of PVC-M particles viewed by reflected light.

Magnification: x60





Guimon[120] points out that bulk density increases very rapidly within the first 2-3 minutes and would soon be at a maximum but for temperature.

Morohashi[122] has suggested that increase in bulk density was due to particle size reduction. But Gale[118] reports mixer discharge temperature has no significant effect on size distribution, the only changes being a shift from 150 μm to 105 μm. It will be shown later (section 4.5.3) by an optical method of size analysis - Zeiss Counter - that there is no significant change in size distribution of blends discharged at various temperatures. Boulton[14] considers the main factor to be a more effective packing resulting from de-agglomeration or collapse of voids between the various particles during blending. He also suggests that the additives incorporated in the blend might lead to surface changes of the particles which could alter considerably the packing characteristics and thus the bulk density. Both suggestions appear to be supported by microscopy. For instance, a close look at Figs. 48 and 49 show the resin particles are more compact and the primary particles more clustered together. Figs. 33-42 which are scanning electron micrographs of blended and unblended PVC particles, show a gradual smoothing of the particle surface.

High bulk density blends are reported to give high extruder outputs[118-122]. An important aim in dry blending therefore is to obtain powders of high density for a given polymer and formulation. The discharge temperature chosen has to be compatible with the thermal stability of the blend. Generally a blend discharge temperature of 100° - 130°C would suffice. Most volatiles and moisture would be expelled within this temperature range.

4.4 Effect of Blending on Glass Transition Temperature (Tg)

The results of measuring the Tg of blends discharged at various

temperatures are presented in Table 13. In the lead formulation there is no significant change in Tg both during the initial DTA run and rerun - only about 2°C. But with the tin blends the Tg is lower (6° - 7°C less), though not as low in the 80°C blends. This may be due to polymer-stabiliser interaction still being in progress. The stabiliser has notcompletely diffused into the polymer particles at that lower blending temperature.

The blend Tg on the rerun is now the same for the tin blends and lowered by 9°-10°C. Having takenthe polymer blend temperature up to 200°C in the DTA before cooling for the rerun, it is reasonable to assume all the resin particles now have a uniform absorbtion of the tin stabiliser. It now gives a unique blend Tg.

In section 4.2 the tin stabiliser was shown to be absorbed into the polymer particle in a manner analogous to plasticisers. Thus there is swelling of the PVC particles, albeit by small amounts, as they imbibe the diluent when heated in an excess of tin stabiliser. Tin stabiliser therefore, should be expected like plasticisers, to disturb the polymer chains, increasing the free volume and thus reduce the Tg; which is what is observed.

Natov and Gancheva[125,126] have studied the effect of stabilisers on Tg of PVC. They showed that some stabilisers are dispersed between the bundles of polymer molecules, that is they are dispersed interstructurally, or within the bundles (between the polymer molecules), that is, they are dispersed intermolecularly. In other words, the stabilisers could be dispersed between the primary particles or within the primary particles.

According to them, inorganic and organometallic stabilisers reduce the Tg to a value specific for the individual stabiliser and interstructural dispersion. For some stabilisers such as epoxide stabilisers the reduction of Tg depends on type and quantity used. At

low concentrations, the Tg is practically unchanged but as the concentration increases the Tg decreases steadily as the stabilisers now function as intermolecular plasticisers.

Noel and King[73] have reported a change in Tg by lubricants and stabilisers which they interpreted in terms of polymer additive interaction. Additives compatible with PVC will diffuse into the polymer in the fluid state and disrupt existing cohesive forces thereby lowering the Tg. McKinney[45,124] has also determined the effects of stabilisers and plasticisers on the Tg of several vinyl chloride polymers and copolymers. He found that while some stabilisers like barium-cadmium laurate do not affect the Tg, some for example, organotin stabilisers, behave like plasticising agents and lower the Tg by 10°-20°C.

From McKinney's work the DTA can easily be used to assess the degree of plasticiser uptake. Such measurements can also detect uniformity of a blend. A non-uniform blend, for example, will have residual transition peaks whereas a properly prepared dry blend will have a unique lower Tg with no inflection at the polymer Tg. Since not all stabilisers affect the Tg of PVC the DTA can only be used in a few cases to assess the uniformity and preparation of rigid dry blend formulations. Besides, the stabilisers are not added in such large amounts as plasticisers to effect big Tg reductions.

Figs. 29-32 are the thermograms of the DTA runs of various blends for both formulations.

Table 13

DTA Determination of Tg (^{o}C) of PVC blends discharged at Different Temperatures

Polymer Type	Blending Temperature ^{o}C	Tin-Blend		Lead-Blend	
		Initial	Rerun	Initial	Rerun
Mass	80	79	75	82	83
(Unblended Tg = 85)	110	78	75	83	82
	120	78	75	82	82
	140	78	75	83	83
Suspension	80	81	76	82	83
(Unblended Tg = 84)	110	78	75	82	82
	120	78	75	82	82
	140	78	75	82	83

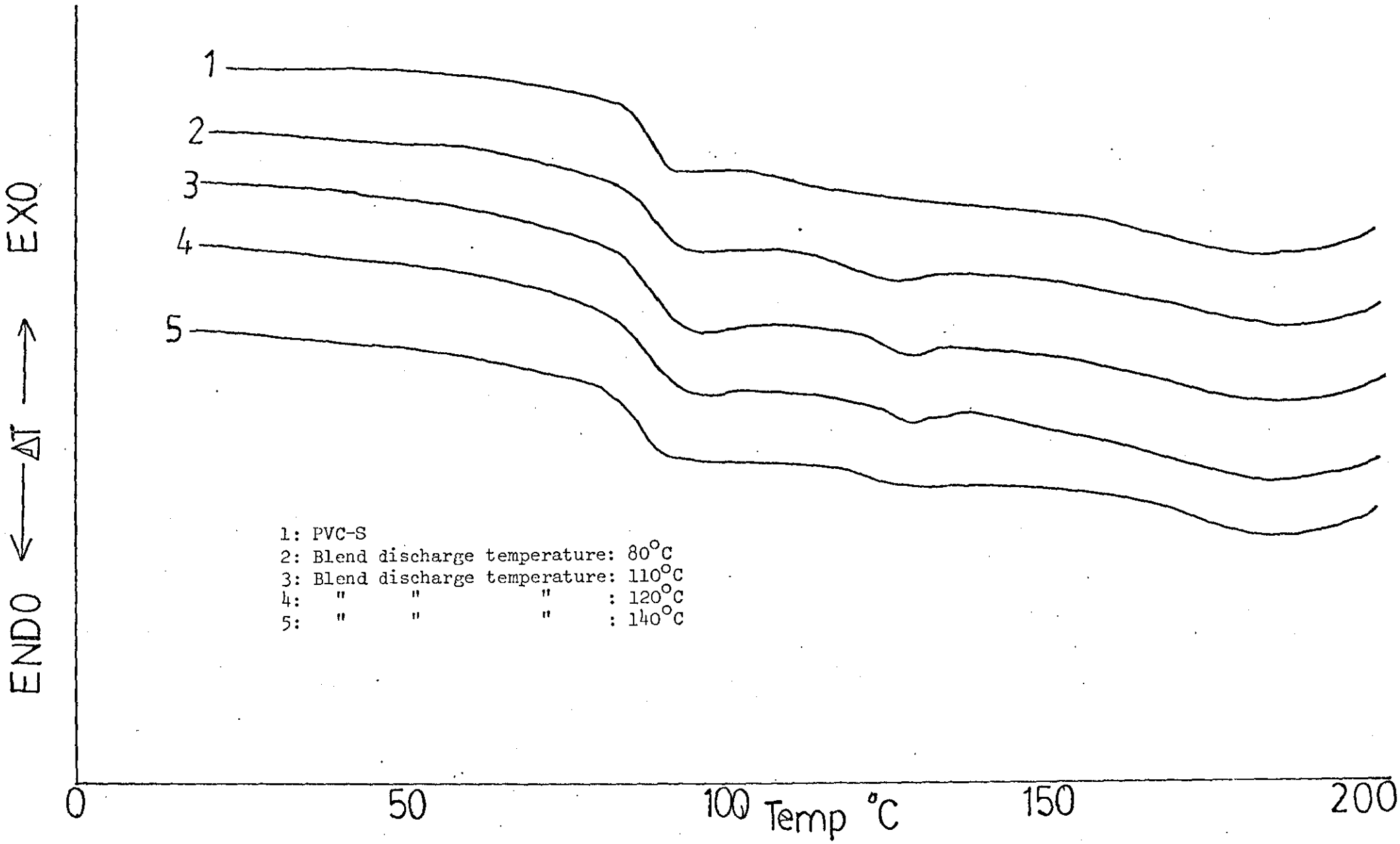


Fig. 29(a): DTA curves of PVC-S (Lead formulation), initial run

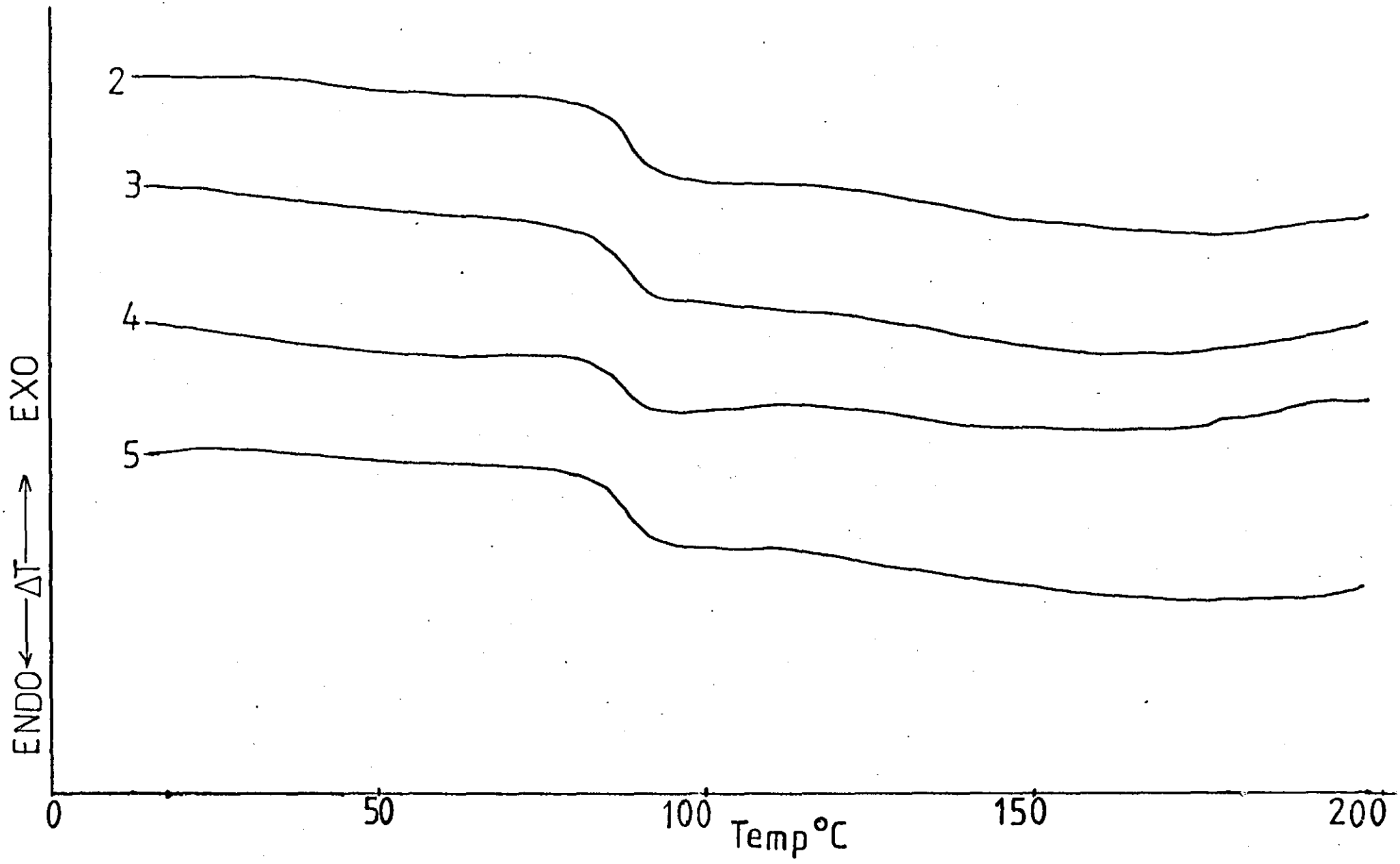


Fig. 29(b): DTA curves of PVC-S (Lead formulation), Rerun

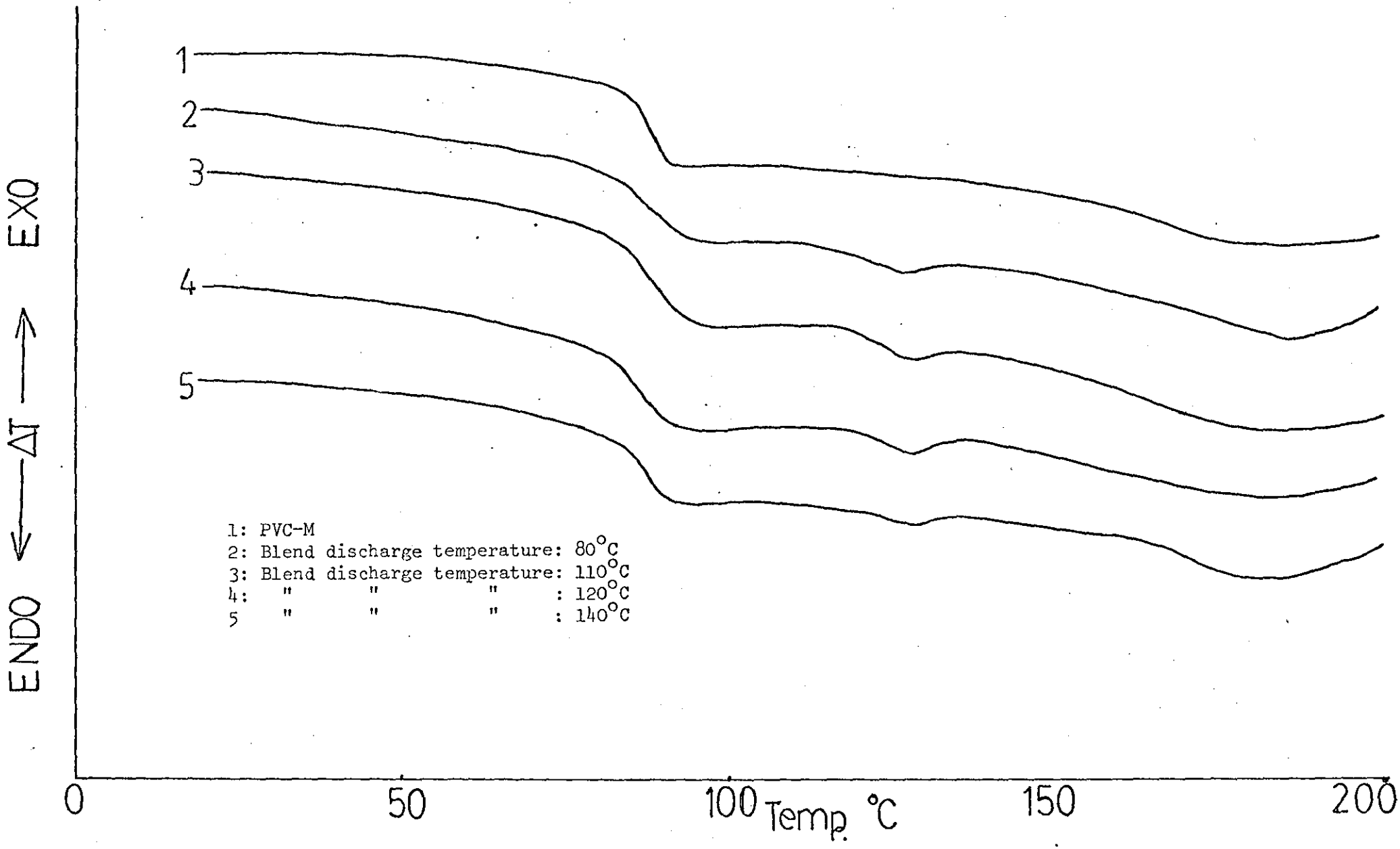


Fig. 30(a): DTA curves of PVC-M (Lead formulation), initial run

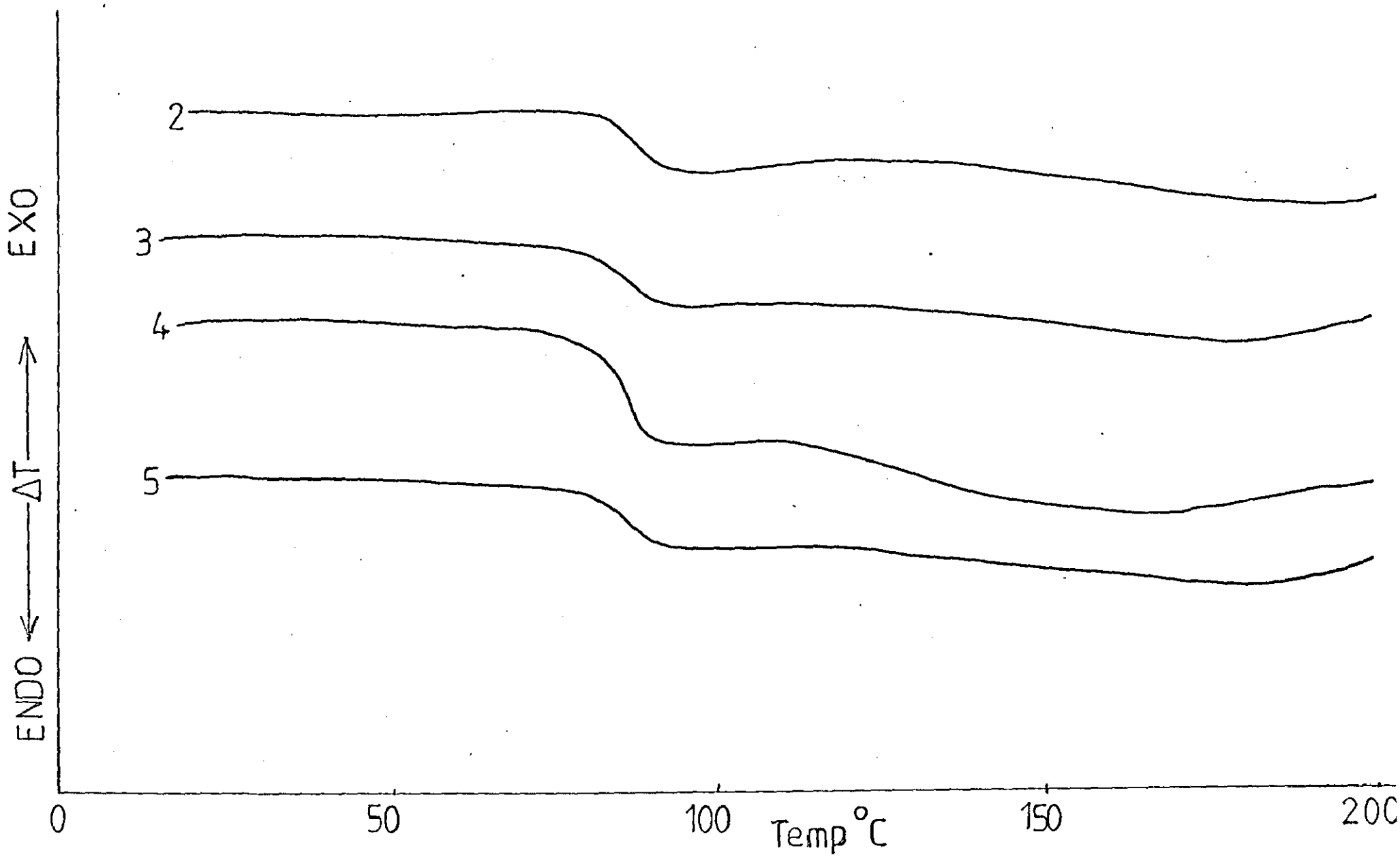


Fig. 30(b): DTA curves of PVC-M (Lead formulation), Rerun

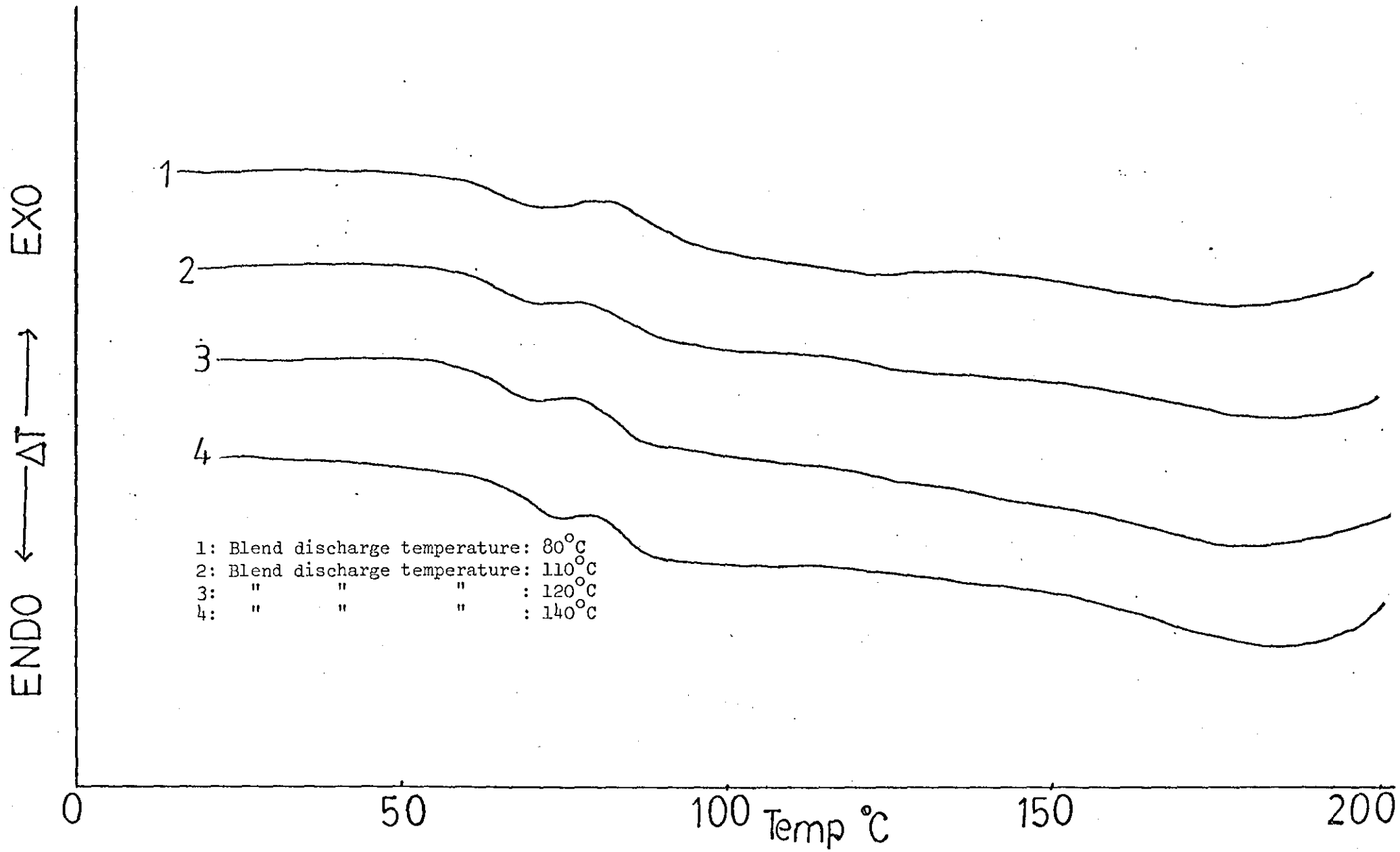


Fig. 31(a): DTA curves of PVC-S (Tin formulation), initial run

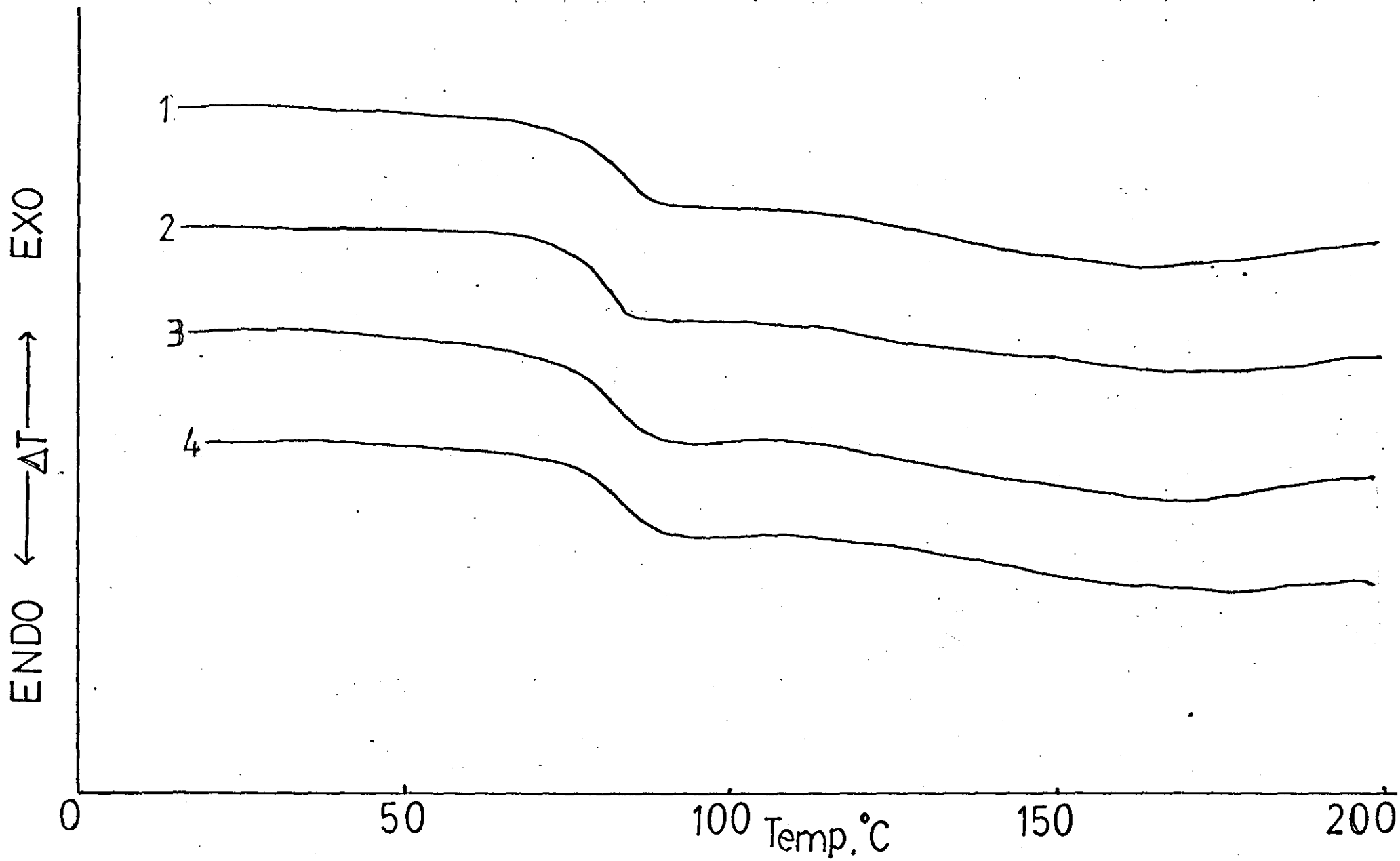


Fig. 31(b): DTA curves of PVC-S (Tin formulation), Rerun

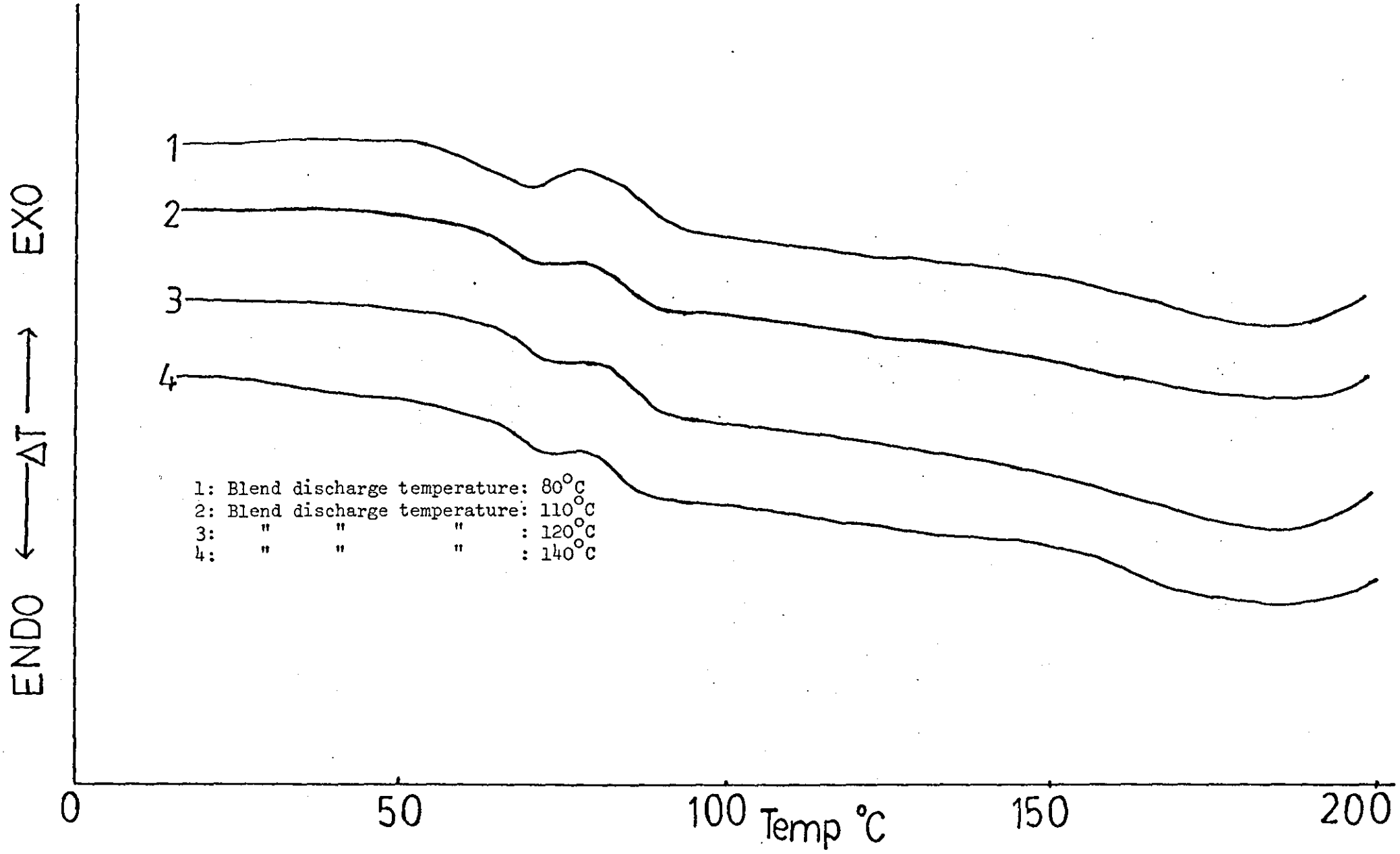


Fig. 32(a): DTA curves of PVC-M (Tin formulation), initial run

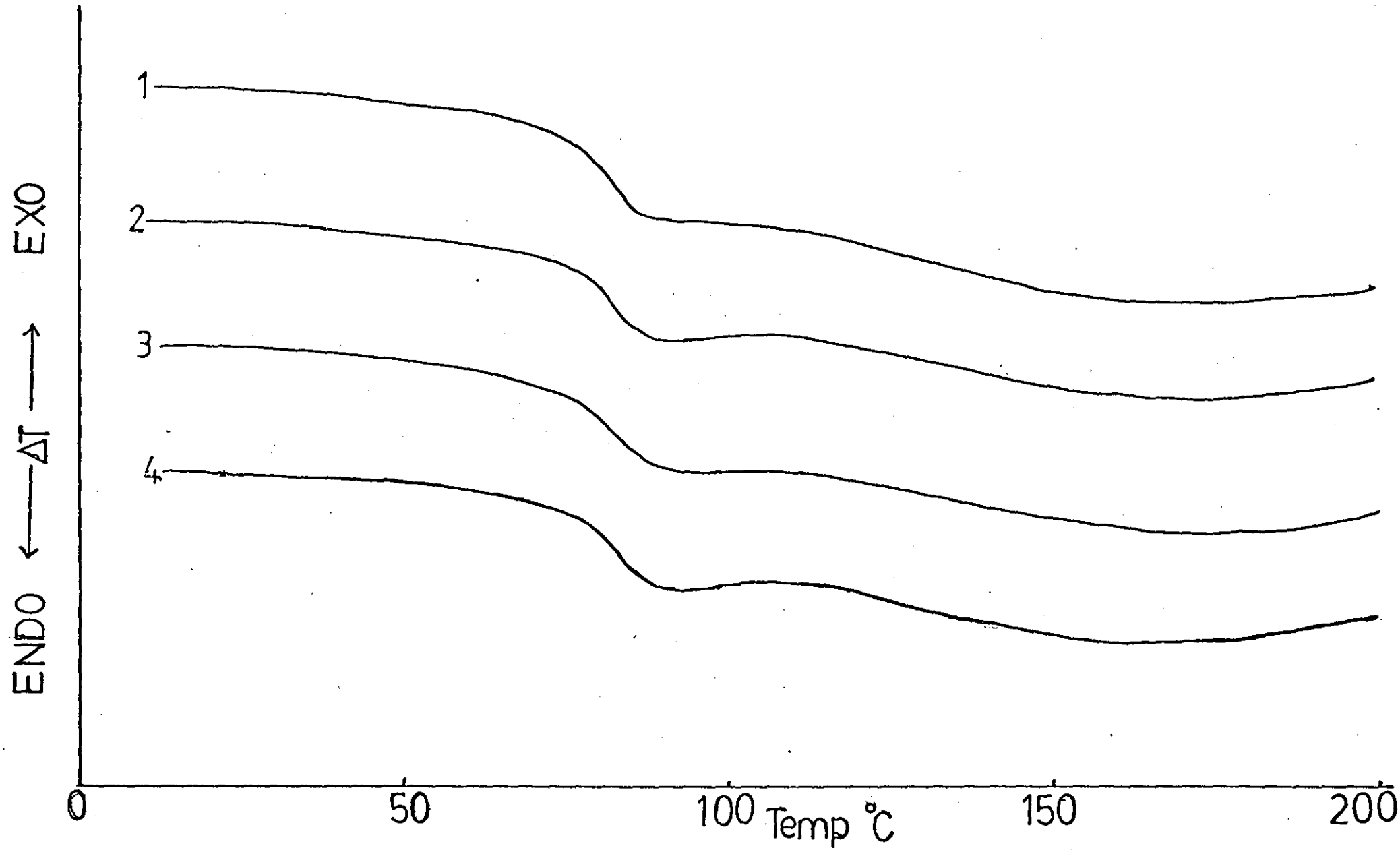


Fig. 32(b): DTA curves of PVC-M (Tin formulation), Rerun

4.5 Effect of blending on Particle Shape, Internal Structure and Particle Size

4.5.1 Particle Shape

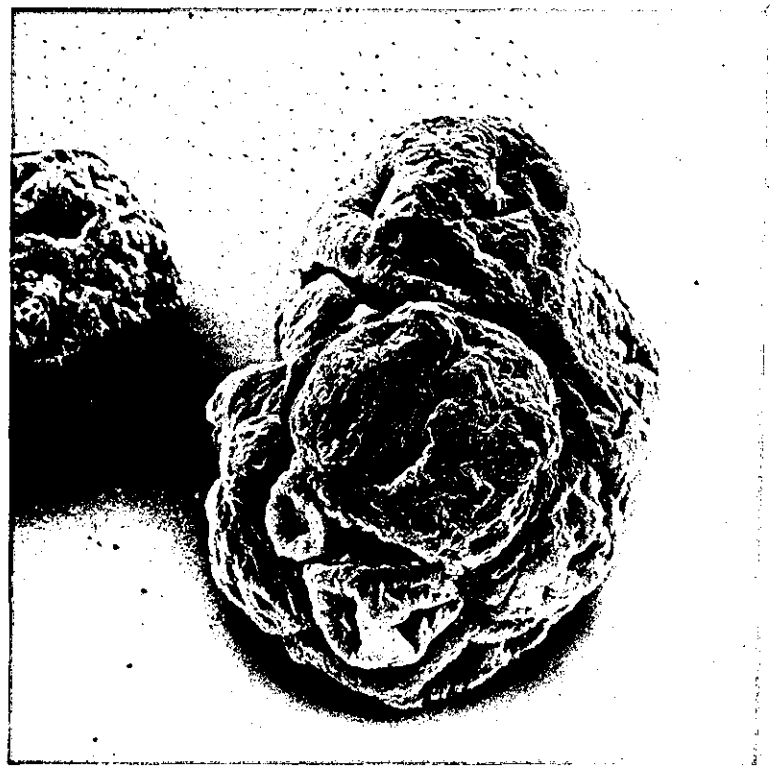
Scanning electron micrographs of PVC particles, before and after blending to 80°, 120° and 140°C are shown in Figs. 33-42. Compared with unblended PVC particles there are no marked changes in particle shape after blending, although a gradual smoothing of the particle surface is observed.

The surface of PVC-S particles is covered by a skin or membrane which obscures the observation of the 1 - 2 μm particles (primary particles). However, there are some areas on the surface where this skin is ruptured exposing these primary particles. Fig. 33(b) is an example. It is not unreasonable to expect the blending operation to lead to large-scale damage or rupture of the skin which would allow additives to penetrate into the polymer much more easily. Rougher surfaces would also lead to greater generation of frictional heat. No such general rupture of the skin as a result of the blending was observed.

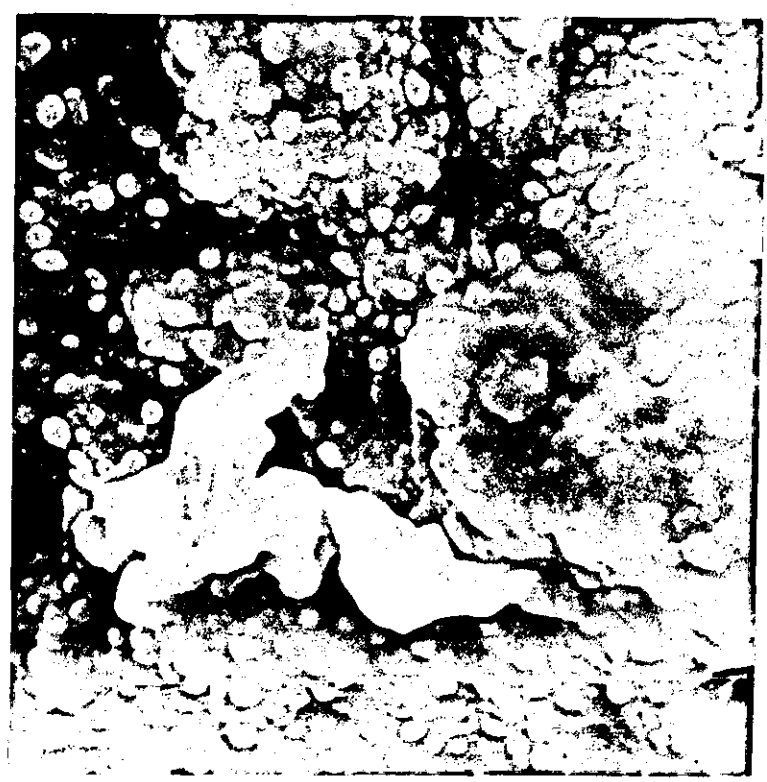
Because of this apparent resistance of PVC particles to breakup or gross deformation during blending, the resin was subjected to more severe impact treatment and freeze grinding. In the former case a jet mill was used. Here no direct heat or shear was applied to the particles, Instead, high velocity impacts were relied upon to reduce particle size and or shape. In the latter, it was hoped that if the resin temperature was further lowered much below the Tg, then the resin would become brittle and friable. Therefore the shape, surface characteristics and size distribution would be affected even by gentle grinding.

Fig. 33: Scanning electron micrograph of PVC-S particle.

Magnification: (a) x500; (b) x10,000



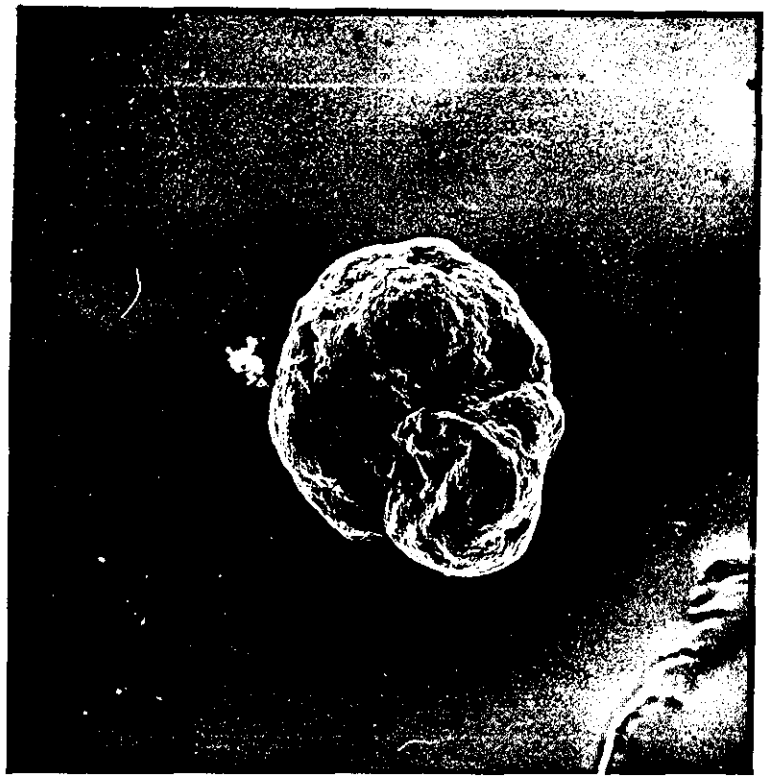
(a)



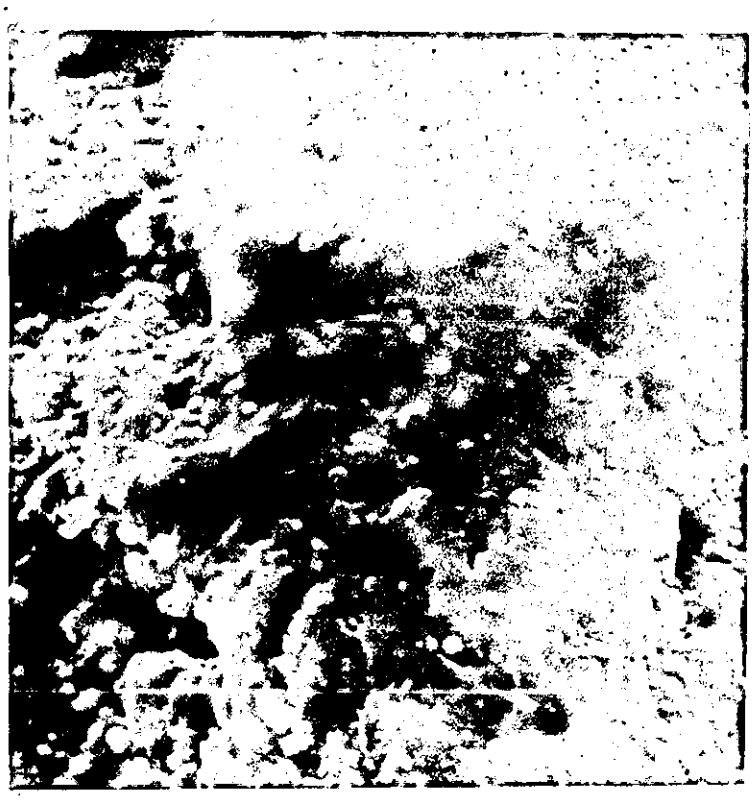
(b)

Fig. 34: Scanning electron micrographs of PVC-S particle (lead blend) discharged at 120°C.

Magnification: (a) x450; (b) x10,000



(a)

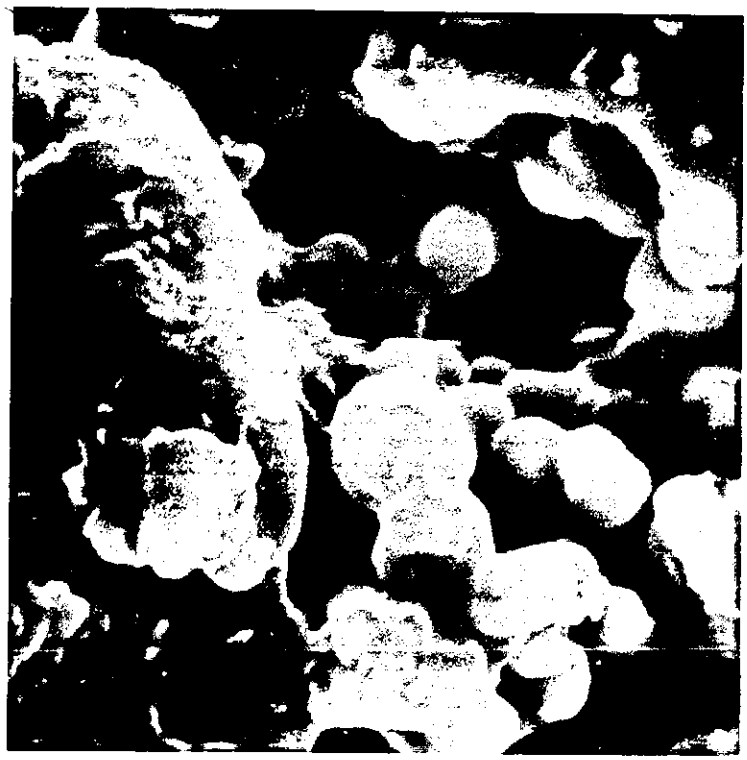


(b)

Fig. 35: Scanning electron micrograph of PVC-S particle (tin blend) discharged at 80°C.

Magnification: (a) x500; (b) x10,000

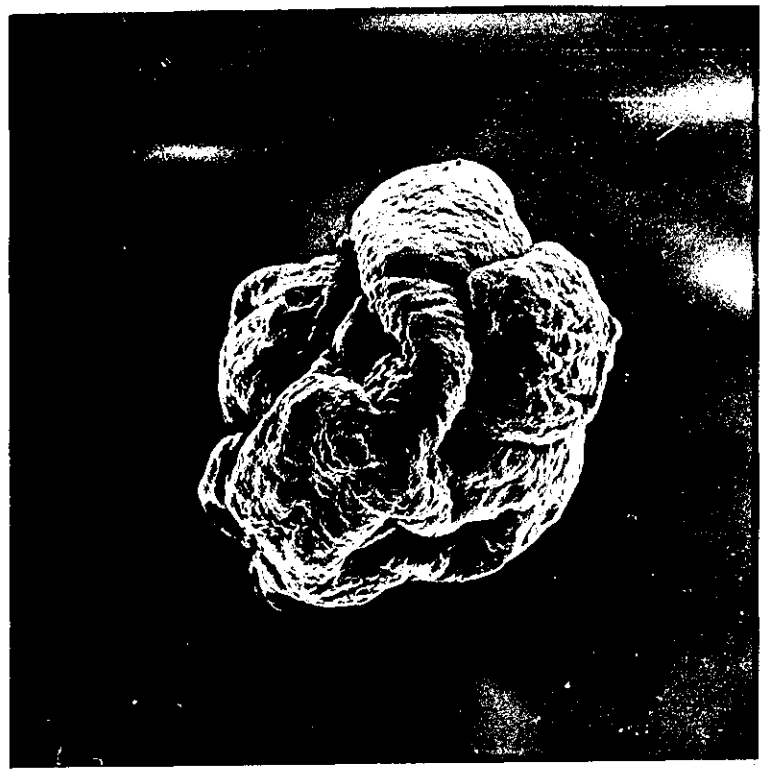
(a)



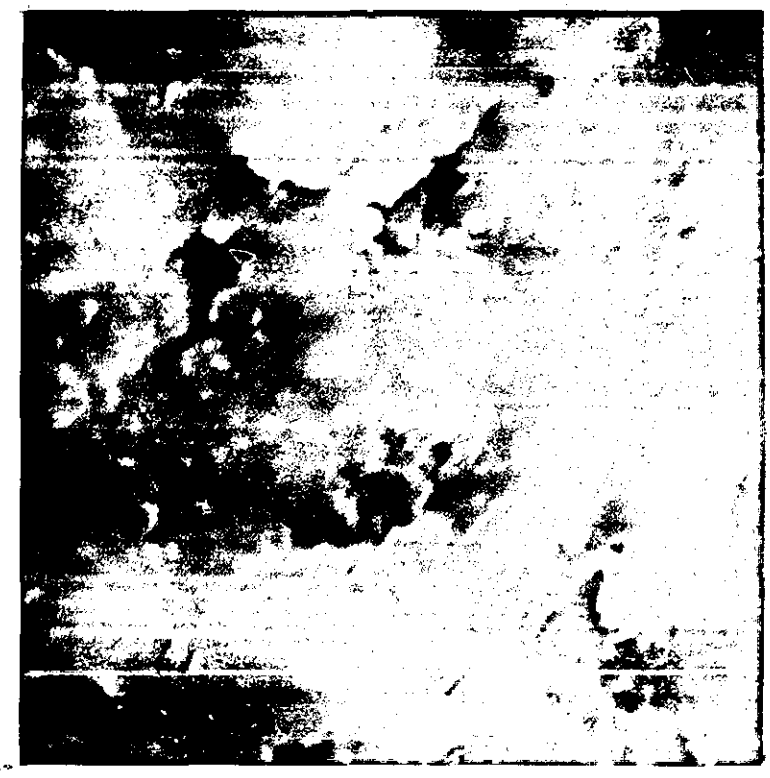
(b)

Fig. 36: Scanning electron micrograph of PVC-S particle (tin blend) discharged at 120°C.

Magnification: (a) x500; (b) x10,000



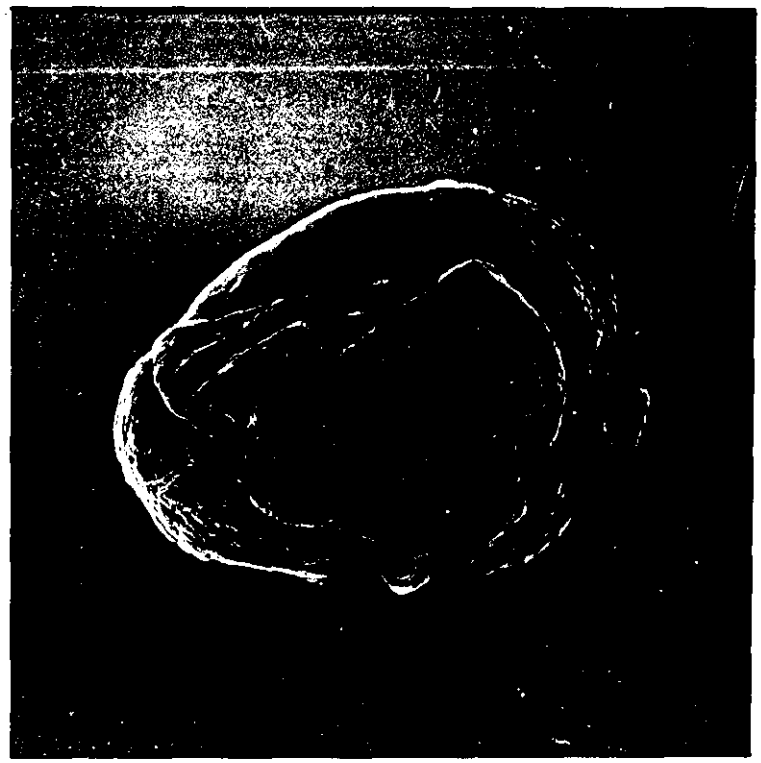
(a)



(b)

Fig. 37: Scanning electron micrograph of PVC-S particle (tin blend) dishharged at 140°C.

Magnification: (a) x450; (b) x10,000

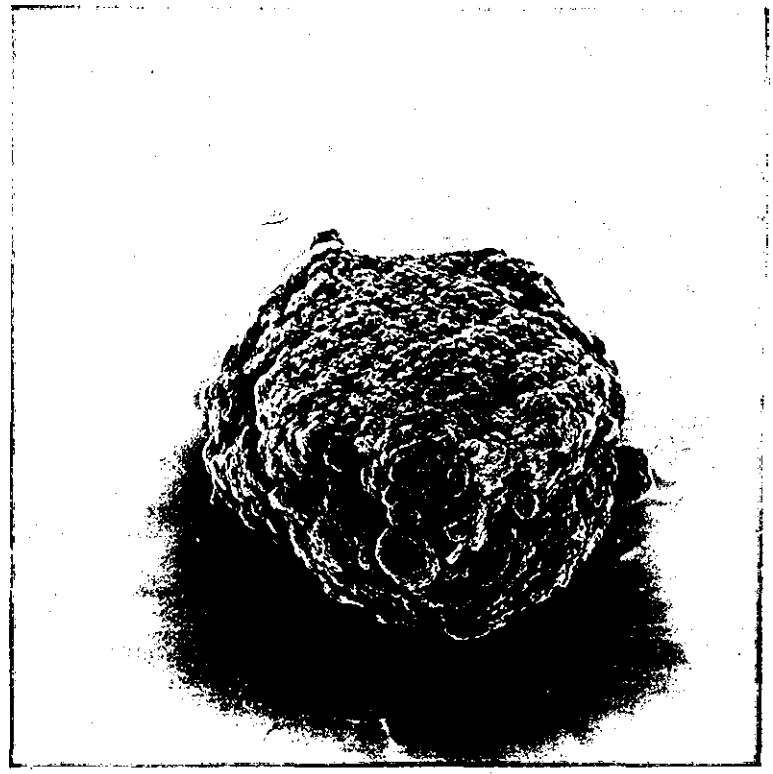


(a)

(b)

Fig. 38: Scanning electron micrograph of PVC-M particle.

Magnification: (a) x450; (b) x10,000

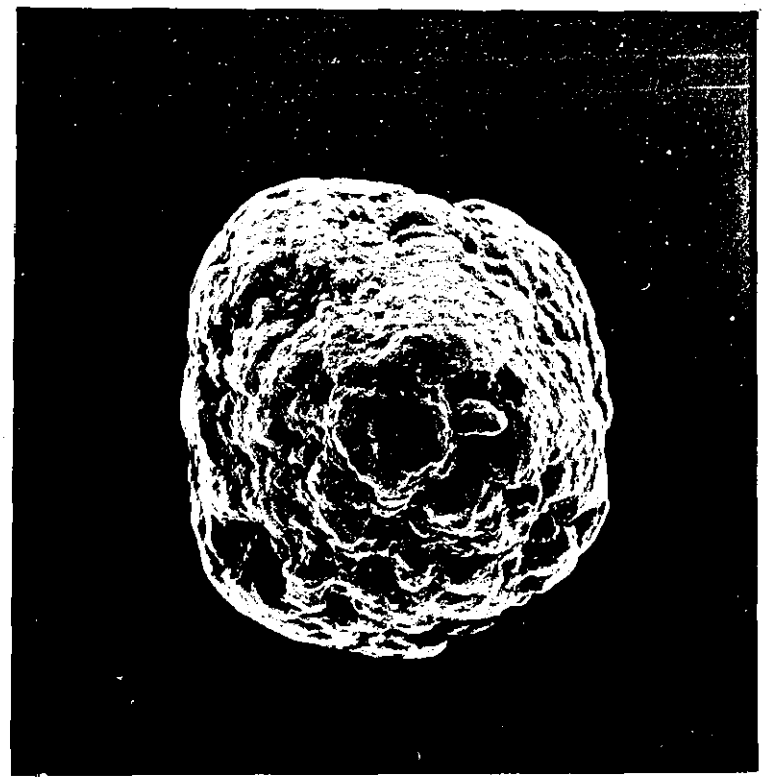


(a)

(b)

Fig. 39: Scanning electron micrograph of PVC-M particle (lead blend) discharged at 120°C.

Magnification: (a) x500; (b) x10,000

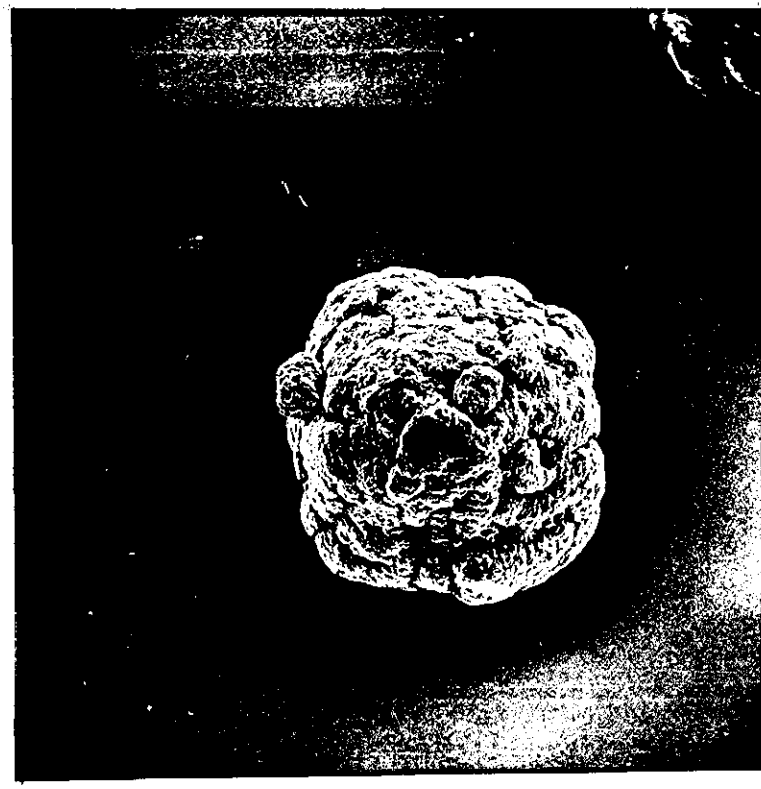


(a)

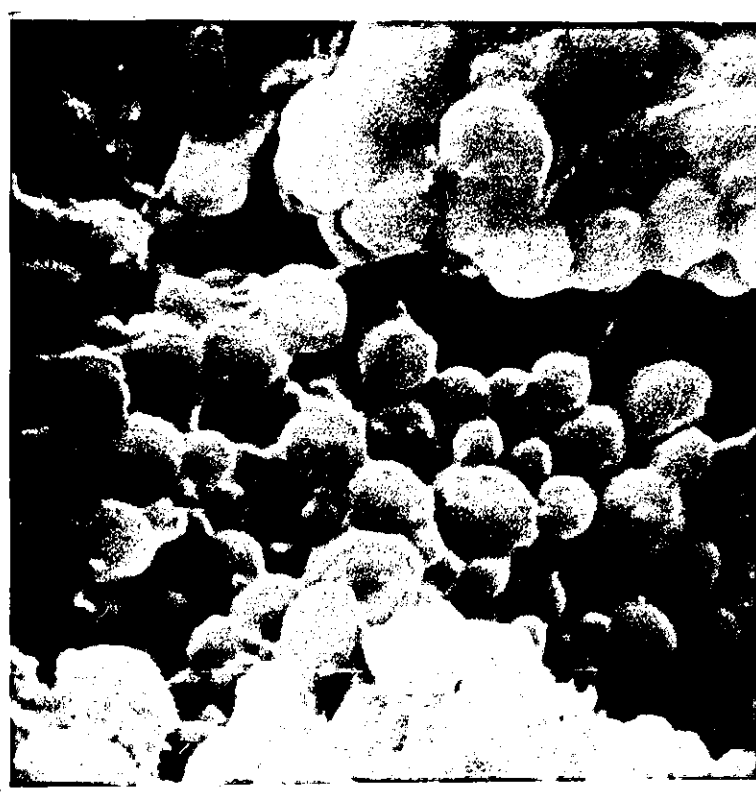
(b)

Fig. 40: Scanning electron micrograph of PVC-M particle (tin blend) discharged at 80°C.

Magnification: (a) x450; (b) x10,000



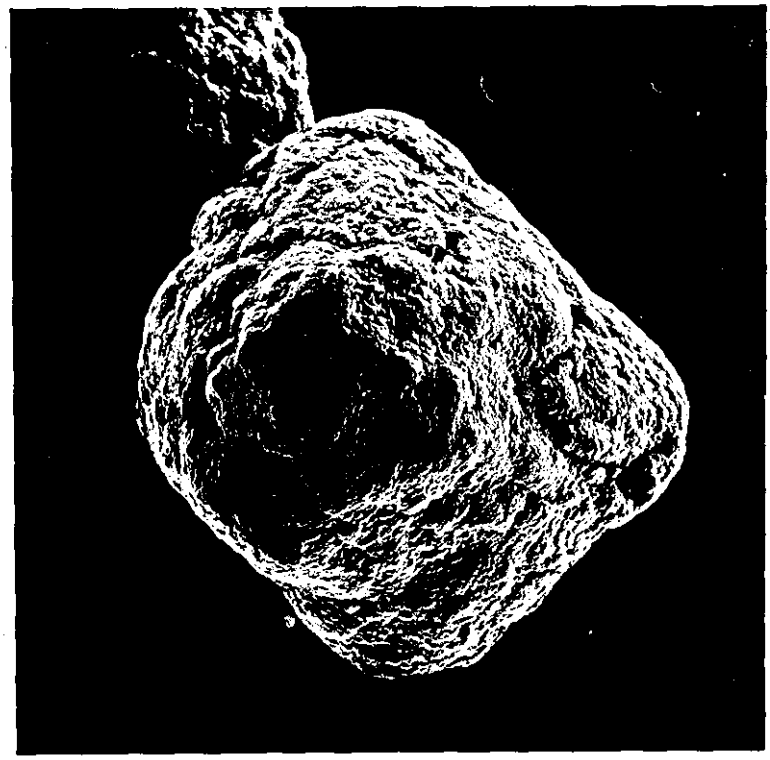
(a)



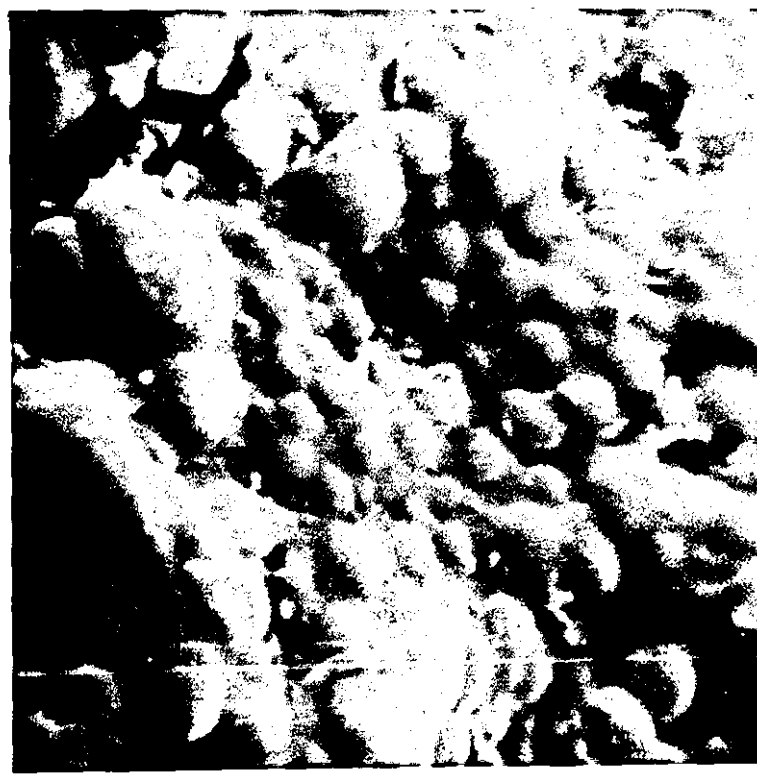
(b)

Fig. 41: Scanning electron micrograph of PVC-M particle (tin blend) discharged at 120°C.

Magnification: (a) x500; (b) x10,000



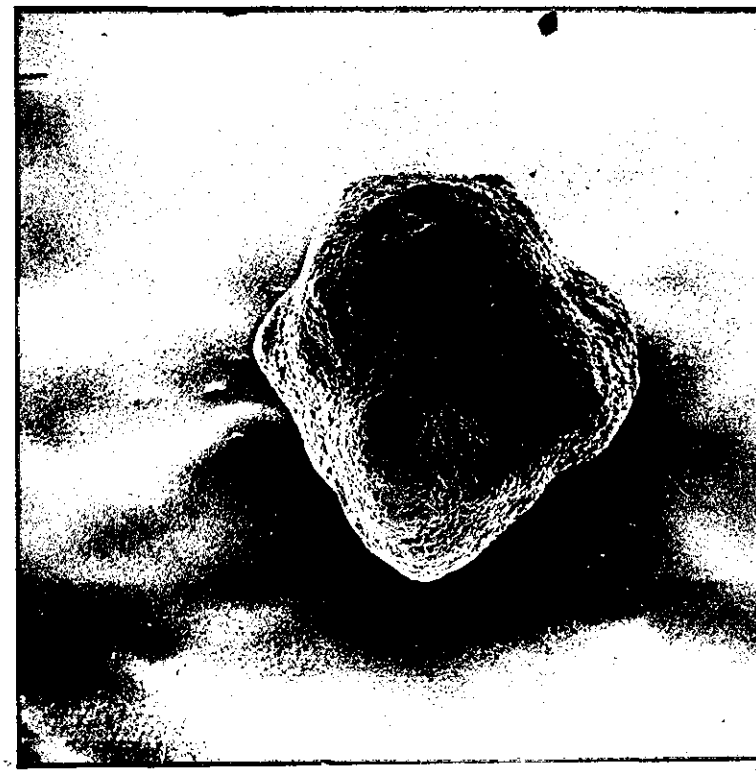
(a)



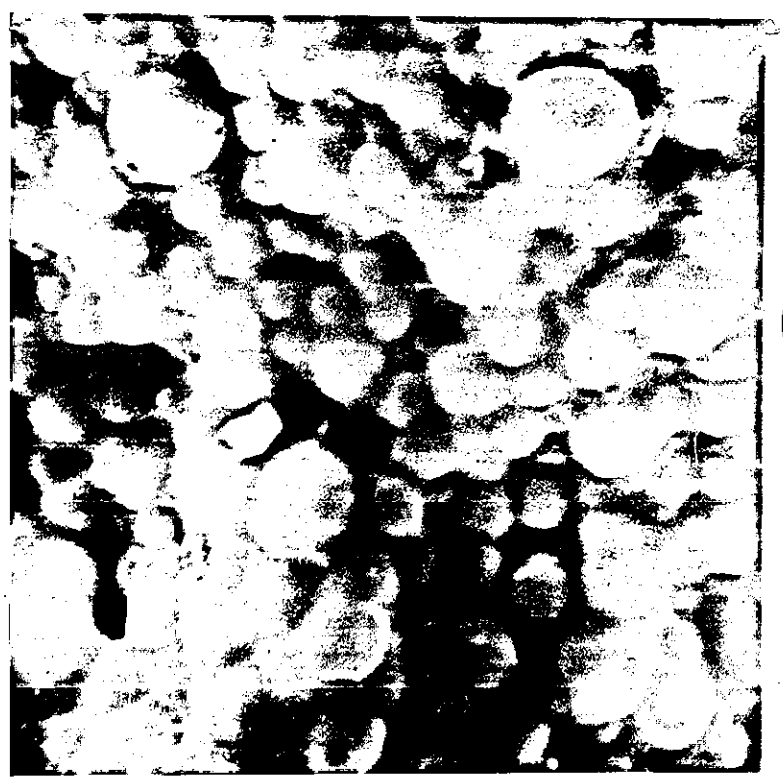
(b)

Fig. 42: Scanning electron micrograph of PVC-M particle (tin blend) discharged at 140°C.

Magnification: (a) x450; (b) x10,000



(a)



(b)

Although there appeared to be some rounding or smoothing of the particle surfaces there was no evidence of particles disintegrating or severe deformation. Fig. 43 shows the surface of PVC-M particle before and after the liquid nitrogen treatment. It shows that shear is needed even under these conditions to break up or modify or deform the resin particles.

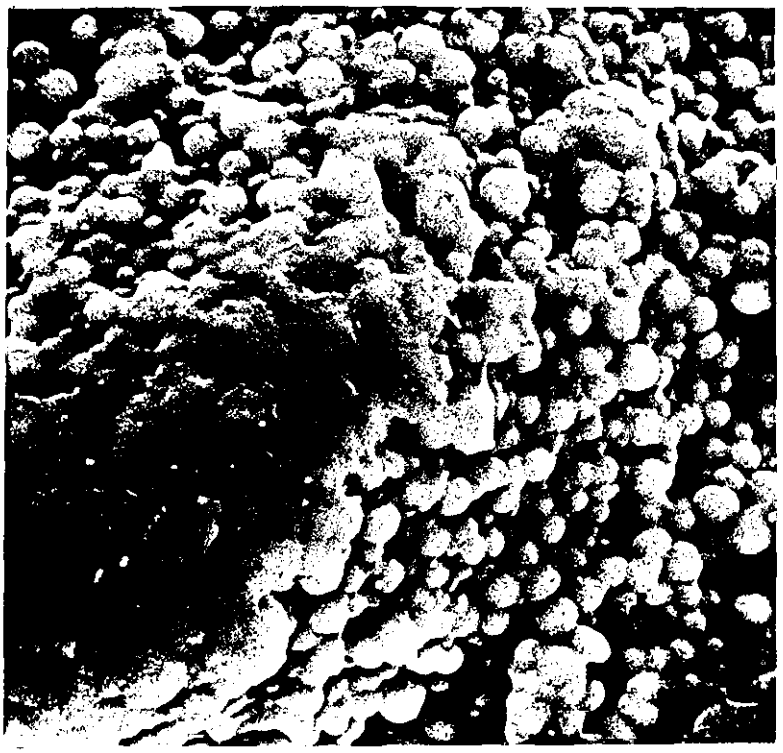
Further attempts were made to deform the polymer particles by thermal treatment alone. PVC powder particles mounted on a stub were heated in an air circulating oven for various lengths of time at different temperatures ranging from 160°C to 200°C and then examined in the scanning electron microscope. Details of sample preparation and SEM examination have been described in section 3.1.3.

Figs 44 and 45 show unblended PVC particles that have been heated at 160°, 180° and 200°C for 30, 15, 10 and 5 minutes respectively. At 160°C the shape and surface characteristics of the particles are still maintained even after 30 minutes heating. (Figs. 44(a) and 45(a)). At 180°C striking differences begin to show up after 15 minutes. The surface becomes smooth and looks devoid of structures though the multicellular nature of the suspension polymer is still preserved (Fig. 44(b)). At 200°C the shape is still retained after 5 minutes heating but the state of fusion of the mass particle (Fig. 45(c)) is more advanced than that of the suspension polymer (Fig. 44(c)). However after 10 minutes at 200°C a dramatic change in shape and surface characteristics is noticed. The particle is now extremely smooth and the original shape lost (Figs. 44(d) and 45 (d)).

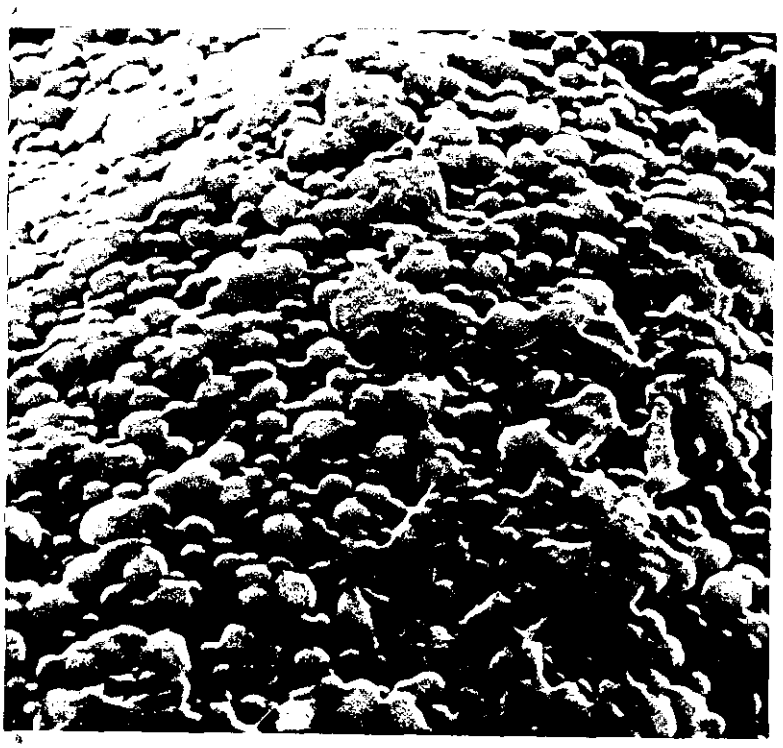
Where the polymer has been blended with stabiliser and lubricants, the smoothing effect and change in particle shape appear even more delayed although the Tg is lowered. For instance, it is only after 20 minutes heating at 200°C (Figs. 46-47) that comparable changes with the unblended polymer are seen. Harsh or severe thermal treatment without

Fig. 43: Scanning electron micrograph of PVC-M particle before (A) and after (B) liquid nitrogen treatment.

Magnification: x5,000



(A)

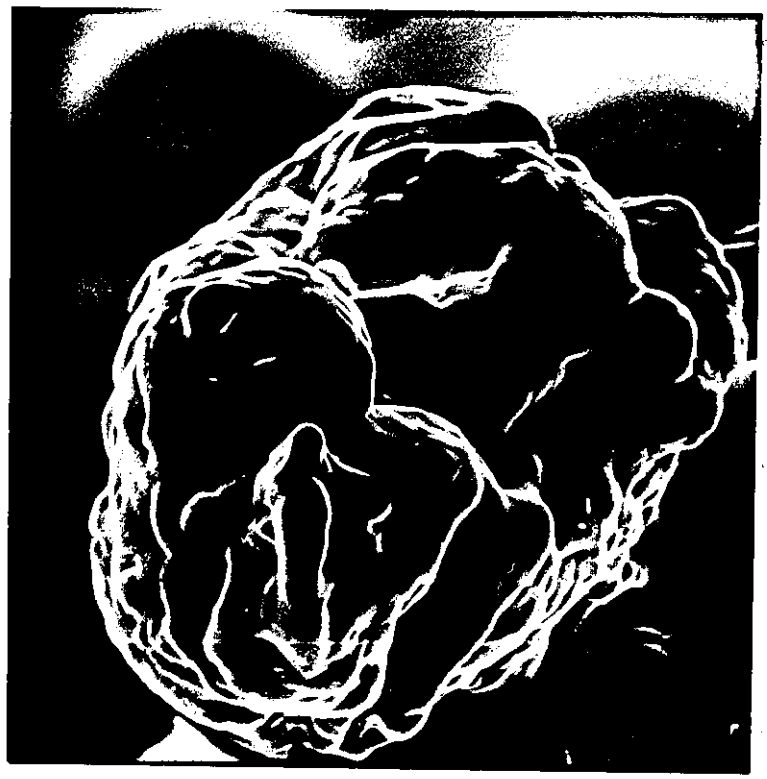


(B)

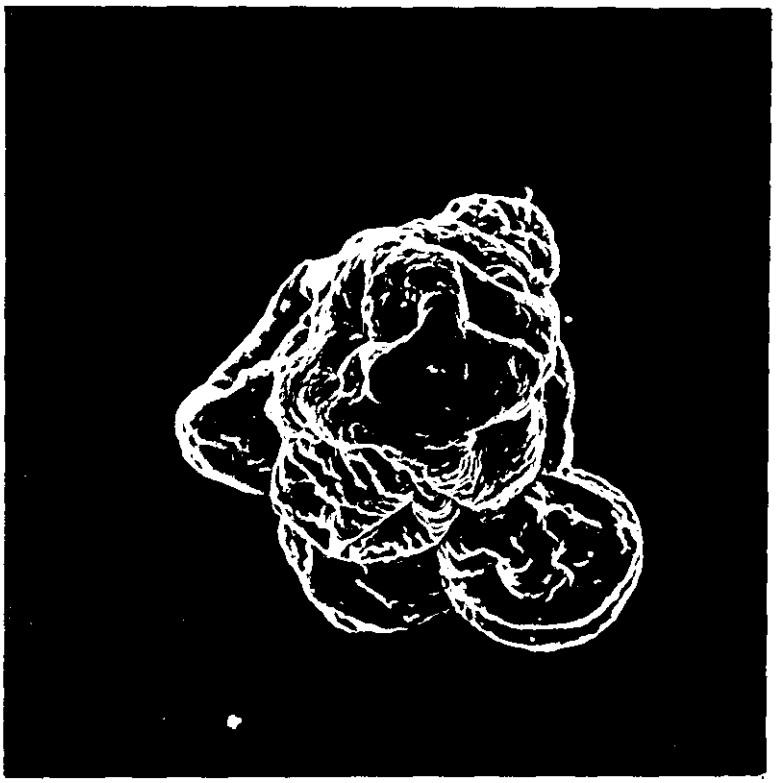
Fig. 44: Effect of heat on PVC-S particle topology.

a) 160°C - 30 min x1,000
b) 180°C - 15 min x1,000
c) 200°C - 5 min x500
d) 200°C - 10 min x500

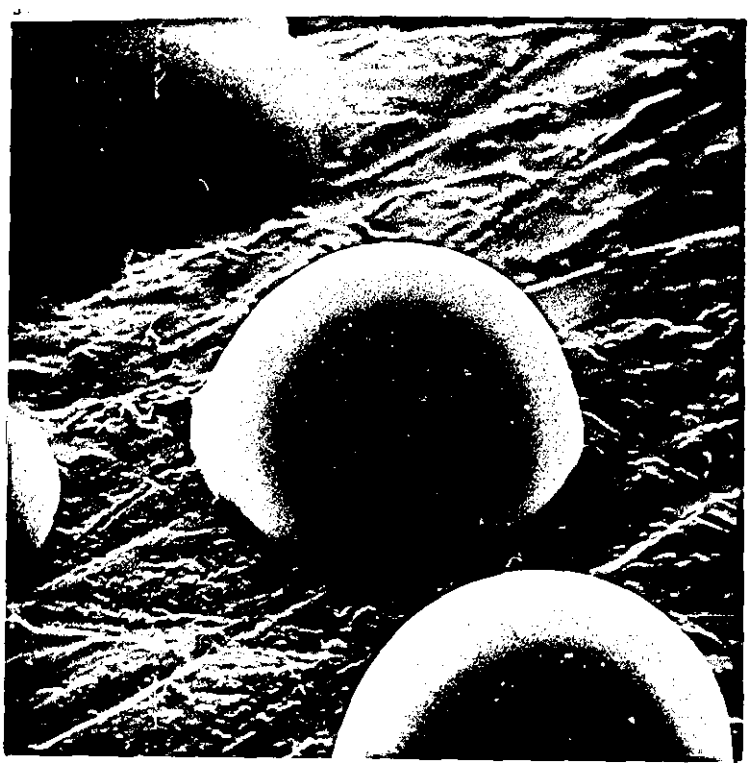
(a)



(b)



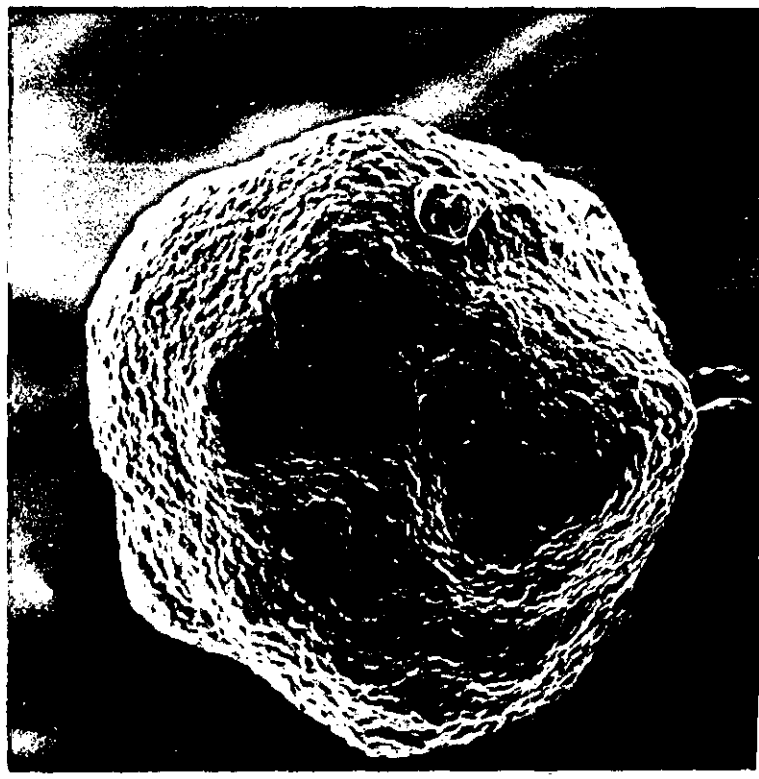
(c)



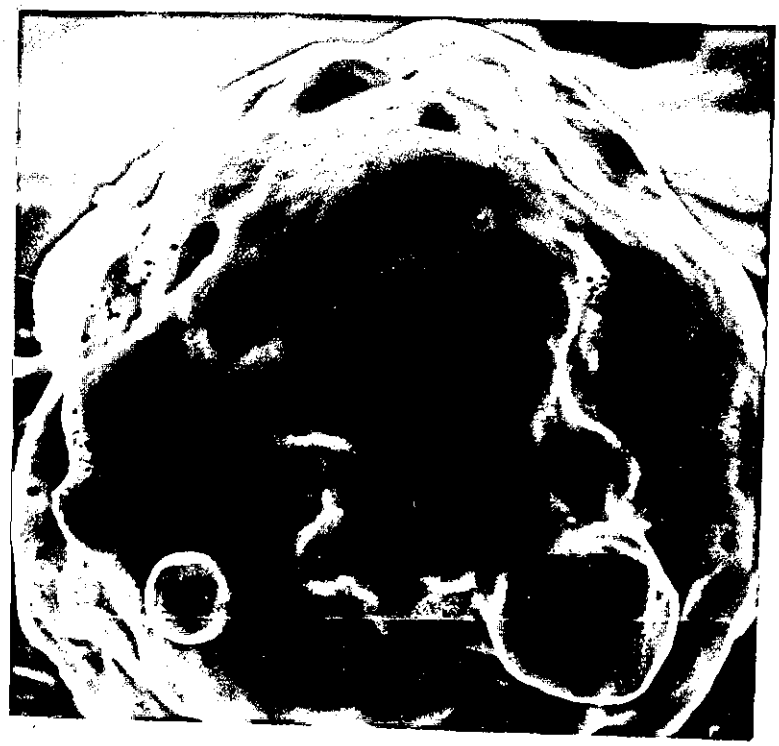
(d)

Fig. 45: Effect of heat on PVC-M particle topology.

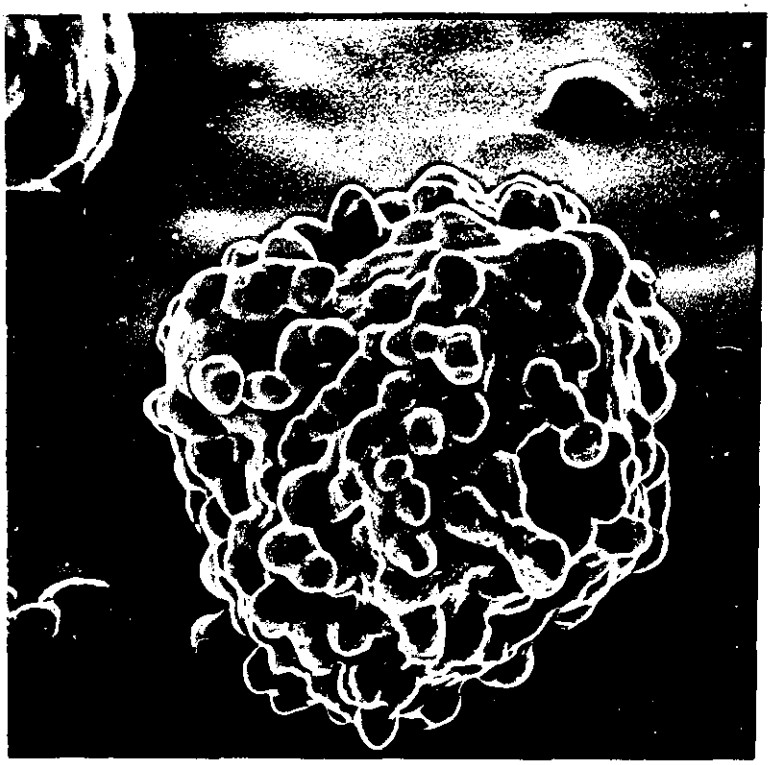
a) 160°C - 30 min x1,000
b) 180°C - 15 min x1,000
c) 200°C - 5 min x500
d) 200°C - 10 min x500



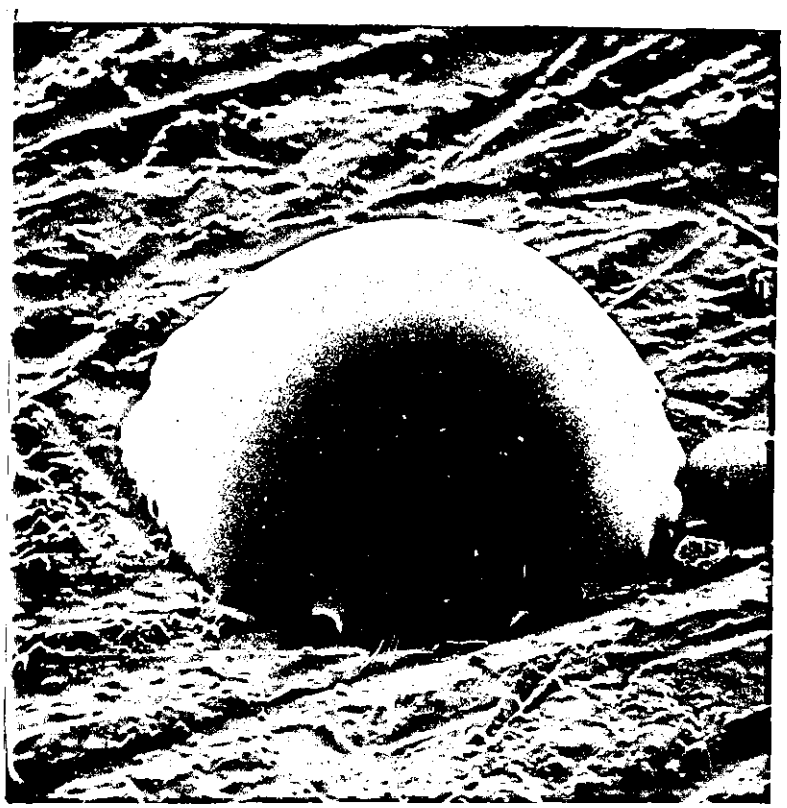
(a)



(b)

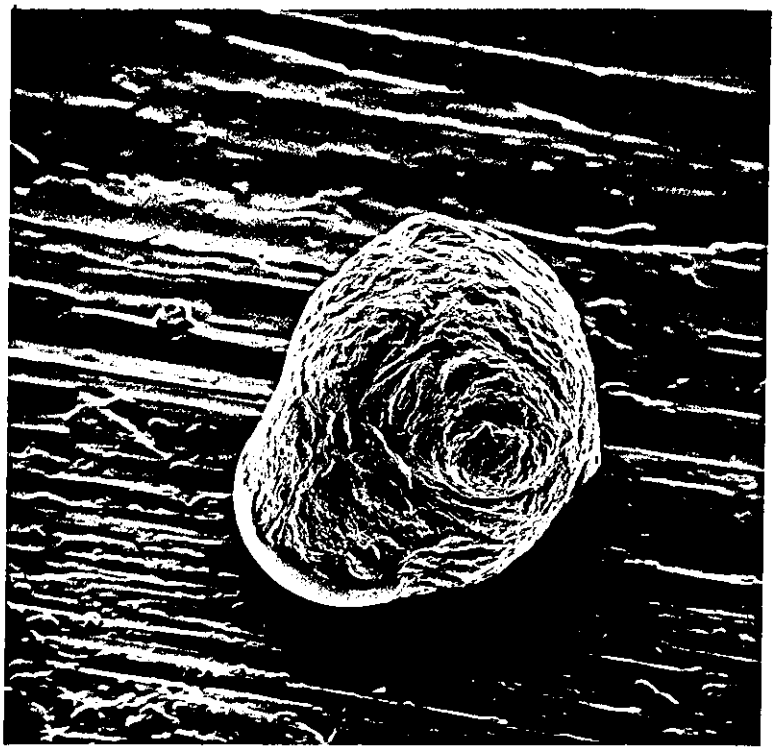


(c)

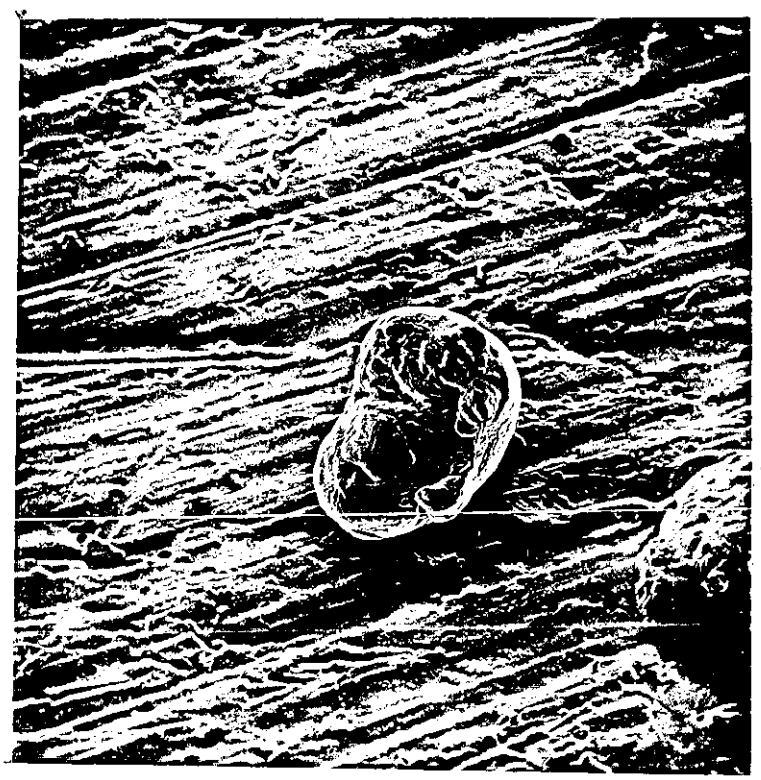


(d)

Fig. 46: Effect of heat on blended PVC-S particle topology.
a) Lead blend: 200°C - 20 min x500
b) Tin blend: 200°C - 20 min x400

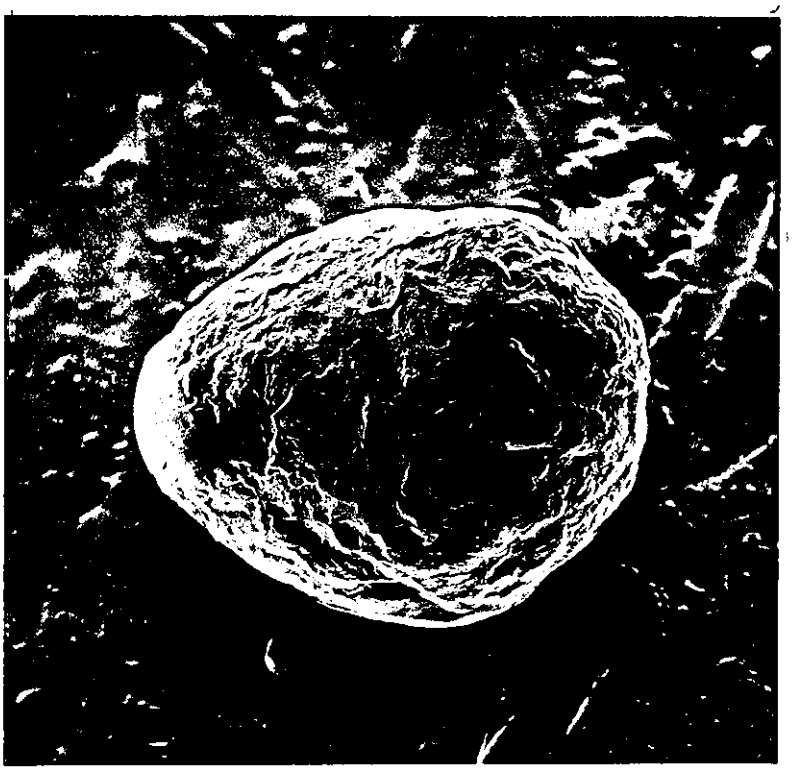


(a)

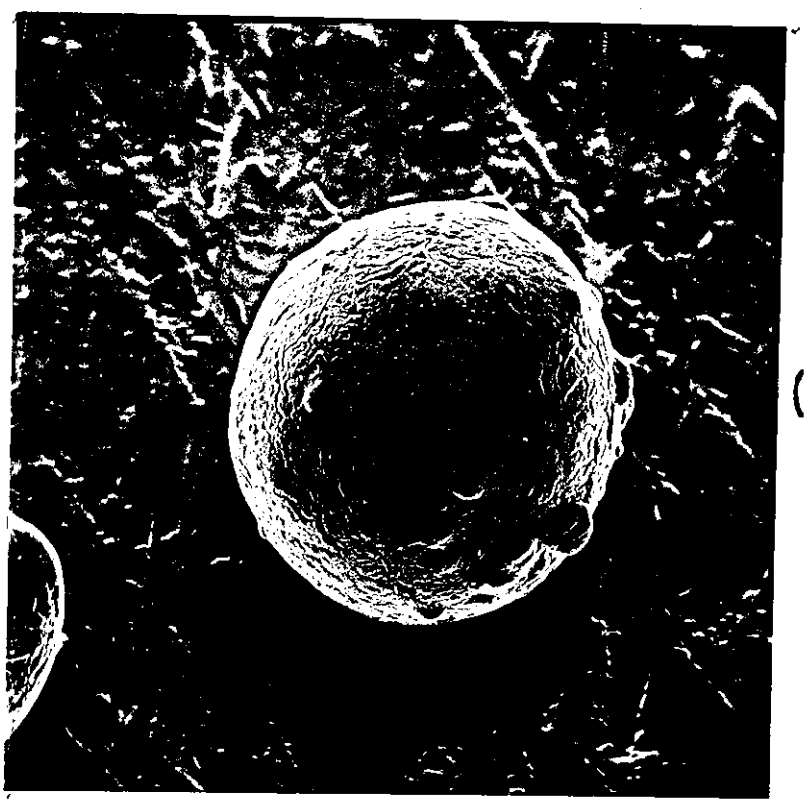


(b)

Fig. 47: Effect of heat on blended PVC-M particle topology.
a) Lead blend: 200°C - 20 min x500
b) Tin blend: 200°C - 20 min x500



(a)



(b)

mechanical energy is therefore needed if the particle shape or surface characteristics are to be significantly affected. Such conditions are not met in the Fielder Laboratory Mixer, unless of course the blending is carried to a point where degradation/gelation occurs.

4.5.2 Internal Structure

Fig. 48 are phase contrast micrographs of thin sections unblended PVC-S particles and Lead formulation blends discharged at 80° and 120°C. Corresponding samples of PVC-M are shown in Fig. 49. Typical micrographs of tin-formulation blends are given in Fig. 50.

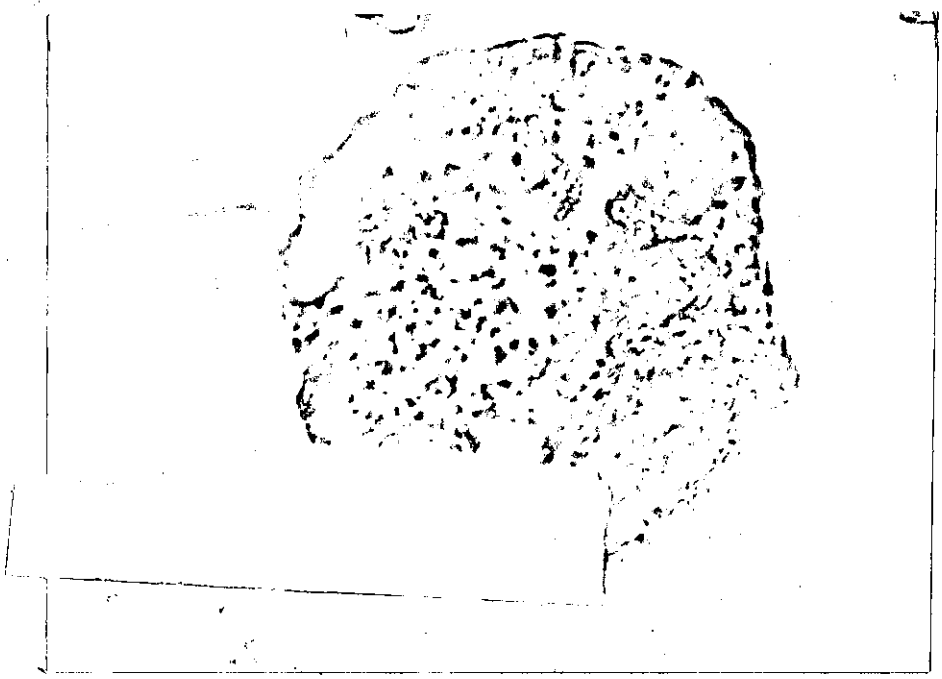
The resin particle structure, that is, the supermolecular structure, is observed in all cases and therefore it is not affected by blending. The 1 - 2 μm structures, the so called primary particles are clearly seen.

Since the electron microscope has a much higher resolution than the optical microscope it was used to examine the resin particles both before and after blending. Figs. 51-52 are typical transmission electron micrographs of ultra thin sections of powder particles. It is apparent the internal structure of a resin particle is not much affected by blending. Hattori et al[31] heated lead stabilised PVC powder particles in an oven at 220°C for 1 and 3 minutes. On examining the internal structure they found the 1 - 2 μm structures were still present in the resin particles heated for 1 minute. But in the case of particles heated for 3 minutes, only fibrillar structures ∿ 300 Å thick were found. They then concluded that while heat could be effective in breaking down the 1 - 2 μm particles, a combination of shear and heat increases the potential for structural modification of PVC. It is reasonable therefore to suggest that in the normal blending process, where shear effects are small, very little particle modification is to be expected.

Fig. 48: Optical micrographs (phase contrast) of microtomed sections of PVC-S particles.

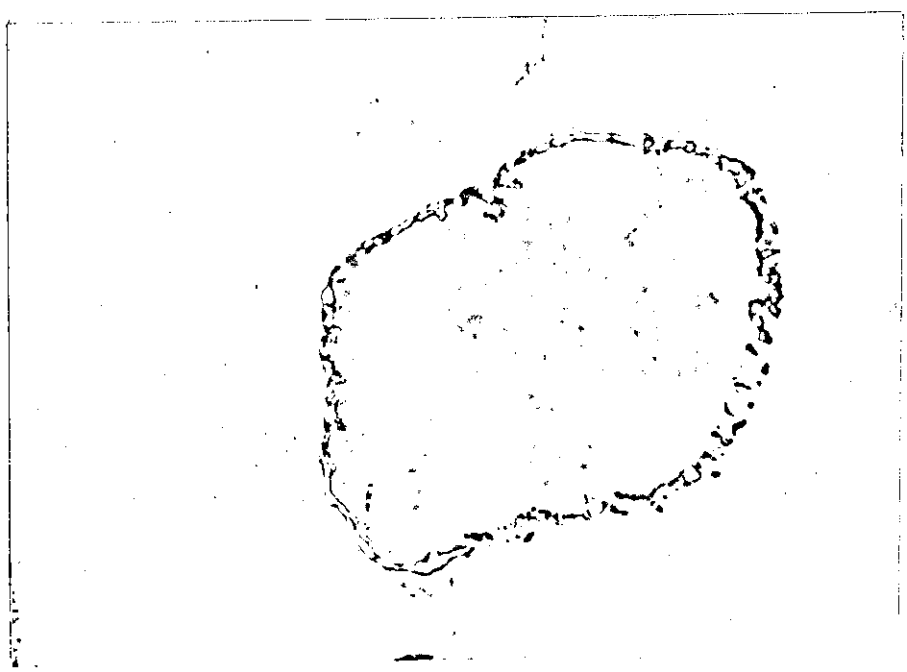
(a) unblended
(b) lead blend discharged at 80°C
(c) lead blend discharged at 120°C

Magnification: x600



(a)

(b)



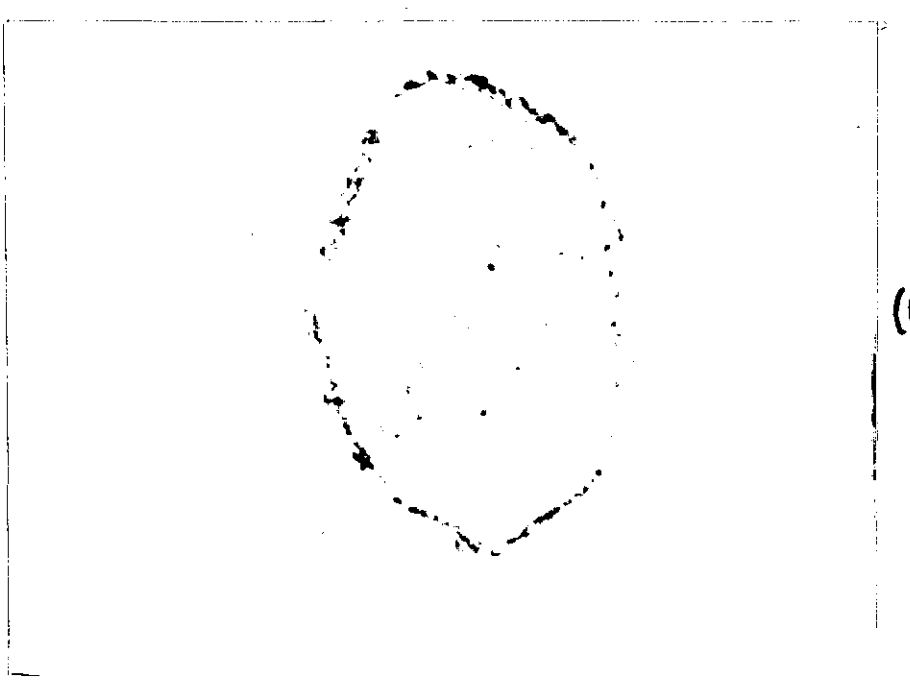
(c)

Fig. 49: Optical micrographs (phase contrast) of microtomed sections of PVC-M particles.
(a) unblended
(b) lead blend discharged at 80°C
(c) lead blend discharged at 120°C

Magnification: x600

(a)

(b)

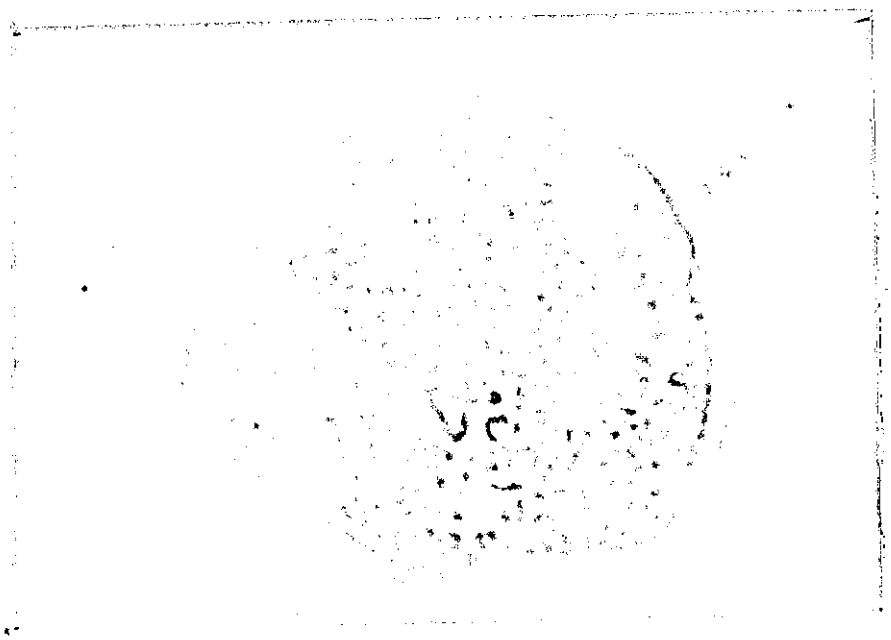


(c)

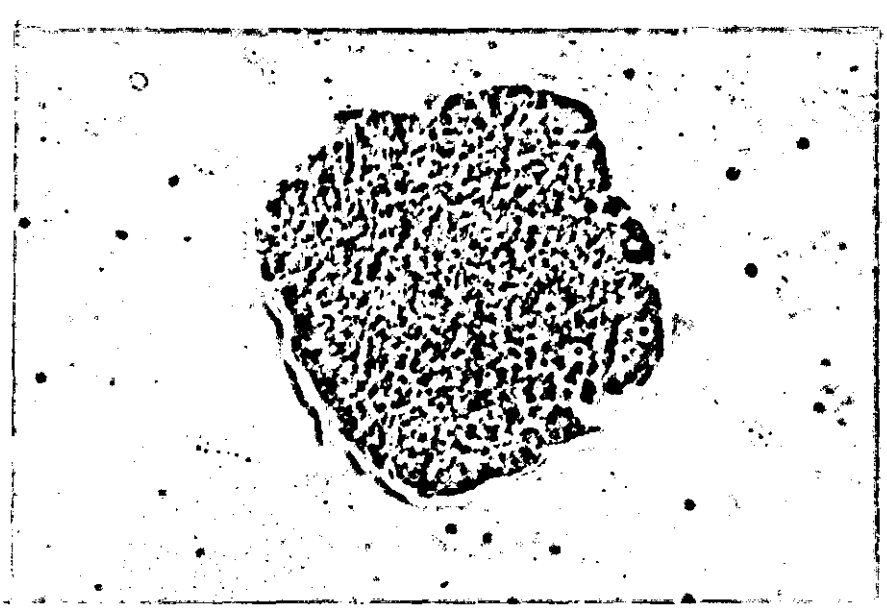
Fig. 50: Optical micrographs (phase contrast) of microtomed sections of PVC particles tin blends discharged at 140°C.

(a) PVC-S; (b) PVC-M

Magnification: x600



(a)



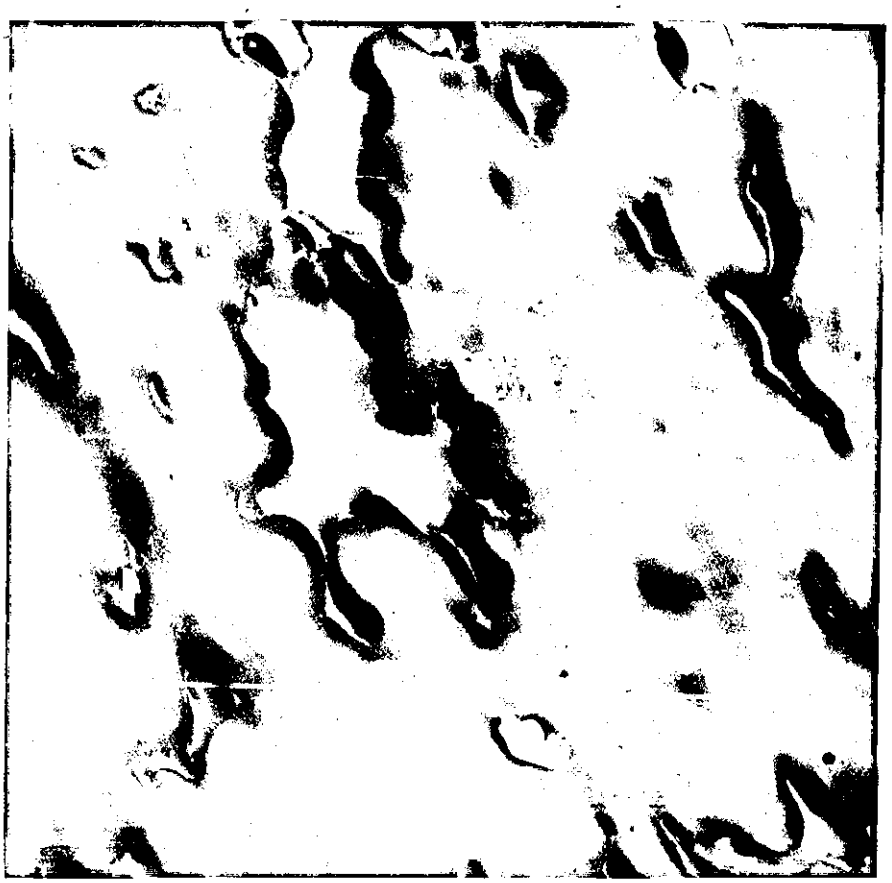
(b)

Fig. 51: Transmission electron micrograph of ultramicrotomed sections of PVC-S particles.

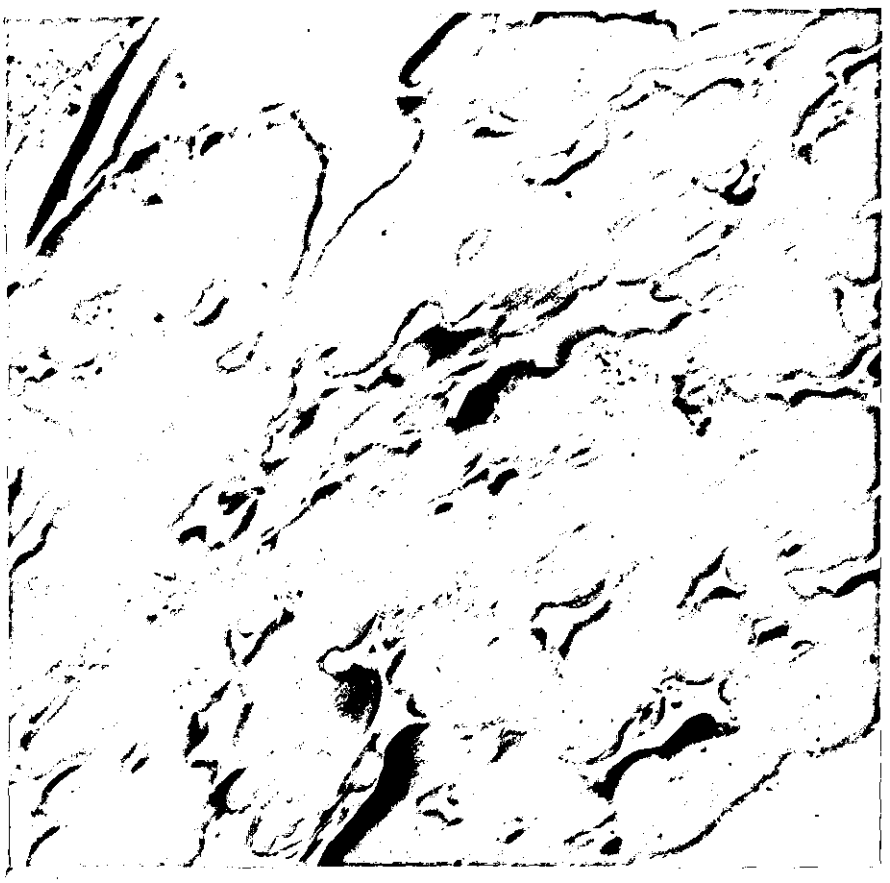
(a) unblended
(b) lead blend discharged at 140°C
(c) tin blend discharged at 140°C

Magnification: x3,000

(a)



(b)

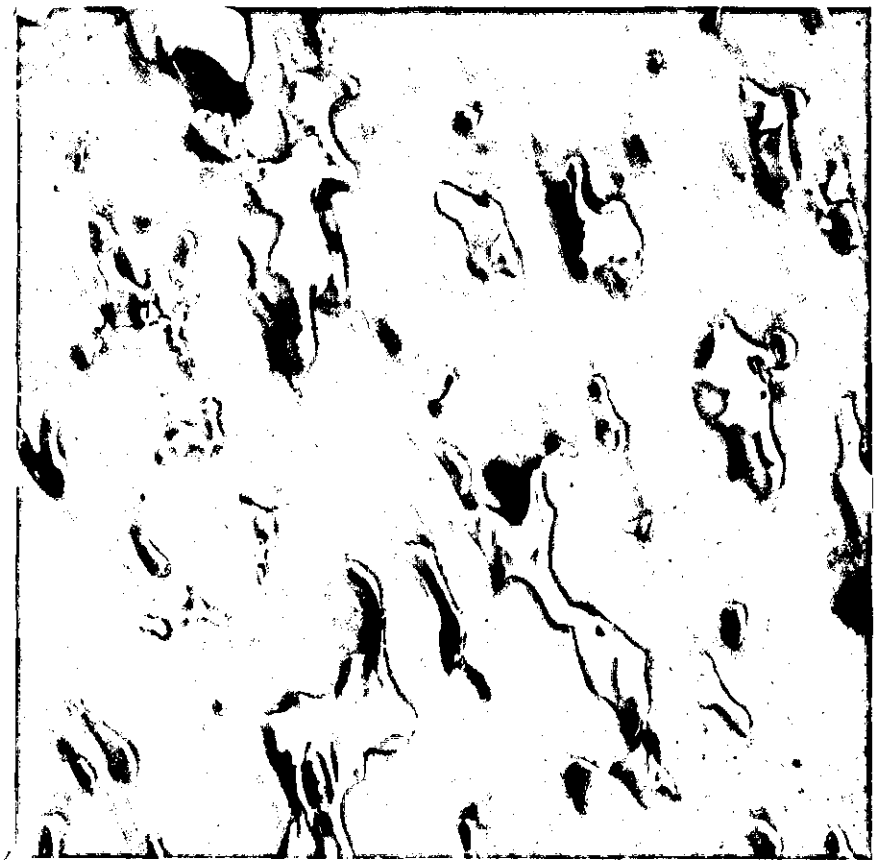


(c)

Fig. 52: Transmission electron micrograph of ultramicrotomed sections of PVC-M particles.

(a) unblended
(b) tin blend discharged at 120°C

Magnification: x3,000



(a)

(b)

4.5.3 Particle Size Distribution

At the outset of the investigation into the effect of blending cycle on the particle size distribution, it was thought prudent to compare closely size distribution results obtained from the Zeiss Counter and by Sieve Analysis.

Each method of particle size determination measures a different parameter. For example, a microscopic method like Zeiss TGZ3, measures the equivalent diameter of a sphere having the same projected area as the particle when viewed in a direction perpendicular to the plane of greatest stability. Sieve Analysis on the other hand, measures the equivalent diameter of a sphere.that corresponds to a square aperture of side A through which the particle just passes.

A recalculation of one set of results so that the data are comparable in terms of the parameter being measured is therefore necessary. To do this two assumptions are made: (1) individual particles are roughly equidimensional; (2) large and small particles have similar density. Microscopy suggests both assumptions are valid (see Figs. 27-28 - optical micrographs of PVC particles viewed by reflected light).

Fig. 53 shows the size distribution of unblended PVC-S. The class intervals of the histogram are dictated by the size of sieves used toobtain the results - illustrated by a full line. The dotted line shows Zeiss Counter results transformed into weight percent and using the same class intervals.

The two sets of results show real differences. They can be interpreted by postulating that particles in the interval 150-180 μm are mainly agglomerates, which are distinguished as such by the subjective sizing counter method but not by the Sieve Analysis. Thus the counter method distributes many of these larger 'particles' over

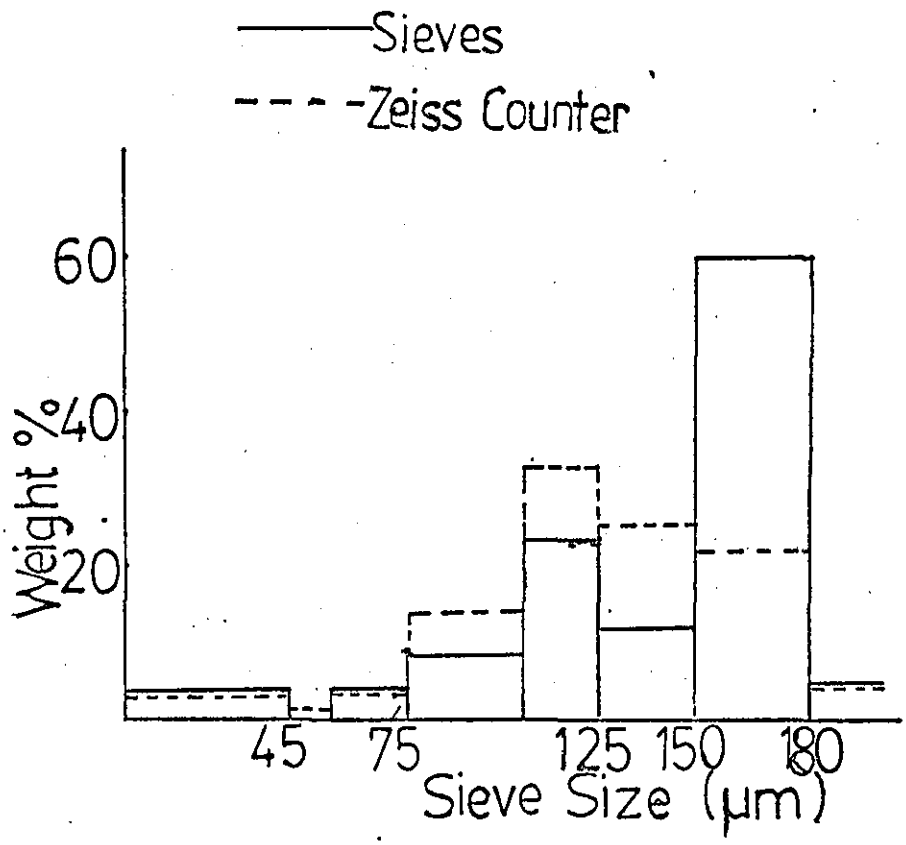


Fig. 53: A comparison of size assessment methods

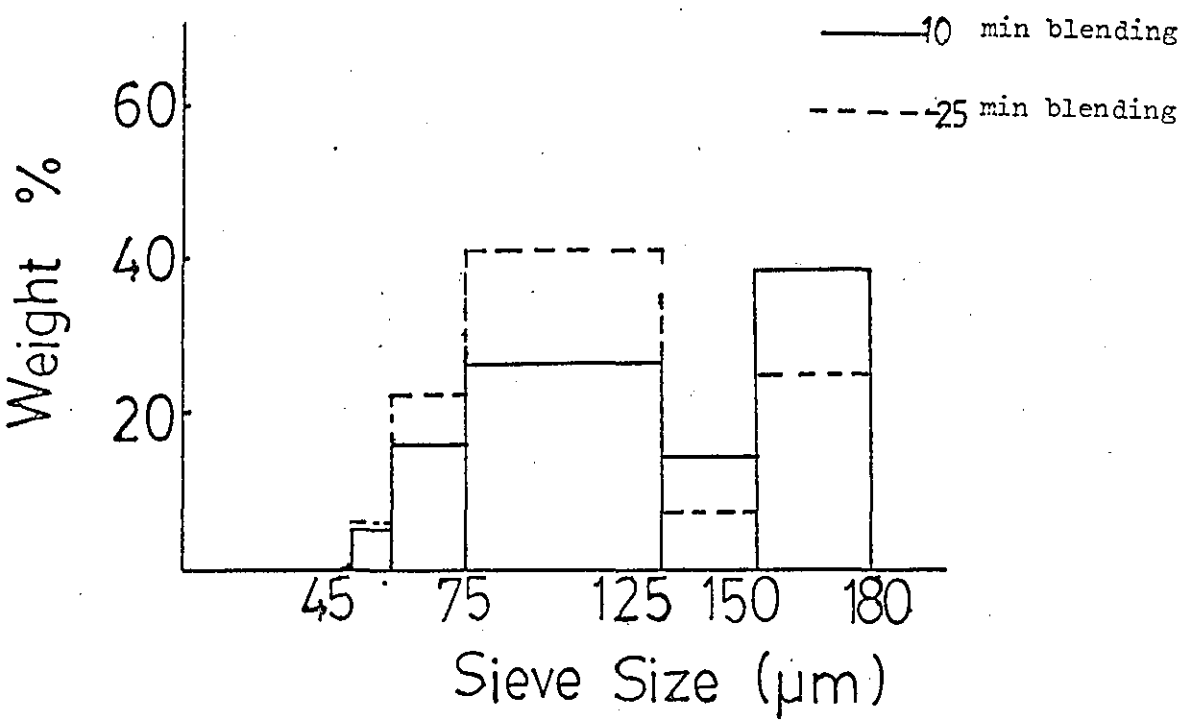


Fig. 54: The effect of blending time on powder size

the smaller class intervals, roughly in proportion to those passing through the 150 μm mesh. It is reasonable then to conclude that a critical analysis of powder particle size distribution is better carried out using the Zeiss Counter. The main drawback of the Zeiss Counter is that it could be tedious as it requires a very large number of particles to be measured in order to obtain a reliable and accurate result. If, for convenience, Sieve Analysis is used, since it is rapid and requires little operator skill, then it is necessary to exercise caution in interpreting differences in distributions in the upper size ranges.

With this in mind the size distribution of the powder after various periods of mixing (with a rotor speed of 600 r.p.m) are compared in Fig. 54. There is a substantial decrease in the number of large 'particles' above 125 μm in diameter and a corresponding increase in the incidence of smaller particles. The similarity between the result of using Zeiss Counter on unblended powder and the effect of blending time, suggests that the result of blending is largely the break up of agglomerates.

Figs. 55-58 show particle size distribution of blends discharged at various temperatures as determined by the Zeiss method. No substantial changes are observed for each formulation. Any changes observed are concerned with large particle diameters or agglomerates. It seems this is achieved quite early in the blending cycle. Gale[118] has also reported mixer discharge temperature does not affect size distribution, the only significant changes being a shift from 150 μm to 105 μm.

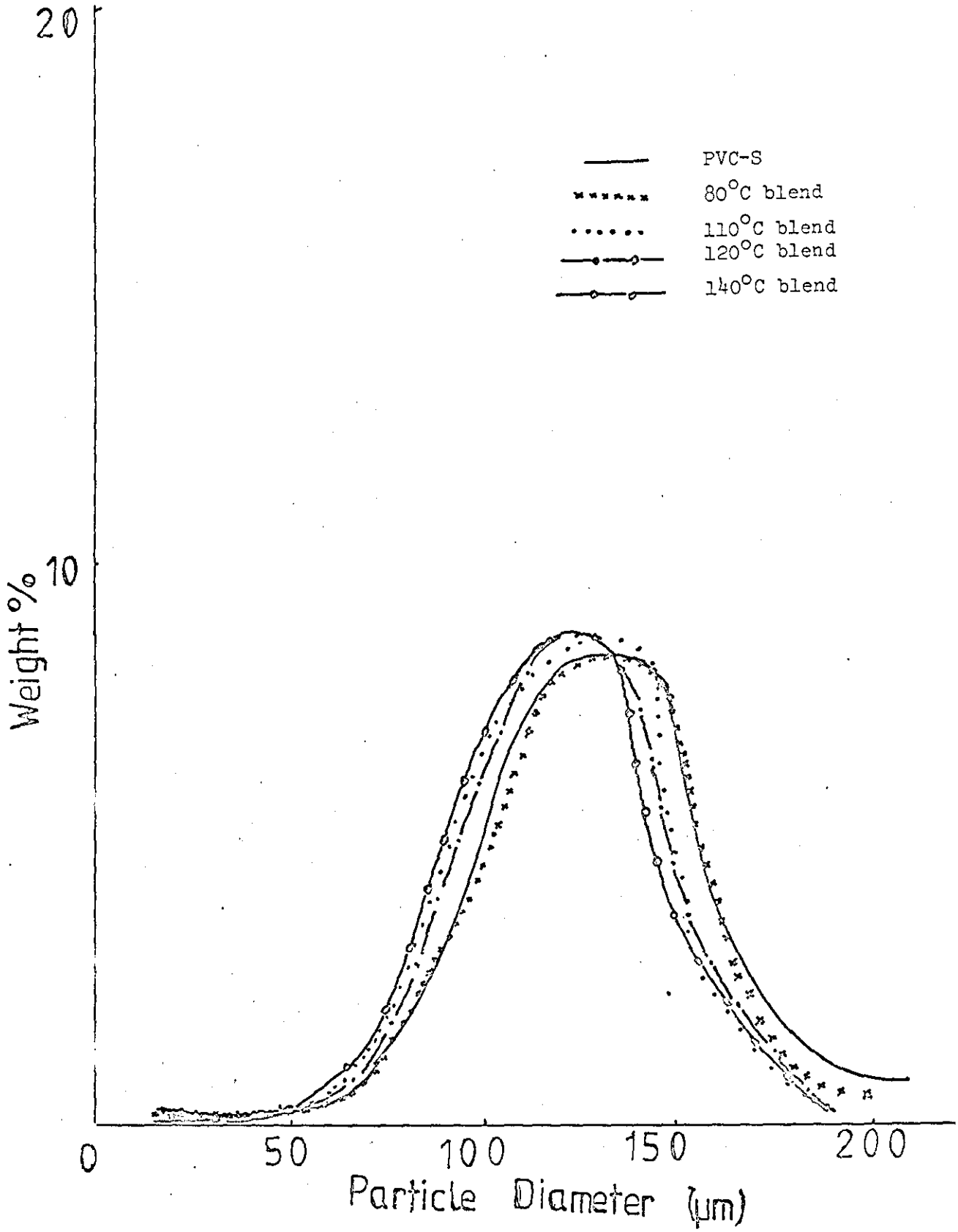


Fig. 55: Particle size distribution of PVC-S (Lead formulation) blends discharged at various temperatures

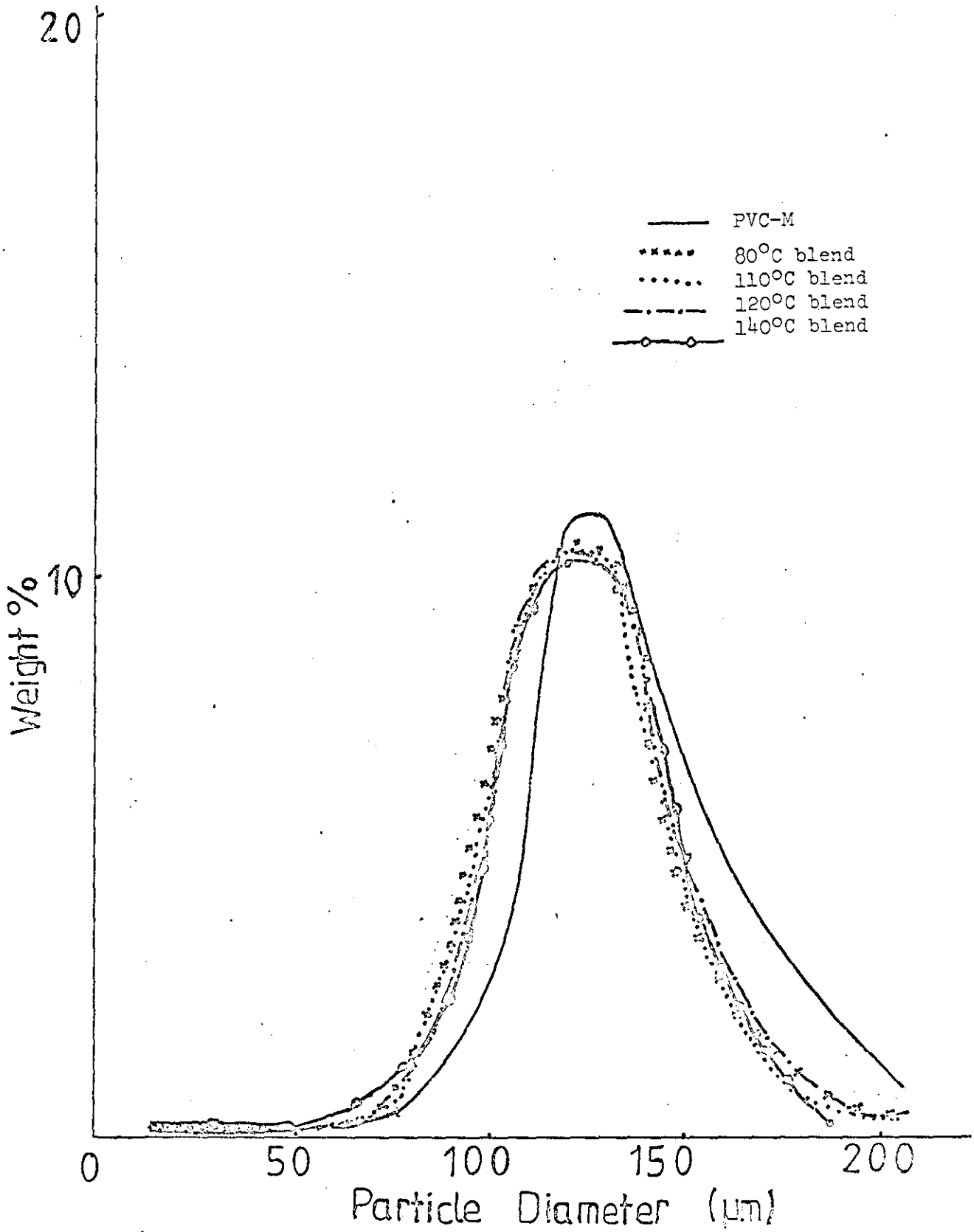
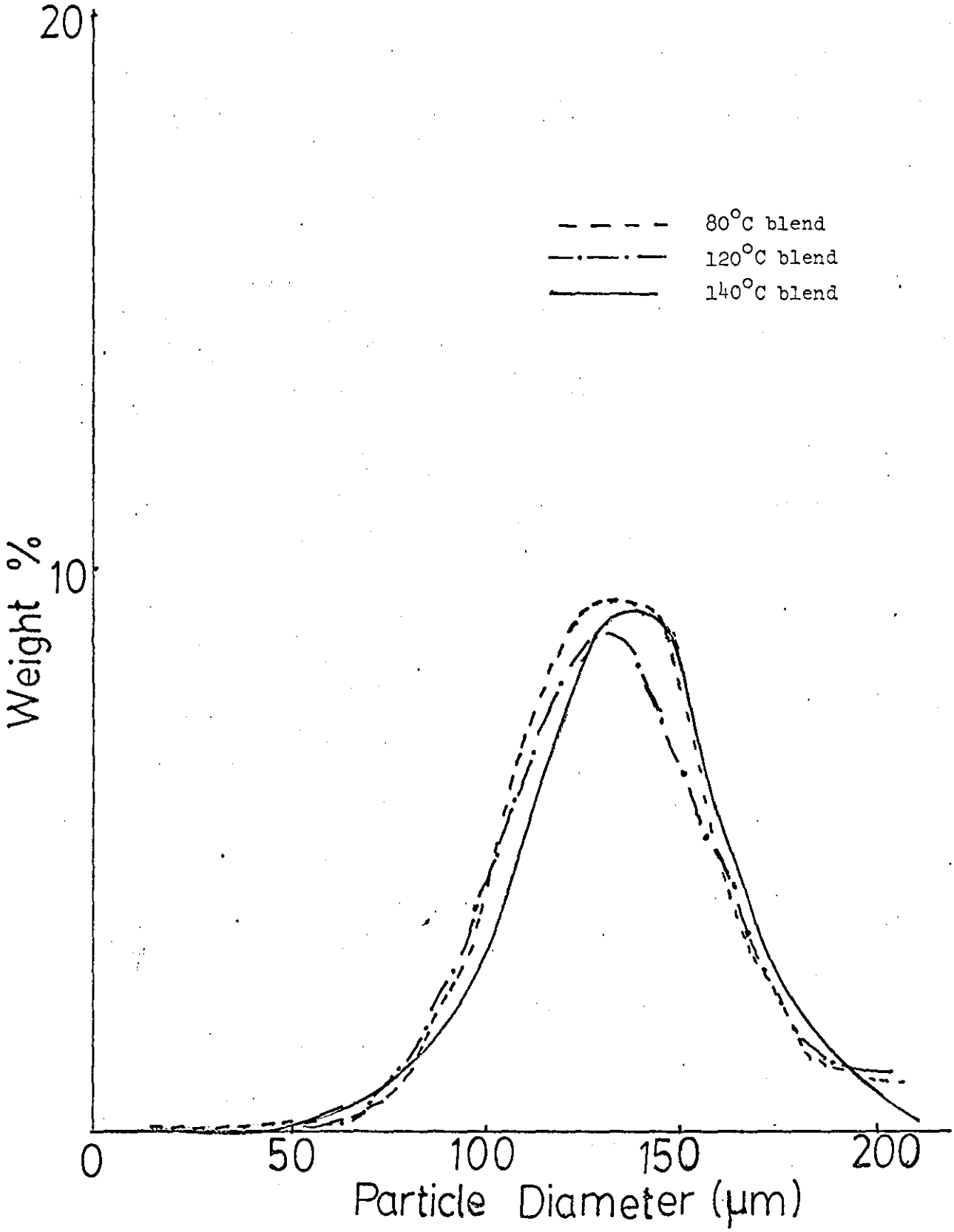


Fig. 56: Particle size distribution of PVC-M (Lead formulation) blends discharged at various temperatures



Fug. 57: Particle size distribution of PVC-S (Tin formulation) blends discharged at various temperatures

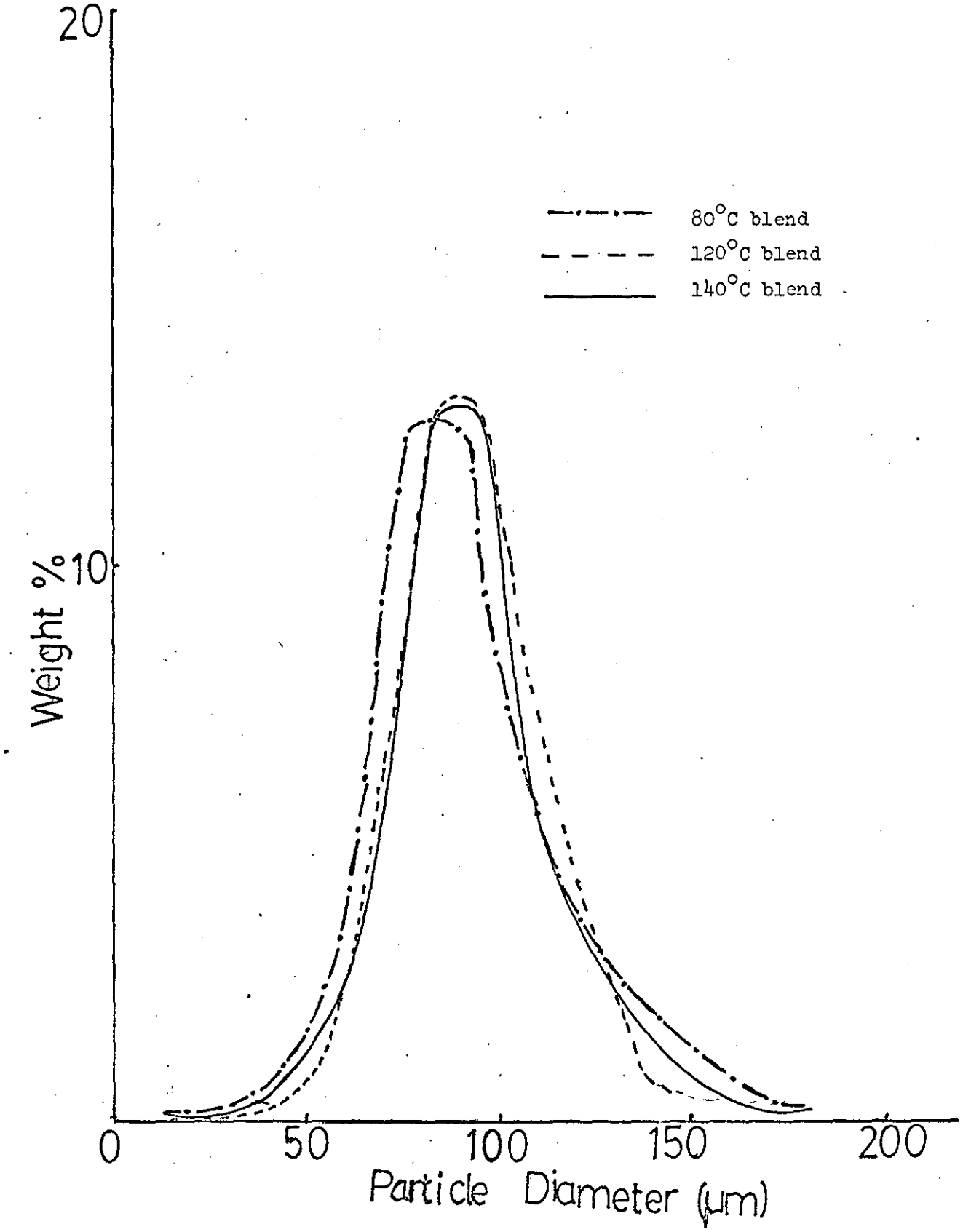


Fig. 58: Particle size distribution of PVC-M (Tin formulation) blends discharged at various temperatures

4.6 Evaluation of Processing Behaviour

4.6.1 Use of Capillary Rheometer

In Figs. 59 and 60 are the plots of extrusion pressure against shear rate for PVC blends discharged at various temperatures. These plots are curves showing non-Newtonian behaviour. The non-Newtonian behaviour of PVC is well known, starting from the early studies of Fukasawa[127], Sieglaff[128], Mayrick and Sieglaff[129] and Collins and Krier[42].

There is no significant change in these flow curves for any given formulation. This means that dry-blending temperature does not affect the flow characteristics of a given PVC composition. The extrusion pressure for the mass polymer is lower than that of the suspension and the difference is more pronounced for the two formulations especially at higher shear rates. That for the tin-blend is much lower than for lead-blends. The tin stabiliser is absorbed into the resin particle breaking up the three dimensional network and creating more free volume in the system. Just like plasticiser it lowers the viscosity of polymer and therefore should be easier to process.

The study of the rheology of PVC is complicated by two main factors. The first is that PVC has to be processed with the incorporation of various additives such as stabilisers, lubricants, fillers, plasticisers and processing aids. Secondly, during compounding and processing PVC undergoes different thermal and shear treatment.

The effects of the various additives on the flow behaviour or processability of PVC have been extensively studied and a recent review is given by Collins[130]. The work reported here was limited to the effect the various blend discharge temperatures have on the processability of a PVC formulation.

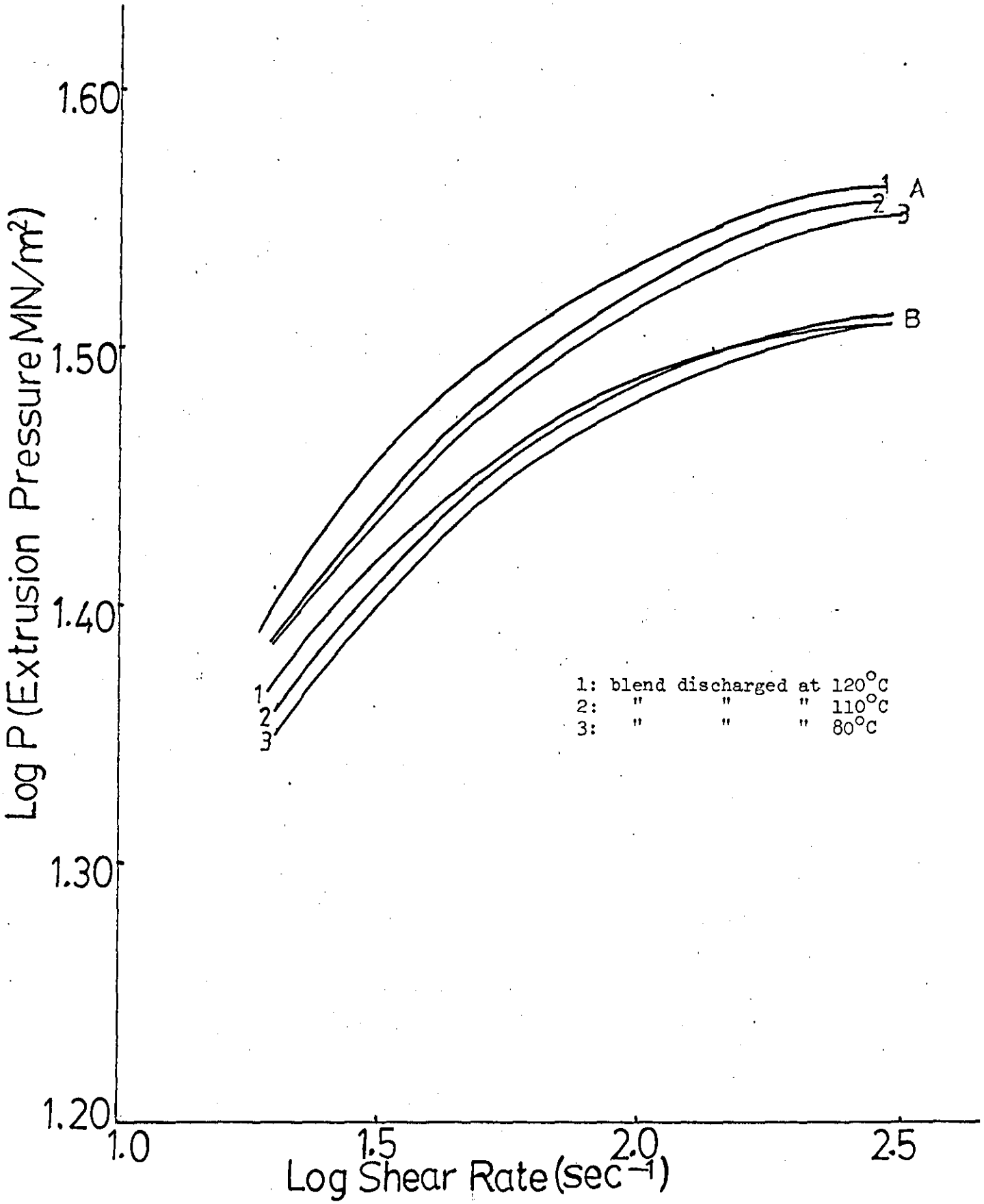


Fig. 59: Flow curves of PVC-S blends discharged at various temperatures
A, Lead formulation; B, Tin formulation

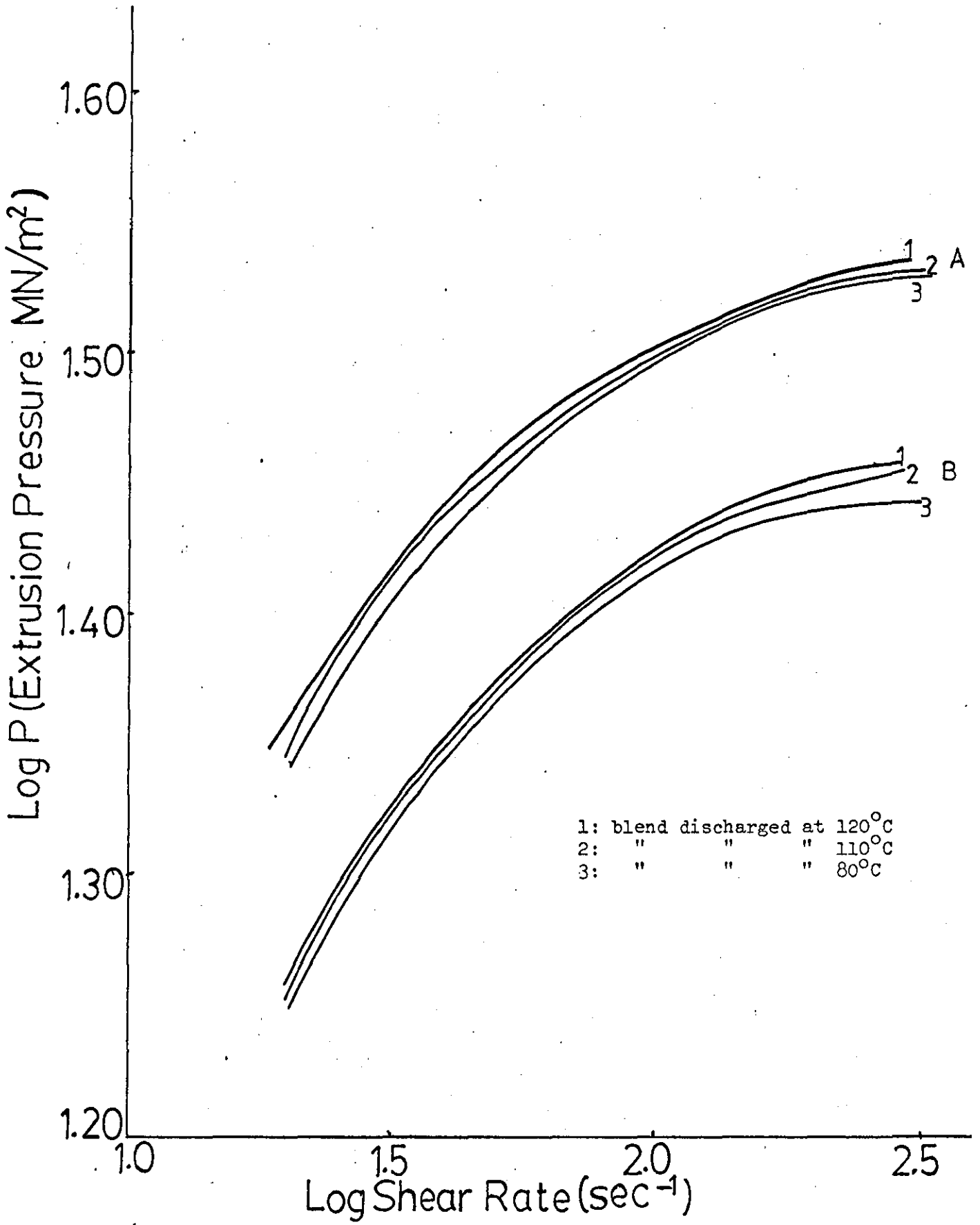


Fig. 60: Flow curves of PVC-M blends discharged at various temperatures
A, Lead formulation; B, Tin formulation

Khama[40] has studied in some detail the effects of pre-extrusion treatments by heat, shear and solvents; polymer variables and extrusion conditions on flow properties of PVC melts. He prepared some PVC samples by Banbury and roll milling, roll milling only and Banbury treatment only. On measuring the flow curves in a capillary rheometer at 150°, 170° and 190°C he found no significant differences.

Since dry blending does not appreciably change the morphology of PVC it seems reasonable that the flow curves of the blends are similar. Recently, attempts are being made to relate morphology to the flow behaviour[33,40,131,132]. Thermal and shear treatment can alter considerably the morphology of PVC. They would therefore be expected to affect the flow curves. Indeed, they have been observed to have a pronounced effect on the flow curves and properties of PVC.

4.6.2 Use of Torque Rheometer

The effect of blending temperature on fusion characteristics is given in Table 14. An example of fusion curves obtained is shown in Fig. 61.

For each formulation, PVC-M shows a higher fusion torque and smaller fusion time than PVC-S. This may be due to the known differences between the two polymers in their bulk density, particle shape, particle size and size distribution, porosity and presence of 'skin' in PVC-S. No marked differences are revealed in the fusion characteristics of the blends discharged at different temperatures. Both Gale[118] and More and Peek[121] have reported similar observations but offered no explanations. Direct comparison of results between formulations (A) and (B) must be avoided because fusion is affected not only by polymer type but also by the nature and level of additives.

Faulkner[34] has interpreted the processing behaviour of PVC

compounds in terms of breakdown of Stage III, Stage II and Stage I particles. The three peaks he observed in the temperature-torque curve correspond to these structural transformations. For a given set of experimental conditions the breakdown of Stage III particles depends on resin properties like particle size and size distribution, and bulk density. Larger Stage III particles would require more processing to break them down and the time to achieve that would depend on the bulk density of the powder resin.

The break down from Stage III to Stage II which is equivalent to fusion is influenced by additives. Additives affect the torque levels either by reducing the cohesive forces between the Stage II particles or by promoting interparticle friction between Stage III particles. Higher torque levels would intensify the breakdown process. Finally, from Stage II to Stage I depends on the K-value of the polymer.

In the foregoing sections it has been shown that the morphology of the PVC is largely unchanged by blending. Therefore the fusion characteristics of the blends for a given formulation should be expected to be similar. In fact Faulkner[34] compared the temperature-torque curves of a dry blend, partially fused granules and reground extrudate of the same PVC compound. He found that the partially fused granules and the dry blend gave a similar curve indicating a large number of Stage III and Stage II particles are still present in the former. This was confirmed by microscopy. But the reground extrudate had a different curve. Microscopic examination revealed it had mostly 'unfused' Stage II particles.

However, it is possible that the Brabender Plastograph is not sensitive enough to detect differences between the processing behaviour of the blends especially if these differences are on a fine scale.

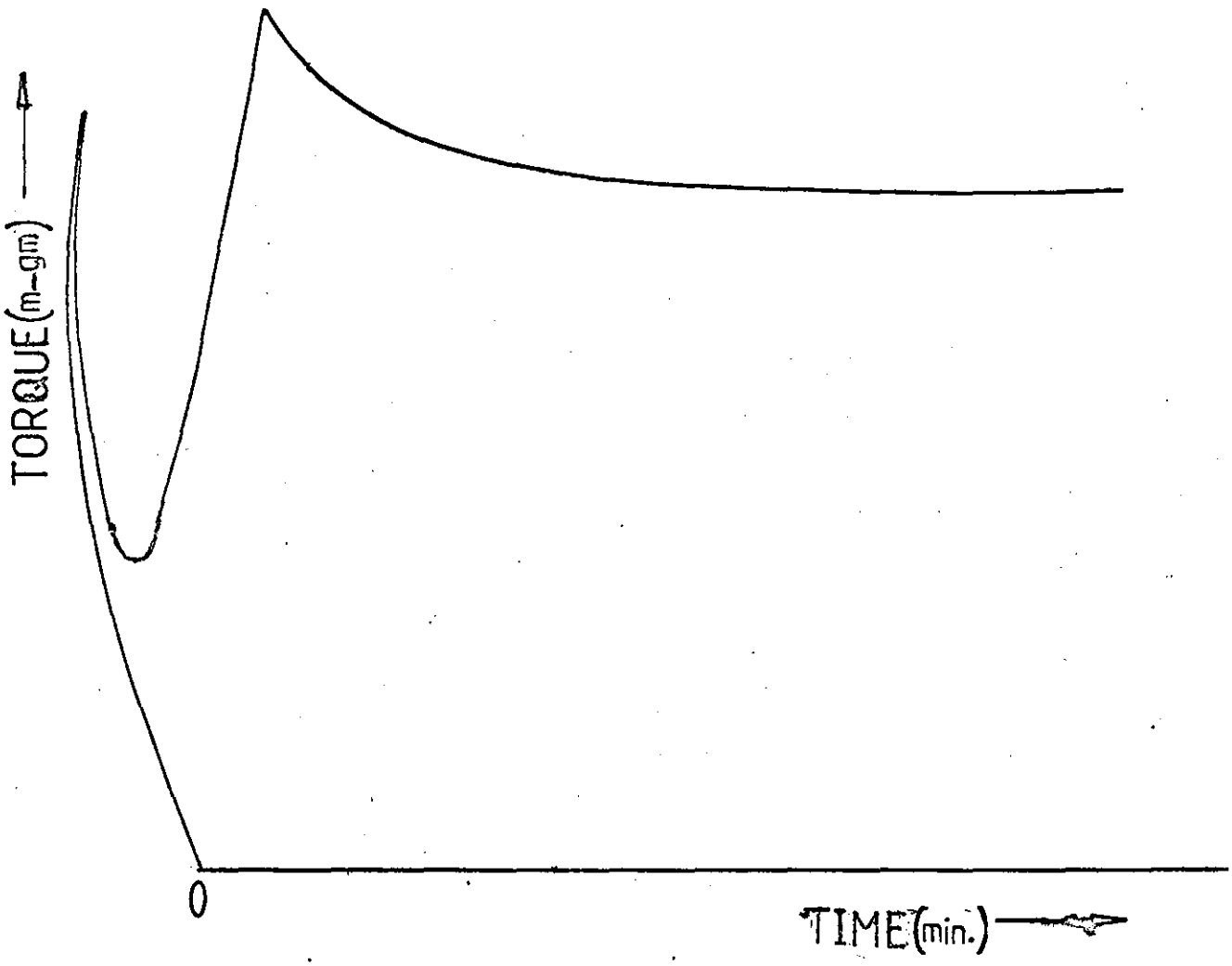


Fig. 61: A torque-time curve of PVC blend obtained in the Brabender plastograph

Table 14: Effect of Blending Temperature on Fusion Characteristics

Type of Blend	Discharge Temperature (°C)	Fusion Time (Min.)	Fusion Torque Metre-gramme	Melt Temperature (°C)
Formulation (A)				
PVC-S	80	2.7	630	154
	110	2.5	610	154
	120	2.4	608	154
	140	2.3	600	155
PVC-M	80	1.6	660	156
	110	1.4	640	157
	120	1.3	630	156
	140	1.3	625	156
Formulation (B)				
PVC-S	80	3.3	660	161
	110	3.2	635	160
	120	3.0	625	161
	140	2.9	620	160
PVC-M	80	1.0	740	152
	110	0.9	730	154
	120	0.8	730	153
	140	0.8	720	154

4.7 Conclusions

While the aim of blending with the T. K. Fielder mixer is to produce a PVC blend that is dry and free-running with the additives homogeneously distributed, certain important conclusions can be drawn from this study.

It is necessary to commence blending with at least one of the additives - TBLS or Calcium Stearate. Although they show contrasting effects on the generation of frictional heat, they both reduce interparticle friction thus maintaining the circulating movement of the powder. Otherwise the polymer powder soon cakes up and the blending operation comes to an abrupt end. Adding the Calcium Stearate at a later stage shortens the blending cycle. But the production time savings this offers has to be weighed against a higher homogeneity of blend that would be expected if all the additives were added at the start of blending.

Solid additives like TBLS with high melting points are not absorbed into the particle but coat the surface. Liquid tin stabiliser on the other hand, diffuses into the resin particle in a way similar to plasticisers. Blending to high temperatures will ensure the liquid stabiliser has fully diffused into the primary particles of the resin. Certainly this intermolecular dispersion of stabiliser would impart better heat resistance to the formulation.

Bulk density increases with blend discharge temperature. However, the rate of increase is not uniform throughout the temperature range studied and depends on the type of polymer and formulation. The biggest increase in bulk density occurs between the start of the blending and 80°-90°C. After 130°C bulk density increase is not substantial. A blend discharge temperature of 100°-130°C would therefore be suitable. Degradation of the polymer would be avoided and most volatiles would be

expelled at this temperature range.

Despite the fact that severe operating variables on the Fielder mixer were chosen with a view to significantly modifying the structure of the PVC powder particles, they remained largely unchanged. The significance of this is that the processing behaviour of blends discharged at different temperatures would be similar.

Scanning electron microscopy shows that particle shape is not markedly changed by blending although a gradual smoothing of the surface may be observed. This is attributed mainly to the coating of the surface by additives.

Both optical and transmission electron microscopy reveal the particulate structure of PVC is not altered by blending.

Particle size analysis using the Zeiss TGZ3 particle size analyser shows no substantial changes in the particle size distribution of the blends discharged at various temperatures. Any changes observed are concerned with large particle diameters suggesting that blending mainly results in a breakdown of agglomerates existing in the starting material. A subsidiary conclusion is that the more reliable method of analysis in this work is the Zeiss counter technique which allows subjective discrimination of agglomeration.

Torque and capillary rheometers have shown no significant differences in the processability of blends discharged at various temperatures for a given formulation. This is understandable in view of the fact that the morphology of PVC particle is largely unchanged by dry blending.

The general conclusion from this work on powder blending, using the equipment described therefore, is that the main effect of blending is a spatial rearrangement of the ingredients, with only minor modifications to particle shape, size and surface texture. Indeed,

attempts made to grossly exaggerate the severity of treatment, for example, by high velocity impact in a jet mill or low temperature grinding in liquid nitrogen, have failed to significantly increase these small modifications. This then suggests that even with much higher peripheral rotor speeds, little modification is to be expected from commercial blending equipments of the Fielder type. In practice, peripheral rotor speeds are independent of the size of the machine.

The PVC particles have shown apparent resistance to break-up, or gross deformation during blending. It is therefore highly probable that only by shearing PVC powder can changes be made to particle structure which would noticeably affect the subsequent handling and processing characteristics of the material.

PART II

PROCESSING OF PVC BLENDS

This section deals with the processing of the blends which were characterised in Part I. Moulding conditions, properties of mouldings studied including experimental techniques employed, results and discussions are treated in this section.

CHAPTER V

COMPRESSION MOULDING OF PVC

In this chapter the compression moulding of powder blends (section 2.3) is described. The objectives to be achieved from studying the properties of the mouldings and a brief review of literature on mechanical properties of PVC are also set out.

5.1 Introduction

PVC is processed by the application of heat, pressure and shear or a combination of any of these on the polymer after blending or compounding with additives. The different routes by which PVC is converted into finished products are shown in Fig. 6. The shear rates usually encountered in PVC processing are as follows:[197]

Compression moulding	$1 - 10\ sec^{-1}$
Milling and calendering	$10 - 10^2\ sec^{-1}$
Extrusion	$10^2 - 10^3\ sec^{-1}$
Injection moulding	$10^3 - 10^4\ sec^{-1}$

Compression moulding clearly involves minimum shear. One of the conclusions drawn in Part 1 of this research project is that shear is

vital to the modification of PVC structure.

The main objectives in this part of the work are to establish whether significant internal structure was present in mouldings made using a minimum of shear. It should provide the opportunity to observe the early stages of any structure modification.

Having examined the microstructure of the mouldings the mechanical properties would then be studied in order to correlate structure, processing conditions and properties.

Since useful information on process variables can be obtained from refractive index of a processed material, the refractive index of the mouldings would also be investigated.

5.2 Literature Review on Mechanical Properties

Mechanical properties have been used to study the structure of PVC. Malac[133] has shown a qualitative connection between processing conditions and properties of PVC samples. Tensile strength is increased, embrittlement temperature raised but impact strength reduced by slow cooling. He explained these results by a freezing-in of free volume during fast cooling. Phillips et al[134] reported annealing above the Tg increases the yield stress but decreases tensile strength and elongation. Retting[135] found that while there was a significant increase in modulus with annealing time at low strain rates, the effect at higher strain rates was small. Illers[136] felt changes in tensile behaviour were due to decrease in free volume for samples heat treated below Tg, and to crystallinity changes for those above Tg.

Pezzin et al[137] investigated the influence of thermal history and crystallinity on tensile properties of PVC. They found that crystalline PVC has lower tensile strength, elongation at break and impact strength

than conventional suspension PVC. Room-temperature modulus and yield properties are little affected by processing history and crystallinity. But elongation at break and fracture energy increased with milling temperature. Scanning electron microscopy of surfaces of specimens fractured at -180°C revealed the persistence of particulate structure in the polymer. Pezzin et al therefore considered the mechanical behaviour to be a consequence of the retention of particulate structure in the PVC.

Shinozaki et al[6] examined the effect of a variety of processing parameters on the mechanical properties of rigid PVC. They showed that yield stress, modulus and density increase with annealing pretreatment, each reaching a limiting value.

A number of authors[138-144] have investigated creep and stress relaxation of both rigid and plasticised PVC. They interpreted their results in terms of a three-dimensional network. Alfrey et al[139] and Walter[140] also added the idea of crystallite cross-linking, explaining the differences in action of different plasticisers as either promoting or retarding crystallization. Further support of the cross-link theory has come from the study of viscoelastic properties of plasticised PVC by Taylor and Tobolsky[141]. Crugnola et al[142] have also attributed the elastic behaviour they observed to crystallite cross-links. Sabia and Eirich[143,144] proposed two mechanisms of creep behaviour. First, there is elongation of the amorphous regions followed by deformation of the crystallites, thereby causing flow and set.

5.3 Preparation of Mouldings

The powder blends (prepared in section 2.3) were moulded into 20x20 cm sheets of 3 mm thickness in a steam-heated press. The blends were left in the mould with full pressure (30 tons on 8 in diameter

ram) for 10 minutes at various temperatures ranging from 130°-200°C. The mould was then cooled down with water to 30°C in 4 minutes.

In the interval between specimen moulding and testing, the moulded sheets were stored at -21°C in a deepfreezer to inhibit any morphological changes which might otherwise take place. Dunn and Turner[145] have shown slow changes occur in modulus and creep behaviour of PVC during prolonged storage. They explained the results in terms of changing free volume. Illers[146] in his study on the influence of thermal history on properties of PVC found that duration of room temperature storage resulted in changes in the samples. For instance, the density of a sample quenched from 130°C to -70°C increased the longer it was kept at room temperature. Specific heat changes were larger in the glass transition range from quenched samples stored at room temperature.

After measuring the refractive indices of the mouldings as prepared above it was thought desirable to correlate these indices with crystallinity and hence moulding temperatures. Amorphous samples were therefore needed for estimating the crystallinity in the mouldings.

To prepare an amorphous sample a piece of moulding was wrapped with aluminium foil and heated for 5 minutes in an air-circulating oven kept at 210°C. It was then quenched immediately in ice/water mixture.

The amorphous nature of the moulding so prepared was checked by X-ray diffraction spectra using Jeol DX-GE-2S generator and a DX-GO-S vertical goniometer with Ni-filtered CuK_α radiation in an air atmosphere. The operating conditions used were as follows:

X-ray tube	:	40 kV 30 mA
Range	:	2×10^3 cps
Time Constant	:	2

Scan speed	:	1°/min
Divergence slit	:	2°
Receiving slit	:	0.2^{o}
Scattering slit	:	2°
Angular Range	:	$12-46^{o}2\theta$

Plots of intensity in arbitrary units versus diffraction angle 2θ were obtained. A typical trace is shown in Fig. 62. Compared with a normal untreated moulding the two peaks at 17° and $19^{o}2\theta$ have merged into one at $17.5^{o}2\theta$. This is typical of non-crystalline patterns observed by other workers[186-190].

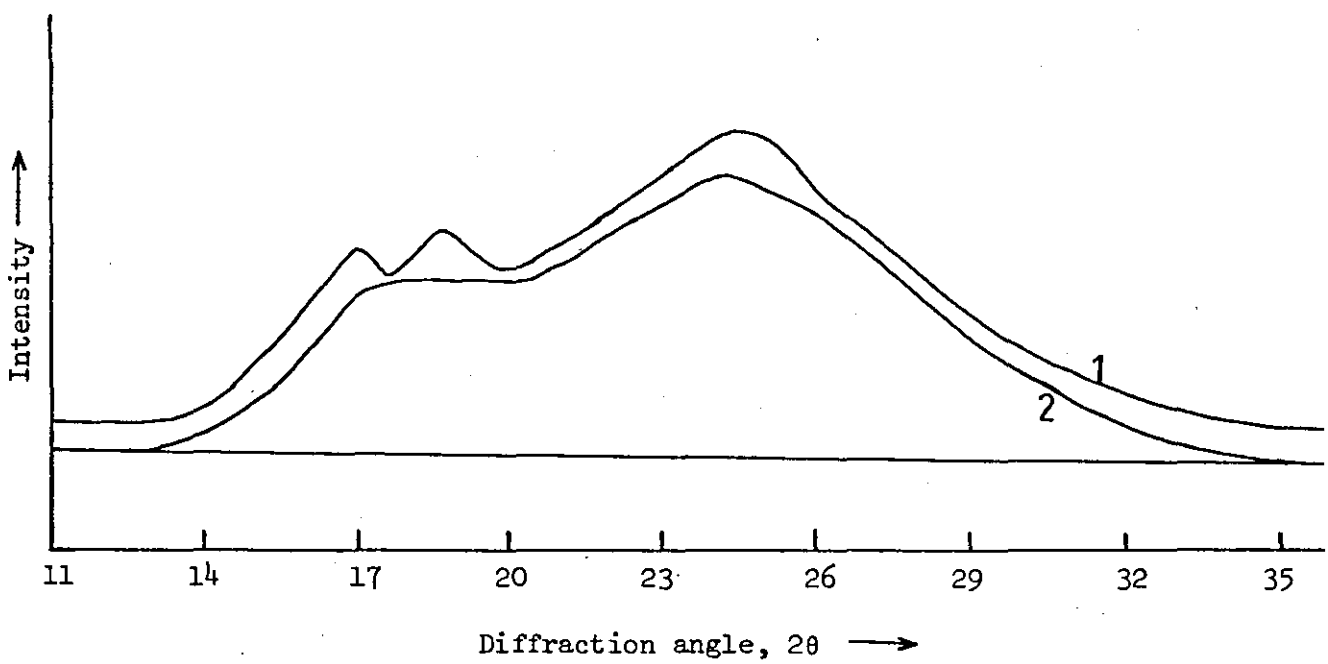


Fig. 62: X-ray diffraction trace for compression moulded PVC:

1, normal moulding; 2, amorphous moulding.

CHAPTER VI

EXPERIMENTAL TECHNIQUES

The experimental methods employed to study the mechanical properties, microstructure and refractive indices of the mouldings are presented. They are principally tensile testing and microscopy.

6.1 Tensile Testing

The literature review shows that the mechanical properties of PVC depend on processing history. Processing history involves mechanical history e.g. injection moulding, extrusion etc; and thermal history such as when a polymer is cooled quickly or slowly from the melt or heated again after solidifying.

The stress-strain curve can provide considerable information about the mechanical properties of a polymer. The form of the curve for a given polymer is profoundly influenced by the rate of strain and temperature of test.

Extreme care in the preparation of tensile bar specimens is vital if reproducible results are to be obtained. After routing out the tensile test bar specimens from the sheets, the machined edges were polished with sand-paper in order to remove any sites of stress concentration. The dimensions of the tensile bar samples are shown in Fig. 63.

Tensile tests were carried out at room temperature (22±1°C) on a J J Tensile Testing Machine Type T5002 having previously kept the samples for 24 hours at this temperature. The operating conditions on the J J are given in Table 15. The yield stress or break stress was calculated from the maximum stress and the initial cross-sectional area.

The strain was calculated from the initial length and the extension recorded on the graph by the instrument. Five specimens were tested for each moulding and the average result reported.

Table 15

Load Cell Full Deflection	:	5 KN
Cross head speed	:	5 mm/min
Paper/Cross head Ratio	:	10/1

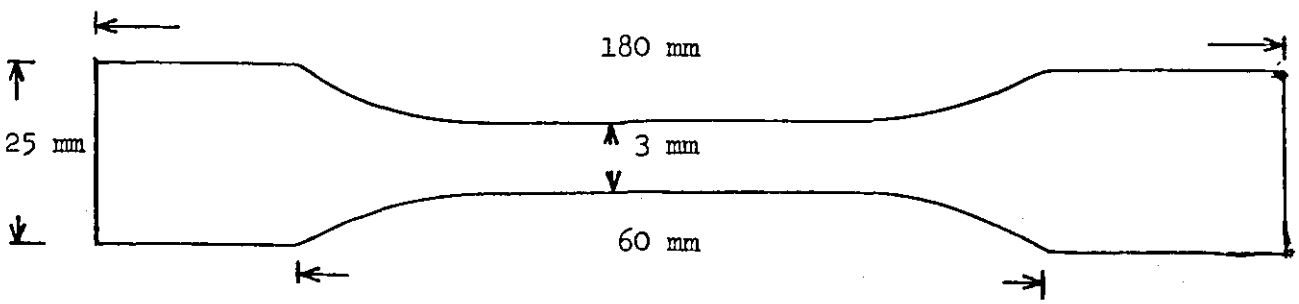


Fig. 63: Tensile bar Sample

6.2 Microscopy

Optical and electron microscopy were used to examine the microstructure of the mouldings. Sample preparation included microtomy and ion beam etching.

6.2.1 Microtomy

Thin sections were prepared directly from the mouldings for optical and transmission electron microscopy using a base sledge microtome and an LKB Ultratome respectively. However, efforts to obtain sections 200-300 Å thick in order to exploit the high resolution of the

transmission electron microscope (see section 3.1) were unsuccessful. Therefore about 800-900 Å thick sections were cut. Even then, many of these sections were 'shredded' or curled up or not coming off easily from the surface of the knife.

6.2.2 Ion Beam Etching

It is more than possible that stage I particles (10-20 nm) are very closely packed in processed material and hence the inter-space voids will be quite small. Therefore even if good quality 500 Å thick sections are successfully cut, they will contain some six to eight layers of stage I particles within their total depth. It is not too surprising that these particles will not be resolved by conventional t ransmission electron microscope.

Ion beam etching technique was therefore employed in the sample preparation for electron microscopy. Ion beam etching basically involves bombarding the surface of a material placed in an evacuated chamber with inert gas ions, usually argon ions. The ions are generated by means of a high frequency coil and accelerated through a direct voltage.

Several articles describing the applications and techniques of ion-etching have appeared in the literature[147-151]. Recent ones by Gloersen[148] and Norgate and Hammond[149] discuss the parameters governing the ion-beam etching of materials. An atom at the surface of a material is removed if the energy transfered to it by the incident ions is greater than the chemical binding energy; or if the momentum imparted to the atom is directed away from the surface. Thus there is a threshold energy for the incident ions before an atom can be removed from the surface of the material. It is characteristic of the material and its crystallographic arrangement and depends on the mass of the incident ion.

The detailed mechanism of etching of polymers is far from clear. It seems the amorphous regions are more easily attacked by the argon ions. Samples of PVC mouldings were first trimmed to a pyramidal shape and the top was then cut on the LKB Ultratome. The parameters for the ion-etching were as follows:

Gas	:	Argon
Pressure	:	0.01 m bar
HF-frequency	:	27 mHz
HF-current	:	80 m A
Time	:	4 hrs.
Direct voltage	:	None

To avoid the surface of the PVC specimen being heated by the concentrated ion bombardment, accelerating direct voltage was not used. After etching, the specimen was then coated with gold and examined in the scanning electron microscope as previously described. (See section 3.1.3).

6.3 X-ray Microanalysis of Mouldings

One of the consequences of a beam of electrons striking a solid surface is the emission of X-rays (see Fig. 9). These X-rays are characteristic of the particular element and therefore by measuring their wavelengths or energies the elements present can be identified. In practice, an electron beam is focused on a small area of a thin specimen. The X-rays emitted are collected by an X-ray detector.

Basically there are three types of X-ray detector: the wavelength dispersive crystal spectrometer; the energy dispersive solid state detector; and gas-flow proportional counter. Each detector has certain advantages and disadvantages but will not be discussed here. These could be found in texts[152] and by comparing manufacturers' claims.

An energy dispersive detector was coupled to a JEM-100CX TEMSCAN electron microscope made by JEOL and used to locate the additives in the ultrathin sections.

6.4 Fracture Surface Examination

Considerable information about the structure and the mechanisms taking place during fracture can be obtained from the study of fracture surfaces of polymers. The path taken by the fracture is such as to proceed through areas of minimum strength. As much as possible it avoids cutting through polymer chains where it has to break strong covalent bonds. In an inhomogeneous material like one containing fillers, the fracture front passes around the fillers which are obstacles but goes through the weak points in the material. Fracture behaviour therefore is not only affected by the structure but the fracture path reveals the microstructure of the material.

Fracture surfaces from the tensile test bars were mounted on a stub and sputter coated with gold as previously described. (See page 38) They were then examined in the 'Cambridge S2A Stereoscan' scanning electron microscope.

6.5 Measurement of Refractive Index of Mouldings

A polymeric material may be identified by comparing its refractive index with a known specimen or with data from the literature. For processed material refractive index can provide significant information on the variables involved in the processing. Thus if the molecules have been oriented during processing, for example by stretching or drawing, the stress introduced can be assessed by measuring the difference in refractive indices in the directions of interest, that is,

the birefringence of the material, and the consequent effect on properties. In practice, the refractive indices measured are usually the "principal refractive indices" corresponding to the direction of the principal stresses.

The refractive indices of the mouldings was measured by an interferometric method. A transmitted light interference microscope - Jamin-Lebedeff System - attached on Zeiss Universal Polarising Microscope was used.

In this system there is complete separation of the image field into reference and measurement regions by the use of polarised light and doubly refracting optical components.

The principle of the system is illustrated in Fig. 64. Light from source S (initially considered monochromatic) is plane polarised by polariser P and then divided by the beam splitter R_1 into two rays polarised at right angles. The beam splitter is a birefringent doubly refracting prism in the 45° position i.e. in the "diagonal position". The ordinary ray goes straight through without change in direction while the extraordinary ray is laterally displaced. Both rays now pass through a half wave plate which rotates their plane of polarisation through 90° i.e. the polarisation planes of the original O and e rays are interchanged. One set of rays pass through the specimen and the others by-pass it through a reference area before both enter the beam combiner R_2 which is identical to R_1 in nature and orientation.

If the specimen, with respect to the reference region has a zero or an integral number of wavelength optical path difference (OPD), recombination results in a plane polarised beam whose plane of polarisation is at right angles to the plane of the analyser A. The image field of view is thus dark. Other cases will result in elliptically polarised light reaching the analyser and a component traverses the analyser giving, in general, a bright image.

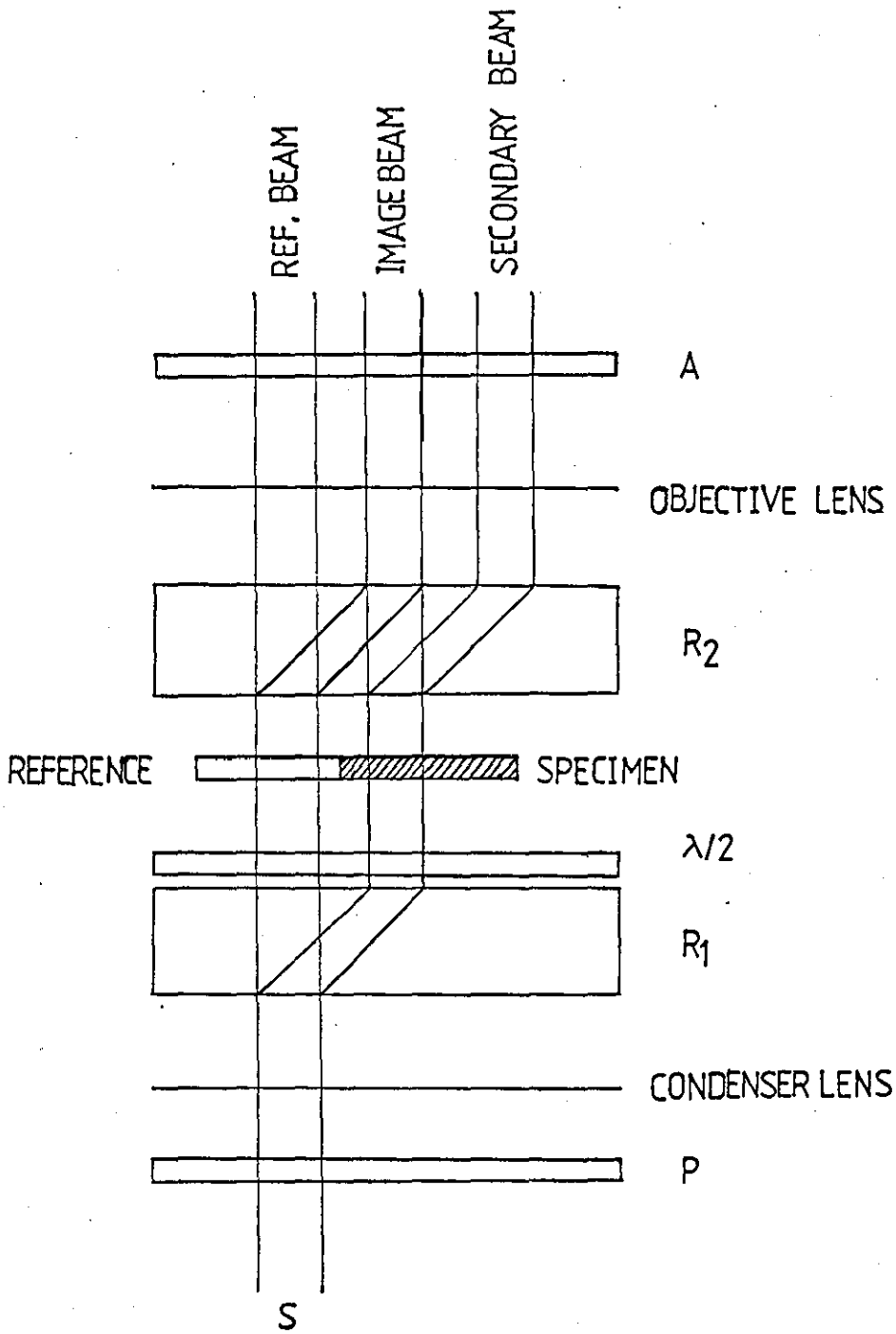


FIG.64: PRINCIPLE OF JAMIN-LEBEDEFF SYSTEM

Details of operation of the microscope can be found in the manufacturer's handbook. The following precautions were taken in order to obtain accurate and reliable results:

1. interference equipment is usually delicate and the performance is adversely affected by dust and dirt. It was therefore important to ensure the absence of dirt and dust from all optical pieces before setting up the microscope with carefully adjusted interference system.
2. Only cover slips and slides that are strain and striation free, flat and not wedge-shaped were used. This was checked by adjusting the interference background to red or purple colour which remained unchanged as the slide and or coverslip was moved or rotated.
3. High quality sections were used - 1 μm thick sections cut with the LKB ultratome.
4. Monochromatic light instead of white light was used. White light will, for increasing OPD, produce a sequence of image colours identical to those of Michel-Levy Colour Chart.

The optical path difference between the rays passing through the specimen and those through the reference medium was measured with the Ehringhaus compensator. The Ehringhaus compensator is of the rotary type and made from Calcite plate. It was inserted into the diagonal body of the microscope and rotated about a horizontal axis until the extinction of the background was transferred to the specimen. This setting was corrected with monochromatic light by inserting green filters, for maximum extinction. To reduce measuring errors the compensator tilt was made on either side of the horizontal zero position and the average angle of tilt (θ) taken. θ was either substituted into the formula

$$\Gamma_\lambda = {}_\omega^\varepsilon\sqrt{\omega^2 - \sin^2 i} - \sqrt{\varepsilon^2 - \sin^2 i}$$

where Γ_λ = phase difference in μm at wavelength λ

ω = refractive index of the ordinary wave

ε = refractive index of the extraordinary wave

i = angle of inclination of the plane of the plate relative to its zero position

or used to obtain the optical path difference of the compensator plate and hence that of the specimen from the tables supplied with the equipment.

The refractive index of the mouldings was determined as follows:

1 μm thick section of the PVC moulding was mounted on a slide and the optical path difference measured as described above. A few drops of paraffin oil placed by the side of the cover slip was allowed to cover the section by capillary action. The path difference was again measured.

OPD is given by the expression

$$d = t\,(n_1 - n_2)$$

where d = optical path difference

t = section thickness

n_1 = refractive index of specimen

n_2 = refractive index of mounting fluid.

n_p, refractive index of paraffin oil, was accurately determined on the Abbe refractometer at 23±1°C; if n = refractive index of specimen then

For air as mounting medium $d_1 = t(n - 1)$ (1)

For paraffin oil as the mounting medium $d_2 = t(n - n_p)$ (2)

From (1) and (2),

$$\frac{d_1}{d_2} = \frac{n - 1}{n - n_p}$$

If $\frac{d_1}{d_2}$ i.e. the ratio of the optical path difference with air and paraffin oil as the mounting media is D then

$$n = \frac{Dn_p - 1}{D - 1}$$

For each moulding five determinations were carried out and the average reported.

Two main difficulties were encountered in this test. First was the problem of finding an entirely satisfactory mounting liquid which will not attack or swell the PVC sections. For instance, when glycerol was used as the mounting liquid the optical path difference measured by the angle of tilt of the compensator, changed rapidly with time. That means the thickness of the section altered as a result of attack by the glycerol.

Secondly, the thickness of the section is critical. If the section is too thin, say less then 1μm, the optical path difference in the mounting medium becomes too small. If it is more than say 2 μm thick then the optical path difference will be too large. In either case the accuracy of measurement is grossly affected. A more suitable method would be the wavelength variation technique. But this would involve extra cost in equipment, particularly a monochromator.

CHAPTER VII

RESULTS AND DISCUSSION

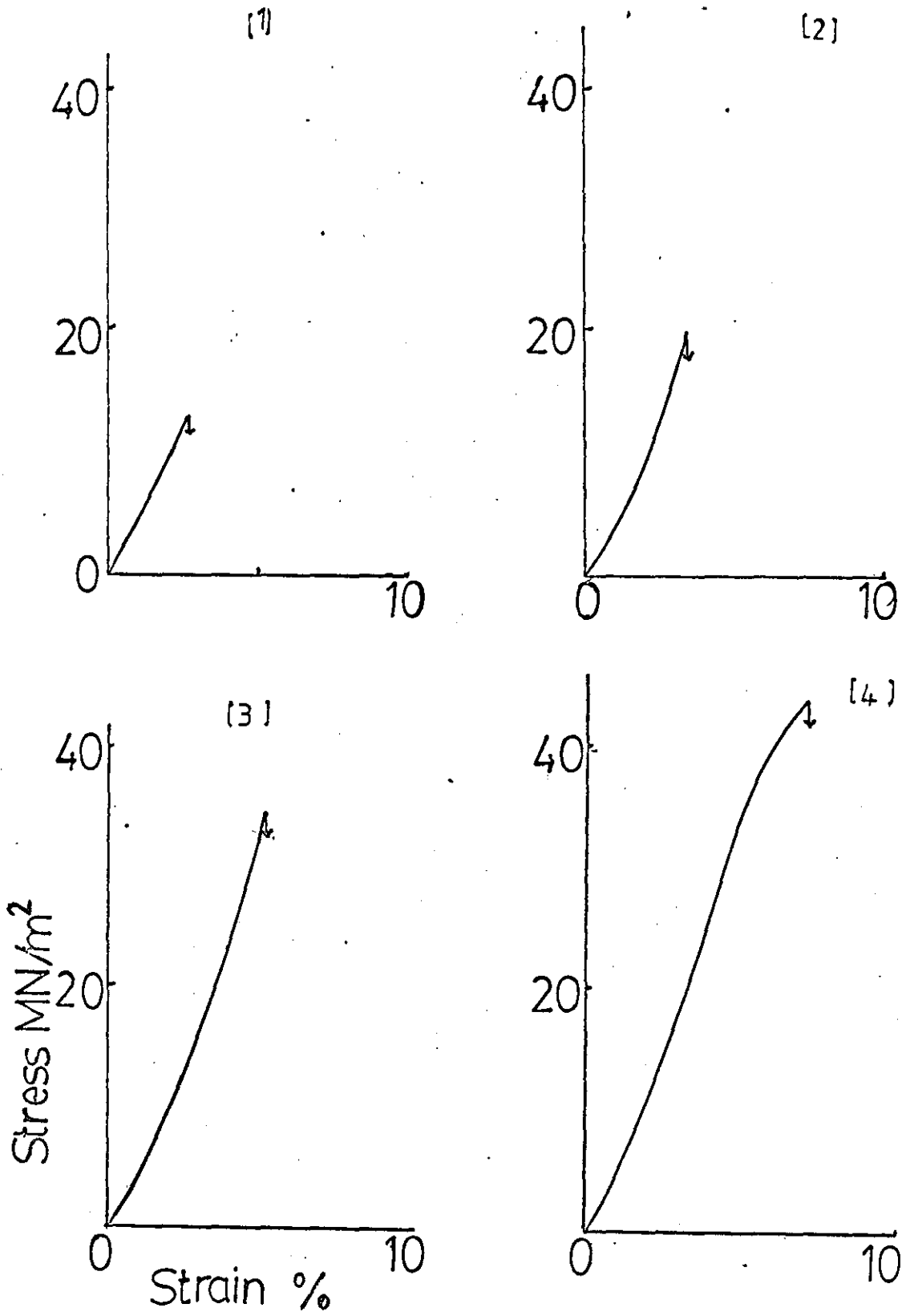
The results of tensile testing, fracture surface and microstructure examination and refractive index measurement are reported and discussed here. Conclusions based on these results on the processing of PVC blends will be formed.

7.1 Tensile Properties

Figs. 65-68 show typical stress-strain curves of mouldings made at different temperatures from the tin and lead-blends. The mode of deformation for a given formulation depends on the moulding temperature. For instance, PVC-M tin-formulation moulded at 130°C underwent a brittle fracture while for mouldings at 200°C, stress whiteming, necking and extension (cold-drawing) occurred. This was followed by the specimen breaking within the necked region. In between these temperatures ductile failure was observed but no stabilised cold-drawing until a moulding temperature of 180°C. That is, as the moulding temperature is raised the type of failure changes progressively from brittle fracture to necking rupture to cold-drawing. It will be shown later (section 7.3) to be related to changes in microstructure with moulding temperature.

Mouldings made from similar blends with PVC-S failed in a brittle manner, without necking or cold-drawing until a moulding temperature of 200°C. That is, for the same moulding temperature the mass polymer failed differently from the suspension polymer. Figs. 69 and 70 show mouldings of PVC-S and PVC-M respectively immediately after fracture.

For lead-formulation, PVC-S exhibited only brittle failure even at 200°C. PVC-M mouldings however, showed necking rupture without


[1]
[2]
[3]
[4]
40
20
0
10
Stress MN/m²
Strain %

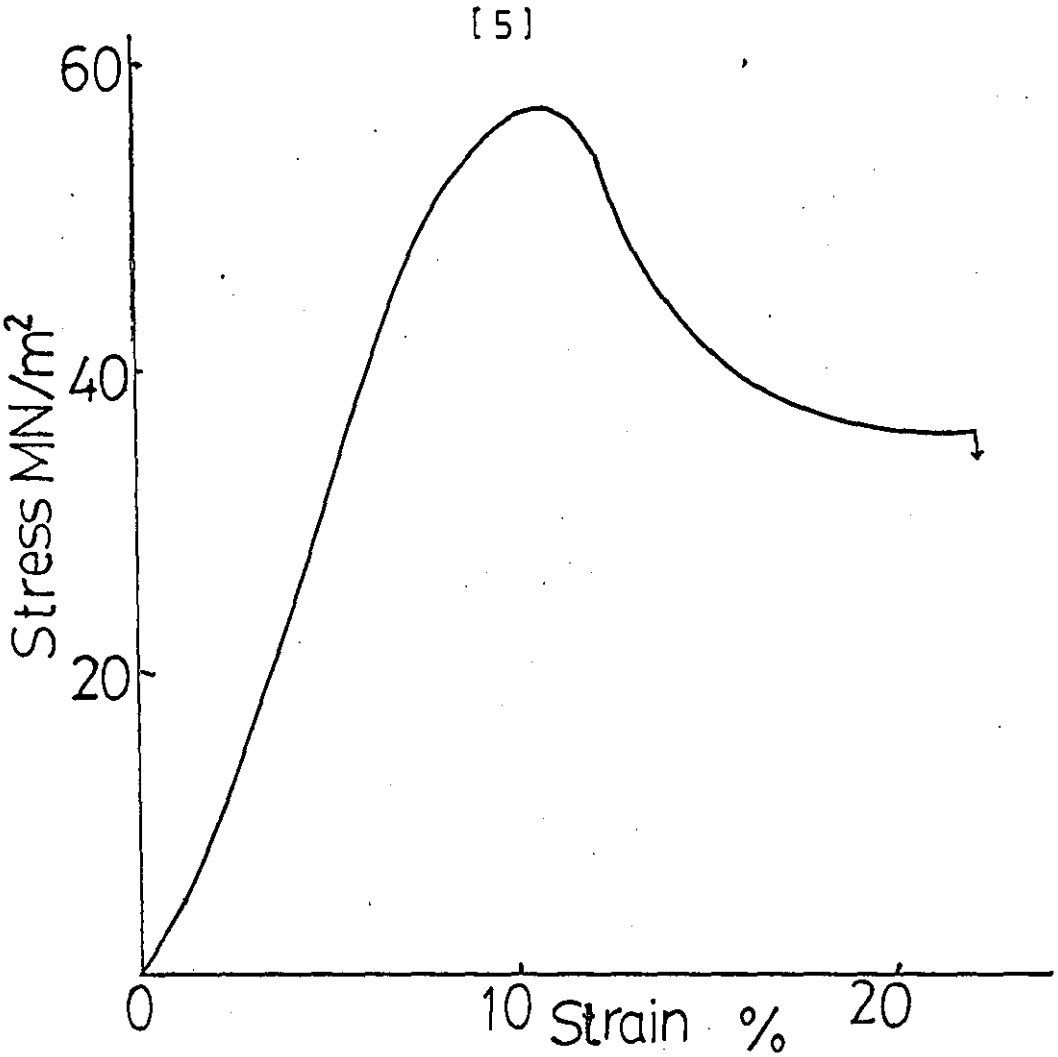


Fig. 65: Stress-Strain Curves for PVC-S (Tin formulation) moulded at: (1), 130°C; (2), 140°C; (3), 160°C; (4), 180°C; (5) 200°C

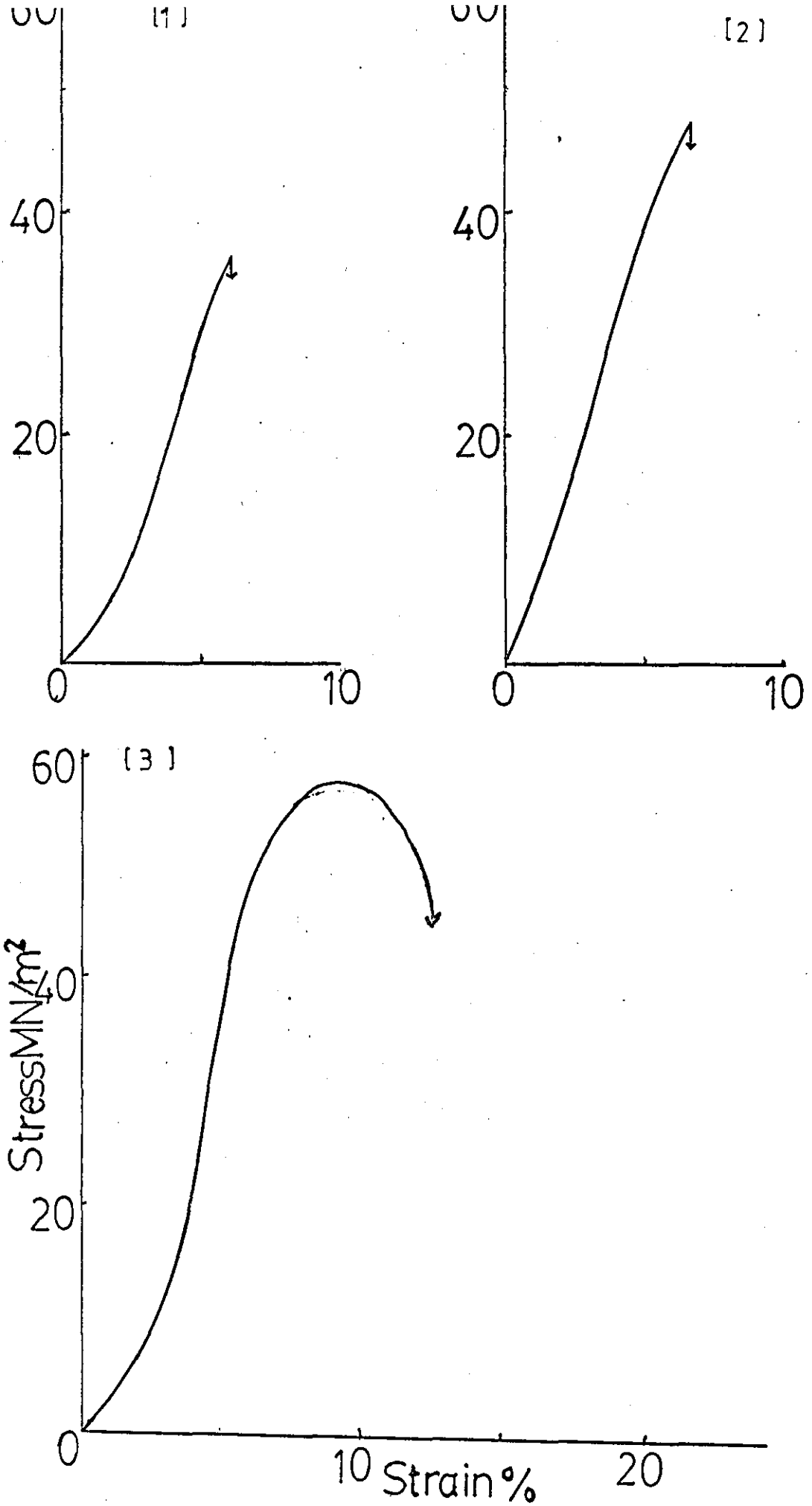
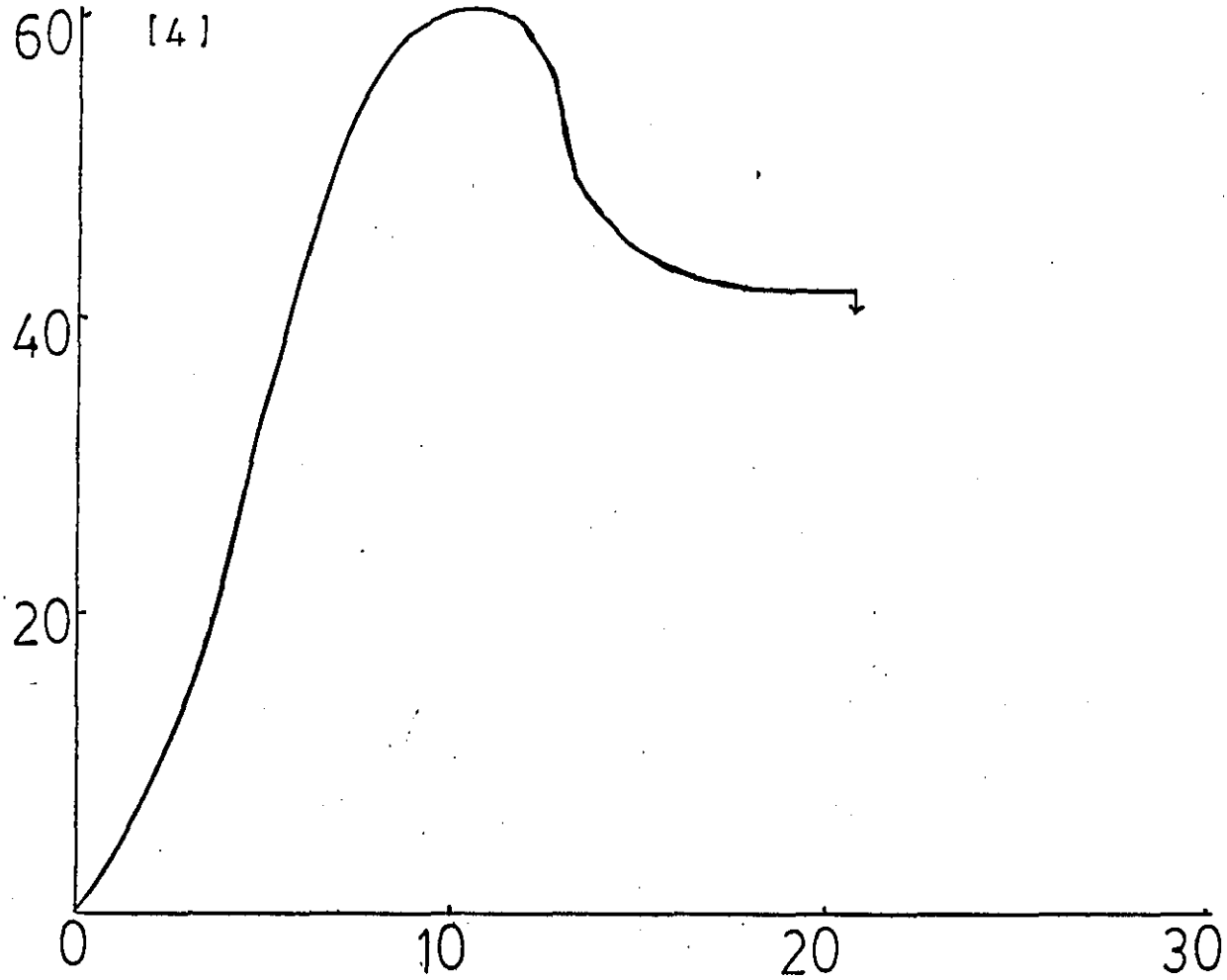
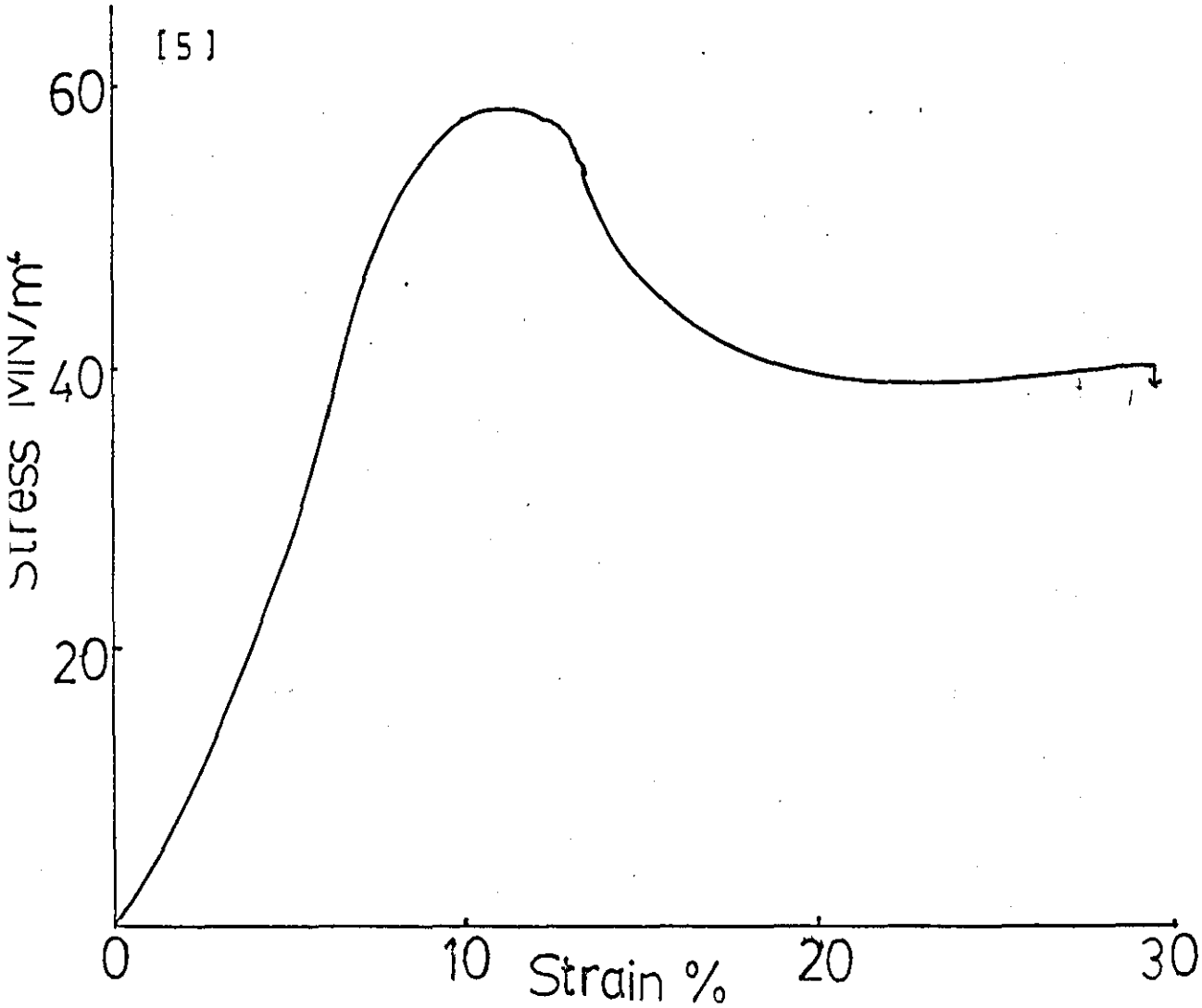


Fig. 66: Stress-Strain Curves for PVC-M (Tin formulation) moulded at: (1), 130°C; (2), 140°C; (3), 160°C; (4), 180°C; (5), 200°C


[4]
60
40
20
0
10
20
30


[5]
60
40
20
0
10
20
30
Strain %

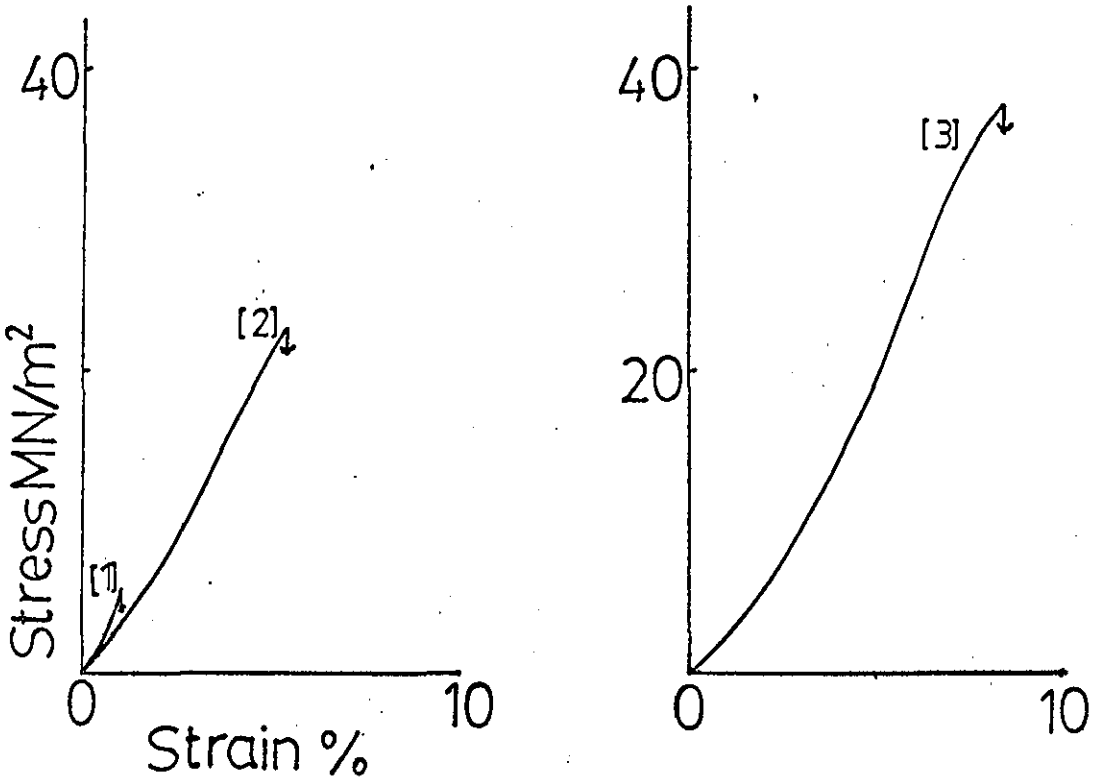


Fig. 67: Stress-Strain Curves for PVC-S (Lead formulation) moulded at: (1), 160°C; (2), 180°C; (3), 200°C

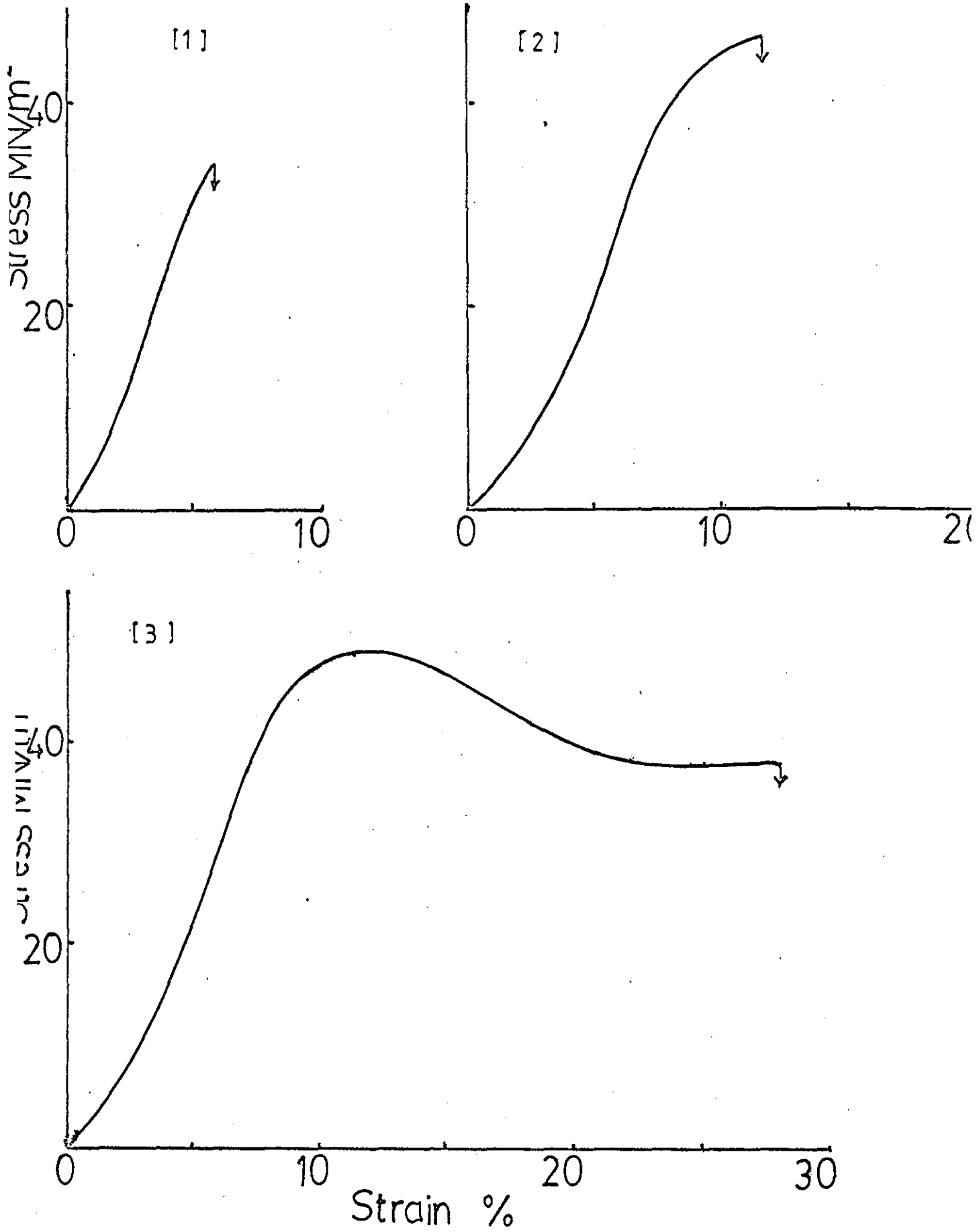


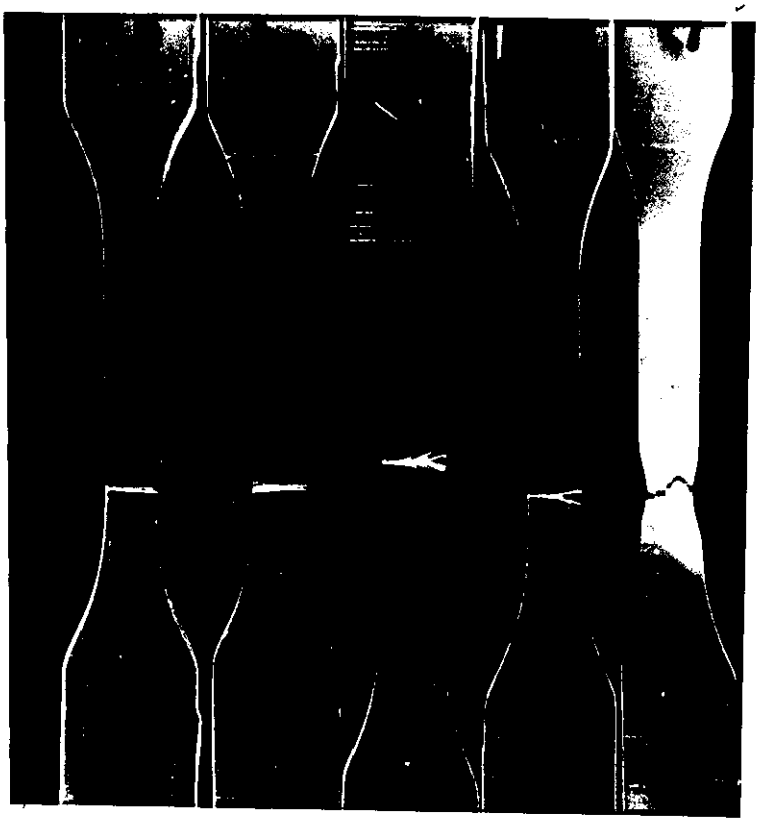
Fig. 68: Stress-Strain curves for PVC-M (Lead formulation) moulded at: (1), 160°C; (2), 180°C; (3), 200°C

Fig. 69: Compression moulded specimens of PVC-S (tin formulation) after tensile testing.

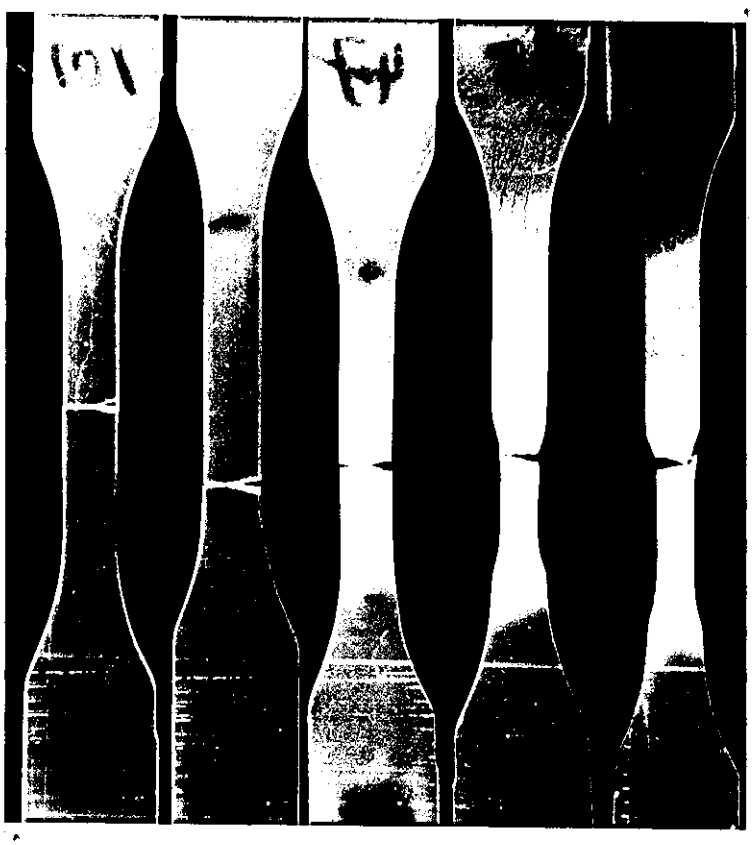
Moulding temperatures: (1) 130°C; (2) 140°C; (3) 160°C; (4) 180°C; (5) 200°C

Fig. 70: Compression moulded specimens of PVC-M (tin formulation) after tensile testing.

Moulding temperatures: (1) 130°C; (2) 140°C; (3) 160°C; (4) 180°C; (5) 200°C



1 2 3 4 5



restabilisation of the neck at 200°C. The whitening observed in the neck has been attributed to the occurrence of very small voids, holes or cracks[153], though other views suggest small crazes are the cause[154]. The neck does not restabilise because the specimen breaks before the orientation hardening is sufficient.

The results of the yield or breaking stress are given in Table 16. These stress values for mass and suspension polymer are shown as a function of moulding temperature in Figs. 71 and 72. The mass polymer has higher yield stress values than the suspension polymer and this can be attributed to the known differences in their morphology. As pointed out in section 1.4, PVC processing involves the structural breakdown of the resin into smaller particles. A network is ultimately formed as molecular entanglement occurs with the disappearance of boundaries between the primary particles. The ease with which this can be achieved, that is, ease of processing, for a given formulation and processing equipment, depends on the type of PVC and the K-value. A higher K-value implies a greater degree of entanglement so a larger force or energy input is required to extend the network and bring about interdiffusion of short chain segments across particle boundaries.

The yield stress for both mass and suspension polymers tends to the same value as the moulding temperature is raised to 200°C. Stresses at corresponding moulding temperatures from PVC blends discharged at 120°C are lower, especially for the lead blends. Blends discharged at 80°C could not be expected to have the additives uniformly dispersed as those discharged at 120°C. Since additives lower tensile yield it is therefore not surprising stress values from PVC blended to 120°C are lower. It is worth pointing out that in a process like injection moulding the powder blends are subjected to considerable shear, further mixing and working and homogenising of the melt also takes place.

Table 16

Type and Formulation of Blend	Moulding Temperature °C	Yield Stress MN/m²	
		80°C Blend Temp.	120°C Blend Temp.
PVC-S	160	5.03	-
(A)	170	14.75	
	180	23.31	6.96
	190	30.75	
	200	37.61	14.28
(B)	130	12.25	9.20
	140	17.83	14.31
	160	35.01	34.71
	180	47.07	45.57
	200	57.37	56.30
PVC-M	160	34.22	11.37
(A)	170	41.01	
	180	46.04	25.73
	190	49.51	
	200	51.18	43.23
(B)	130	35.09	30.05
	140	50.37	42.08
	160	59.28	57.49
	180	60.45	58.45
	200	57.86	56.37

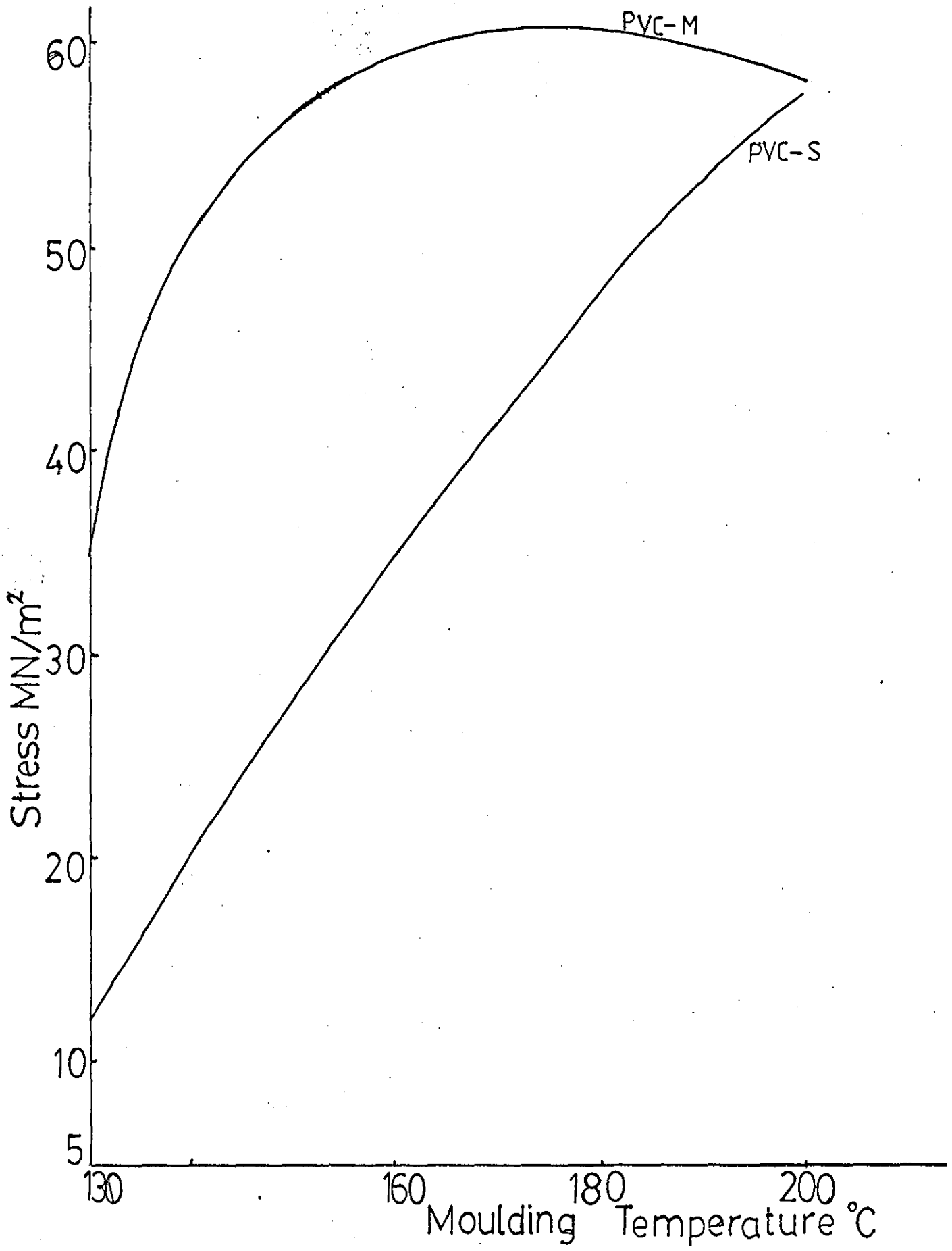


Fig. 71: Yield or Breaking Stress as a Function of Moulding Temperature (Tin formulation)

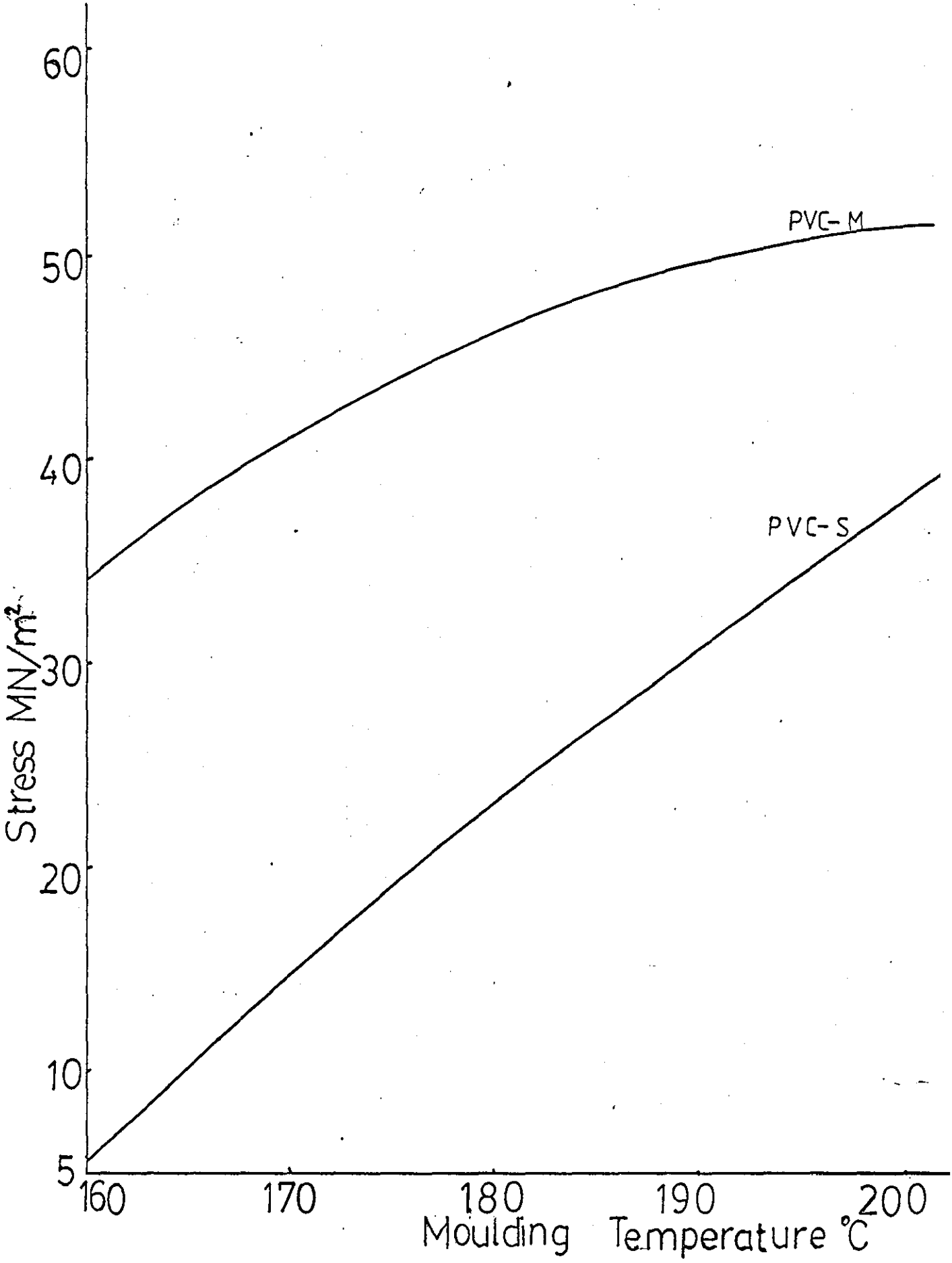


Fig. 72: Yield or Breaking Stress as a Function of Moulding Temperature (Lead formulation)

Consequently stress values would be the same from blends discharged at different temperatures. Subsequent work here has confirmed this to be the case[155].

The basic reason for necking in tensile samples is non-uniformity. The stress is higher at the thinner part of the specimen. This results in further deformation being concentrated at this point and thereby increase the local stress. The system thus becomes unstable and a neck is formed. The necking phenomena based on the construction of Considere has been rigorously treated by Vincent[159].

Three mechanisms have been proposed to explain yield and cold-drawing phenomenon. Marshall and Thompson[156], Muller[157], and Jackell[158] all rely on a mechanism in which localised heating causes softening. That is, during the stretching process a large amount of heat is generated which goes largely into heating the neck region. As a result, yielding and cold-drawing occur.

But yielding and cold drawing are known to occur very slowly in creep tests when the temperature is constant. Vincent[159] based his explanation not on temperature rise but on the stress lowering the softening temperature to about the temperature at which drawing occurs.

Yielding occurs in shear, where there is no volume change, and in compression where the volume decreases under stress. It cannot be connected with viscous flow in the usual sense since the deformation is recoverable. Lazurkin[160] based his explanation therefore on the Eyring model[177]. The effects of thermal motion and mechanical stresses during stretching combine to rupture intermolecular bonds and allow large scale configurational changes. Confirmation of this mechanism that cold-drawing is due to biased segmental motion was made by Robertson[161]. Yielding occurs therefore when stresses or strains create increased segmental mobility.

Fig. 73 is Bartenev and Zuyev[175] illustration of elementary types of failure in the tensile testing of materials. From Fig. 70 it is seen that at low moulding temperatures the type of failure is I, a tear in a plane normal to greatest stress. At the other end of high temperature moulding the fracture is a complicated process that commences with type V, necking and cold-drawing and then ends up with type I.

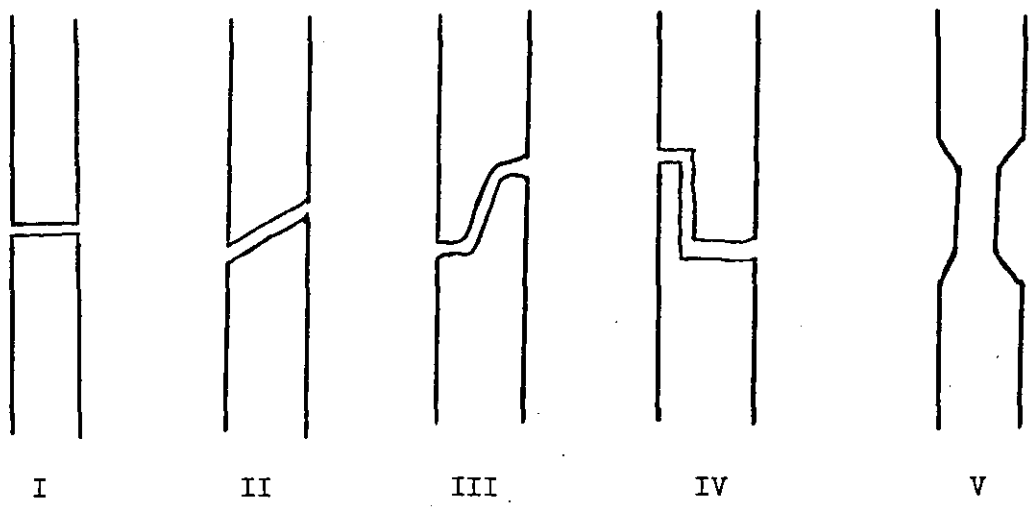


Fig. 73 Elementary types of failure under tension.[175]

I) Tear in plane normal to greatest stress

II) Failure in plane of greatest stress

III) Tear and Shear

IV) Tear and shear in the direction of tension

V) Change of shape through the forming of a neck.

7.2 Fracture Surface Morphology

The fracture surface morphology of the mouldings will be examined in terms of inter or intra particulate failure. According to Zhurkov and Kursukov[169] the hypotheseswhich have been proposed for the mechanism of fracture of polymers can be divided into three groups based on whether strong chemical bonds binding the atoms in polymer

chains or weak van der Waals bonds between macromolecules are involved in the fracture process. One group involves the breaking of intra-molecular (covalent) bonds in polymers under stress[170,171]. Another group is based on the breaking of intermolecular bonds[172]. Chain molecules slip past one another under load and fracture ensues. The third group which is a combined hypothesis, states that either mechanism of fracture can occur depending on the conditions of testing, structure and temperature[173,174]. At low temperatures for instance, fracture of a glassy polymer occurs through scission of chemical bonds and at high temperatures through slippage and rearrangements.

Fig. 74 are scanning electron micrographs of some fracture surfacesof the tensile bars (lead-formulation). In Fig. 74a the fracture at the lowest moulding temperature is wholly interparticulate. The fine scale structure visible is the additive on the powder particle surface. At the moulding temperature of 180°C (Fig. 74b) there is some intraparticulate failure but at 200°C the failure is clearly wholly intra particulate and ductile (Fig. 74c). The fracture surface of the suspension polymer moulded at 200°C (Fig. 74d) shows that failure is almost totally inter-particulate, that is, similar to the mass polymer moulded at 160°C. By raising the moulding temperature it is possible to achieve a similar breaking stress for suspension polymer when moulded at 200°C to that found for mass polymer at 160°C and the appearance of the fracture surfaces are similar.

In Figs. 75 and 76 (tin formulation) the fracture is again mostly interparticle at low moulding temperature. But at 160°C (Fig. 76c) changes begin to appear, some areas having cellular or honeycomb appearance and some areas pitted. At 180°C and 200°C the morphology is entirely different.

Fig. 74: Scanning electron micrographs of fracture surfaces of PVC (lead blend) Tensile Test Bars.

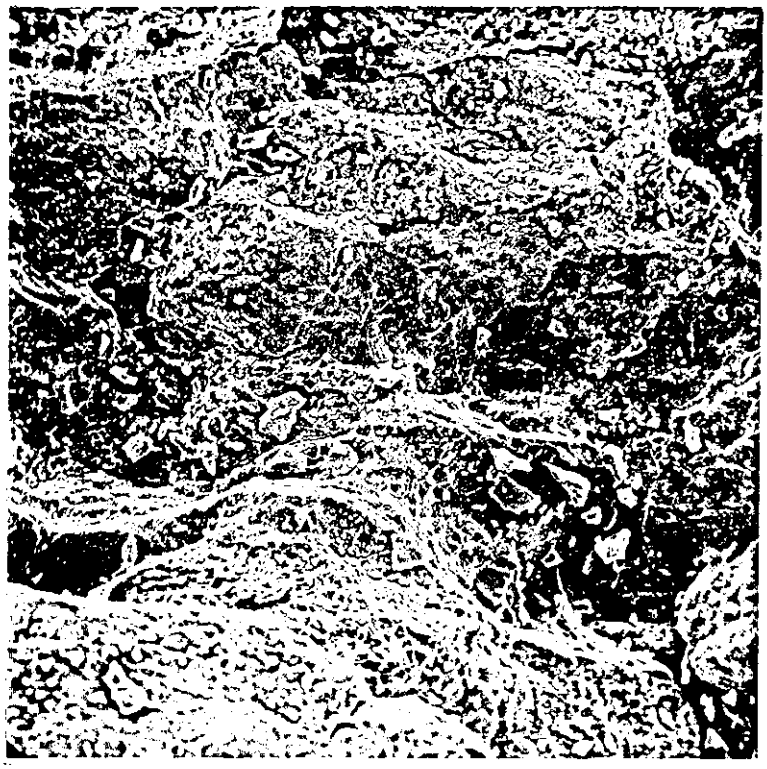
(a) mass polymer 160°C
(b) mass polymer 180°C
(c) mass polymer 200°C
(d) suspension polymer 200°C

Magnification: x600

(a)

(b)

(c)

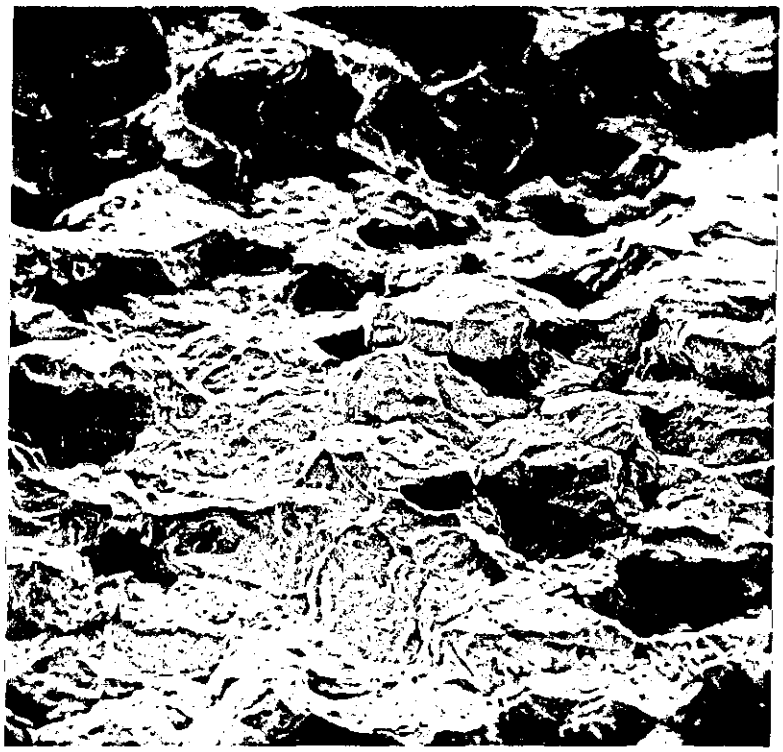


(d)

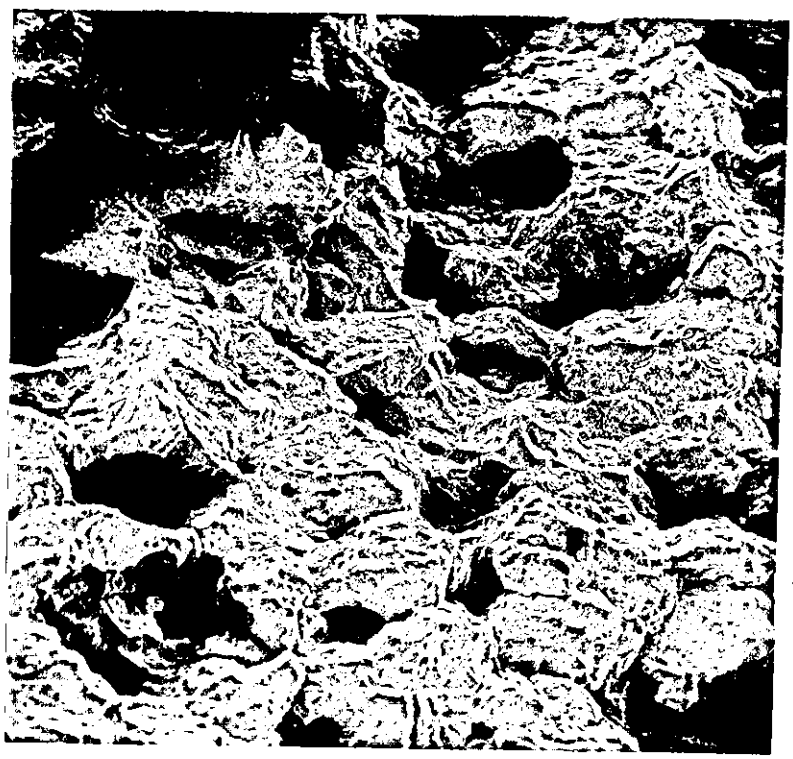
Fig. 75: Scanning electron micrographs of fracture surfaces of PVC-S (tin blend) Tensile Test Bars.

Moulding temperature: (a) 130°C; (b) 140°C; (c) 160°C; (d) 180°C; (e) 200°C

Magnification: x240

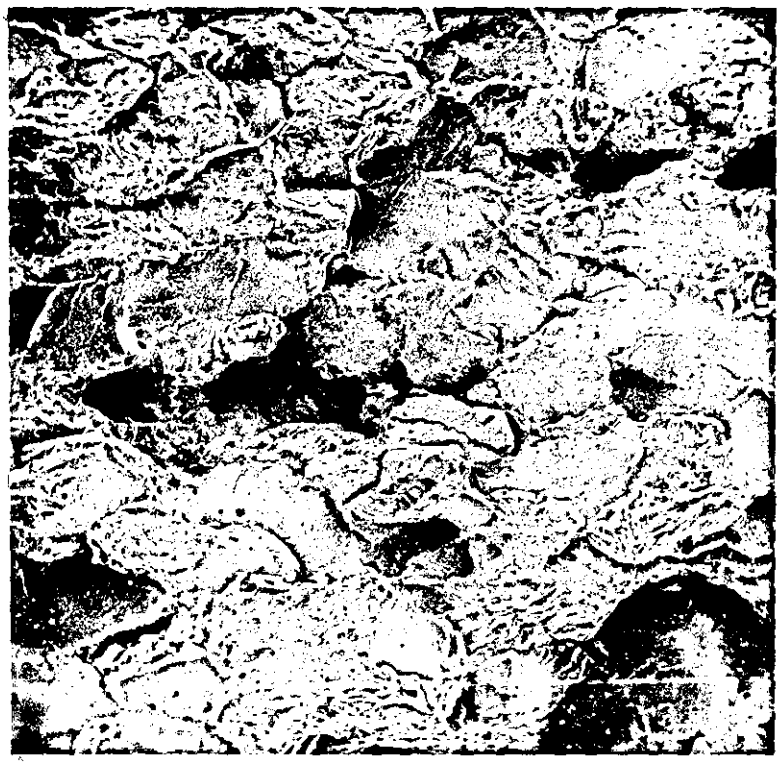


(a)

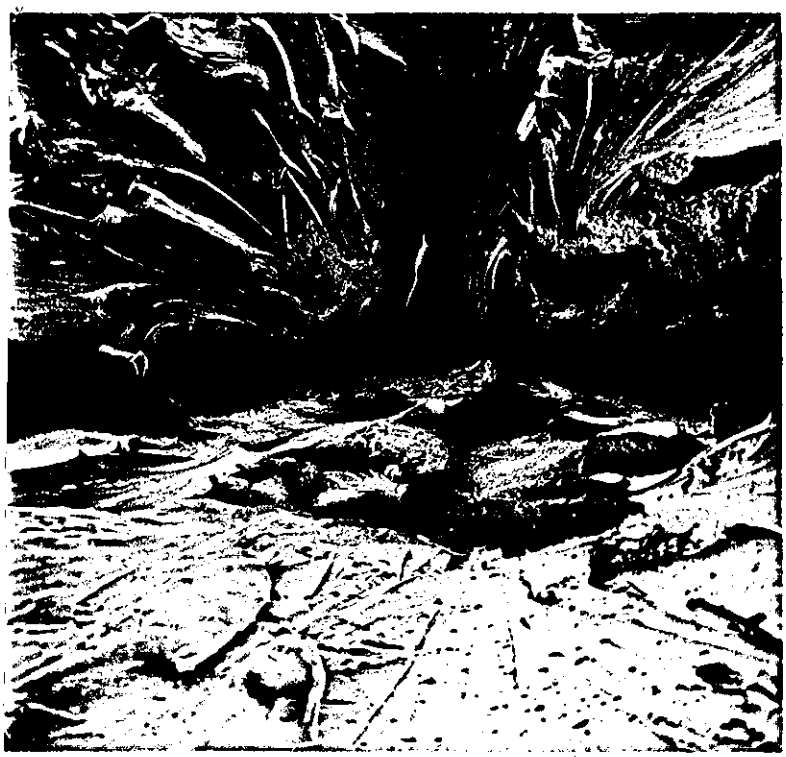


(b)

(c)



(d)

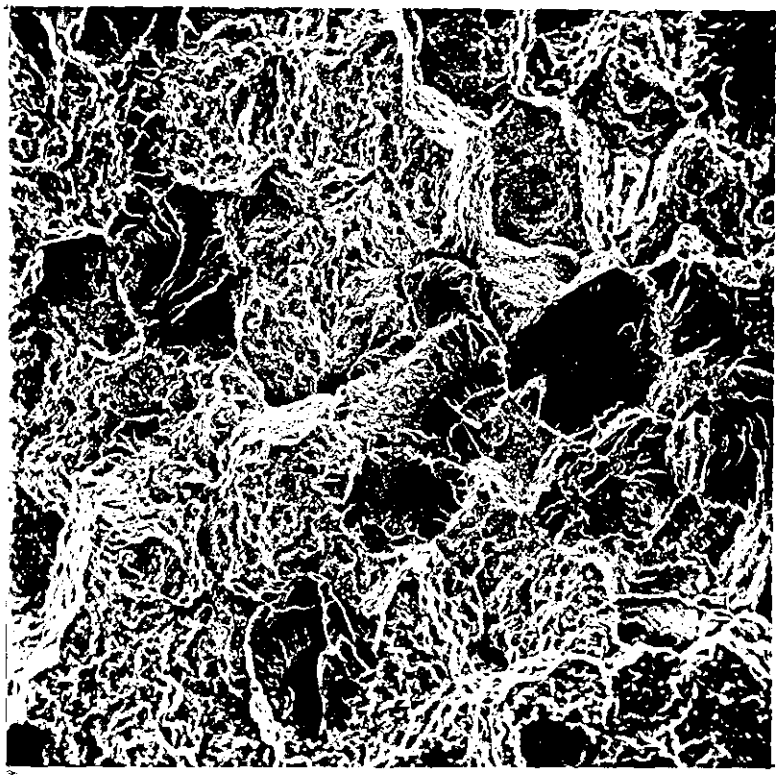


(e)

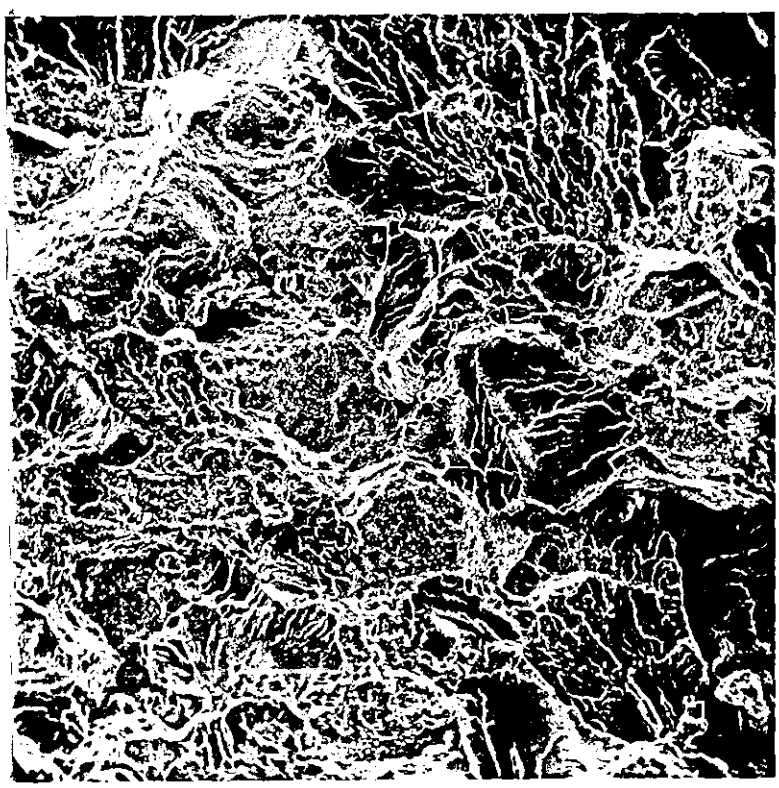
Fig. 76: Scanning electron micrographs of fracture surfaces of PVC-M (tin blend) Tensile Test Bars.

Moulding temperature: (a) 130°C; (b) 140°C; (c) 160°C; (d) 180°C; (e) - (g) 200°C

Magnification: x240



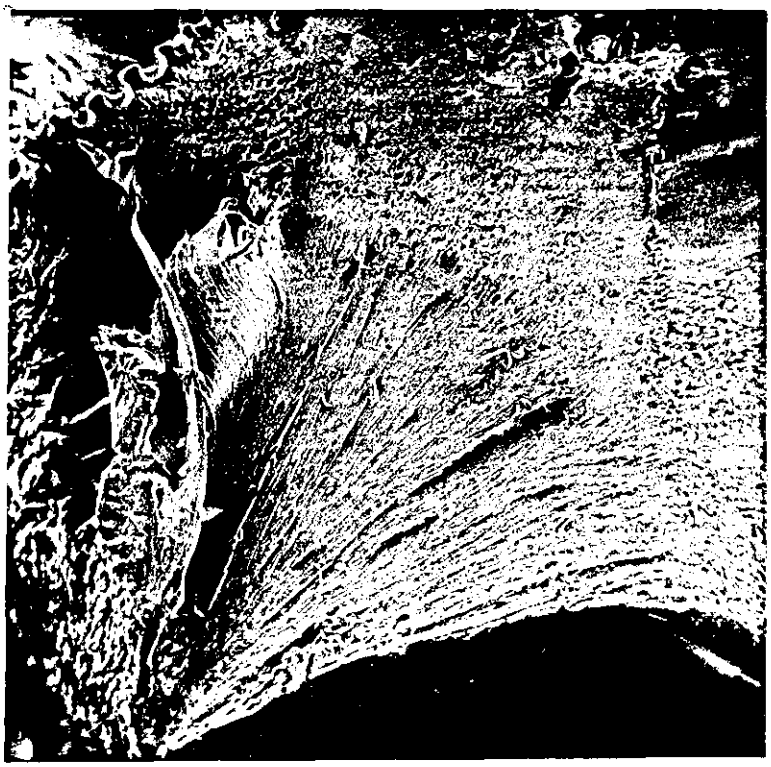
(a)



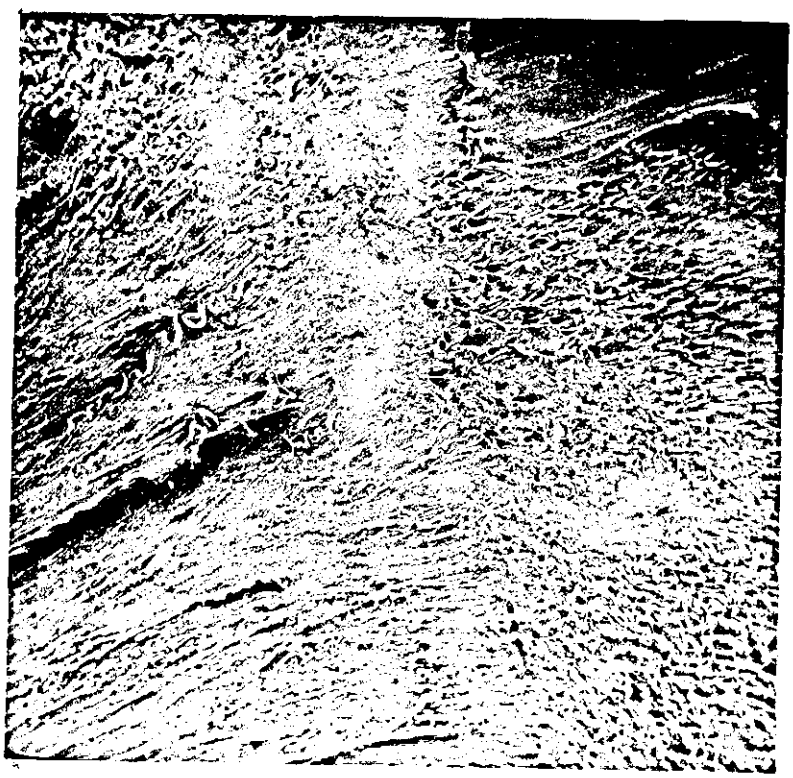
(b)

(c)

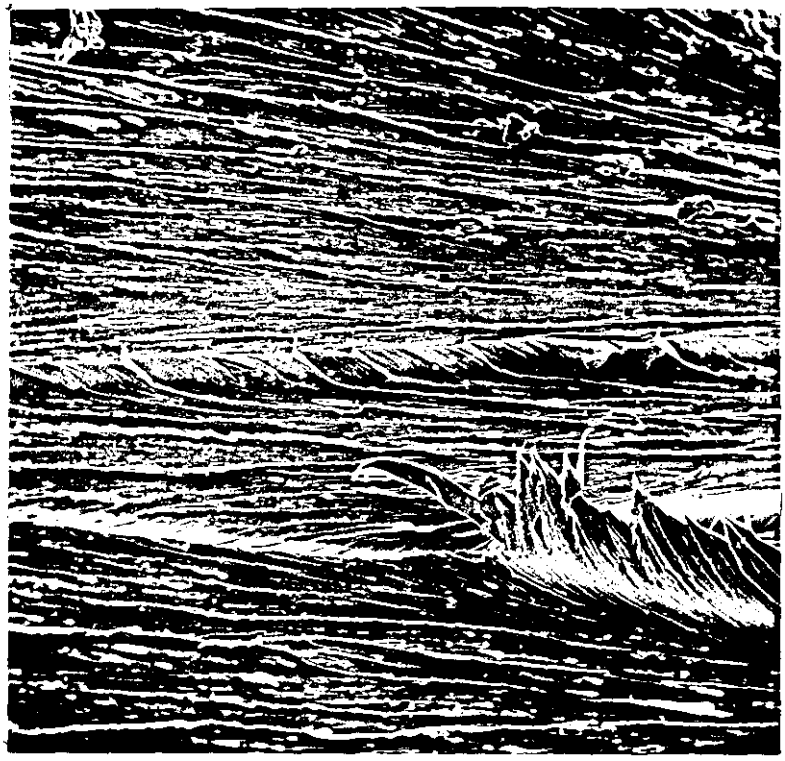
(d)



(e)



(f)



(g)

Tormala et al[164] have examined the fracture morphology of injection moulded commercial rigid suspension and emulsion PVC compounds. They observed a number of cavities on the fracture surfaces, being fewer in the emulsion where cold drawing phenomenon was rather vague. These cavities resembled the diamond cavities of Cornes and Harward[168]. SEM showed they grow by ductile tearing of the material in a direction parallel to the tensile axis. Their walls are made up of small and large strips, with wedge-like points. The strips are arranged with the small ones on the surface of large strips, forming lamellar structures. These are typical structures found in Figs. 75e, 76g where the moulding was done at high temperatures and some form of cold drawing occurred.

In Fig. 76e a fracture resulting from an edge failure is seen. It starts with a smooth area in one corner and spreads out until it changes abruptly to a rougher surface. (Fig. 76f). The smooth area is associated with slow tearing and the rough region with rapid fracture.

In the tin formulation samples it is again observed that the fracture surface of the suspension polymer moulded at 200°C is similar to that of the mass moulded at 180°C. It shows then that even though the fracture surfaces of the two polymers appear different, they can be made similar by raising the moulding temperature of the suspension polymer to an appropriate level. This agrees with the observation in section 7.1 that the yield stress of both polymers tends to same value as the moulding temperature is raised to 200°C (see Figs 71 and 72).

No evidence of crazing or fibrous structures was observed on any of the surfaces. Some workers have also reported the fracture of PVC without crazing[162-164]. However, there are reports of formation of crazes[165-168].

It is clear then that the fracture surfaces change from

interparticle to intraparticle failure or from brittle to ductile or a more complex ductile failure where there is a cold-drawing phenomenon depending on the moulding temperature. The slope of the curve in Fig. 71 or 72 therefore appears to be related to a steady transition from interparticle to intraparticle failure.

Later (section 7.3), it will be shown that the microstructure of the mouldings varied with moulding temperature. At lower temperatures the internal particulate structure of the powder resin is retained. But as the moulding temperature is raised the boundaries of these sub particles become substantially diffused and at 200°C a network of molecular entanglements is left. Therefore interparticle failure results where particulate morphology is substantially retained. In other words, inter or intra particle failure is governed by the degree of disappearance of particulate structure. The path taken by the fracture is such as to proceed through areas of minimum strength. As much as possible it avoids cutting through polymer chains where it has to break strong covalent bonds.

7.3 Microstructure of mouldings

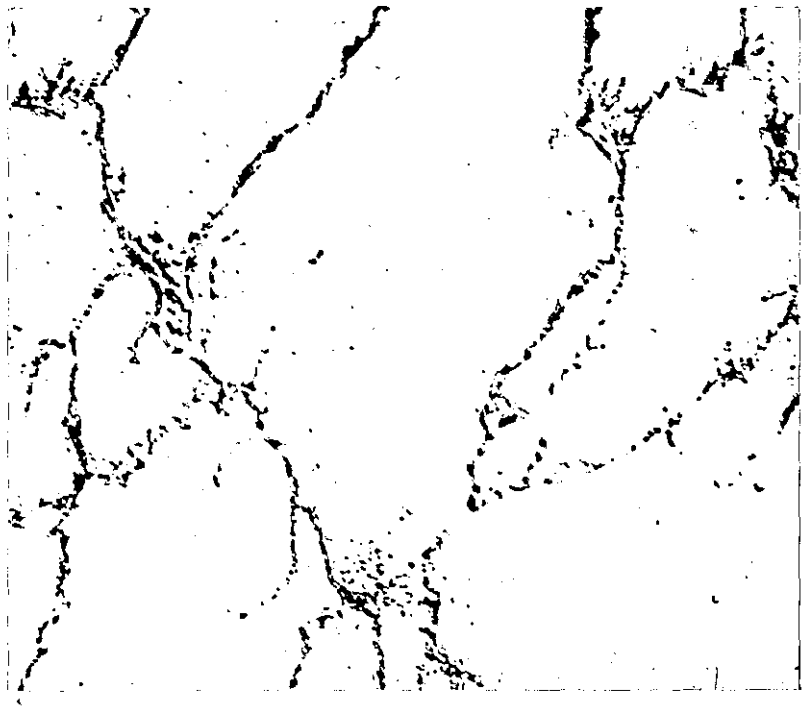
Optical micrographs (DIC) of mouldings made at different temperatures are shown in Figs. 77-80. The outlines on the micrographs are the additives and their location appear unchanged as they remain at the periphery of the powder particles. In the tin-formulation mouldings these additives appear as droplets or melts at 200°C.

Apart from mouldings at low temperatures, for example at 160°C, the internal structures of the particles seem to have been destroyed. However, electron microscopy revealed the existence of particulate structures in all the mouldings. Figs. 81-87 are the transmission electron micrographs of ultra microtomed sections of the mouldings.

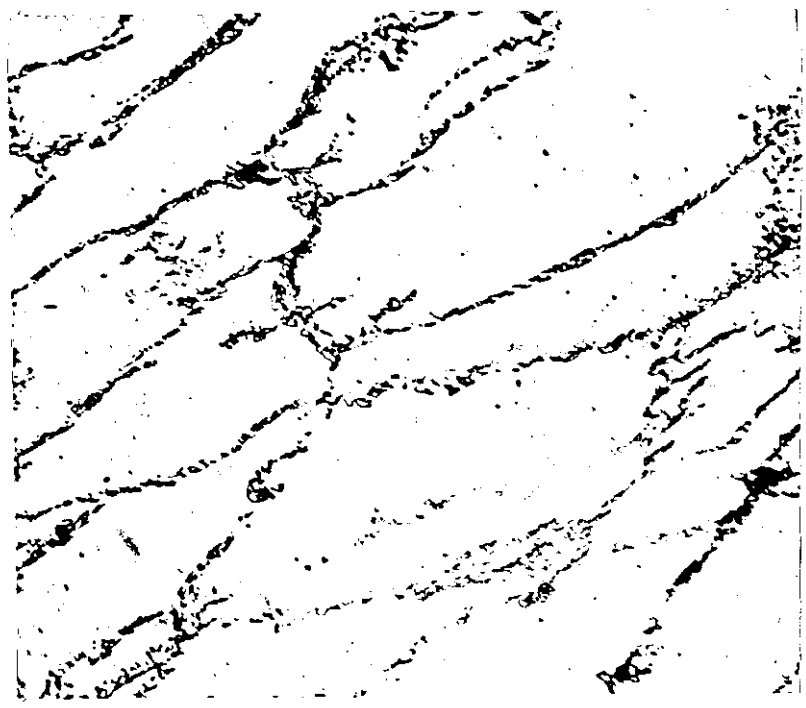
Fig. 77: Optical micrographs of thin sections of PVC-S mouldings (lead blend) viewed by differential interference contrast (DIC).

Moulding temperature: (a) 180°C; (b) 200°C

Magnification: x500



(a)



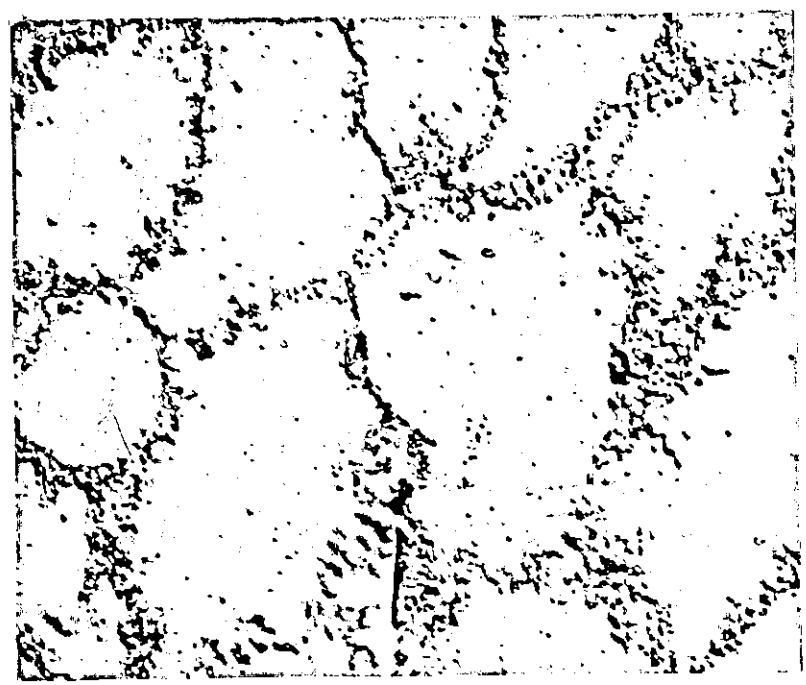
(b)

Fig. 78: Optical micrographs of thin sections of PVC-M mouldings (lead blend) viewed by differential interference contrast (DIC).

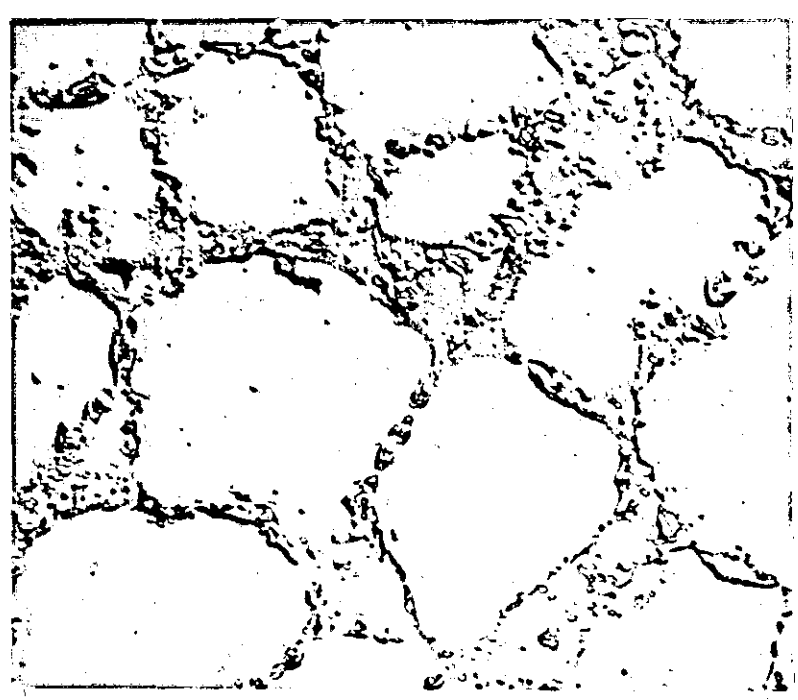
Moulding temperature: (a) 160°C; (b) 180°C; (c) 200°C

Magnification: x500

(a)



(b)

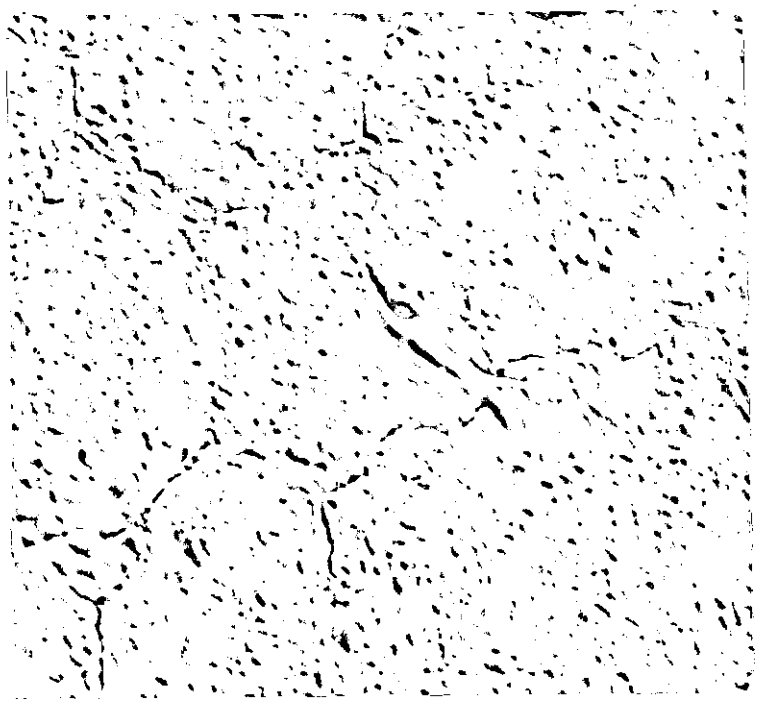


(c)

Fig. 79: Optical micrographs of thin sections of PVC-S mouldings (tin blend) viewed by differential interference contrast (DIC).

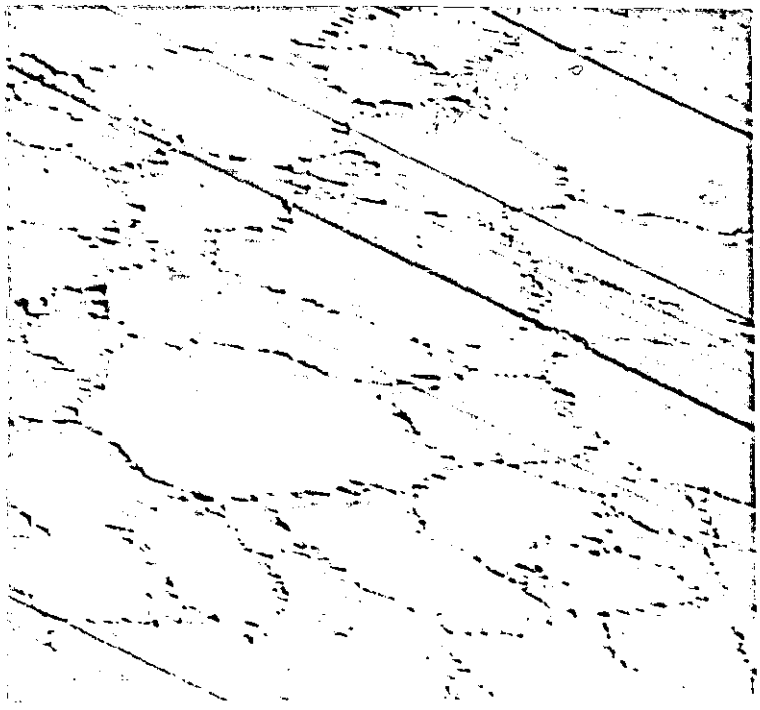
Moulding temperature: (a) 140°C; (b) 180°C; (c) 200°C

Magnification: x500



(a)

(b)

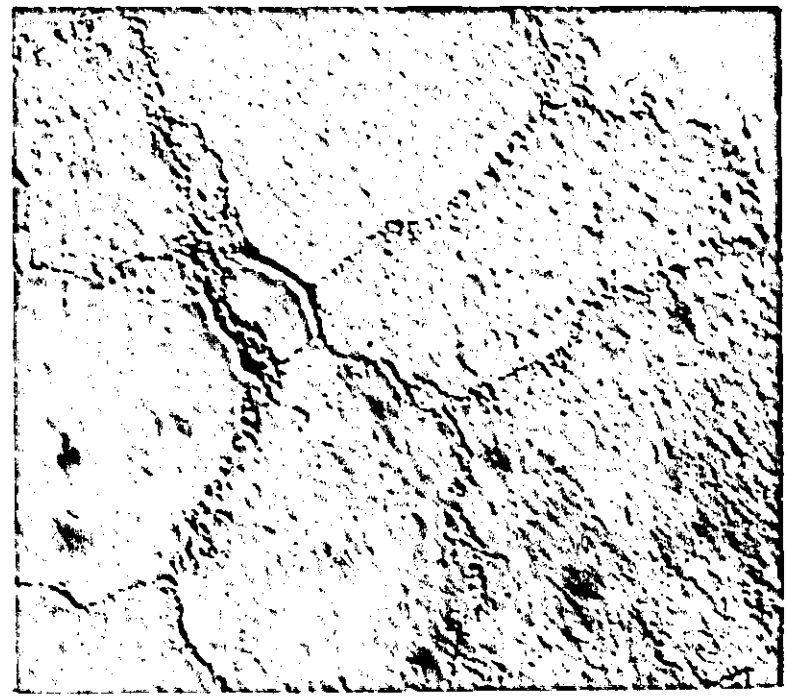


(c)

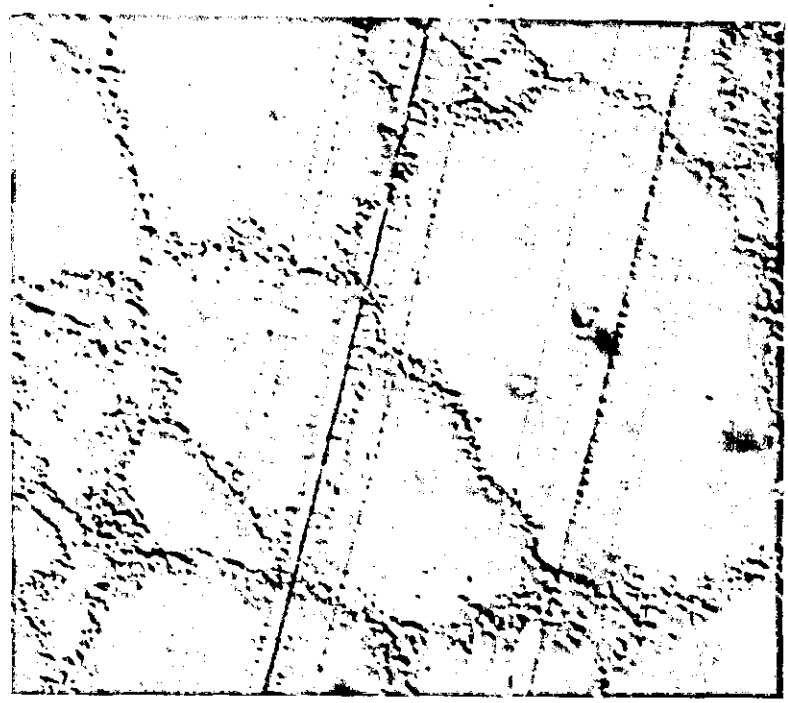
Fig. 80: Optical micrographs of thin sections of PVC-M mouldings (tin blend) viewed by differential interference contrast (DIC).

Moulding temperature: (a) 140°C; (b) 180°C; (c) 200°C

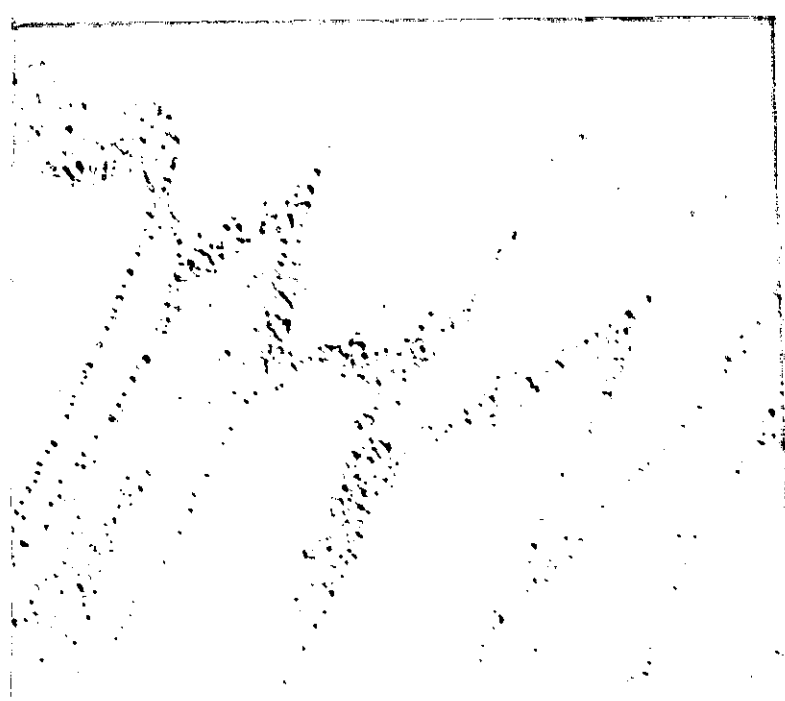
Magnification: x500



(a)



(b)



(c)

Fig. 81: Transmission electron micrograph of ultramicrotomed section of PVC-S moulding (lead blend).

Moulding temperature 160°C. Magnification x5,000

Fig. 82: Transmission electron micrograph of ultramicrotomed section of PVC-S moulding (lead blend).

Moulding temperature 180°C. Magnification x12,000

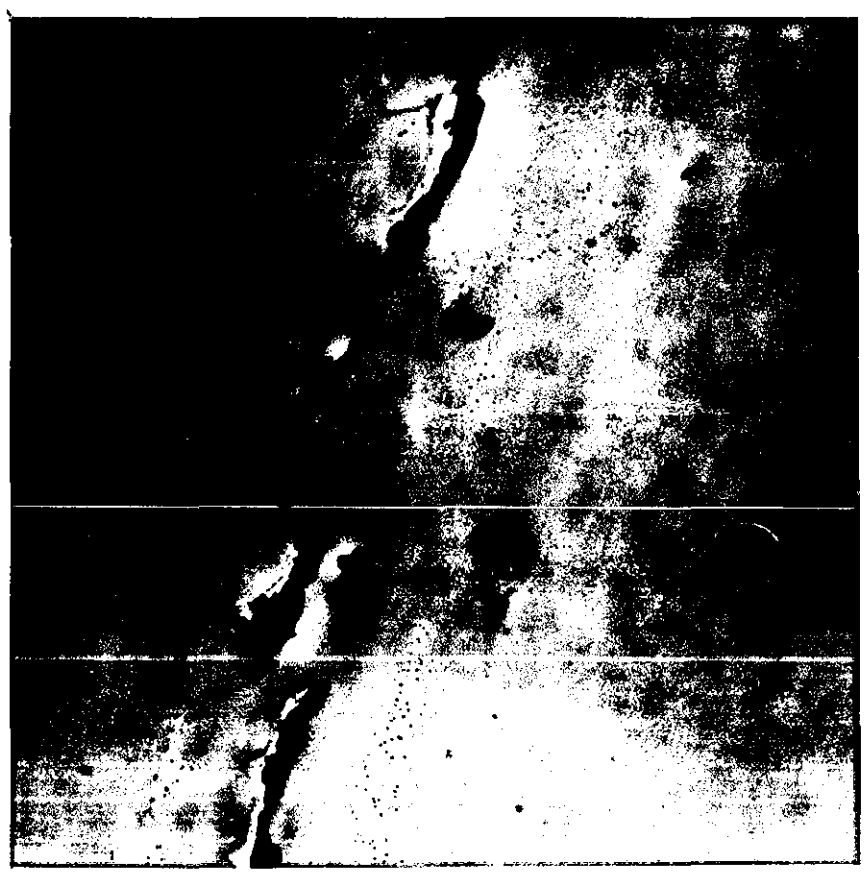


Fig. 83: Transmission electron micrograph of ultramicrotomed section of PVC-M moulding (lead blend).

Moulding temperature 160°C. Magnification x8,000

Fig. 84: Transmission electron micrograph of ultramicrotomed section of PVC-M moulding (lead blend).

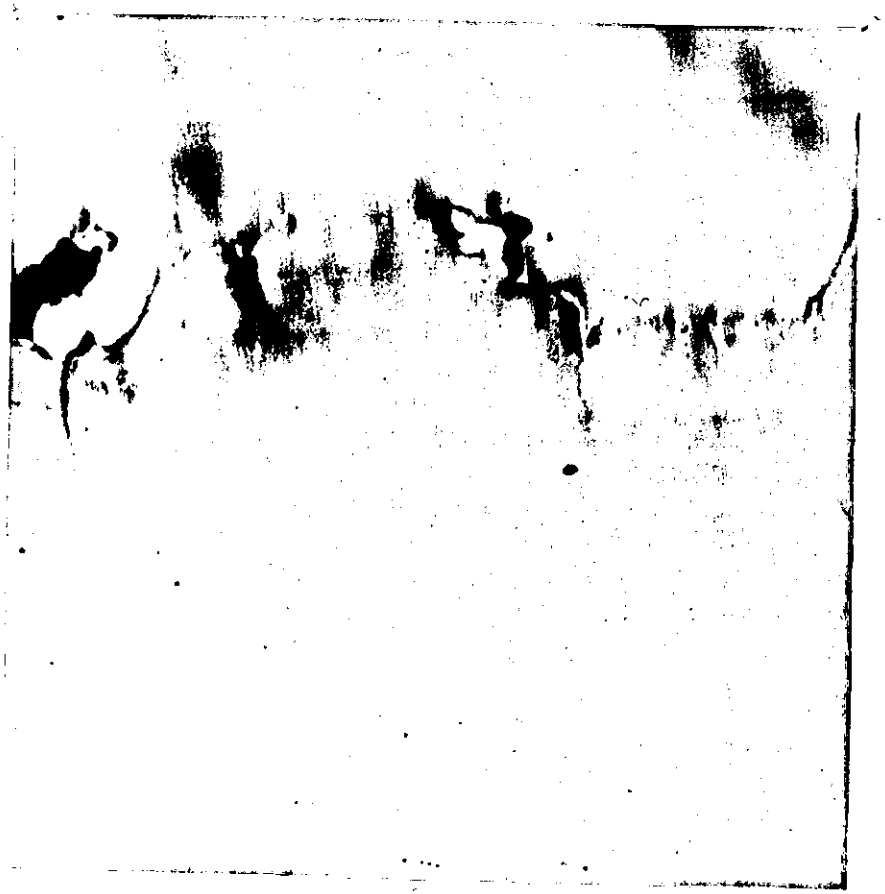
Moulding temperature 180°C. Magnification x8,000

Fig. 85: Transmission electron micrograph of ultramicrotomed section of PVC-S moulding (tin blend).

Moulding temperature 160°C. Magnification x10,000

Fig. 86: Transmission electron micrograph of ultramicrotomed section of PVC-S moulding (tin blend).

Moulding temperature 180°C. Magnification x8,000



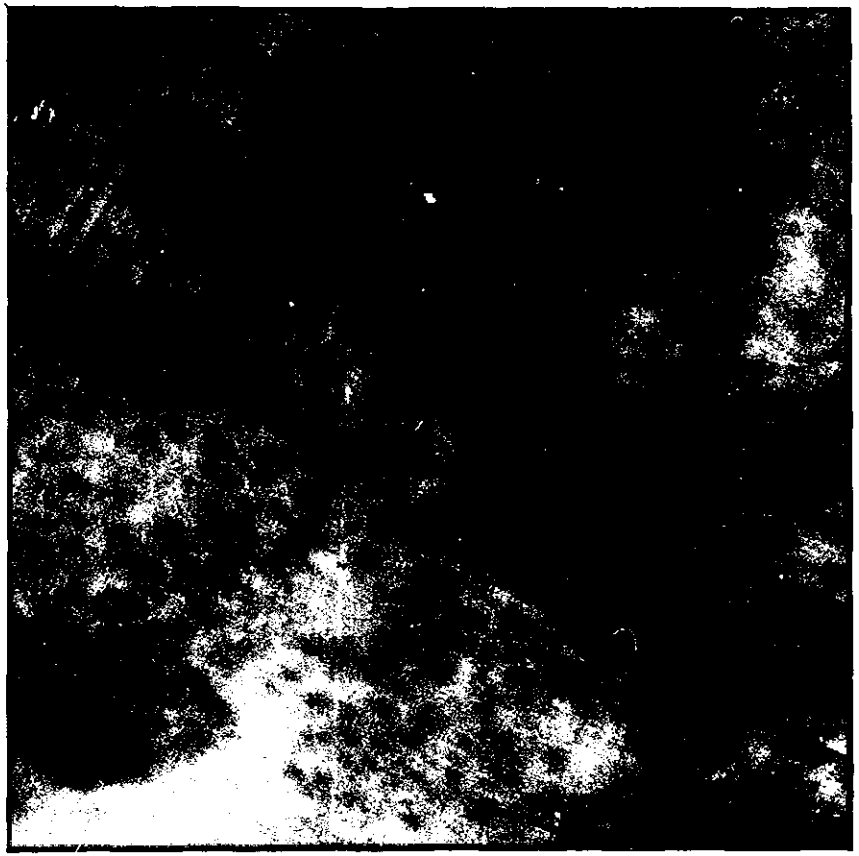
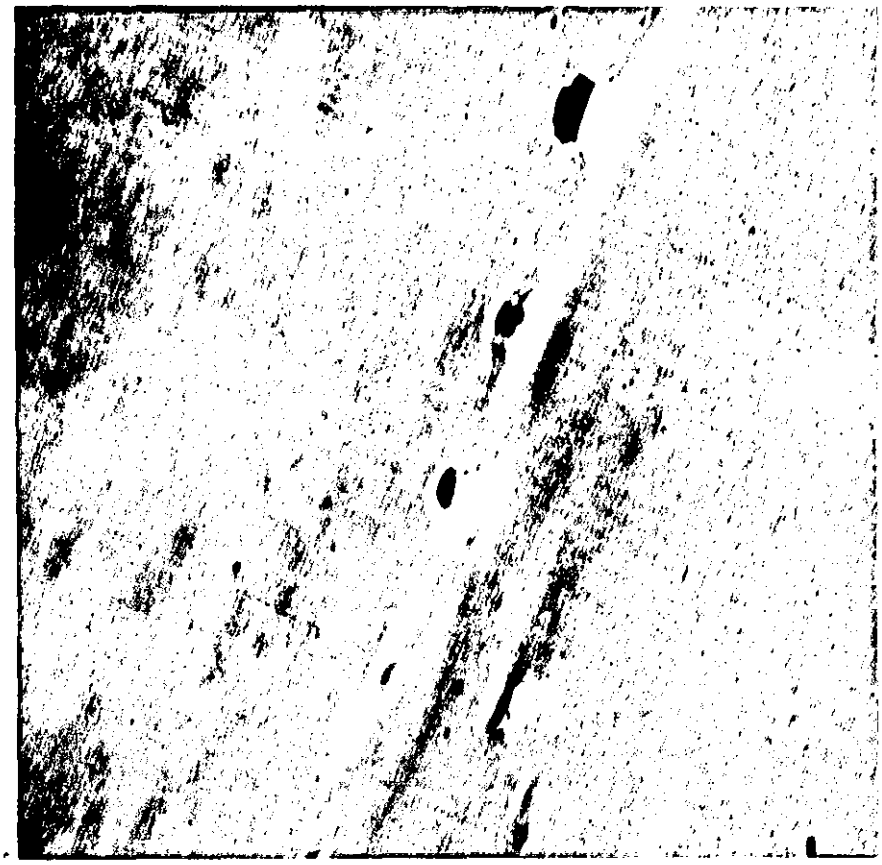


Fig. 87: Transmission electron micrograph of ultramicrotomed section of PVC-M moulding (tin blend).

Moulding temperature 180°C. Magnification: x8,000



These particulate structures, depending on the moulding temperature, on the average range from ca. 0.3 - 2 μm to ca. 0.1 - 0.7 μm. The breakdown of particle structure seems faster in mass than in suspension polymer. For example, the particulate structure in the lead-formulation mouldings at 160°C and 180°C respectively are 0.3 - 1 μm and 0.1 - 0.6 μm in size for mass polymer and 0.3 - 2 μm and 0.2 - 0.9 μm in size for suspension polymer. It is best illustrated by the scanning electron micrograph of ion-etched surfaces of mouldings of the two polymers made at 200°C. In the case of the suspension polymer (Fig. 88a) the globular structures, 0.3 - 0.6 μm in diameter are clearly seen. But in Fig. 88b the particle structure is strongly marked for the mass polymer.

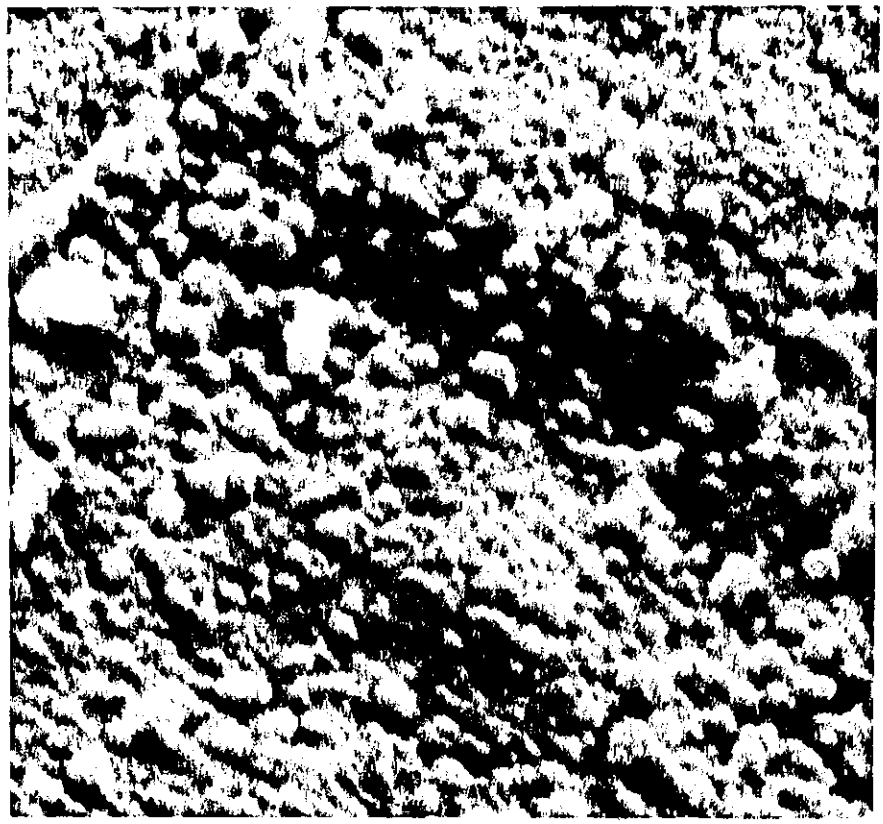
There is also a remarkable difference between mouldings from lead and tin formulations. In appearance the former are brown and the latter fairly transparent. Fig. 89 compared with Fig. 88 shows no particulate structure. The particulate structures in tin-formulations are smaller in size than those in lead-formulation. Thus in Fig. 82 the particles are 0.3 - 2 μm but 0.1 - 1 μm in Fig. 86. Since the tin stabiliser was originally absorbed into the resin particles it is reasonable to suggest that liquid additives 'soften' the polymer particles and therefore make it easier for them to be broken down.

Scanning transmission electron micrograph of PVC-M moulding at 200°C is shown in Fig. 90. Particles ranging in size from 300-700 Å can be seen. It demonstrates an obvious advantage of STEM over CTEM - higher resolution for a section of given thickness. These particles would be the 300 Å 'fibrils' of Hattori et al[31] or Stage I (10 nm) particles of Faulkner[34]. The difference in size range with the results of these workers may be due to the level of processing the material has undergone. Further processing at higher temperatures or by applying more shear would reduce all the particles to 300 Å or less.

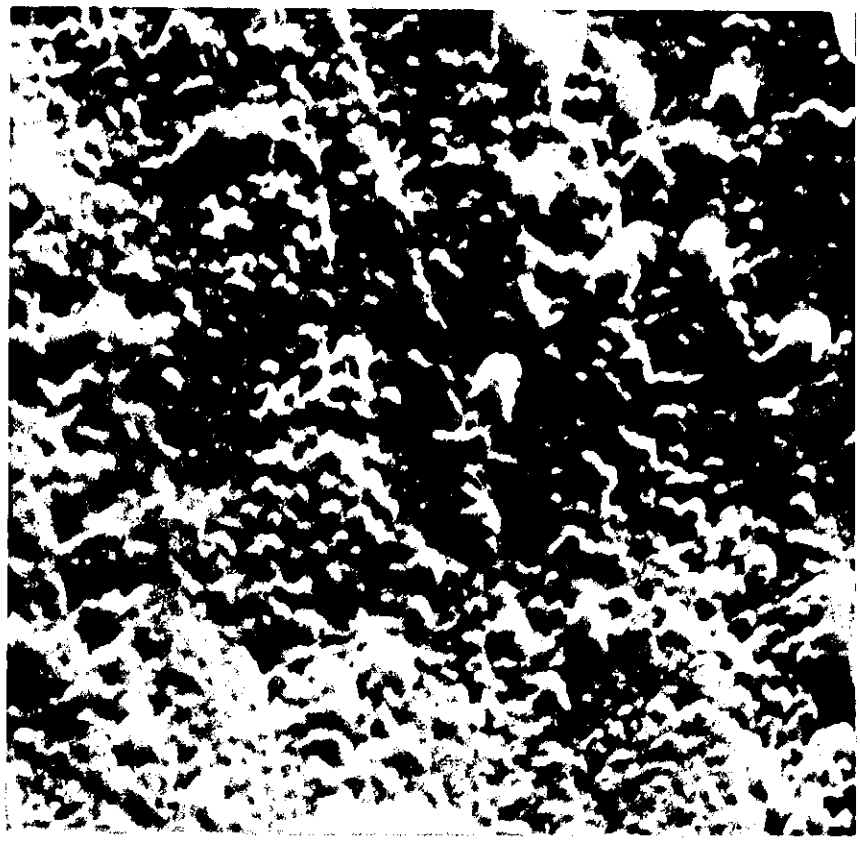
Fig. 88: Scanning electron micrographs of ion-etched surfaces of PVC mouldings (lead blend). Moulding Temperature 200°C.

(a) Suspension polymer (b) mass polymer.

Magnification: x13,000



(a)

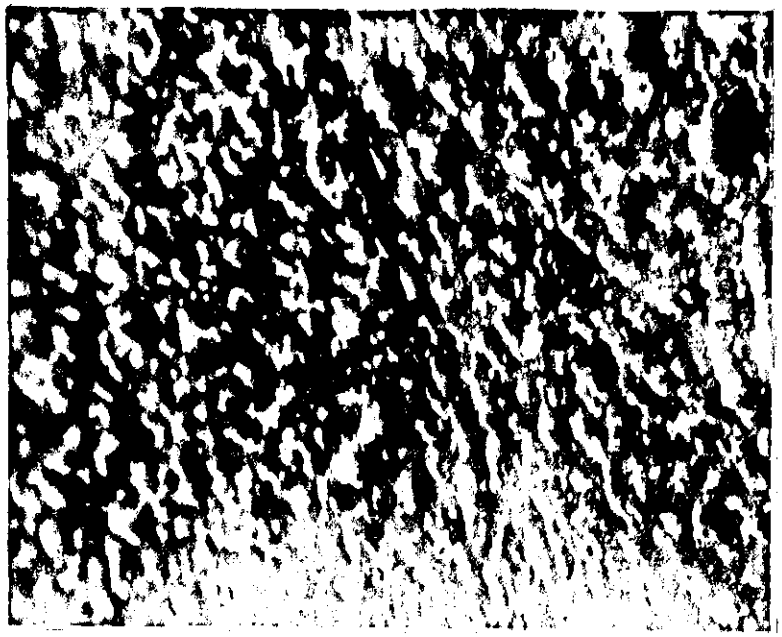


(b)

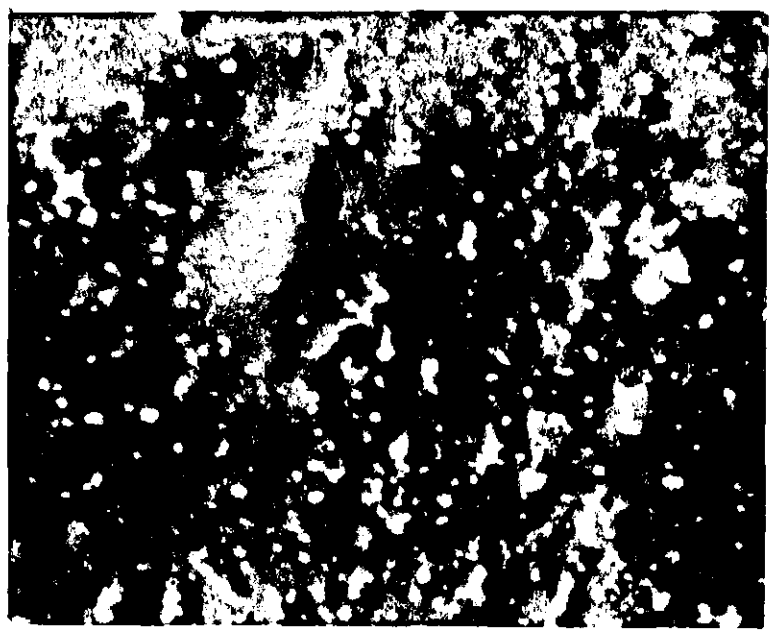
Fig. 89: Scanning electron micrographs of ion-etched surfaces of PVC mouldings (tin blend). Moulding Temperature 200°C.

(a) Suspension polymer (b) mass polymer.

Magnification: x10,000



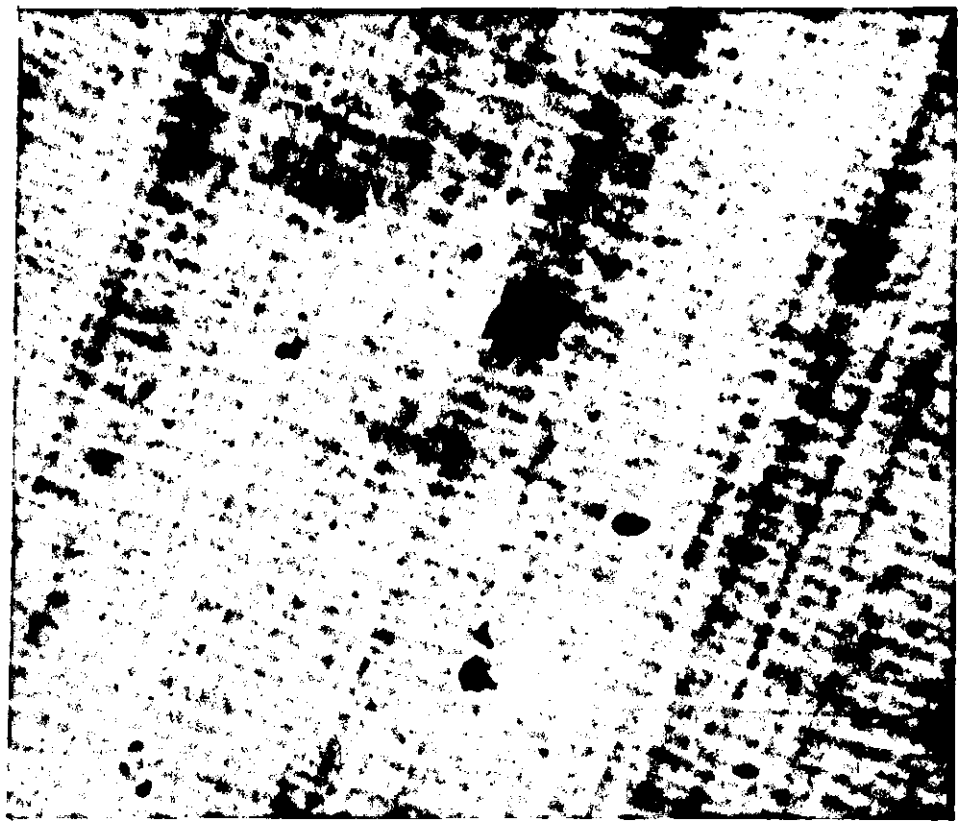
(a)



(b)

Fig. 90: Scanning transmission electron micrograph of ultramicrotomed section of PVC-M moulding (tin blend).

Moulding temperature 200°C. Magnification: x26,000



It is evident from these micrographs that for a given formulation the retention of particulate structure and their size depends on the moulding temperature. It was shown in sections 7.1 and 7.2 that the mouldings had different tensile properties and behaviour depending on the moulding temperature. These changes therefore are determined by the microstructure present. Thus a desired property can be achieved by controlling those process parameters that give the right microstructure.

A closer examination of Figs. 81-84 reveals that one component migrates into the interior of the particles to a depth of around 1 or 2 μm where it exists as discrete droplets some 50 nm in diameter. Both these droplets and the big 'blotches' have been examined with the energy dispersive X-ray analyser coupled to a scanning transmission electron microscope. The droplets were found to contain mostly lead and chlorine. The chlorine presumably comes from the stabilisation action on the PVC (see section 1.5). In Fig. 91 they are marked as A. The big blotches, marked B in Fig. 91 contain mostly calcium and chlorine.

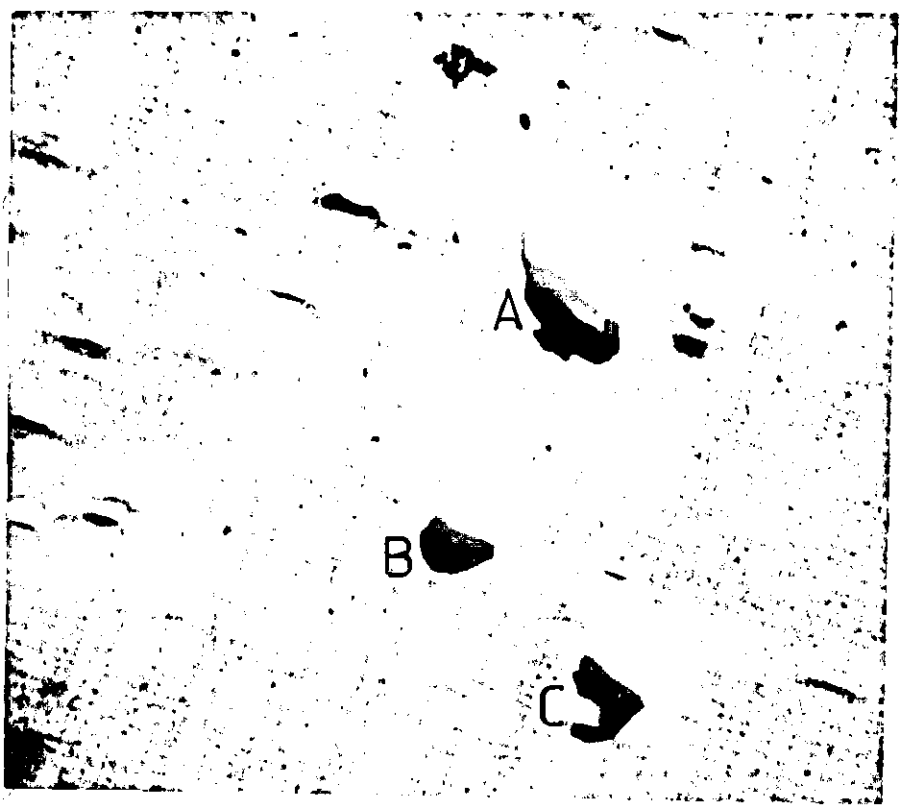
In Fig. 92 the 'blotches' contain calcium, chlorine and sulphur. They are marked A, B, C. Similar result is obtained from Fig. 90.

A combination of techniques have been used in this study of the microstructure of the mouldings. STEM, together with its other facilities e.g. X-ray analyser seems to be the most suitable especially where finer details or structures are required. Geil et al[33] have called for further development of various etching techniques to study the morphology of PVC. One of the setbacks of ion-etching is that structural features observed may not be characteristic of the material but may be 'artefacts'. For instance, it is known that with lengthy etching a polymer surface undergoes considerable changes, probably due to local overheating, decomposition, fusion of separate parts, etc.

Fig. 91: Ultramicrotomed section of PVC moulding (lead blend) showing additives examined by energy dispersive X-ray analyser.

Fig. 92: Ultramicrotomed section of PVC moulding (tin blend) showing additives examined by energy dispersive X-ray analyser.


B
C
A


A
B
C

However, the use of oxygen plasma for etching should be considered. Since Jakopic's[178] device for etching with active oxygen in the preparation of electron microscopy specimens significant improvements have been made on the existing devices and commercial instruments are now available[179-181]. In contrast to ion beam etching, oxygen plasma etching action is inherently gentle. This is because the ions in the former require energies of 2000 eV or more compared with oxygen species of ∿ 10 eV or less. It also uses radio frequency (RF) to excite the oxygen under reduced pressures so that a highly active plasma is produced which has a low operating temperature. According to Thomas and Hollahan[191] the etching action is due mainly to the formation of volatile compounds from the highly active plasma species interacting chemically with the specimen surface.

Still, scanning transmission electron microscope with its higher resolution capability could provide the best results and its use should be further explored.

7.4 Refractive Index

The results of the refractive index of the mouldings are given in Table 17. All the samples were isotropic so the compression moulding process did not introduce any stress into the mouldings. Fig. 93 is a graph of refractive index against moulding temperature. There is a gradual decrease in refractive index with increasing moulding temperature. At low moulding temperatures the change in refractive index is very small. But after 160°C moulding temperature there is a marked drop in refractive index. This decrease in refractive index suggests crystallinity was being destroyed with increasing thermal treatment. Ansari[182] has measured the crystallinity of similar

mouldings by X-ray diffraction and found that it changed from ∿ 10% to 7% for the mass polymer and from ∿ 15% to 12% for the suspension polymer. His results are plotted against moulding temperature in Fig. 94.

A decrease in density with increasing mould temperature for compression moulded samples of the same compounds has been shown by thermal analysis, to be due to breakdown of crystallites[183]. The breakdown of crystallites it would seem begins at ∿ 160°C since that is when the breakdown of particulate structure becomes apparent or perceptible. For instance, in Figs. 77-80 the primary particles are clearly visible only at 140°C moulding temperature.

These results show that PVC property changes can also be followed by measuring the refractive indices of the mouldings. The advantage of using interference microscopy is that morphological studies as well as accurate quantitative measurements may be undertaken. Most important is the fact that refractive index determination is a quick and useful method of detecting molecular orientation.

Table 17: Refractive Index of Mouldings

Polymer Type	Moulding Temperature °C	Refractive Index n_D^{23}	Amorphous Sample n_D^{23}
Mass	130	1.5410	1.5375
	140	1.5406	1.5372
	160	1.5405	1.5374
	180	1.5383	1.5374
	200	1.5376	1.5370
Suspension	130	1.5421	1.5375
	140	1.5420	1.5378
	160	1.5410	1.5375
	180	1.5392	1.5377
	200	1.5378	1.5372

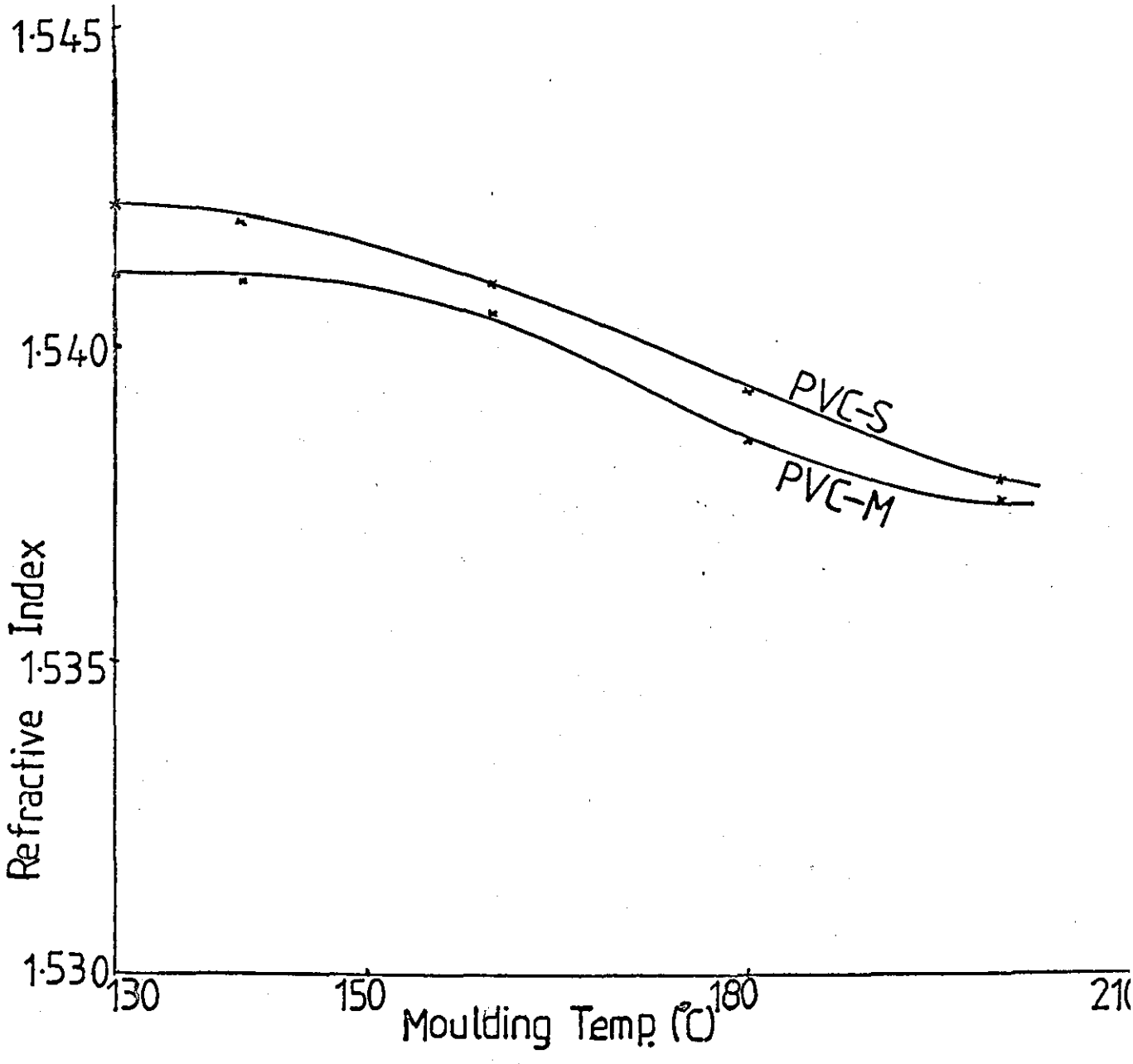


Fig. 93: Refractive Index as a function of moulding temperature

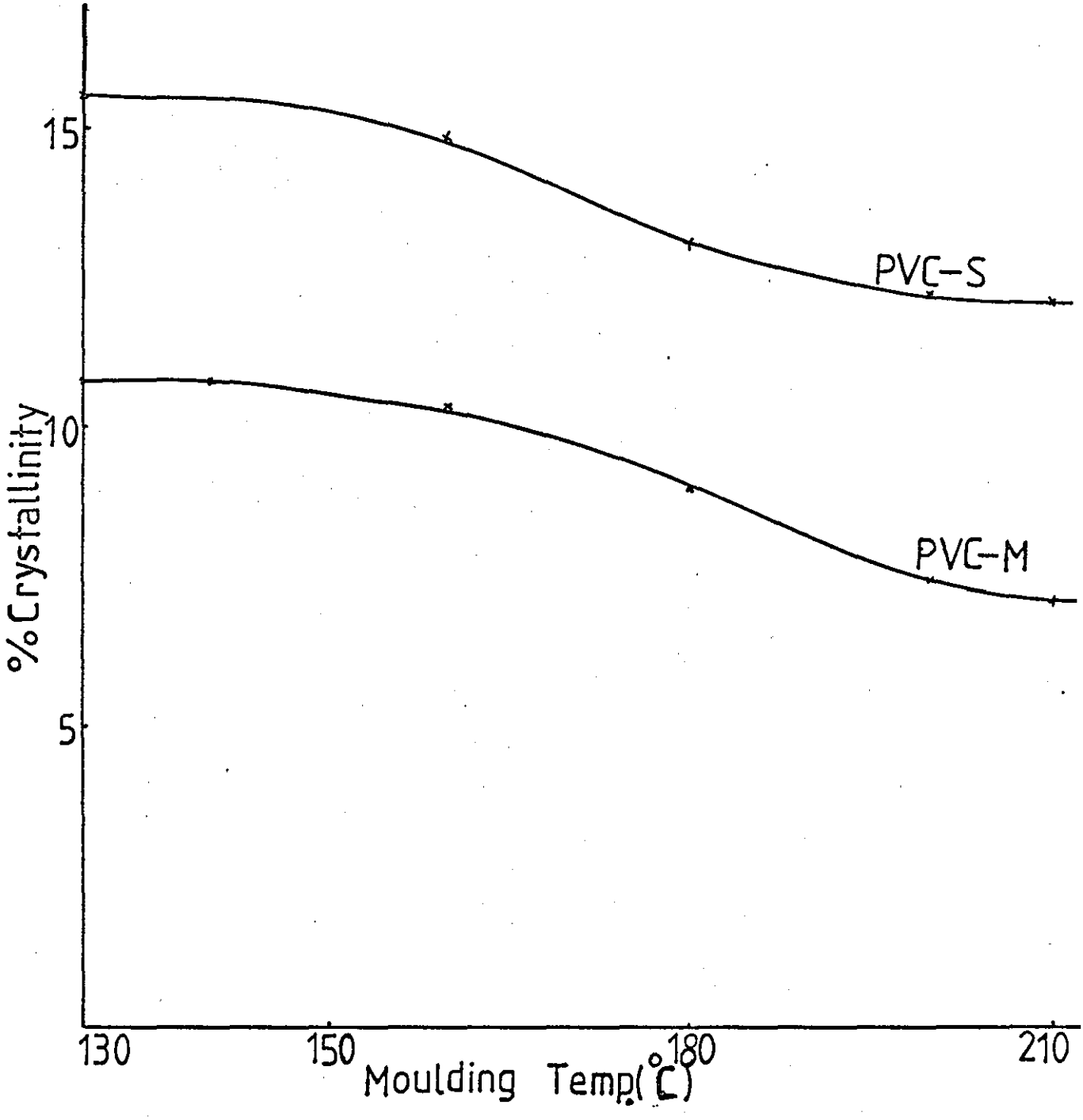


Fig. 94: Change in crystallinity with moulding temperature

7.5 Conclusions

The tensile behaviour of the compression moulded sheets has been found to be strongly affected by the moulding temperature. At low moulding temperatures the type of failure is brittle but with increasing moulding temperature necking rupture and finally cold drawing occurs. There appears to be substantial agreement between the appearance of the fracture surfaces and the yield or breaking stresses regardless of whether the PVC is of the mass or suspension type. The large difference in breaking stress between suspension and mass polymer when pressed at lower temperatures, for example at 160°C, can be attributed to the known differences in particle surface morphology. However, by raising the moulding temperature appropriately it is possible to achieve a similar breaking stress for the two polymers and the appearance of the fracture surfaces is similar.

The examination of the microstructure of the mouldings has shown it is altered by raising the moulding temperature. Where the particulate structure is largely retained the failure is brittle. But as the particulate structure is obliterated with increasing moulding temperature ductile failure takes place. It therefore follows that since the microstructure determines the behaviour of the polymers then by controlling the process parameters a material of specific or desired mechanical properties can be obtained.

The elucidation of microstructure of the PVC mouldings has required a combination of techniques. Scanning transmission electron microscope (STEM) offers the most promise as 'artefacts' normally associated with ion-beam etching are absent from thin sections. Besides, with its X-ray energy dispersive analyser attachment the location and identification of additives have also been achieved. Their location is unchanged as they remain at the periphery of the powder particles.

The calcium stearate melts at high temperatures and stays as big blotches while the lead stabiliser is still as discrete particles.

The trend of decrease in refractive index with increasing moulding temperature is in agreement with other property results obtained in the research school here. Therefore, not only can molecular orientation be detected from refractive index measurements by interferometry but also property changes in PVC processing may be quickly measured and with a high degree of accuracy.

CHAPTER VIII

GENERAL REVIEW OF RESEARCH PROJECT AND RECOMMENDATIONS FOR FURTHER WORK

8.1 General Review

A close study of PVC dry blending, from mixing PVC powder particles, stabiliser and lubricant in a T. K. Fielder Laboratory Mixer to compression moulding into sheets has been undertaken. Direct processing of PVC powder blends instead of pellets or granules may be viewed as a significant breakthrough in PVC processing technology. Besides reducing the thermal history of PVC, the pelletising costs are eliminated which is an enormous saving. For these advantages to be realised a thorough understanding of blending and its consequent effects on PVC morphology is essential. There is a need to choose the right blending conditions to yield suitable blends whose batch-to-batch variations of such properties as particle size and size distribution, particle shape, bulk density, powder flow and moisture content are minimal.

In establishing the right blending conditions. certain questions are bound to be asked. When should the ingredients be added and in what order? At what temperature should the blend be discharged? This study has shown that blending cannot be commenced with PVC only or the friction between the particles will become too high and stop the circulating movement of the mix. Thus abruptly ending the blending operation. The effect of each additive on frictional heat is specific. For instance, calcium stearate decreases frictional heat being a lubricant, while TBLS promotes interparticle friction. Adding calcium stearate later in the blending cycle cuts down blending time. It does suggest then that a knowledge of the effect of each additive on

frictional heat would be useful in deciding on the order of addition. However, this could be at the expense of higher homogeneity of blends especially short cycle blends. Jacket heating was found necessary in the case of liquid additives if the temperature of the mix was to be raised to over 100°C.

Bulk density was shown to increase with blend discharge temperature although not at the same rate throughout the range of temperatures investigated. It has been reported that higher bulk densities yield increased extruder outputs. The temperature at which the blend is discharged will depend on a number of factors but first and foremost, it must be compatible with the thermal stability of the blend. The design of the machine for processing the blend will also have to be considered. For example, a single screw extruder with greater flight depth and higher compression ratio could deal with blends of lower bulk density. In that case blending to higher temperatures may be unnecessary. For the grade of PVC used in this study a blend discharge temperature of 100°-130°C is adequate. There will be no degradation of the polymer and most volatiles would be expelled.

Detailed examination of the effects of discharge temperature on absorption of additives show that solid additives e.g. TBLS, are not absorbed into the resin particles but coat the surface. Liquid additives e.g. tin stabiliser, on the other hand, diffuse into the resin particle like plasticisers. As a result of this absorption of the tin stabilier into the particle, the Tg of the polymer is lowered. The extent to which it is lowered obviously depends on the nature, concentration or amount and the dispersion of the stabiliser in the polymer. On a routine basis therefore, a dry blend preparation may be checked by measuring the Tg particularly as the Du Pont Thermal Analyser is relatively simple

to operate and it is not time consuming. Unfortunately not all stabilisers affect the Tg of PVC so the DTA would have only limited application in assessing blend preparation. Tg measurement would be most useful in cases where Tg is appreciably affected by the stabiliser. Those stabilisers that lower the Tg would suggest that they are absorbed into the resin particle. Consequently better heat resistance of the blend should be expected. An initial guide on the heat stability of a formulation may be obtained from the effect of the additive on Tg.

Having established the optimum blending conditions another important aspect of the study was to find a set of operation parameters that would significantly modify the morphological features of the PVC particles. If blending modifies PVC particle morphology then processing will yield products of varied properties. This objective was largely unsuccessful. PVC particles were found to be resistant to gross deformation or structural modification during blending. For example, particle shape, particle size analysis, surface texture and particulate structure are not markedly affected by blending. One of the problems with suspension PVC is the presence of 'skin' on the surface which prevents easy penetration of additives into the polymer. With plasticisers it could lead to 'undigested grains' which cause 'fish eyes' in mouldings. If blending were to damage or destroy this 'skin' the polymer would more readily absorb additives. Blending operation variables could then be chosen accordingly.

The inference then is that all blending does is a repartition of additives with a breakdown of agglomerates existing in the starting materials and a densification of the powder. It seems this is achieved quite early in the blending because particle size analysis of blends discharged at 80°, 120° and 140°C are not significantly different and the biggest increase in density is between the start and mix temperature of 80°-90°C.

These agglomerates need to be examined further. It is worth considering whether on breaking up the agglomerates the size distribution of the broken parts is similar to that of the unbroken unagglomerated material. If different, many fines in the polymer should be expected to agglomerate during blending. Conversely many fines occurring during blending may actually agglomerate. Since too many fines lead to uneven plasticiser absorption blending operation could be so modified to add the plasticiser after the fines may have agglomerated to larger particles. The problem with such an investigation is obtaining sufficient quantity of agglomerates to make up a Fielder mixer charge. Perhaps a small laboratory planet mixer may be used initially.

As a result of the PVC morphology remaining largely unchanged by the blending the ease of processing should not be affected by blend discharge temperature. This was confirmed by torque and capillary rheometry where no appreciable difference is seen in fusion time or flow curves among the blends discharged at different temperatures.

It is realised that commercial equipments are much bigger than laboratory mixers. However, since peripheral rotor speeds are independent of size of machine, it is not expected that PVC particles should be substantially modified when blended with production size mixers. In the absence of shear PVC powder particles are largely unchanged in character.

All this information should suffice to formulate the right blending procedure for each specific case without undue expectations of morphological changes in the PVC particles which might improve subsequent handling and processing. Each grade of PVC, stabiliser or lubricant, for a given equipment, requires its own individual dry blending conditions.

The work on compression moulded sheets correlates

the relationships between structure, processing conditions and properties. By moulding at different temperatures mouldings having different microstructure were produced. Their mechanical properties also varied with moulding temperature. Thus at low moulding temperatures it is found that the particulate structure is largely retained and this results in brittle failure. But as the moulding temperature is raised the primary particles are gradually obliterated with corresponding change to ductile failure. At sufficiently high moulding temperatures only subprimary particles are left as the microstructure - Stage I particles of Faulkner[34] or 'fibrils' reported by Hattori et al[31]. Necking and cold-drawing occur in such mouldings. It is interesting to note that inspite of the known differences in the morphology of mass and suspension PVC it is possible to produce mouldings of similar mechanical properties from both polymers by choosing appropriate moulding temperatures. Thus PVC-S blend (tin-formulation) moulded at 200°C produced mouldings similar to PVC-M blend moulded at 160°C. This is a highly significant point for it clearly demonstrates a material of desired properties can be produced by controlling the processing parameters. In other words, the PVC processor by controlling his set of operation variables to develop the right morphology, can produce the desired properties in the final products.

Before this objective can be achieved however, the appropriate technique by which the microstructure can be readily studied must be established. In this work two techniques namely, microtomy and ion-beam etching have been used. While microtomy is of general application in specimen preparation for electron microscopy several difficulties were encountered. Firstly, good quality sections were not easy to obtain. The difficulties may be attributed to the additives present since samples without them were much easier to section. Secondly, an

ultrathin section of processed PVC could have several layers of 10 -20 nm subparticle structures which conventional transmission electron microscope could not resolve - a handicap that could be overcome by using scanning transmission electron microscope by virtue of its greater resolving power. Ion-beam etching not only requires time to identify the best etching conditions but extreme care must be taken to avoid producing 'artefacts'. Further work is urgently needed on etching techniques for PVC especially oxygen plasma etching.

The results of the refractive index measurements are in general agreement with the other properties - they are affected by the moulding temperature. As already pointed out, both morphological studies and quantitative measurements can be made with an interference microscope. Other possible areas of application of refractive index measurement are PVC mixtures with processing aids or having multiphases. By careful and accurate measurements of refractive index the components or phases in the PVC matrix may be identified.

To summarise, this study has shown that the morphology of PVC powder particles is largely unchanged by dry blending. Processing parameters e.g. moulding temperature, have a pronounced effect on the microstructure and hence on properties. A PVC processor therefore should be fully aware of the effect of his processing conditions on the morphology for that determines the properties of his finished products. This is extremely important in improving and optimising properties. Finally, a more suitable technique that can be readily applied to study the microstructure of PVC down to very fine details e.g. 10 - 20 nm structures is required.

8.2 Recommendations for Further Work

Temperature profile of the mix during blending has been investigated,

but the stirrer used had a fixed configuration hence the construction could not be altered. Stirrers of different configuration or construction should also be used in order to find out if they have any influence on heat generated during blending. Again, in view of the reported observation that ∿ 15% PVC-M blend stuck to the walls of the mixer, other stirrers giving better sweeping action should be tried.

Blending can also be controlled by observing the power input. Therefore for easy and reliable readings to be obtained continuous recording facilities for temperature and motor current should be installed on the Fielder mixer. The thermocouple probe on the cooler should be located at the bottom of the vessel so as to be in continuous contact with the blend during the cooling stage.

A number of other additives should be used for a more thorough examination of any relationships between blending cycle and absorption of additives with consequent effects on bulk density, size distribution and glass transition temperature, Tg. Preferably additives with low melting points should be used to find out at what stage of the blending they are absorbed into the particles. Also various levels of additives especially lubricants should be used to examine their effect on frictional heat and densification of the particles.

The use of fluorescence microscopy and microprobe (fitted on STEM) to study the distribution/dispersion of additives should be explored. It will thus be possible to follow more closely additive distribution during blending operation. Either method would give the distribution of additives on individual particles unlike X-ray fluorescence spectroscopy which gives an average result over a number of particles. A knowledge of how the additives are distributed or dispersed on each single particle would be of immense value in clarifying their role or performance during processing.

A new electron microscope, JEM-100CX, made by Jeol is now being installed in I.P.T. Since Scanning transmission electron microscope (STEM) has a higher resolving power and it can operate on thicker sections than conventional electron microscope, the JEM-100 CX, STEM mode, should be used to study the structure of the primary and subprimary particles.

Commercial PVC has low crystallinity, generally put at <15%. However the size, perfection or form of the crystals is not certain. Using the JEM-100CX in the dark-field mode may resolve this problem. This is because in dark-field electron microscopy the bright parts of the 'dark field' image are derived from crystalline regions.

Further development of methods of sample preparation for electron microscopy studies of microstructure of PVC mouldings is required.

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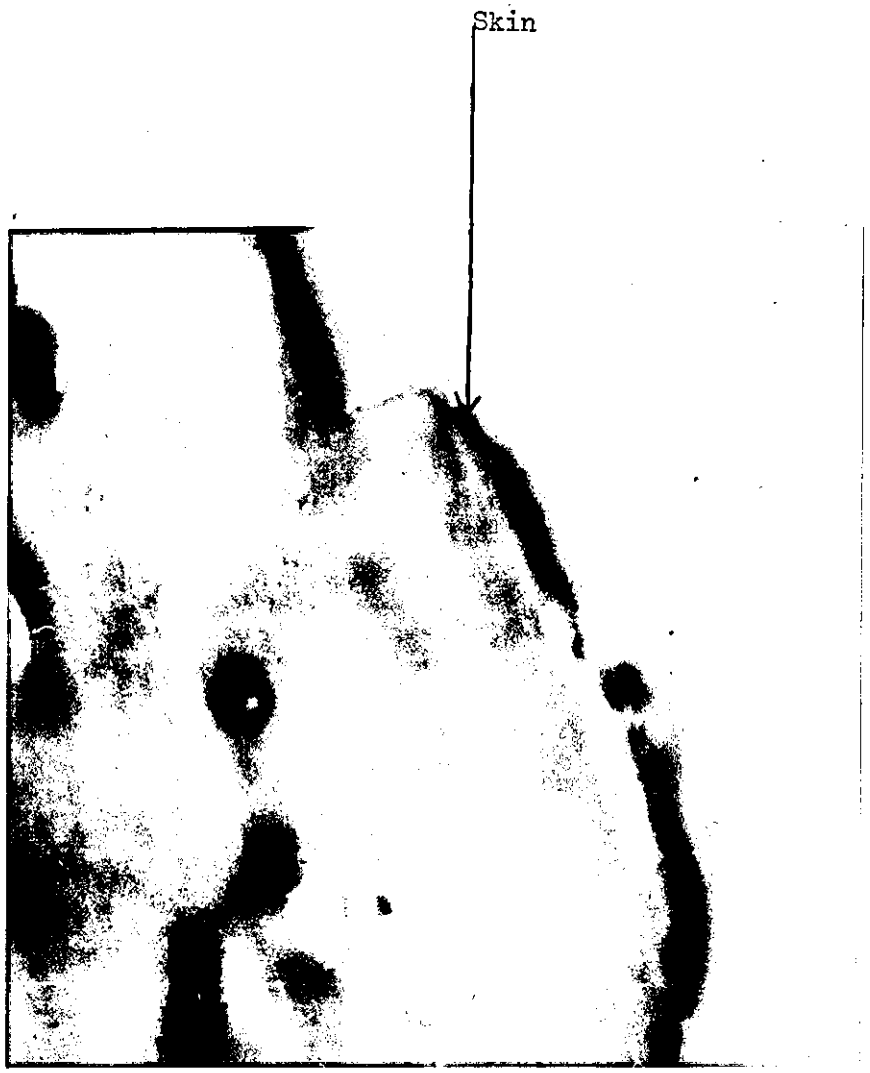
APPENDIX

Computer programme to convert the Number-size distribution result from the Zeiss TGZ3 Counter to Weight-size distribution.

```
      MASTER STA
      DIMENSION F(50), W(50), P(50), D(50), Q(50), WW(50,50), DD(50,50),MSTOR
     1(50)
C     SIZE ANALYSIS OF PVC PARTICLES (WT. PERCENT)
  101 FORMAT (I0)
  100 FORMAT (50 F0.0)
  102 FORMAT ('    FREQUENCY    DIAMETER    DIAMETER3    PRODUCT    WEI
     1GHT PER CENT ')
  103 FORMAT (5F15.3)
  104 FORMAT (1H0)
      ICOUNT=0
   10 READ (1,101)M
      IF (M.EQ.0.0) GO TO 999
      ICOUNT=ICOUNT+1
      READ (1,100) (F(I),I=1,M)
      READ (1,100)(D(I),I=1,M)
      DO 5 I=1,M
      Q(I)=D(I)**3
    5 CONTINUE
      DO 1 I=1,M
      P(I)=F(I)*Q(I)
    1 CONTINUE
      SUM=0.0
      DO 2 I=1,M
      SUM=P(I)+SUM
    2 CONTINUE
```

```
      DO 3 I=1,M
      W(I)=(P(I)*100.0)/SUM
    3 CONTINUE
      WRITE (2,102)
      DO 4 I=1,M
      WRITE (2,103) F(I), D(I), Q(I), P(I), W(I)
    4 CONTINUE
      WRITE (2,104)
      MSTORE (ICOUNT)=M
      DO6 I=1,M
      WW(I,ICOUNT)=W(I)
      DD (I,ICOUNT)=D(I)
    6 CONTINUE
      GO TO 10
  999 CONTINUE
C     PLOTTING SECTION
      WRITE (2,120)
  120 FORMAT (5X,' GRAPH OF WEIGHT PER CENT VS DIAMETER.',/)
      CALL LU1934
      DO 131 J=1,ICOUNT
      CALL DEVPAP (210.,310.,1)
      CALL WINDOW (2)
      CALL AXIPOS (1,50.,30.,140.,1)
      CALL AXIPOS (1,50.,30.,200.,2)
      CALL AXISCA (1,10,0.,200.,1)
      CALL AXISCA (1,10,0.,20.,2)
      CALL AXIDRA (1,1,1)
      CALL AXIDRA (-1,-1,2)
      M=MSTORE(J)
      DO 130 I=1,M
```

```
      W(I)=WW(I,J)
      D(I)=DD(I,J)
130   CONTINUE
      CALL GRASYM (D,W,M,J,O)
      CALL PICCLE
131   CONTINUE
      CALL DEVEND
      STOP
      END
      FINISH
```


Skin