AMINOSILANE CROSSLINKING
OF PLASTICIZED POLYVINYLCHLORIDE) :
PROCESSING, PROPERTIES AND CHARACTERIZATION

by

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A Doctoral Thesis

Submitted in partial fulfillment of the requirements

for the award of

Doctor of Philosophy

of the Loughborough University of Technology

1994

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ACKNOWLEDGEMENTS

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TO THE MEMORY OF MY FATHER

SYNOPSIS

The extensive use of Poly(vinyl chloride) (PVC) is partly due to the modification of properties which is possible by the addition of plasticizer. Although plasticized PVC is used at temperatures well above Tg, the properties are favourable and the material has a rubberlike behaviour. This is generally considered to be due to the presence of a physical network consisting of small crystallites. However, its service range is limited by its thermoplastic nature. At temperatures above 100 $^{\circ}$C it has a tendency to flow and to have a reduced mechanical strength.

One way to increase the maximum application temperature of plasticized PVC is to introduce a permanent chemical network.

The reaction of plasticized PVC with [N-(2-amino ethyl)-3-aminopropyl trimethoxy silane] yielded silane-grafted PVC that was crosslinked by a hydrolitic mechanism. The grafting of the aminosilane was carried out during processing in both a roll mill followed by compression moulding and in a single screw extruder. A controlled reaction was observed when a tin stabilizer was selected. It was found that other thermal stabilizers accelerate the grafting reaction, but destabilize the polymer.

The crosslinking of the grafted PVC has been studied in water at different temperatures. The crosslinking

occurred faster at high temperatures and was diffusion controlled.

It was found that crosslinking resulted in improvement of mechanical properties (tensile strength and elongation at break) specially at temperatures higher than 80 $^\circ$C. Properties at 130°C were substantially enhanced showing a four fold increase in ultimate tensile strength (UTS), and a twofold increase in elongation at break. There was a unique relationship between UTS at 130°C and gel content irrespective of processing conditions, with UTS starting to increase sharply around 30 % gel content , and reaching a plateau at about 60%. Also the softening temperature was improved. The crosslinked material had a higher softening temperature (up to 165°C compared to 95°C for the compound without crosslinking agent), indicating that the hydrolitic crosslinking of PVC yielded a material with improved properties.

The grafting and crosslinking reactions were followed by measuring the gel content and by determination of the concentration of different structures ($-Si-OCH_3$), ($-Si-O-Si$) using FTIR.

The changes in molecular weight distribution before crosslinking were also followed using Size Exclusion Chromatography (SEC); increases in both Mw and Mn were found. Mw increased from 1.6 x 10^5, in the virgin polymer to up 3.5 x 10^5 after processing; Mn increased from 0.7 x 10^5 in the virgin polymer to 1.4 x 10^5.

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CHAPTER 1
INTRODUCTION

1.1 GENERAL.

Poly(vinyl chloride) is produced from the polymerization of the vinyl chloride monomer, CH2=CHCl. It is a thermoplastic homopolymer, commonly abbreviated to PVC, with the repeat unit:

$$[CH_2 - CH]_n$$
$$Cl$$
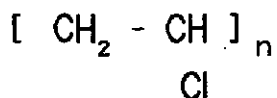
where "n" denotes the degree of polymerization.

The formation of vinyl chloride was first observed by Liebig, but the preparation was first reported in a paper by Regnault in 1835[1]. Despite these earlier works, the first mention of vinyl polymerization was more than 100 years ago. At that time the product was reported to be a white solid that could be heated to $130^{\circ}C$ without degradation, but thereafter became a black brown melt with the evolution of acid vapours.

Perhaps because of this apparently intractable nature and because of the whole industrial background, PVC remained a laboratory curiosity for many years. There were some attempts in the 1920s to exploit copolymers that were easier to process, but the first really significant breakthrough came in around 1930. At that time several workers discovered that PVC could be plasticized by esters such as dibutyl phtalate to give an easier processing material of lower softening point, which was flexible, almost rubberlike, at room temperature.

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Industrial production of PVC sprang up from the 1930s. Its production was started in Germany in 1931; in the United States in 1933; in Japan in 1939; in Great Britain in 1940 and in Italy in 1951. The outbreak of the Second World War was a boost to the PVC industry. It was during this period that PVC substituted the highly costly rubber in some applications. PVC is now one of the top five thermoplastics commercially used (along with high and low density polyethylenes, polypropylene and polystyrene), with a total production of about 20 million tonnes in 1993.

1.2 PVC POLYMERIZATION.

Vinyl chloride monomer is polymerized commercially by four main methods: Bulk (mass), suspension, emulsion and microsuspension. Mass polymerization is, in principle, the simplest of these processes. Briefly monomer and initiator (which is soluble in the monomer) are heated to, and then held at reaction temperature for a given period of time whilst being agitated. During this process the liquid vinyl chloride is converted to a solid PVC which precipitates at a very low conversion. In suspension polymerization, the same process occurs except that the monomer is dispersed as fine droplets, ranging from about 50 - 250 μm, in a continuous aqueous phase. The stability of the dispersion is achieved by combination of agitation plus dispersing agents such as poly(vinyl alcohol), cellulosic derivatives, etc. The microsuspension and emulsion processes produce a powder, which while still in latex form has a mean particle size

ca. 1μm, but when spray dried , agglomeration occurs and then the mean particle size goes up to 50 μm. Emulsion polymerization also involves a dispersion of monomer in a continuous aqueous phase. An important difference between emulsion and suspension polymerization is that in the later case monomer soluble initiators are invariably used, whereas it is more common to use water soluble initiators for emulsion polymerization. In all these processes free radical sources are used as initiators.

1.2.1. THE SUSPENSION POLYMERIZATION PROCESS.

In this process the monomer is dispersed as droplets in water in an autoclave and polymerized using free radical initiators until 80 - 90% of the monomer is converted to PVC. The residual monomer is then removed from the suspension PVC in water, the slurry is dewatered, dried and then stored.

A typical suspension polymerization recipe may consist of:

Water	5000 kg
Dispersant	3.5
Buffer	0.7
Initiator	1.5
Vinyl chloride	3500

Water is first charged to the autoclave and other polymerization ingredients such as initiator, buffers and protective colloid are added. The autoclave is then sealed and evacuated. Monomer is added. The autoclave is heated up to the polymerization temperature. Reaction

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temperature is commonly between 40 - 80°C[2] until ca. 75% conversion of VCM to PVC, when there is no free VCM phase remaining.

The molecular weight of the PVC is controlled by the polymerization temperature and:

a) Molecular weight is inversely proportional to temperature.

b) Granule porosity is inversely proportional to temperature[8].

Combining facts a) and b) it follows that high molecular weight polymers have high granule porosity.

1.2.2. ROLE OF WATER IN THE PROCESS.

Water is present to carry out three main functions: to act as a continuous phase, to act as a heat transfer medium and as a carrier for the protective colloid. The quantity of water used is determined to some extent by each of these activities but principally by the nature of the VCM and PVC particles, normally called granules or grains, which are produced during the process[3].

1.2.3. ROLE OF DISPERSANT.

The dispersants commonly used in PVC manufacture are water soluble substituted celluloses, and/or various partially hydrolysed polyvinyl acetates (PVA). By carefully selection of the right cellulosic or PVA and appropriate agitation conditions, it is usually possible to achieve the type of PVC granule that is desired[4]. The dispersant contributes by stabilizing the

polymerizing droplets against too much agglomeration (controlling the particle size) and to produce porous grains[4-6].

1.2.4. REACTOR AGITATION.

Reactor agitation is critical in determining the size, shape and internal structure of the PVC granules. The agitator has the functions of producing the necessary droplet size, maintaining a suspension of the droplets and ultimately of PVC grains, and ensuring good heat transfer from the polymerizing mass to the autoclave walls. Johnson[7] has found, that as the agitation increased, the granule size and size distribution at first decreased, reached a minimum and then increased due to the agglomeration of the granules. At the same time the granule porosity progressively increases. At low levels of agitation, the final PVC granules were large, spherical in shape and very dense.

1.2.5. INITIATORS.

Two major factors are important in the choice of initiators: the first is the half-life, i.e. the time taken at a particular temperature for the initiator concentration to fall to half its original value. Initiators with half-life times of about 2 hours are commonly used in the polymerization of VCM. The radical efficiency is the second factor, for example, while the peroxides in general have a high radical efficiency, the azo compounds are less effective.

At the present time the most popular initiators are the peroxydicarbonates which are gradually replacing lauroyl peroxide, at least for the lower temperature polymerizations. t-Butyl perpivalete and azobis -2,4(dimethyl-valeronitrile) are used to some extent, but their use is declining.

1.3 STRUCTURAL DEFECTS.

The thermal dehydrochlorination of PVC starts at about $100^{\circ}C$[9],which is much lower than the degradation temperatures for low molecular weight compounds taken as a model for the ideal PVC structure[10,11,12]. On heating to above $180^{\circ}C$ the polymer begins to decompose with the evolution of HCl and discolouration[13,14]. The colour changes from white to yellow to brown then black[14]. It has been assumed that the low stability of PVC is caused by irregular structures in the polymer. Although commonly called "irregularities", they are more or less regularly formed during the polymerization of vinyl chloride. They appear as:

    a) Unsaturation.
    b) End groups.
    c) Branching.
    d) Head to head structures.
    e) Oxidized structures.

a) Unsaturation.

Chain-end unsaturation could arise by disproportionation during bimolecular reaction of polymer radicals[15]

$$2-(CH_2-\overset{\bullet}{C}HCl) \longrightarrow -CH_2-CH_2-Cl + -CH=CHCl \quad (1.1)$$
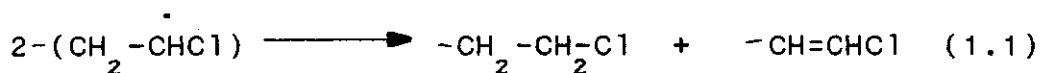
Chain transfer reactions involving the monomer could also result in unsaturation at the chain ends[16] according to the following two reactions:

$$\sim CH_2-\overset{\bullet}{C}H + CH_2=CH \longrightarrow CH_2-CH_2 + CH_2=\overset{\bullet}{C}$$
$$\qquad\quad | \qquad\qquad | \qquad\qquad\qquad | \qquad\qquad\quad |$$
$$\qquad\quad Cl \qquad\qquad Cl \qquad\qquad\qquad Cl \qquad\qquad\quad Cl$$

$$VCM \qquad (1.2)$$

$$CH_2=C-CH_2-CH-$$
$$\qquad | \qquad\quad |$$
$$\qquad Cl \qquad\quad Cl$$
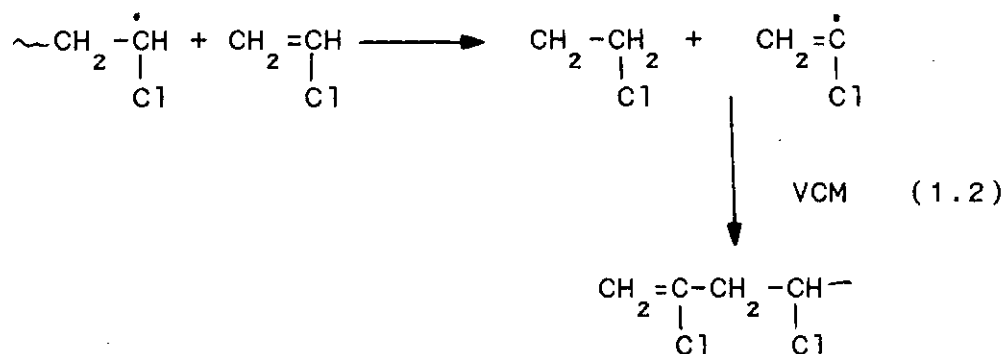
Braun and Schurek[17] assumed that during polymerization a reaction can occur between the polymer and free radicals which leads to the elimination of hydrogen chloride and formation of a double bond.

Starnes et al[18] appear to have evidence for the following mechanism of formation of a double bond next to the chain end. Hjertberg and Sorvik[19,20] have also presented evidences of this mechanism:

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$$\overset{\displaystyle\cdot}{\underset{\displaystyle \overset{|}{Cl}}{\sim CH_2-CH}} \xrightarrow[\text{head to head addition}]{\text{VCM}} \overset{\displaystyle\cdot}{\underset{\displaystyle \overset{|}{Cl}\ \overset{|}{Cl}}{\sim CH_2-CH-CH-CH_2}}$$

$$\Big\downarrow \begin{array}{l}\text{1,2 Cl}\\ \text{migration}\end{array}$$

$$\text{Polymer with } CH_2Cl \text{ branch} \xleftarrow{\text{VCM}} \overset{\displaystyle\cdot}{\underset{\displaystyle \overset{|}{Cl}\qquad \overset{|}{Cl}}{\sim CH_2-CH-CH-CH_2}} \qquad (1.3)$$

$$\Big\downarrow \text{-Cl}$$

$$\overset{\displaystyle\cdot}{Cl} \; + \; \underset{\displaystyle \overset{|}{Cl}}{\sim CH_2-CH=CH-CH_2}$$
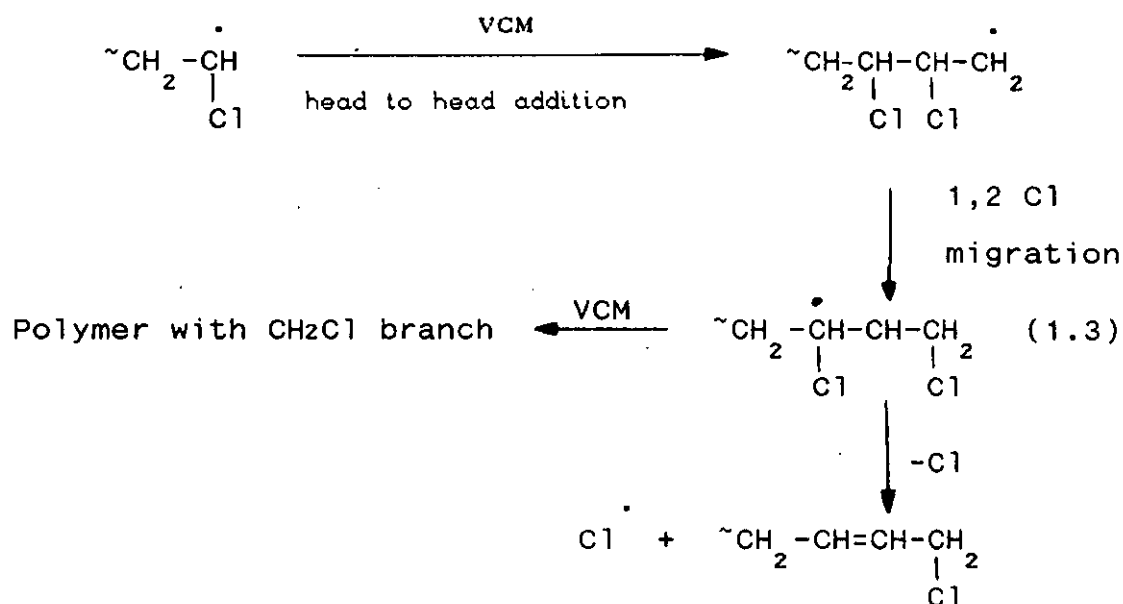
There are many conflicting reports regarding chain end unsaturations as initiation sites for thermal degradation. Arlman[21] found a linear dependence between the rate of dehydrochlorination and the reciprocal value of the average molecular weight of several PVC samples. The same linear dependence was found by Bengough and Sharpe[22,23] and Talamini and Pezzin[24]. However, Bengough and Varma[25] affirm that there is no systematic relationship between the rate of dehydrochlorination and molecular weight for samples obtained by fractionation of a commercial PVC. Crosato-Arnaldi and coworkers[26] investigated the thermal decomposition of fractions of PVC; they found that fractions having lower and higher molecular weights were less stable than the medium fractions. This is in agreement with the findings of Onozuka and Asahina[27]. Studies on model compounds also suggest that unsaturated chain end-groups should not have an important influence on the thermal stability of PVC[28]. In conclusion, it may be said that the effect of unsaturated end groups on the stability of PVC is minor.

A direct connection between the number of internal double bonds and the rate of dehydrochlorination of PVC has been established[29], and it seems that the allylic chlorines associated with internal double bonds along with tertiary chlorines at branch points are mainly responsible for the low thermal stability of the polymer. With respect to this Hjertberg and Sorvik[30] consider that tertiary chlorines are the most important labile structure in PVC. This conclusion is in line with Berens[31]. This is in contrast to the opinion expressed by Braun[29] and Mayer[32]. They mentioned that chlorine atoms allylic to internal double bonds are the most labile and play the most significant role in the thermal degradation of PVC.

b) End groups.

The problem of the effect of the decomposition products of the polymerization initiator incorporated at the beginning of the chain is a controversial one. Cittadini[33] and Corso[34] found that the product obtained by polymerization initiated with peroxides is thermally more stable than PVC obtained with azo initiators. However Park and Skene[35] have found that the rate of dehydrochlorination increases with the content of the initiator end groups and that PVC obtained with peroxides undergo decomposition more readily than PVC-azo. It seems therefore, that the end groups originating from the decomposed initiator do not bear the main responsibility for the low thermal stability of PVC.

c) Branching.

Branches in PVC can be formed by transfer to polymer during polymerization. Short branches in PVC have usually been considered to be formed by a backbiting mechanism similar to those occurring in polyethylene. Such branches should have a tertiary chlorine at the branch point.

Branching in PVC has been suggested as a possible source of instability for a long time. Caraculacu[36] studied the degradation of a polymer obtained by copolymerization of vinyl chloride with 2-chloropropene and showed that tertiary chlorines atoms readily initiate degradation at temperatures lower than is usual for pure PVC. Berens[31] has suggested that only 0.1 - 0.2 mol% of such groups would be needed to account for the instability of PVC. On the other hand, investigations with copolymers from vinyl chloride and 2,4 - dichloropentene - 1 led to the conclusion that because of steric reasons PVC could not contain branch points with tertiary chlorine atoms[37]. Braun and Weiss[38] also found the same relationship between the number of branch points and the rate of degradation. Short branches in PVC are mainly chloro methyl groups with a hydrogen attached to the tertiary carbon. The methyl content is thus a measure of structures which are more stable than tertiary chlorines. Abbas and Sorvik[39] found no obvious correlation between dehydrochlorination rate and the methyl content in reduced PVC. There was a slight trend toward higher degradation rates at higher amounts of branching but the data were rather scattered. Suzuki et al[40] found

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similar results. For a very high degree of branching they observed a much higher dehydrochlorination rate.

The development of ^{13}C-NMR has allowed a more direct determination of tertiary chlorines and different authors[41,42] have found different branch structures with tertiary chlorines. Hjertberg and Sorvik consider tertiary chlorines to be the most important labile structures in PVC[20,42]. This conclusion is in line with Berens[31] and Starnes et al.[43]

d)Head to head structures.

Head-to-head units can either be formed through termination by combination or by head-to-head addition during propagation. It has been difficult to determine head-to-head structures in PVC and there are not conclusive studies of its quantification. In a recent investigation Hjertberg et al[44] studied various PVC samples: they were able to measure the content of saturated 1,2-dichloroethyl chain end groups. Head-to-head PVC prepared by adding chlorine to cis-polybutadiene has been found to be less stable than ordinary head-to-tail polymer[45].

From the results obtained by thermal decomposition of both low molecular weight vicinal dichlorides in the gas phase and of the copolymers of vinyl chloride and trans-1,2-dichloroethylene, it is not possible to attribute the cause of low thermal stability of PVC to the individual head-to-head structures.

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The extent of head-to-head units in PVC and their effect on stability of the polymer is yet to be conclusively demonstrated although it would seem that compared to other structural defects their contribution to polymer instability is a minor one.

e) Oxidized structures.

Various oxygen-containing structures[46], arising either by reaction with traces of oxygen already present during polymerization or by oxidation during storage or treatment of the finished polymer in air, are also sometimes considered to be the possible labile sites in the PVC molecule. The unfavourable effect of oxygen during the polymerization of vinyl chloride on the thermal stability of the product has been proved[47]. Under these conditions a partial copolymerization of vinyl chloride and oxygen takes place. The splitting of the peroxide bond in the copolymer gives rise to the oxy radicals which can initiate further polymerization leading to a thermally unstable product.

As far as oxidation of the polymer with oxygen of the air is concerned, the β hydrogen atom in the neighborhood of the C=C double bond is the most likely one to be attacked by oxygen with the formation of hydroperoxide which undergoes further decomposition[27]. OH and CO groups have been detected spectroscopically in the polymer[27].

1.3.1. EFFECT OF STRUCTURAL DEFECTS ON CROSSLINKING.

As mentioned before, thermal stressing of PVC induces degradation reactions (dehydrochlorination, oxidation and scission of primary macromolecules) on one hand and reactions leading to network formation on the other. The mechanism of these reactions is not quite clear yet. The most likely crosslinking reaction seems to be the reversible (Diels-Alder) diene synthesis of conjugated double bonds[50].

Irregularities in the chemical structure of PVC are the cause of poor thermal stability of the polymer[13,14,42-44]. They play, however, an important role in the chemical (non-degradative) crosslinking of PVC[51], although some authors[52] claim that a PVC macromolecule contains only negligible amounts of these defects which are unlikely to affect the degree of crosslinking reaction. It is assumed[53] that structural defects accumulate in the low molecular weight fractions of PVC.

1.4 MORPHOLOGY OF SUSPENSION PVC.

Whereas the behaviour of other polymers may be concerned with molecular weight distribution, rate or level of crystallization , density, melt flow behaviour, etc., the success of a PVC polymer depends largely on its grain structure or morphology.

The grain structure or morphology of a PVC polymer is developed during the polymerization process. Allsopp[54]

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examined the PVC grain during polymerization and reported that microdomains are formed and precipitated from the monomer phase at the very early stage of polymerization and consist of coiled macromolecules of about 0.02 μm size. At less than 2% conversion, these particles aggregate to form the domains (0.2 μm size) and thereafter become primary particles. The primary particles are stable and form an important feature of PVC morphology. At more than 2% conversion the primary particles flocculate and growth proceeds in these flocs until a macrosize (of 100 μm average size) is attained.

Table 1.1 presents the terminology used to describe PVC morphology, as summarized and published by Geil[55].

1.5 MOLECULAR STRUCTURE AND CRYSTALINITY.

PVC has a fundamental repeating unit $^{\sim}CH_2$-CHCl-. The chlorine atom can be disposed in three different ways with respect to the backbone giving rise to configurational isomers namely isotactic, syndiotactic and atactic. Two of these, syndiotactic and isotactic arrangements are regular, but the third, atactic is random and irregular. A minimum of three monomer units, a triad, is required to define these three types of configurational isomers, but it is possible to describe their stereoregularity, and that of longer sequences, in term of two types of diads, meso (*m*) with the substituents on the same side of the backbone and racemic (*r*) where they alternate. In this notation the three triads become *rr, mm, mr.*

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TABLE 1

PVC NOMENCLATURE

Term	Approx. Rang (μm)	Size Avg. (μm)	Origin or Description	Previous Terminology (with ref.)
Grain	50-250	130	Visible constituents of free flowing powders made up of more than 1 monomer droplet.	Granule [56] Cellular grain [57]
Sub-grain	10-150	40	Polymerized monomer droplet.	Sub-granule [56] Unicell [57]
Agglomerate	2-10	5	Formed during early stages of polymerization by coalescence of primary particles (1-2μm). Grows with conversion to size shown.	Aggregate Cluster [57] Macro-globule [58]
Primary particle	0.6-0.8	0.7	Grows from domain. Formed at low conversion (less than 2%) by coales cence of micro domain: grows with conversion to size shown.	Microgranule Primary particle [56] Granule [57] Micro-globule [58]
Domain	0.1-0.2 (200nm) (2000A)	0.2	Primary particle nucleus. Contains about 10^3 micro-domains. Only observed at low conversion (less than 2%) or after mechanical working. Term only used to describe 0.1μm species; becomes primary particle as soon as growth starts.	Primary nucleus [56] Granule [57]
Micro-domain	0.01-0.02 0.02		Smallest species so far identified. Aggregates polymer chains probably about 50 in number.	Basic particle

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First indications of crystallinity in PVC stemmed from the creep resistance of plasticized samples. The creep resistance was explained on the basis of permanent network junctions formed by crystals[59]. The ability of a PVC macromolecule to pack in an orderly crystalline array is determined by the regularity of the polymer chain. The syndiotactic sequence is the main crystallizable unit and the syndiotactic fraction decreases with increasing polymerization temperature[60]. The first proof of the existence of crystallites was provided by Natta and Corradini[61] based on studies using wide angle X-ray diffraction.

It had been mentioned that the degree of syndiotacticity correlated well with the reported degrees of crystallinity[62] (10 % for commercial PVC) However, Juijn[63] concluded that the crystallinity of atactic PVC cannot be explained satisfactorily by assuming that only the syndiotactic part of the polymer crystallizes.

1.6 PVC STABILIZATION.

Degradation which occurred during early attempts to process PVC homopolymers led investigators to the conclusion that the polymer would not be workable without modification. It was not until the development of copolymers and techniques for plasticizing homopolymers that commercialization was possible. Since that time, resins with improved heat stability and processing characteristics have been developed. In addition, more effective heat stabilizers and efficient processing

equipment which reduce processing time and temperature have also been developed.

1.6.1. CLASSIFICATION OF STABILIZERS.

There are now many stabilizers and some classification is necessary to avoid confusion. The stabilizers, by virtue of their composition, fall into relatively well defined groups. The four main groups are as follows:

- Organo-tin compounds.
- Metal soap or salts.
- Organic and miscellaneous stabilizers.
- Lead salts or soaps.

1.6.1.1. ORGANO-TIN STABILIZERS.

The organo-tin stabilizers are normally compounds of either dibutyl tin or dioctyl (or diisooctyl) tin with various organic materials such as certain fatty acids (frequently lauric or maleic) and thio compounds (mercapto acids).

These compounds are powerful stabilizers and the best among them are undoubtedly the most effective stabilizer available, unequalled in the degree of stabilization, both long and short term, and the clarity they confer on PVC compounds.

Most of the stabilizers in general use have structures of the type $RnSnX_{(4-n)}$ where R is normally an alkyl group, usually methyl, butyl or octyl, and X is one

of a large number of saturated or unsaturated carboxylates or mercaptide derivatives. The relative order of efficiency of the range of possible compounds is as follows:

$$R_2SnX_2 \; > \; RSnX_3 \; > \; R_3SnX \; >> \; R_4Sn$$
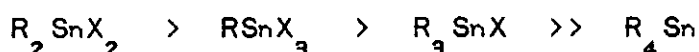
It has been generally confirmed by several workers that varying the structure of the R group in dialkyl tin compounds, R_2SnX_2, has relatively little effect on the stabilizer efficiency, but that the nature of X is much more important. For dibutyl tin, for example, diacetates or dilaurates are poor stabilizers, the dilauride mercaptide much better and the di(isooctyl-mercaptoacetate) extremely good.

Stabilization Mechanism.

The stabilization process is as complex as the degradation process.[69] At least six of such processes are now clearly definable:

- Reaction with HCl and its removal from the system.
- Reaction with and stabilization of "abnormal" structures.
- Interference with the chain mechanism.
- Non-chain decomposition of peroxide or hydroperoxide compounds.
- Reaction with conjugated polyene sequences.
- Rendering harmless of prodegradant substances.

- Reaction of organotin compounds with HCl.

$$Bu_2 SnX_2 \quad + \quad HCl \longrightarrow Bu_2 SnCl_2 \quad + \quad RX \quad (1.4)$$
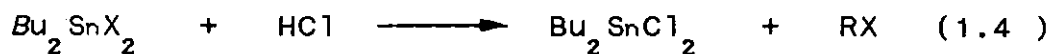
The reaction product $Bu_2 SnCl_2$, has the advantage of being a relatively weak Lewis acid and therefore unable to catalyze further degradation.

- Reaction of organotin with PVC.

Since the work of Frye et al[64] which first showed that the X component of an organotin stabilizer becomes chemically bound to the polymer during the thermal ageing of stabilized PVC, the mechanism has subsequently been confirmed many times by different workers using a variety of experimental techniques. Experiments with model compounds for allylic and tertiary chlorines, showed that the stabilizer functioned not only as an acceptor of HCl, but replaced the allylic chlorine formed by the dehydrochlorination with an X group thus interrupting the "zipper" elimination of further HCl which normally follows allylic activation[65].

$$2 \; CH{=}CH{-}CH{-} \; + \; R_2 SnX_2 \longrightarrow 2 \; CH{=}CH{-}CH \; + \; R_2 SnCl_2 \quad (1.5)$$
$$\qquad\quad | \qquad\qquad\qquad\qquad\qquad\qquad\qquad | $$
$$\qquad\quad Cl \qquad\qquad\qquad\qquad\qquad\qquad\;\; X$$
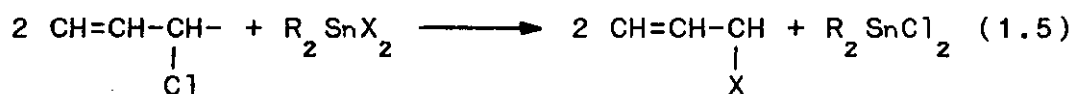
Experiments with labelled stabilizers showed that effectively the thiol group of mercaptide stabilizers react with allylic chlorides on PVC[66]. Starnes and Plitz[67] have shown that treatment of PVC with a relatively large quantity of stabilizer, in some cases with a requisite amount of catalyst, gave a polymer whose thermal stability was considerably improved.

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The following broad generalizations about reactions
with PVC may be made[68]:

1) Stabilizers react with and remove certain
destabilising structures which are almost certainly
allylic chlorines.

2) A limiting stabilising effect is reached which
does not correspond to absolute stability of the polymer
and may reflect some inherent instability of the normal
PVC structures.

3) Whether destabilising structures exist in the
virgin polymer or are introduced during processing, the
contribution of this mechanism to the efficiency of the
stabilizer is considerable and allows greatly increased
flexibility in processing conditions.

4) The reactions concerned are almost certainly
catalyzed to an extent which depends on the conditions.

- Organotin compounds as radical scavengers and
peroxide decomposers.

Sulphur-free organotins are not able to react with
peroxides below a certain level; on the contrary,
sulphur-containing organotins can reduce the level of
peroxide formation almost to nil, but not at the
beginning of thermooxidation, when they even seem to
increase the rate of peroxide concentration. This initial
increase in peroxide concentration is higher depending on
the amount of stabilizer introduced[69]. Cooray[69]
explains that the tin mercaptides convert hydroperoxides
to tin sulphenates, which at elevated temperatures
produce sulphur acids having an antioxidative action.

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The other important function of stabilizers is that of radical deactivation. According to Mori et al[70] organotin stabilizers are effective in the deactivation of radicals. Ayrey and Poller[71] presented a mechanism of radical deactivation. Their findings are interesting, since a similar mechanism describing the action of organotins during thermal degradation was proposed by Gupta and Pierre[72].

- Reactions of organotin compounds with double bonds.

Addition of organotin mercaptides or maleates to partially degraded (coloured PVC) can bring about decolouration which must be do to reaction with conjugated polyenes sequences[73]. Cooray and Scott[69] presented a detailed comparison of the effect of organotin stabilizers on PVC. They evaluated two main classes of dialkyltin stabilizers during processing (dibutyltin maleate (DBTM) and dioctyltin thioglycolate (DOTG)); they found that both stabilizers have a profound effect in reducing the rate of formation of unsaturations, but only DOTG is able to destroy the unsaturation formed during the early stage. During the secondary stage DBTM continues to react with allylic chlorine and with further HCl liberated giving rise to the corresponding dialkyltin chlorides and maleic anhydride. In addition there is a progressive removal of conjugated unsaturations as a result of the Diels-Alder reaction. The reason that the initial unsaturation is not removed is because maleic anhydride is unable to react with the isolated double bonds which account for the initial unsaturation. DOTG on the other hand is able to

react with and remove the isolated double bonds completely.

1.6.1.2. METAL CARBOXYLATES STABILIZERS.

These are molecules having the general formula $(RCOO)_2M$ where M is Cd, Zn, Ba or Ca, and R is a linear or branched alkyl group often stearate ($C_{18}H_{35}$). They are normally used in synergistic combination. Although the carboxylates of cadmium or zinc alone provide thermally processed PVC with good initial colour, they confer poor long term stability. The carboxylates of barium or calcium on the other hand act in the reverse way and so Ca/Zn and Ba/Cd mixtures are used.

It has been demonstrated that metal carboxylates are good HCl acceptors. Frye and Horst[74], showed that esterification of the polymer to form PVC-carboxylate esters occurred, the by-products of this esterification, metal chlorides are active catalysts of the dehydrochlorination. $ZnCl_2$ is most active in this respect, closely followed by $CdCl_2$, and $BaCl_2$ and $CaCl_2$ are much less reactive. There is an exchange reaction[75] between the carboxylates and chlorides that explains the synergistic effect.

$$ZnCl_2 + Ca(OOCR)_2 \rightleftharpoons Zn(OOCR)_2 + CaCl_2 \quad (1.6)$$
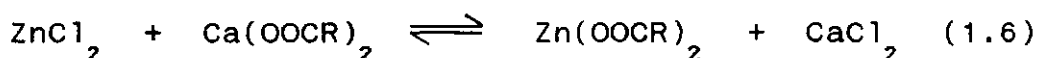
Thus, $Ca(OOCR)_2$, inactive (towards stabilization/esterification) reacts, with $ZnCl_2$, reactive (towards dehydrochlorination) to form $Zn(OOCR)_2$

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active towards stabilization and $CaCl_2$ inactive towards dehydrochlorination. In absence of calcium or zinc, cadmium or barium carboxylates function only as HCl acceptors.

1.6.1.3. ORGANIC PHOSPHITES.

Organic phosphites have been used to stabilize PVC as well as polyolefins, and natural rubber. As well as having an overall stabilizing effect they have usually been assumed to contribute towards preserving the original colour of the polymer during processing and use and in the case of PVC are most often used as synergistic combinations with the other stabilizer components, antioxidants, etc.

Phosphites function as terminators of chain processes by reacting with peroxy radicals and suppressing degenerate chain branching by decomposing peroxides. Phosphites are also able to react in other ways. They can react with labile structures in the polymer, suppressing the catalytic action of HCl and metal halides.

1.6.1.4. LEAD COMPOUNDS.

These are either lead salts or lead soaps. The main technical advantages of these stabilizers are good heat-stabilizing power and particular suitability for use in electrical insulation. Lead compounds represent a health hazard, and exposure must be minimized.

The main mechanism whereby the lead stabilizers exert their effect is thought to be neutralization of HCl[76]. This view accords with their basic nature, their mode and rates of reaction with HCl[77], and the fact that lead chloride is formed in lead-stabilized PVC materials in the course of their heat treatment and service. Unlike the chlorides of some other stabilizer metals, lead chloride does not promote degradation of PVC polymer.

1.7 THE PROCESSING OF PLASTICIZED PVC.

Penn[78] and Matthews[79] have described the processing and compounding of PVC. Practically every kind of plastics processing can be applied to PVC in one form or another. The various different routes by means of which PVC or copolymers and additives can be converted to finished products are presented by Menges[80]. The various processes may be broadly classified into three classes: (1) mixing, (2) melt compounding and (3) finishing. In the present context "mixing" is seen as any process in which the various components are blended together mechanically to produce a free flowing powder (dry blend). "Melt compounding" is the operation (commonly carried out on a mixed preblend) whereby the constituents of a composition are intimately combined with the resin in the melt, under heat and shear. "Shaping" comprises those processes which produce the final product.

1.7.1. DRY BLENDING.

Dry blending[76,78] is a technique involving the mixing of all the ingredients in a single operation to produce a completely dry free-flowing powder. This process is carried out in a high speed mixer . Normally the polymer and minor solid ingredients are mixed at the beginning of the cycle and then the plasticizer is run in with any other liquid ingredients, at a prescribed temperature, generally between 60 and 90°C. Mixing then continues to a peak temperature in the region of 90-110°C, after which the blend is transferred to the cooling chamber. This procedure facilitates the even dispersion and absorption of plasticizer into the polymer granules. Optimum distribution of the additives is only assessed if the mixing temperature exceeds the melting temperature of one of the additives. Well dispersed or preferably adsorbed stabilizers are essential to stop degradation which will occur if unprotected polymer regions exist. The rate and effectiveness of the dry blending process depends critically on the nature of the polymer granules and the plasticizer employed.

1.7.2. EXTRUSION PROCESSING.

Most of the conversion processes used in the plastic industry can be applied to PVC powder compounds. There are two main processing possibilities, either the dry blend is extruded in order to melt and then produce pellets which are subsequently re-extruded into finished products, or it is extruded directly into finished products.

Twin screw extruders are more usually used for rigid
PVC in Europe, and single screw extruder for plasticized
PVC. The principle of the machine is widely known but it
is worth reviewing the functions of the various parts
with particular reference to PVC powder. PVC presents
some characteristics that make it different from other
thermoplastics:

a) Low powder to metal friction.

b) Limited heat stability.

c) High melt viscosity (unplasticized).

In the feed zone of an extruder the objective is to
convey the powder away from the feed hopper and to
develop sufficient pressure to enable the powder, and
subsequently the melt, to overcome any downstream
obstacles in the extruder. An initial requirement is to
have a good flow from the hopper to the screw. This means
that the powder compounds must not agglomerate. For good
conveying in the extruder feed zone it is desirable that
the powder slips on the screw surface and tends to stick
to the barrel.

Once adequate conveying is obtained, the PVC powder
is subjected to gradually increasing pressure and
temperature as it moves away from the hopper. As the
pressure and temperature rise the powder will be softened
slightly and compacted. Further along the screw the PVC
grains start to show a high level of densification, the
point at which this occurs is dependent upon the preset
extrusion barrel temperatures and the variation of the
frictional forces with the developing temperatures and
pressures. As soon as this process starts to develop in

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a correctly designed extruder the screw profile will change to compress the material. In this, the melting zone of the screw, further pressure increases are likely and the shearing forces becomes larger. As a consequence the fusing PVC powder which is still constrained from breaking down into smaller particles but which is now being sheared and softened will be elongated. Ideally, when the PVC reaches the end of the melting and compression zone no powder will still be present, melting having been completed. It is the function of the final or pump zone of the extruder to ensure complete homogenization and to pump the melt through the head and die at a uniform rate.

1.7.3. POLYMER/PLASTICIZER INTERACTION.

Since the interaction of polymer and plasticizer is central to the formation of plasticized compositions, it is pertinent at this point to consider the mechanism of this interaction. Three major theories have been proposed to account for the main effects produced by plasticizers: the lubricity theory, the gel theory and the free volume theory.

In the lubricity theory, the plasticizer thought to act as a lubricant reducing intermolecular friction of the polymer chains between which it is interposed, and thus making the bulk material[83] less resistant to deformation[81,82]. The gel theory, ascribes the deformation resistance of amorphous polymers to the existence of a quasi cross-linked structure, linked to a loose three dimensional honey comb with the cross-links

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operating between "active centres" along the polymer chains. The structure is envisaged as non-static, but existing in a state of an aggregation-disaggregation equilibrium, with the cross-links continually breaking down and reforming. When a plasticizer is introduced into the polymer it takes part in the interaction within the resulting two-component system, so that temporary links are now formed also between the plasticizer molecules and the polymer "active centres". In consequence, a proportion of the centres is engaged (masked or solvated) by the plasticizer and hence it is not available to polymer-to-polymer linking, the polymer structure being correspondingly loosened. The free volume theory takes into account the lowering of glass transition temperature Because an increase of hole free volume permits increased motion of polymer molecules, a study of plasticization is a study of ways to increase free volume. Free volume comes from three principal sources: (1) the motion of chain ends, (2) the motion of side groups, and (3) the motion of the main chain. These motions and therefore the free volume of a resin may be increased by:

- Increasing the number of end groups (lower Mol. Weight).
- Increasing the number or length of side chains (Internal plasticization).
- Increasing the chance for main chain movement by decreasing the steric hindrance and the intermolecular attraction (Internal plasticization).
- Inclusion of a compatible compound of lower molecular weight that acts as it does all of 1 through 3 above (External plasticization).
- Raising the temperature.

1.7.4. THE EFFECT OF FORMULATION INGREDIENTS.

PVC polymers, because of their poor thermal stability, cannot be processed without additives. In plasticized compounds the plasticizer and stabilizer are the two most important constituents apart from the resin. In some cases, other ingredients such as lubricants, modifiers and fillers are also included.

1.7.4.1. THE POLYMER.

The requirements for acceptable processing behaviour are less restrictive on K value for plasticized PVC than in the case of rigid compositions. K values are typically in the range of 65 - 72, with the higher end of the range being employed where mechanical properties, particularly performance at high temperatures are important, and lower K value where the emphasis is on easy processing.

An essential quality in any polymer for flexible applications is that it should absorb plasticizer readily, but homogeneously. The plasticizer absorption characteristics are reflected not only in the performance during dry blend manufacture, but also in the ease with which a homogeneous melt, free of dispersion faults, may be produced. A key requirement is that the polymer grains should possess a relatively high level of porosity.

1.7.4.2. PLASTICIZERS.

A plasticizer is incorporated in a polymer to increase its workability and its flexibility. Addition of plasticizer may lower the melt viscosity, the temperature of the second-order transition or the elastic modulus of the plastic.

A wide variety of substances are employed as plasticizers for PVC. Whilst phthalate esters comprise the largest family, esters of aliphatic acids and organic phosphates are also widely employed. The choice of plasticizer is generally dictated by end product requirements. These may include not only mechanical properties at ambient temperatures, but high-temperature or low-temperature performance, permanence, electrical properties, etc.

In section 1.7.3 the mechanism of polymer/plasticizer interaction was briefly described.

1.7.4.3. STABILIZERS.

Stabilizers are added to PVC compositions to protect against degradation, to which PVC is susceptible, under the influence of heat and mechanical shear in processing, and also to afford long-term protection in service, mainly against the effects of heat, light and oxidation. They were described in section 1.6.

1.7.4.4. FILLERS.

Mineral fillers are commonly employed in plasticized PVC formulations and range in type from fine precipitated calcium carbonate to ground chalk and limestone, clays and talc. As a general rule, this incorporation leads to a deterioration in most mechanical properties, and the main rule is to cheapen the composition; there are, however, important exceptions to this generalization.

1.7.4.5. LUBRICANTS.

The addition of internal lubricants is, of course, inapplicable since the plasticizer provides the desired decrease in bulk viscosity of the melt to a very marked degree. On the other hand, external lubricants to reduce and control adhesion at the metal/polymer interface, are commonly required in the processing of plasticized PVC.

1.7.5. THE INFLUENCE OF PROCESSING ON PROPERTIES.

The effect of increasing the process temperature is to increase fusion level, hence the tensile properties of plasticized PVC. Summer[84] carried out measurements of mechanical properties on the extrudates obtained at different extrudate temperature. Maximum tensile strength and tear strength were found to increase with increasing melt extrusion temperature especially for the more highly plasticized compound. Patel and Gilbert[85,86] also have found that the tensile strength and elongation at break of plasticized PVC increased with the degree of fusion up to a maximum, which is reached asymptotically.

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Ghersey[87] investigated the effect of concentration of dioctyl phthalate (DOP) in suspension type PVC. There is some critical concentration at which the tensile strength reaches a maximum, the elongation at break reaches a minimum, and the material becomes quite brittle. At slightly higher concentration, the plasticization threshold, the tensile strength and elongation reach the original values. Beyond this the material becomes softer and tougher with lower tensile strength and higher elongation, as expected.

1.8 CROSSLINKING OF PVC.

Poly(vinyl chloride) constitutes one quarter of the world production of plastics. The extensive use of PVC is partly due to the large possibilities of modifying its properties by the addition of plasticizer. Although plasticized PVC is used at temperatures well above Tg, the properties are favorable and the material has a rubberlike behaviour. This is generally considered to be due to the presence of a physical network consisting of small crystallites[88]. However, its service range is limited by its thermoplastic nature. At temperatures above 100°C it has a tendency to flow and to have a reduced mechanical strength.

One way to increase the maximum application temperature of plasticized PVC is to introduce a permanent chemical network. There are two ways to introduce such network: by radiation or by chemical methods.

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1.8.1. RADIATION CROSSLINKING.

For practical industrial purposes, PVC materials are irradiated with a view to crosslinking as this upgrades properties important in certain applications.

The degree of crosslinking achieved in a suitable polymer or polymer-based composition depends on the radiation dose. At relatively low doses, the crosslinks formed increase the average size of the polymer chains; this is reflected in improvements in some bulk properties, as well as in an increase in the viscosity (melt and solution) of the polymer. With increasing dose levels, crosslinks are formed between the enlarged but initially still separated molecules, resulting in the formation of closed "meshes" of a three-dimensional network. The portion of the polymer involved in such networks becomes insoluble in solvents which dissolve the polymer in normal circumstances. This portion is usually referred to as the "gel fraction".

The radiation treatment is applied to otherwise finished PVC products for direct upgrading of their properties. Ordinary PVC compositions suffer unacceptable degradation on exposure to high-energy radiation; to achieve satisfactory crosslinking it is necessary to incorporate in the formulation special additives which participate in the crosslinking process. These additives are unsaturated compounds capable of polymerizing under irradiation, and believed to knit simultaneously into a three-dimensional network with the PVC polymer[89-91]. The presence of such additives reduces the radiation dose

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necessary for the desired level of crosslinking. A crosslinking additive often used in PVC compositions is trimethylolpropane trimethacrylate(TMPTMA). These special additives also have some plasticizing action during the production and processing of the composition, and in the product before irradiation. For this reason they are sometimes referred to as crosslinkable plasticizers.

The main effects of irradiation treatment of plasticized PVC products are: increased resistance to heat distortion and abrasion; increased tensile strength and modulus; reduced elongation at break; increased hardness; reduced creep; increased resistance to solvents; reduced tear propagation. Salomon and Loan[92] have shown, in irradiation using a high energy electron beam on PVC with crosslinkable monomers, an increase in tensile strength and decrease in elongation.

1.8.2. CHEMICAL MODIFICATION.

Poly(vinyl chloride) could be considered as an ideal base for chemical modifications, due to its chemical structure. Presumably, the chlorine may react as in other chlorine-containing aliphatic compounds, but secondary degradation reactions will occur at the same time, due to irregularities in the polymer structure, and this will reduce the number of reactive sites. Nevertheless, various functional modification reactions (grafting and crosslinking), have been carried out in solution and in the condensed state. Some of these reactions, mainly concerning grafting and crosslinking, will be discussed next.

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1.8.2.1. GRAFTING.

Grafting by radical synthesis.

The grafting reactions of unsaturated monomer radicals onto a preformed backbone are relatively easy to carry out and generally result from the transfer of a growing polymer or a free radical onto the labile site of a preformed chain. The reactions may take place on particles in emulsion or in suspension by adding a further amount of grafting monomer; or, after previous dissolving of the preformed polymer in the monomer to be polymerized.

In the case of PVC, a large number of grafting reactions are possible. Prabhakara[93] pointed out that PVC with the side chains of poly(methylmethacrylate) or poly(ethyl methacrylate) was synthesized by solution polymerization of methyl or ethyl methacrylate with PVC. The same reactions have been studied by Kawai et al[94] when initiation took place under irradiation. (The main advantage of the radiation methods is that it is possible to graft directly onto films or fibres). Shapiro et al[95] studied the graft polymerization of methacrylic acid onto PVC film by gamma irradiation.

Methods of activating polymers.

Radical or cation formation in PVC molecules by gamma-ray irradiation, redox reaction of PVC with metal ions, mechanochemical bond scission, and the use of PVC as co-catalyst in a cationic polymerization catalyst system have been studied. Minoura et al[96] studied the radical graft polymerization of styrene onto PVC using

chromium ions (Cr^{2+}) as the initiator. These can polymerize styrene with alkylhalide as the co-catalyst[96]. The grafting efficiency is more than 0.88 and crosslinking also occurs through the recombination of polystyrene radicals on increasing the conversion. It has also been established with model compounds that the graft polymerization chiefly initiates from carbon atoms with the labile chlorines in PVC.

Guyot et al[97] pointed out that the mechanochemical graft polymerization of methacrylate ester onto PVC in a Brabender plastograph results in the considerable improvement of dynamic thermal stability.

Gaylord et al synthesized cis-1,4-polybutadiene grafted PVC with diethyl aluminium chloride[98], which can be used to polymerize cationically styrene and isobutene using organic halides as co-catalyst[99]. In this case, the graft polymerization seems to be cationically initiated from the PVC carbon atom which carry the labile chlorine atoms. Actually, the graft PVC produced by this method exhibits extremely good thermal stability.

Polycondensation.

It is possible to initiate the graft polymerization by polycondensation from certain chemically active group previously introduced into PVC. Mori and Nakamura found that the treatment of PVC with thiol compounds and ethylenediamine (EDA) produces PVC with sulphide structures[100].

$$(-CH_2-CH-)_n + C_6H_5CH_2SH \xrightarrow[20-70\ C^o]{EDA} -(CH_2-CH)_n \quad (1.7)$$

with the Cl below the left structure, and on the right the S and CH_2-C_6H_5 branch.

$(-CH_2-CH-)_n + C_6H_5CH_2SH$ where Cl is the substituent, reacting via EDA at $20-70\ C^o$ to give $-(CH_2-CH)_n$ with an S substituent bearing $CH_2-C_6H_5$.   (1.7)
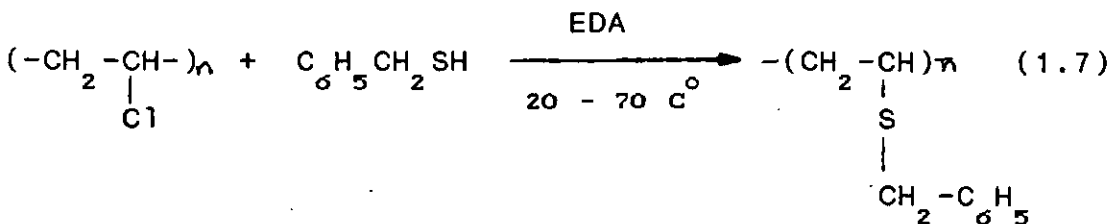
The reaction of PVC with p-(2-dichloroethyl) thiophenol[101] in EDA gives PVC with side chains of polythioether in the same way as the above reaction.

$$-(CH_2-CH-) + HSC_6H_5C_2H_4Cl \longrightarrow -CH_2-CH- \quad (1.8)$$

with Cl below the left structure and $(S-C_6H_5C_2H_4)_nCl$ below the right.

Jump reaction.

This covers the methods of combining PVC with anionic living polymer. Gallot et al indicated that polystyrene grafted PVC can be produced by reacting PVC, as deactivator, with polystyrene anion-polymerized by phenylisopropyl potassium as the initiator in tetrahydrofuran[102].

Furthermore, Leichermeier et al studied the graft polymerization with the living polymer initiated by n-butyl lithium[103]. Also, the graft co-polymerization of styrene and butadiene onto PVC was studied[104]. On the other hand, a typical jump reaction can be seen in the reaction of polymeric carbonium ion of PVC with cis-1,4-poly-butadiene[98]. Namely, the reaction of PVC with diethyl-aluminium chloride, and cis-1,4-polybutadiene generates the following crosslinking.

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$$
\begin{array}{c}
|\\
CH_2\\
|\\
\sim\!\!C+\\
|\\
CH_2\\
|\\
CHCl\\
|
\end{array}
\quad + \quad
\begin{array}{c}
|\\
CH_2\\
|\\
CH\\
\|\\
CH\\
|\\
CH_2\\
|
\end{array}
\quad \longrightarrow \quad
\begin{array}{cc}
| & |\\
CH_2 & CH_2\\
| & |\\
\sim\!\!C\!\!-\!\!-\!\!-\!\!-\!\!CH\\
| & |\\
CH_2 & HC+\\
| & |\\
CHCl & CH_2\\
| & |
\end{array}
\qquad (1.9)
$$
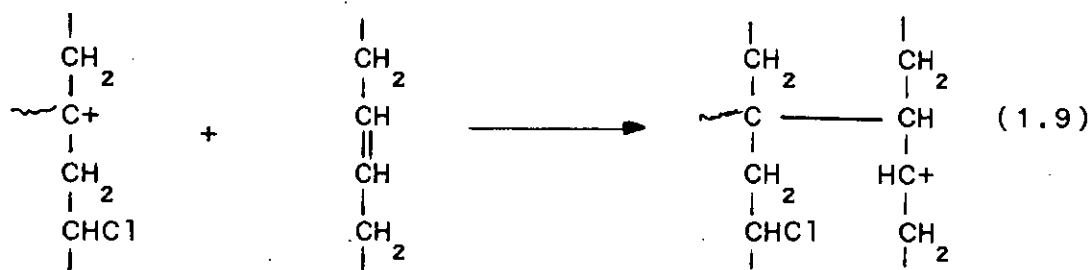
Diethyl aluminium chloride reacts with labile chloride such as tertiary or allylic chlorines in PVC to produce the carbonium ion, and then the crosslinking occurs between PVC and polybutadiene.

Nucleophilic substitution.

Nucleophilic displacement of chlorine from poly(vinyl chloride) either in suspension, solution or in condensed state using different nucleophiles have been carried out. Marian and Levin[105] studied the reaction of PVC with sodium thiolate ($R\text{-}S^- Na^+$), They found that the nucleophilicity of the salt increases if an ether linkage exists in a β position to the thiol group [$R\text{-}O\text{-}(CH_2)\text{-}S^- Na^+$]. Addition of a solvent such as cyclohexanone to the slurry increased substantially the degree of substitution. They also studied the reaction of PVC suspended in water with diethyldithiocarbamate It was found that after 24 hours at $100^{\circ}C$, 33% of the chlorine was replaced by a dithiocarbamate group. The degree of substitution is increased with the reaction time and with the temperature. Elemental analysis showed that one dithiocarbamate replaces a chlorine. However, whenever the percent of sulphur on the polymer was higher than 2%, the polymer obtained was insoluble in common solvents. They suspected that the following reaction took place:

$$\text{(structure 1)} \quad C = S \; + \; \text{(structure 2)} \; C = S \longrightarrow \cdot C - S - S - C \cdot \quad (1.10)$$
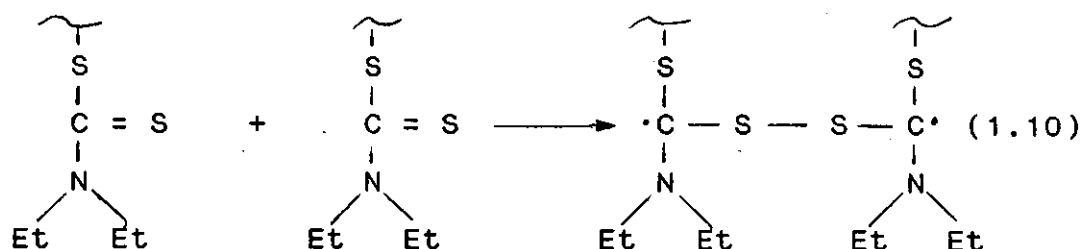
The same effect also was found when lauryl thiolate was used. On the other hand when they used a bifunctional thiolate such as bis-(2-mercapthoethyl) ether not only an increase of substitution was obtained, but also an insoluble material. Martinez and co-workers have studied extensively the reaction of PVC with sodium benzenthiolate. They found that the nucleophilic substitution in solution proceeds by a stereoselective mechanism in that a fraction of isotactic triads react very quickly and both the remaining isotactic triads and all the heterotactic react more slowly. Syndiotactic triads were quite unreactive[106,107]. They also studied the same reaction in aqueous suspension in the presence of a phase transfer catalyst, using two samples of PVC of different tacticities. The kinetics showed two well defined periods: in one period reaction is very fast and involves low conversion, the conversion at the end of this period being higher as the isotactic content of PVC increases, while in the second period reaction is slow and its rate seems to depend on physical features, e.g. molecular weight and crystallinity.

Mijangos et al[108] studied the nucleophilic substitution on a commercial sample of PVC with sodium

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benzenthiolate in the melt state using a Plasticorder. They found that mixing conditions affect both the kinetics and the shape of the rheogram but they scarcely influence the final conversion. The reaction efficiency has been proved to depend linearly on the total amount of nucleophile. They also studied the substitution of PVC in the melt using a twin screw extruder[108,110] and similar conclusions can be drawn from this study.

1.8.2.2. CHEMICAL CROSSLINKING.

Modification of Poly(vinyl chloride) by crosslinking has aroused wide interest due to the improvements of the thermal properties of PVC. Although a number of thermal crosslinking methods for PVC have been presented in the literature, and through patents, the crosslinking products are rarely used practically and commercially. This is most probably due to practical problems during the processing (rheology/premature crosslinking) and product quality (thermal stability). Several attempts using different reactive chemicals have been reported either in solution, suspension or in the molten state.

During the 60's several Japanese workers reported different techniques. Okawara et al[136] for instance, found that the reaction of PVC with sodium dialkyl - dithiocarbamate in dimethyl formamide at $50 - 60^{\circ}C$ results in the introduction of alkylthiocarbamate of about 35 mole % into PVC without dehydrochlorination[111].

$$\text{PVC} \xrightarrow{\text{NaSCSNRH}} \text{PVC} - \text{SCSNRH} \quad \text{(A)} \quad \text{(R = H or alkyl)}$$

$$\text{(A)} \xrightarrow{\text{NHR}_2} \text{PVC} - \text{SH} \xrightarrow{\text{O}_2} \begin{array}{c} \text{PVC} \\ | \\ \text{S} \\ | \\ \text{PVC} \end{array} \qquad (1.11)$$
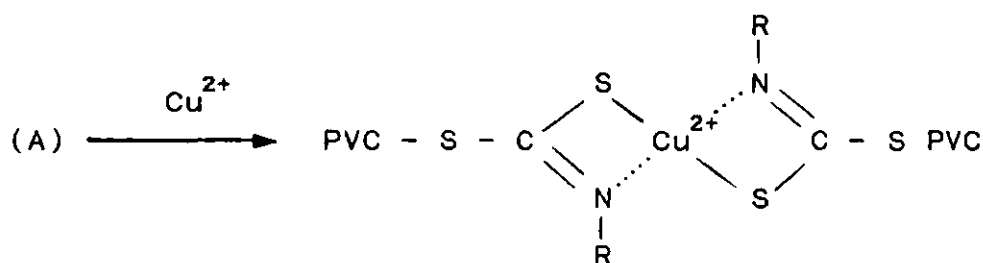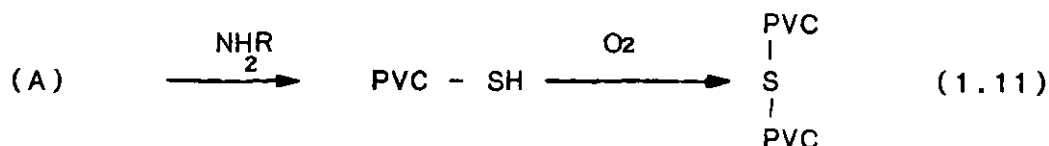
The amine treatment of (A) easily gives PVC with thiol structures, which then cause crosslinking by air oxidation. Immersing the film of (A) into aqueous metal solution causes crosslinking through the chelate structure[112,113].

Furthermore, the reaction of PVC with sodium azide even introduces about 80 mol % of an azide group into PVC, though the azide anion has extremely weak nucleophilicity. The introduction of chemically active groups such as azide groups into PVC facilitates the secondary chemical modifications[114,115]. Namely, azide – PVC (B) gives phosphoimine polymer (C) by reacting with triphenylphosphine. The treatment of (C) with salicylaldheyde produce polyimine (D). The gel (E) is formed by mixing tetrahydrofuran solution of (D) with a dimethylformamide solution of copper acetate at room temperature.

$$PVC - N_3 + P(C_6H_5)_3 \longrightarrow PVC - N = P(C_6H_5)_3 \quad (1.12)$$

(B)   (C)

(C) + [benzaldehyde with CHO and OH groups] $\longrightarrow$ PVC $- N = CH -$ [phenol ring with OH]

(D)

$$(1.13)$$

(D) $\xrightarrow{Cu^{2+}}$ [copper complex structure]

(E)

$$(1.14)$$
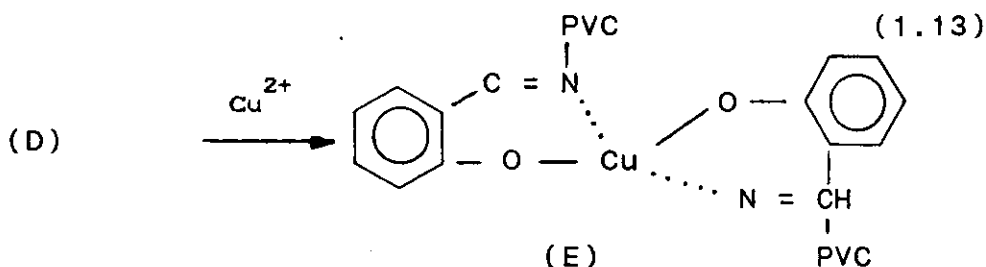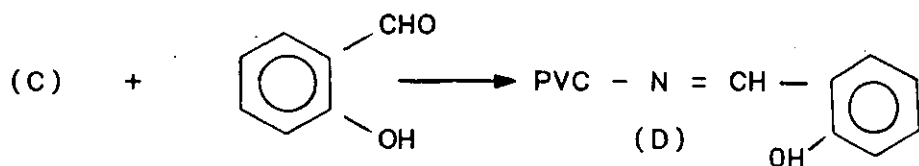
The rapid gel (F) formation can be also observed upon introducing carbon dioxide into the tetrahydrofuran solution of (C)

$$(C) + CO_2 \longrightarrow \underset{O=C-O}{N-P}(C_6H_5)_3 \xrightarrow[-(C_6H_5)_3 PO]{} \underset{O}{\overset{N}{\underset{\|}{C}}} \quad (1.15)$$

$$\longrightarrow \quad PVC - N = N - PVC$$

(F)
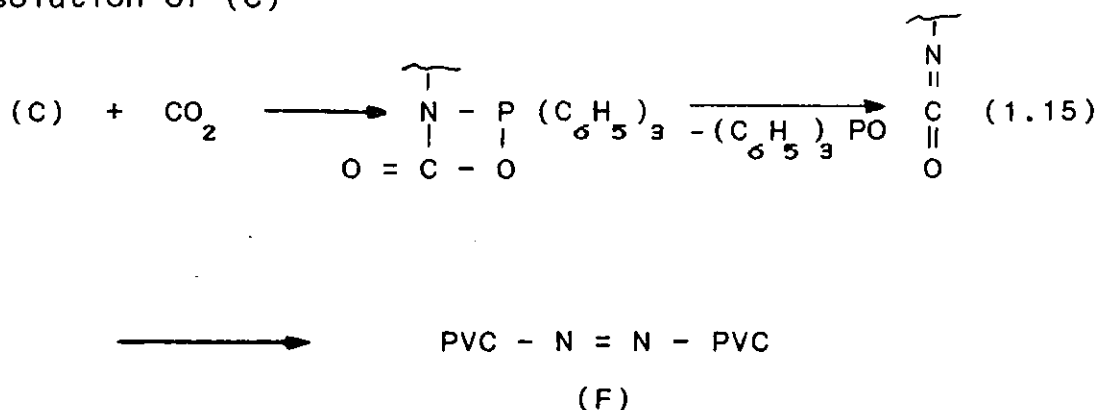
The thermal treatment of (B) and thiokol on a mixing mill at 120 – 140°C gives the gel (G), which is almost insoluble in tetrahydrofuran[115]

(B) + HSRSH $\longrightarrow$ CH$_2$—CH—NH—S—R—S—NH—CH—CH$_2$ (1.16)

with CHCl and CH$_2$ groups

(G)

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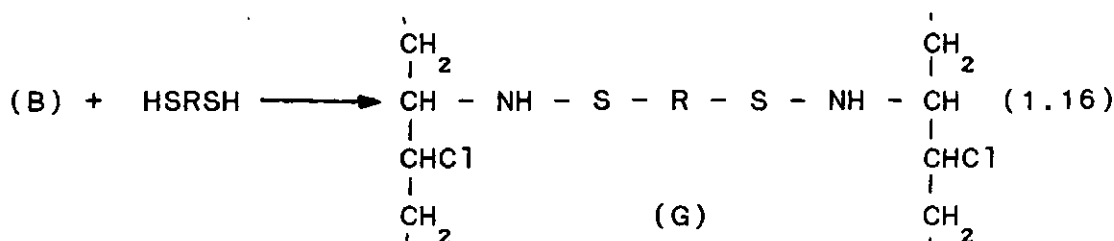
On the other hand, starting from the studies of the reaction of PVC with morpholine[116] Nakamura et al have found a lot of new crosslinking reactions of PVC with sulphur compounds. Morpholine is introduced into PVC by being heated with PVC at more than 100°C. The products are easily crosslinked upon hot mixing with di- or tri-thiol compounds such as thiokol and tricyanuric acid on a mixing mill. The same reaction products seem to be produced when PVC is mixed in a roll mill with morpholine and the thio compounds at the same time[117].

Subsequently, the crosslinking method was further improved to immersing the film of PVC and thiol compounds in liquid ammonia at room temperature[118]. A similar reaction occurs in aqueous ammonia when hexamethylphosamide is used as an activator. In the old methods, the amount of morpholine is the same as that of PVC during the thermal treatment on a mixing mill, whereas the improved method is more practical because of just immersing the film in liquid ammonia.

Furthermore, it was found that primary and secondary diamines are also useful as crosslinking accelerators. Mori and Nakamura[135] have also reported the crosslinking of PVC with dithiols of different chain length. The blends were processed in a two - roll mill and then immersed in ethylene diamine (EDA) at different temperatures for 90 - 120 min. The immersion temperature of up to 30°C of PVC film in EDA seems efficient for the crosslinking judging from its THF insoluble fraction and swelling ratio. At immersion temperatures higher than 50°C, the products were coloured, and a small amount of

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nitrogen was detected; these results suggested the presence of a conjugated double bond and EDA – type crosslink in the products.

The reaction mechanism that they proposed is a condensation reaction between PVC and thiol compound, which is accelerated by the formation of a complex of EDA with thiol compounds:

$$2 -[-CH_2 - \overset{\displaystyle |}{\underset{\displaystyle Cl}{CH}}] + HSRSHn \cdot EDA \longrightarrow \begin{array}{c} [CH_2 - CH] \\ | \\ S \\ | \\ R \\ | \\ S \\ | \\ [CH_2 - CH] \end{array} \quad (1.17)$$
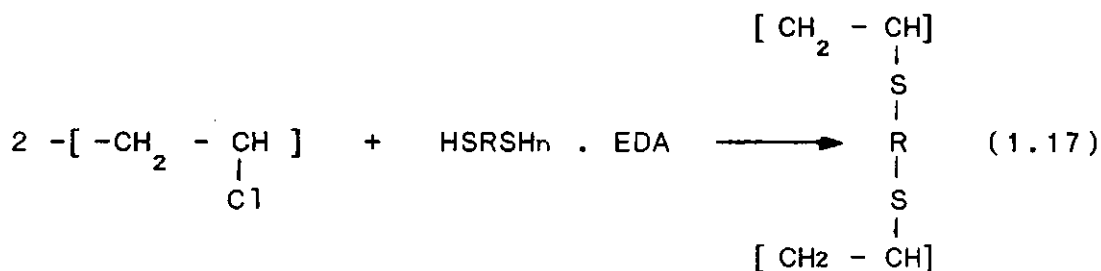
These methods can be applied for crosslinking of PVC with other kinds of thiol compounds. For example, the reaction product (H) of potassium alkyl-o-xantate changes into PVC with the sulfide crosslinking structure (I) via the formation of the thiol structure by the EDA treatment[119].

$$-(CH_2 - \overset{\displaystyle |}{\underset{\displaystyle SCSOR}{CH}})- + NH_2-R-NH_2 \longrightarrow -(CH_2 - \overset{\displaystyle |}{\underset{\displaystyle SH}{CH}})- \quad (1.18)$$

(H)

$$-(CH_2 - \overset{\displaystyle |}{\underset{\displaystyle SH}{CH}})- + -(CH_2 - \overset{\displaystyle |}{\underset{\displaystyle Cl}{CH}})- \longrightarrow \begin{array}{c} -(CH_2 - \overset{\displaystyle |}{CH})- \\ | \\ S \\ | \\ -(CH_2 - CH)- \end{array} \quad (1.19)$$

(I)

44
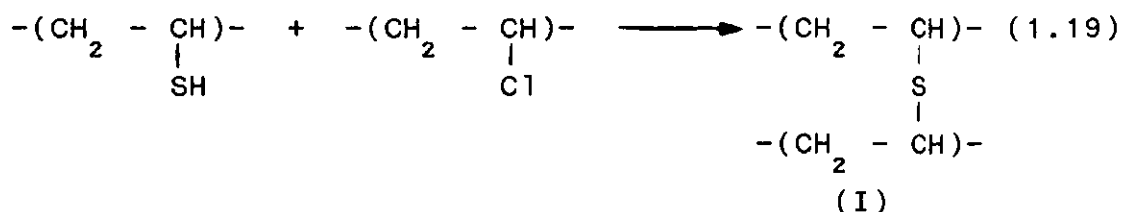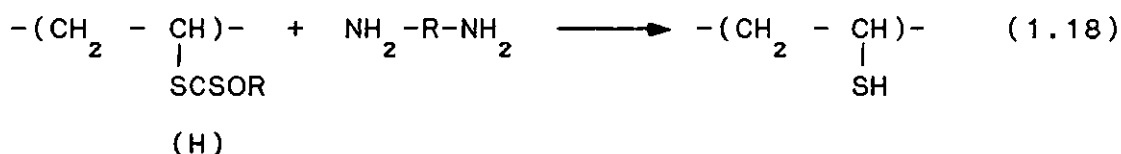
However the mechanical properties of the produced PVC are hardly improved, though there is considerable crosslinking. This lack of improvement in the mechanical properties seems to be due to the formation of the short crosslinking chains.

Since then, a series of studies has been developed in in the direction of forming PVC crosslinking with polysulphide chains[120-122]. The reaction of sulphur with dimethylamine forms the following complex molecule[120]:

$$2 (C_2H_5)_2NH + S_8 \longrightarrow (C_2H_5)NS_8H_2N(C_2H_5)_2 \quad (1.20)$$

The similar reaction between sulphur and ethylendiamine gives the complex molecule ($EDA.H_2S_{2-3}$). Adding PVC powder to $EDA.H_2S_3$ solution of ethylendiamine results in forming the crosslinked structure (J), which is almost insoluble in tetrahydrofuran. The same reaction can be observed upon immersing PVC film made by hot mixing of PVC and sulphur into ethylendiamine.

$$-(CH_2 - CH)- + EDA.H_2S_{2-3} \longrightarrow \begin{matrix} -(CH_2 - CH)- \\ | \\ S_{2-3} \\ | \\ -(CH_2 - CH)- \end{matrix} + \begin{matrix} -(CH_2-CH)- \\ | \\ S_{2-3} \\ | \\ H \end{matrix} \quad (1.21)$$
$$\quad\quad\quad | \\ \quad\quad Cl$$

(J)
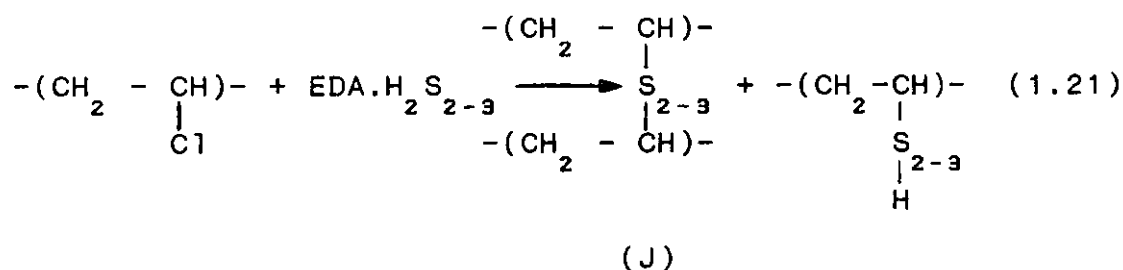
On the other hand, the reaction between PVC and alkylhydropolysulphide gives PVC with side chains of alkylpolysulphide (π)[123]. Alkylhydrosulphide is

synthesized in dimethylformamide (DMF) solution through the reaction between thiol and amine - activated sulphur. Alkylpolysulphide(π) easily crosslinks by U.V. or gamma - ray[123-124] irradiation.

$$C_6H_5CH_2SH \xrightarrow[S_8/N(C_2H_5)_3]{In\ DMF} C_6H_5CH_2S_9H \quad (1.22)$$

$$\xrightarrow[N(C_2H_5)_3]{C_6H_5CH_2SH} C_6H_5CH_2S_xH \quad (1.23)$$
$$x = 2-3$$

$$C_6H_5CH_2S_xH + PVC \longrightarrow -(CH_2-\underset{|}{C}H)- \quad -(CH_2-\underset{|}{C}H)- \quad (1.24)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad Cl \qquad\quad \underset{|x}{S}$$
$$\qquad\qquad\qquad\qquad\qquad (\pi) \qquad\quad CH_2C_6H_5$$
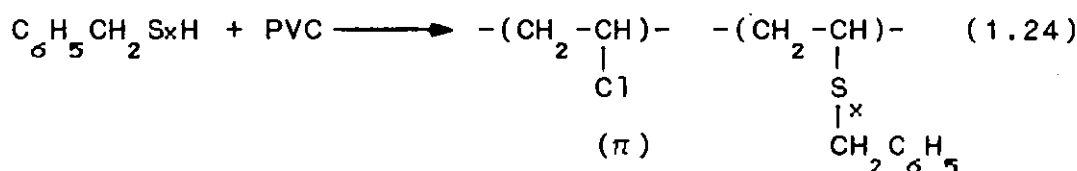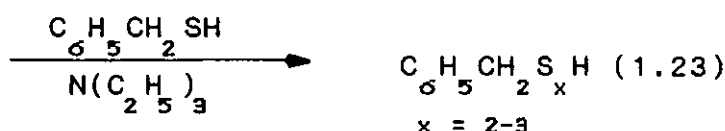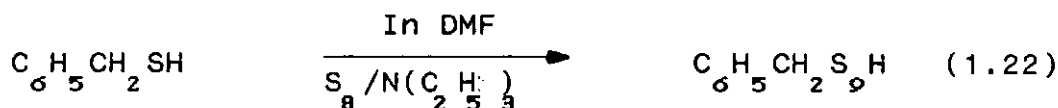
In the late 70's in a series of papers Mori and Nakamura have discussed the use of dithioltriazines for the crosslinking of PVC[125-129]. By converting, e.g. 2-dibutylamino-4,6-dithiol-s-triazine (DB) to a metal salt, they have been able to obtain complete crosslinking in reasonable times without simultaneous dehydrochlorination. If DB is used as such, crosslinked PVC is obtained but with simultaneous dehydrochlorination[126]. There is evidence that crosslinking at least partly occurs via the nitrogen atom in the isocyanuric ring. If an acid acceptor such as MgO is added the crosslinking rate increases and virtually no dehydrochlorination occurs[126]. Mori and Nakamura have given the following reaction scheme for the reaction of PVC and DB in the presence of MgO.

(1) Formation of DB-Mg from DB and MgO.

+ MgO ⟶
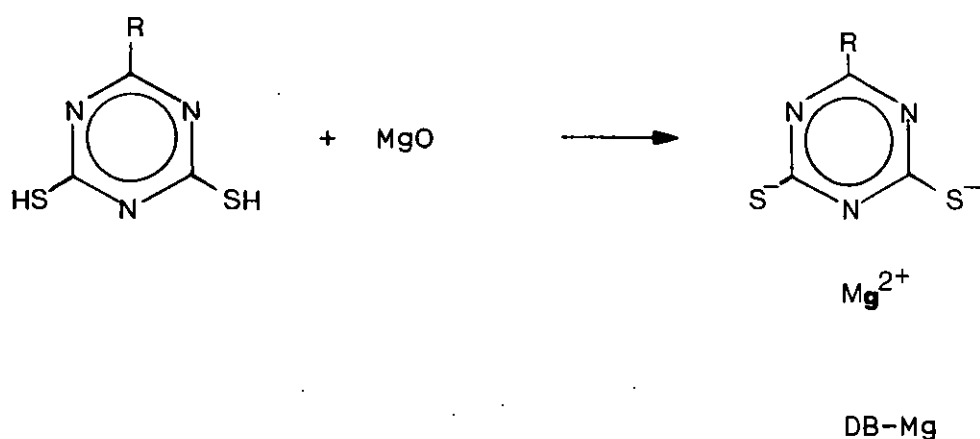
DB-Mg

(1.25)

(2) Formation of DB-Mg pendant PVC - DB by the reaction of PVC with DB-Mg.

+ DBMg $\xrightarrow{k_1}$

PVC-DB

(1.26)

47
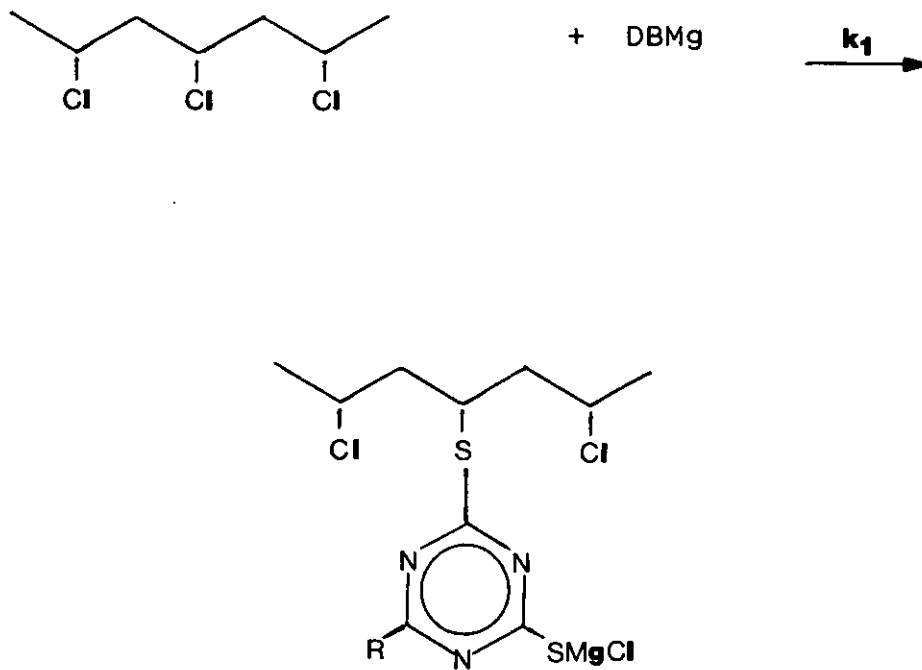
(3) Formation of crosslinking by the reaction of PVC with pendant DB-Mg.

PVC-DB   +

(1.27)

DB-PVC-DB
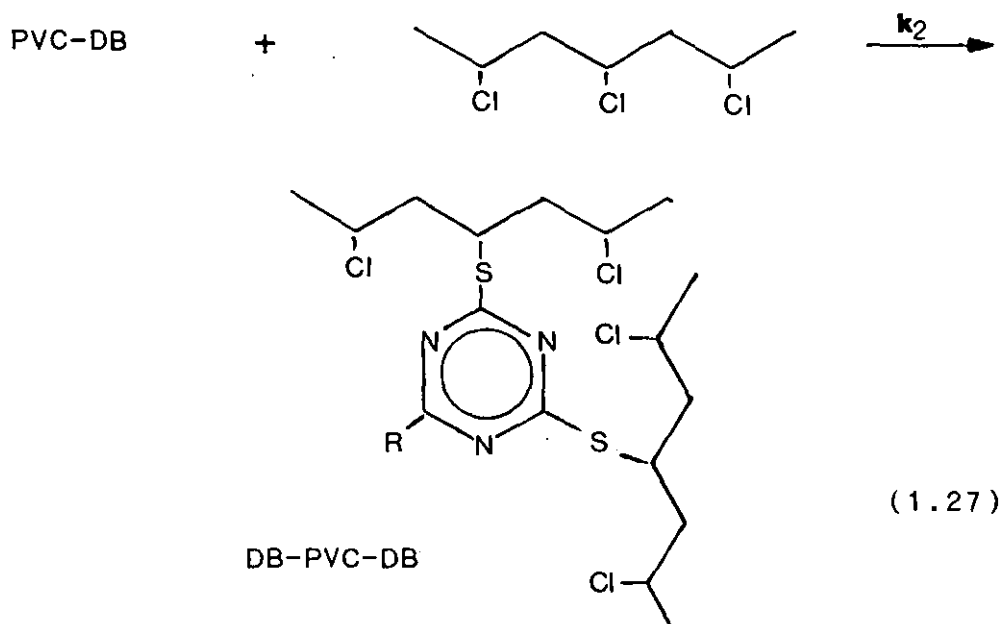
It may be pointed out that the structure of the magnesium dithioltriazine salt (DB-Mg) is only represented schematically. The magnesium ion cannot bind to both thiolate ions in one molecule as its radius is not large enough. A structure including the dimer or oligomer is much more plausible.

The increased rate in the presence of MgO is an effect of converting the thiol group to a thiolate anion, which is a stronger nucleophile. The reaction rate should increase with increased polarization of the thiolate - metal bond, i.e., with decreased electronegativity of the metal. This was indeed found by Mori and Nakamura[127], who reported increased crosslinking rate in the series Sn <Pb <Mg <Ca <Ba <Na. Also they found that the R substituted group strongly influenced the crosslinking rate and the increase is as follows R'O << R'NH < $(R')_2N$, where R' is an alkyl or aryl group.

It should be noted that reaction (1.26) is considerably faster than (1.27)[126]. This is a consequence of the fact that the first thiol group is much more easily dissociated than the second one. The pKa values vary between 4-6 and 11-14, respectively, depending on the third substituent on the triazine ring[127].

Although conversion to a thiolate salt increases the crosslinking rate, the time to reach complete crosslinking may still be too long. Mori and Nakamura[126] have pointed out the necessity of adding certain accelerating compounds, such as diphenylguanidine, tetraalkylammonium chloride, hexamethylphosphoamide and polyethers. Except for polyethers the accelerating agents are very impractical, since the decomposition is vigorously accelerated; polyethers, such as polyethylenglycol do not accelerate the decomposition of PVC.

The formation of longer polymer chains has been found to be possible by using thiol - s - triazines. Nakamura[130] mentioned that (2 - aniline - 4,6 - dithiol - s - triazine), which hardly reacts as a crosslinking agent for PVC, has been shown to bond chemically with PVC and that the reaction takes place with allylic chlorines.

Mori et al[131] also have pointed out the effect of this triazine, as a thermal stabilizer in a synergistic

mixture with zinc and barium stearate; they mentioned
that the zip dehydrochlorination initiated at allylic
chlorines units is, therefore, retarded by the stable
PVC-triazine crosslinked structure (DB-PVC-DB).

In a more recent paper Hjertberg et al[132] discuss
the effect of certain catalysts on the rate of
crosslinking of PVC with dithioltriazines and also the
changes in molecular weight distribution before
crosslinking. With respect to catalyst they found that
the dimer trimethylolpropane (DITMP) gave the best
results, with much faster crosslinking. The catalytic
effect is explained by the possibility of the four
hydroxyl groups coordinating with metal ions, e.g., Mg^{2+}.
The coordination between DITMP and Mg - DB is explained
in two ways. First, the shielding of the polar part of Mg
- DB by DITMP should lead to increased solubility and
mobility. Second, the coordination should increase the
polarization between Mg^{2+} and the thiolate ions. This
should increase the nucleophilic strength and thus the
reacting rate. On the other hand, the GPC analysis showed
an extensive molecular enlargement before crosslinking.
Large changes in molecular weight distribution for a
sample crosslinked with catalyst were observed; Mw
increased from 1.2×10^5 in the virgin polymer to $5.3 \times$
10^5 after 15 minutes in a roll mill at 145^oC. The sample
without catalyst also showed an increase in Mw up to
1.9×10^5.

The increase in Mw was relatively more than Mn. Mn increased as much as 100% without gel formation; this lead to the conclusion that a selective reaction favouring low molecular weight material should be operative.^{1}H NMR measurements on low molecular weight extracts showed that DB effectively reacts with allylic chlorines in the 1 - chloro -2.alkene end groups.

Recently Jando and Mori[133,134] studied the crosslinking of PVC fibre by nucleophilic substitution with 2-dibutyl-amino-4,6-dimercapto-1,3,5-triazine (DB), in the presence of sodium hydroxide and tetra-n-butylammonium bromide (TBAB) in water. They prepared an alkaline aqueous solution of DB; in a second step tetra-n-alkylammonium (TAA) salts were added. PVC fibers were immersed in this solution. The effect of reaction time and temperature on both the gel content and crosslink density is reported. As regards temperature of the solution, the found that if the temperature of the solution is under the Tg of PVC, the reaction hardly occurs. In these conditions the gel content is always under 5%, on the other hand if the temperature of the solution is higher than the Tg of the fibers, the gel content increases sharply and reaches its maximum value at 86°C for 60 minutes. This shows that the segment movement of the polymer chains is a necessary condition for the crosslinking reaction to take place.

With respect the reaction time, it was found that an increase in reaction time produced an increase in gel content. However, the crosslink density in the gel

decreased up to a certain reaction time and then increased. They attributed this to an incomplete polymer network formation, that is, the crosslinked polymer has been formed only on the surface of the fiber.

The effect of the concentration of the crosslinking agent, TAA salts and alkali was also studied. It was found that the gel content increased sharply up to a critical DB concentration. Without using TBAB the gel content is under 5%. The DB/TBAB ratio is an important parameter controlling the reaction rate. Using the graphs of crosslink density versus reaction time, they obtained certain kinetic parameters; the reaction order was regarded as pseudo-first-order. The activation energy was calculated to be 55.5 KJ/mol. They propose a similar mechanism to that of Mori and Nakamura[126], i.e. the reaction takes place in two main steps. In the first step, a substituted branched structure and in the second step, the crosslinked structure forms.

Conventional rubber crosslinking systems have been used to crosslink PVC. The presence of sulphur impairs the thermal stability of PVC. It has been established that sulphur atoms bonded to the polymeric chain induce activation of the adjacent chlorine atoms[127]. These labile chlorine atoms can initiate the PVC dehydrochlorination; they provide, however, reactive sites for the crosslinking reaction in the presence of suitable agents. Mori and Nakamura[135] suggest that the crosslink distribution in the crosslinked sample is

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unlikely to be a random one. Namely the formation of a crosslink containing a sulphur atom will activate the adjacent vinylic chlorine atom and further crosslinks will be grouped around the original initiation site.

Similar conclusions are reported by Okawara and Ochiai[136], who have investigated the chemical modification of PVC by alkali metal salts of the dithiocarbamic acid. They found,e.g., that the sodium salt of the N,N-dialkyldithiocarbamic acid prefers ·the nucleophilic substitution to the otherwise much easier elimination, and the sulphur atoms in the residue of the agent bonded in a PVC chain activate the adjacent vinylic chlorine atoms:

$$
-CH_2 - \underset{Cl}{CH} \underset{\delta^-}{\overset{CH_2}{\diagdown}} \underset{Cl}{\overset{\delta^+}{CH}} \quad + \quad Na^+ S - \underset{\underset{S}{\|}}{C} - N \overset{R}{\underset{R}{\diagup}} \quad \longrightarrow
$$

(1.28)

$$
\overset{-CH_2}{\diagdown} \underset{Cl}{CH} \overset{CH_2}{\diagdown} \underset{S}{\underset{\|}{CH}} \underset{S=C-N \overset{R}{\underset{R+}{\diagup}}}{} \quad + \; NaCl \longrightarrow \overset{CH_2}{\diagdown} \underset{S}{CH} \overset{CH_2}{\diagdown} \underset{\underset{C \; -NR_2}{\overset{+}{\diagup}}}{CH} \underset{Cl^-}{S}
$$
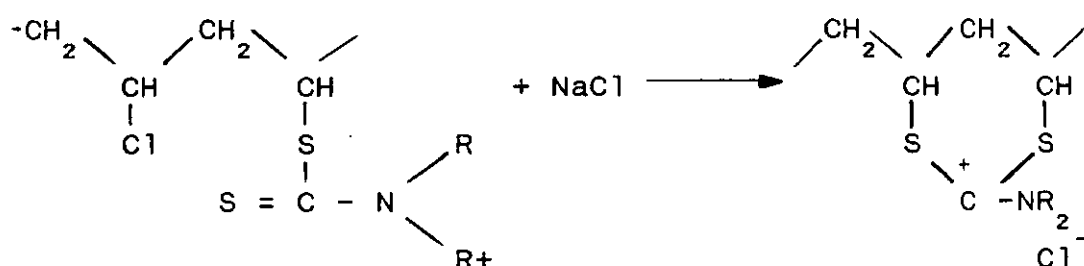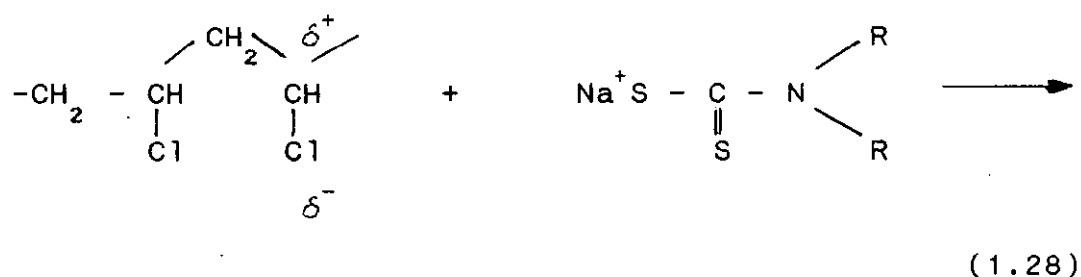
Duchacek and Kuta[137] have crosslinked PVC by tetramethylthiuramdisulphide (TMTD) in presence of zinc

oxide. They found that the activation energy of the crosslinking reaction (106 KJ/mol) is very close to the activation energy of the sulphur-free thiuram vulcanization of natural rubber and proposed a similar mechanism for this reaction. In the first step ZnO reacts with TMTD to produce a perthioanion. The sulphurating agent formed attacks the PVC chains by nucleophilic substitution, and the intermediate product formed is further decomposed, presumably by a radical mechanism, generally leading to formation of a polysulphidic crosslink.

$$
\begin{array}{c}
\text{—CH}_2\text{—CH(Cl)—CH}_2\text{—CH(Cl)—} \;+\; {}^-S-S_x-X \;\longrightarrow
\end{array}
$$

Where $X = (CH_2)_3)_2\, N - C(S)$

(1.29)

$$
\text{—CH}_2\text{—CH(Cl)—CH}_2\text{—CH(}S-S_x-X\text{)—} \;+\; Cl^- \;\longrightarrow
$$

$$
X - S_{x-z} - S^{\bullet} \;+\; \text{—CH}_2\text{—CH(Cl)—CH}_2\text{—CH(}S_z{}^{\bullet}\text{)—} \;\longrightarrow
$$

$$
\text{CH} - S_y - \text{CH}
$$
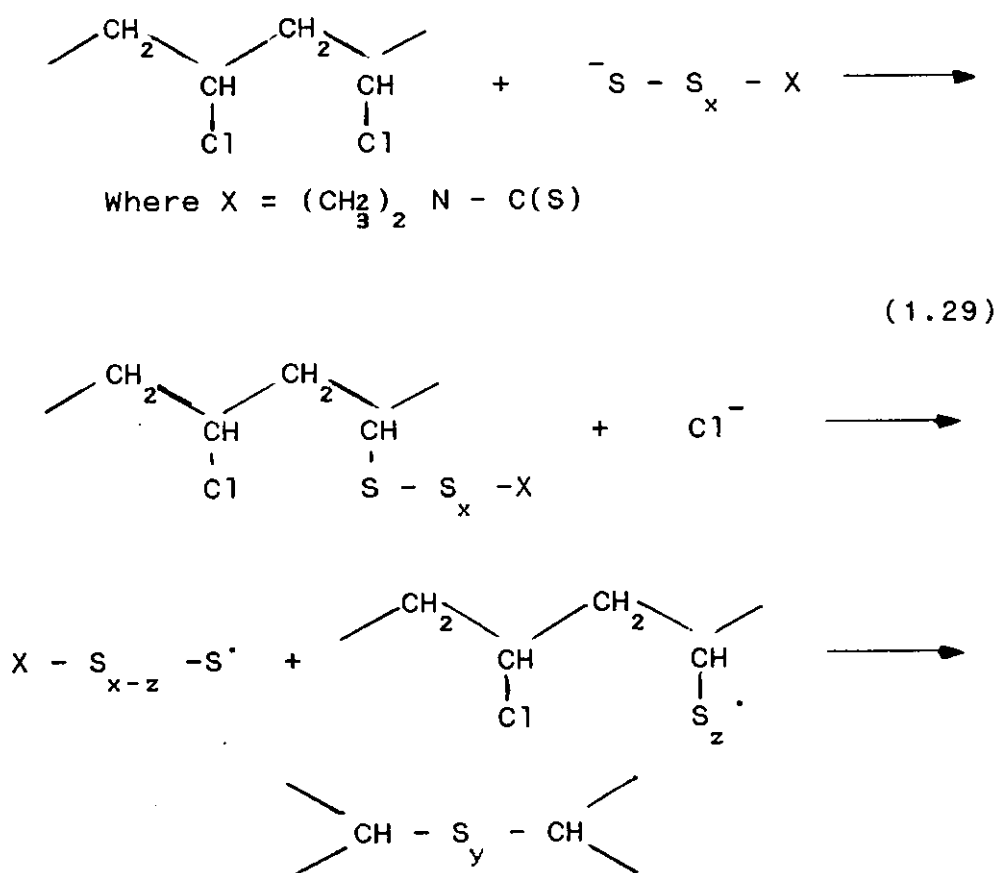
The supposed radical mechanism of this reaction is in good agreement with the high activation energy value of

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crosslinking and the observed effect of thiourea on the course of the sulphur-free thiuram vulcanization[138]. The crosslinking of PVC in the presence of zinc oxide, magnesium oxide, ethylenthiourea (ETU), TMTD and sulphur has been also studied by Behal and Duchacek[51] who found that the course of the PVC crosslinking reaction is almost independent of the concentration of the crosslinking agent (TMTD). This observation supports the assumption that in the PVC chain there is a limited number of sites in which chlorine atom bonds are more labile[126] and thus susceptible to substitution by nucleophilic agents[136].

The bonded carbonyl groups seem to promote the reactivity of adjacent chlorine atoms inducing higher polymer dehydrochlorination rates and leading finally to spontaneous degradation crosslinking. With increasing TMTD concentration this effect is suppressed and the spontaneous degradation shifted towards longer times. This effect was observed previously[137].

Unreacted TMTD or zinc dimethyldithiocarbamate (ZnDMDC) formed[137] tend to attack labile chlorine atoms and to block the zipper mechanism of PVC dehydrochlorination. Behal and Duchacek[51] pointed out that in absence of heat stabilizers TMTD or ZnDMDC act like antidegradants, which however, tend to intensify and accelerate the PVC dehydrochlorination, and thus the "chemical" PVC crosslinking is to a great extent accompanied by the degradation crosslinking. They observed that sulphur has only a negligible effect on PVC

crosslinking in the presence of TMTD, and that with increasing sulphur concentration the degradation crosslinking is significantly suppressed and the range of controlled crosslinking is prolonged. On the other hand the presence of ETU increases the rate of the PVC crosslinking reaction with TMTD and reduces the induction period.

Several attempts to crosslink PVC have been made using different chemicals. Kucera et al[139] studied the crosslinking reaction of PVC both in solution and in suspension in alkanes using carbanions. Previously Gallot et al[140] grafted PVC using anionic polystyrene with K^+ as a counter ion. Carbanions which are capable of grafting may be produced by the transformation of macrocations[141]. When macroanions are used they should undergo the grafting reaction with PVC, while the dianions should lead to the formation of crosslinkages. Kucera[139] using α-methylstyrene tetramer dianions obtained a crosslinked PVC of a slightly rosy colour. The character of this coloration is indicative of the formation of sufficiently long PVC sequences containing conjugated double bonds and is an indirect proof of dehydrochlorination. In this experiment, it was observed that an increase in the reaction temperature from -10°C to 25°C decreases the gel formation, also it was observed that the chain length of the dianion has little effect on gel formation. It is worth mentioning that the gel obtained was as low as 20% and the concentration of dianions used was as high as 20% w/w with respect to PVC.

Using dianions formed by the transformations of dications, Kucera[139] pointed out that dications such as poly(tetramethylene oxide) may be, under suitable conditions, transformed by oligomeric dianions (e.g. α-methylstyrene) tetramer dianion sodium salt) to give polymeric dianions[142]. Such dianions were used to crosslink PVC in solution. The gel formation was very low (15%), and similar results were obtained when the crosslinking process was carried out in suspension.

Ghosh et al[143] studied the crosslinking of PVC using diamines such as ethylendiamine (EDA) as the crosslinking agent. Previously Mori and Nakamura[119] had noticed that EDA forms part of the crosslinked PVC produced with dithiols and catalyzed with EDA. Chosh studied the effect of different diamines on plasticized PVC stabilized with lead compounds, and also the effect of filler. The crosslinking of a band previously prepared on an open mill at 140 – 150°C, was carried out in a heated press in the temperature range 160 – 190°C. It was found that only aliphatic diamines were effective in crosslinking PVC, and the crosslinking took place not at the stage of band formation, but during compression moulding. In a detailed study with EDA, gel content improved from 0% to 50 – 90%. However, the diamine crosslinking lowered the stability, as indicated by the congo red test, from 500 min for uncrosslinked polymers to 20 – 40 min for the crosslinked polymer. When 50 phr of calcium hydroxide were used the stability reached a value of 211 min. The following mechanism was proposed:

$$2PVC \quad + \quad H_2NR\text{-}NH_2 \quad \xrightarrow[\text{limited dehydrochlorination}]{-2HCl} \quad 2 \sim CH = CH - \underset{\underset{Cl}{|}}{CH^-} + H_2NR_1NH_2$$

$$
\begin{array}{c}
\sim CH = CH - CH \sim \\[4pt]
\underset{(-)}{Cl} \quad \underset{(+)}{\overset{|}{NH}_2} \\[4pt]
\overset{|}{R} \quad (1.30) \\[4pt]
\underset{(-)}{Cl} \quad \underset{(+)}{\overset{|}{NH}_2} \\[4pt]
\sim CH = CH - CH \sim \\[4pt]
(M)
\end{array}
$$
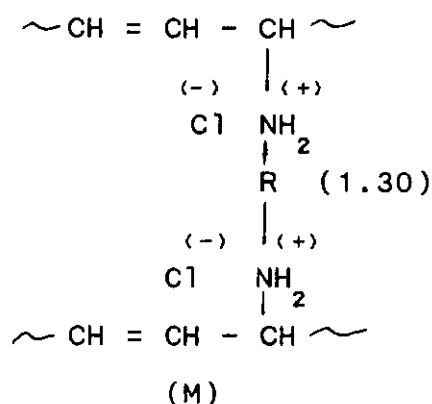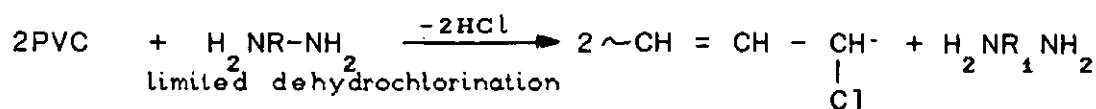
Heating the crosslinked structure (M) leads to ready elimination of HCl forming a more stable structure (N) in the crosslinked polymer.

$$
(M) \quad \xrightarrow{-HCl} \quad
\begin{array}{c}
-CH = CH - CH \sim \\[4pt]
\overset{|}{NH} \\[4pt]
\overset{|}{R} \quad (N)\ (1.31) \\[4pt]
\overset{|}{NH} \\[4pt]
-CH = CH - CH \sim
\end{array}
$$
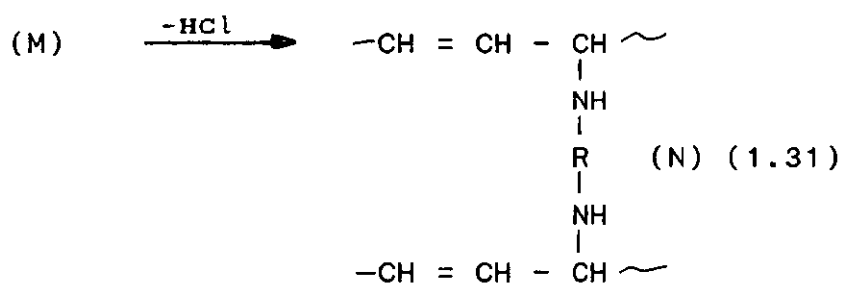
Crosslinking may also take place through amine additions at unsaturation points.

$$2 \sim CH = CH - CH = CH \sim \quad + \quad H_2NRNH_2$$

$$
\begin{array}{c}
\sim CH - CH_2 - CH = CH \sim \\[4pt]
\overset{|}{NH} \\[4pt]
\overset{|}{R} \qquad\qquad (1.32) \\[4pt]
\overset{|}{NH} \\[4pt]
\sim CH - CH_2 - CH = CH \sim
\end{array}
$$
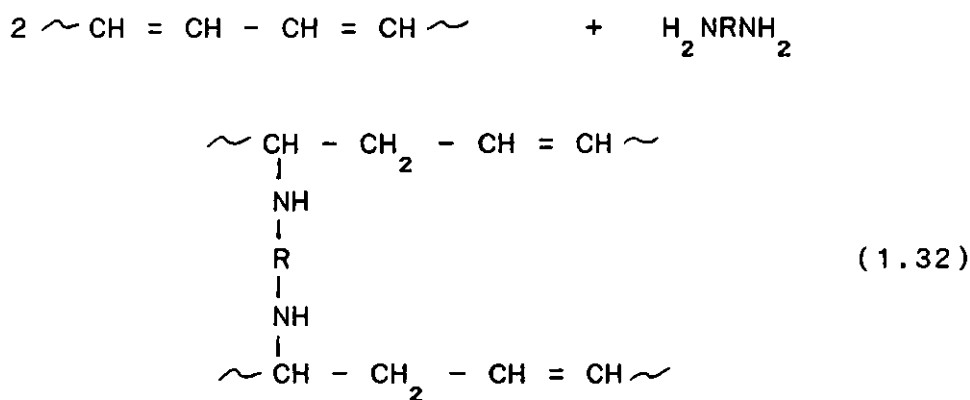
Ready elimination of HCl is viewed as the main reason for lowering of the congo red stability. From the Brabender study, Ghosh etal[143] were able to obtain some curing parameters such as scorch time, cure time, and curing speed. Using a high proportion of EDA leads to lower scorch time and an increased rate of curing. Activation energy of EDA induced crosslinking of PVC was also determined using the Brabender equipment; the calculated activation energy was 63 KJ/mol.

Wejchan[144] reported the crosslinking of PVC using dithiols such as 1,4-benzendithiol and 4',4-diphenylsulphidedithiol. He reports gel formation up to 85%. However, the solubility was determined by immersing 0.5 gr sample in 10 ml THF for 3 h. at 25°C; these conditions are not sufficient to extract the soluble fraction completely. This report does not present or suggest any reaction mechanism.

As mentioned by Nakamura et al[125-129] PVC can be crosslinked with dithiols in presence of metal compounds.

Using a similar approach Gonnu and Michel[145] studied the reactivity of alkaline and alkaline earth salts of either o-mercaptobenzoic acid or of dimercaptans synthesized by esterification of o-mercaptobenzoic acid with α,ω diols for the crosslinking of PVC. The reactivity of the thiolates was assessed with a Haake plasticorder. The efficiency of o-mercaptobenzoic acid esterified with aliphatic diols and diols with ether linkages as barium salts was tested. It was found that

an increase in the length of the alkyl chain of the aliphatic diols increases the crosslinking rate and the gel formation. On the other hand, the introduction of an ether linkage in the crosslinking reagent does not modify the reactivity (crosslinking rate). However, its efficiency is better (higher gel formation). They suppose that these improvements are probably due to better compatibility of the crosslinking agents with the polymer. Different metal salts were studied, and it was found that salts of alkaline metals have higher reactivity than salts of alkaline earth metals. Salts of transition metals such as zinc have a very low reactivity. In the same group reactivity increases with atomic weight. Salts of Na and K gave 76 and 100% of gel respectively.

It was also found that the crosslinking rate is roughly proportional to the crosslinking agent concentration from 20 and 40 mmol per kg of PVC, for the potassium salt of ethylene bis(o-mercapto-benzoate) and of o-mercaptobenzoic acid respectively. Furthermore, the concentration of reagent must be about 150 mmol per kg of PVC to reach a gel fraction of 100%.

Michel and Gondard[146] also studied the crosslinking of PVC with alkaline and alkaline earth salts of dimercaptanes and they proposed the following mechanism:

$$\sim CH_2 - \underset{\underset{Cl}{|}}{CH} - CH_2 - \underset{\underset{Cl}{|}}{CH} \sim \quad + \quad \underset{(SH)}{C_6H_4} - \underset{\underset{O}{\|}}{C} - O - R - O - \underset{\underset{O}{\|}}{C} - \underset{(SH)}{C_6H_4}$$

$$\sim CH_2 - \underset{\underset{S}{|}}{CH} - CH_2 - \underset{\underset{Cl}{|}}{CH} \sim \qquad (1.33)$$

$$C_6H_4 - \underset{\underset{O}{\|}}{C} - O - R - O - \underset{\underset{O}{\|}}{C} - C_6H_4$$

$$\underset{\underset{Cl}{|}}{-CH_2 - CH - CH_2 - CH -}$$

$$\sim CH_2 - \underset{\underset{Cl}{|}}{CH} - CH_2 - \underset{\underset{Cl}{|}}{CH} \sim \quad + \quad \underset{(SK)}{C_6H_4} - \underset{\underset{O}{\|}}{C} - OK$$

$$\sim CH_2 - \underset{\underset{S}{|}}{CH} - CH_2 - \underset{\underset{Cl}{|}}{CH} \sim \qquad (1.34)$$

$$C_6H_4 - C - \underset{\underset{\underset{CHCl}{|}}{\underset{CH_2}{|}}}{\underset{\underset{CH_2}{|}}{CH}}$$
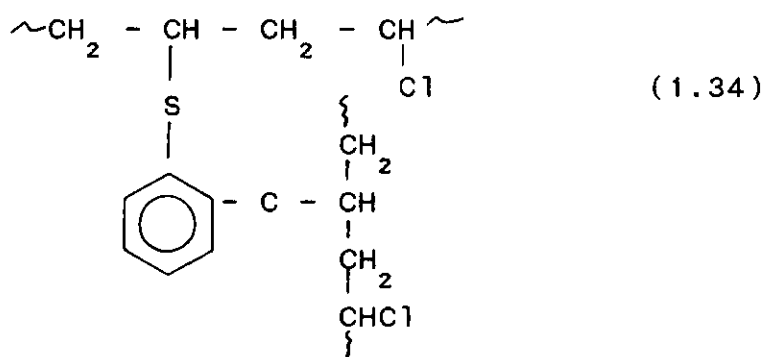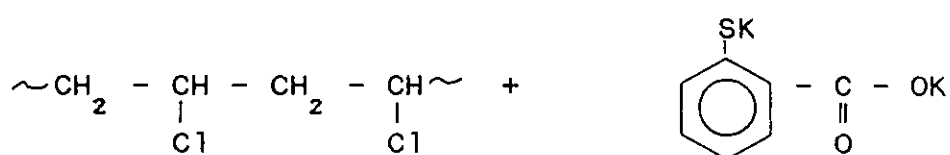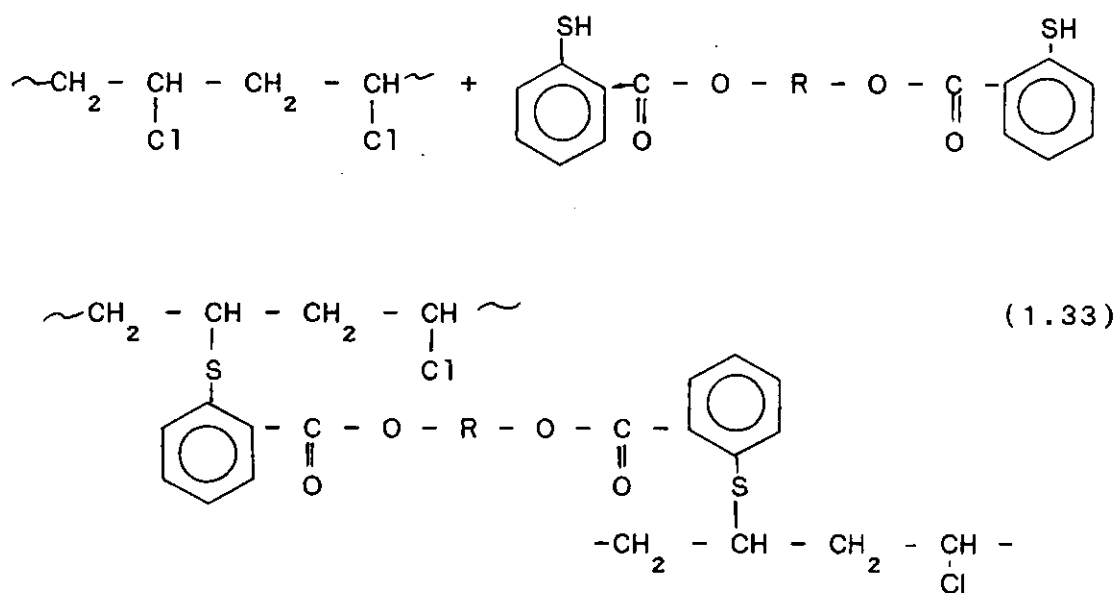
They also studied the crosslinking of PVC with alkyl tin alkoxide according to (1.35).

However in this report no technical data are presented.

$$-CH_2 - CH - CH_2 - CH- \quad + \quad R_2 - Sn \underset{O}{\overset{O}{\diamondsuit}} R$$

with Cl on the CH groups (as shown below):

Structure: $-CH_2 - \underset{|}{CH} - CH_2 - \underset{|}{CH}-$ with Cl below each CH, plus $R_2 - Sn$ with a dioxa ring to R.

$$(1.35)$$

$$-CH_2 - \underset{\underset{R}{\overset{O}{|}}}{CH} - CH_2 - \underset{Cl}{CH}$$

(structure showing)

$-CH_2 - CH - CH_2 - CH$
with O–R–O bridge, Cl

$-CH_2 - CH - CH_2 - CH$
Cl

$$+ \quad R_2SnCl_2$$
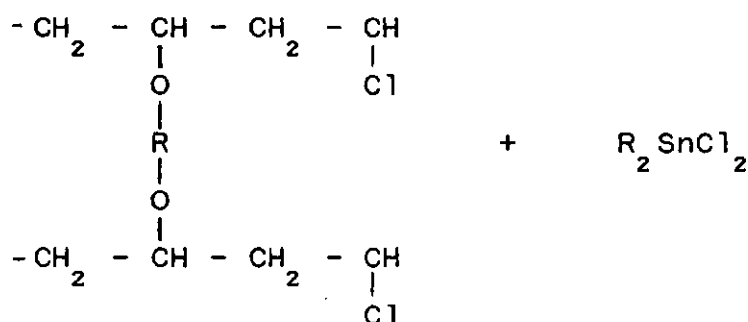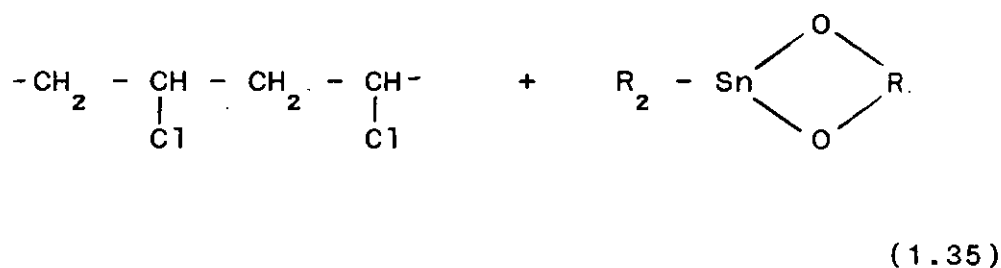
The methods discussed so far have the disadvantage that the crosslinking process is promoted thermally and it is difficult to separate the grafting from the crosslinking process, even when the reactivity of the polymer towards grafting is greater than the reactivity to crosslinking as reported by Mori and Nakamura[126]. Due to this is likely that crosslinking occurrs during the processing step, causing practical problems.

1.8.2.2.1 ORGANOSILANES CROSSLINKING.

For polyolefins, especially polyethylene (PE) silane crosslinking has been used successfully since the 1970s, and is a commercially established process. The polyethylene is grafted with unsaturated silanes containing hydrolysable groups which form crosslinks by hydrolysis

and condensation in the presence of water, preferably in presence of a silanol condensation catalyst. This method has a number of advantages compared to peroxide or radiation crosslinking[147].

The two commercial processes are Sioplas[148] and Monosil[149]. The Sioplas is basically a two-step process in which the base polymer, silane, peroxide and a small amount of antioxidant are fed to an extruder where grafting proceeds at about 200°C. The grafted resin is pelletized. This pelleted polymer can then be fed with a catalyst masterbatch to a thermoforming process.

The Monosil process is a single step process, in which polyethylene pellets along with peroxide and antioxidant and other additives are metered to the hopper of an extruder. Liquid silane and catalyst are fed via a metering pump to the throat of the hopper. Grafting proceeds in the extruder at about 200°C.

It is also possible to produce copolymers of ethylene with vinyl silanes during copolymerization at high pressure[150-152]. The basic chemical reactions are shown in scheme 1.36.

Attempts to crosslink PVC using silane crosslinking agents have also been reported. In 1969 Dow Corning[153] patented a process in which vinyl chloride is bulk copolymerized with vinyl silanes in presence of peroxide type initiators. It was mentioned in this patent, that the copolymer can be crosslinked by exposure to

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POLYETHYLENE

$$+ \quad _2HC = CH - \underset{\displaystyle OR}{\overset{\displaystyle OR}{\underset{|}{\overset{|}{Si}}}} - OR$$

$180\text{-}200^{\circ}C$ $\downarrow$ OR

```
              |
              CH₂
              |
              CH₂ - Si(OR)₃
```

$\downarrow$ H_2O

catalyst

```
              |
              CH₂
              |
              CH₂
              |
     OR - Si - OR
              |
              O
              |
     OR - Si - OR
              |
              CH₂
              |
              CH₂
              |
```

(1.36)
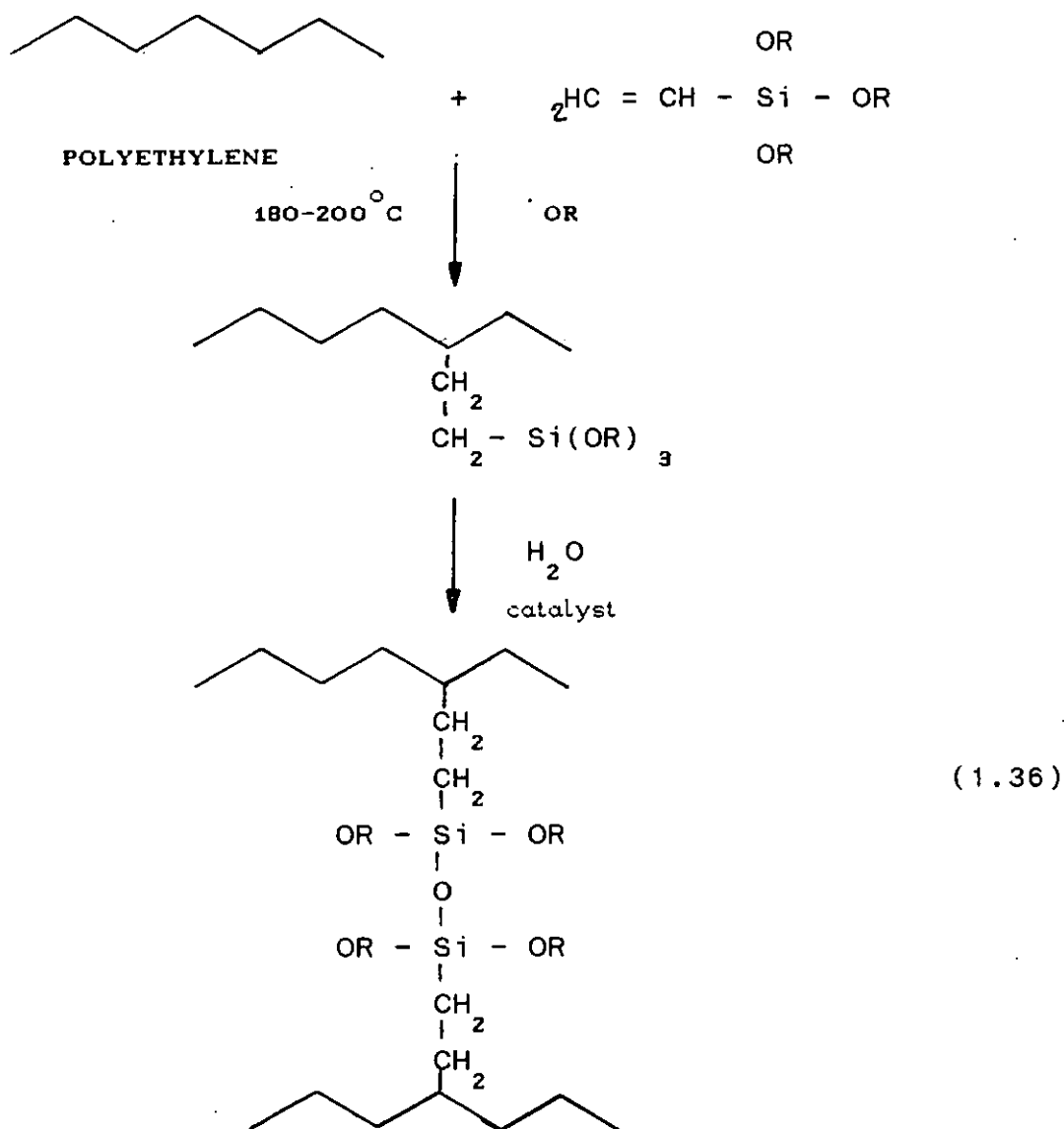
atmospheric moisture, but it is preferable to expedite crosslinking by contact with water at elevated temperatures. The use of a silanol condensation catalyst is recommended, especially tin carboxylates. The catalyst may be added as such or generated in situ. The first option is preferred to avoid premature crosslinking even during storage. It was also noticed that certain organic tin compounds which are commonly employed as stabilizers will serve to catalyze the crosslinking of the copolymeric products.

A similar process was patented by Dynamit Nobel[154]. Vinyl chloride monomer is copolymerized with vinyl silanes containing hydrolyzable groups; the copolymers, according to this invention, are not crosslinked and can be thermoformed as normal PVC. The crosslinking is carried out by immersion in dilute strong acids such as hydrochloric or nitric acid. It was found that as the vinyl silane content increased in the copolymer a highly crosslinked material was obtained; that the incorporation of vinylacetate as the copolymer promoted the crosslinking reaction, and finally by increasing the immersion temperature the crosslinking is more efficient.

A further patent by Dow Corning[155] describes the use of aminosilanes to crosslink the PVC. Here the aminosilane is grafted onto the PVC during processing and then crosslinked by immersion in an aqueous emulsion containing 5% by weight of dibutyl tin dilaureate. It is reported that after processing on a two roll mill at 160°C for 5 min, before immersion in water the gel content was 0% and after immersion at 80°C for 24 hrs the gel content was 59%.

More recently some interesting work has been done by Japanese workers at Fujikara Cable Works. This is concerned with the reaction of alkoxysilanes containing mercapto or amino groups, specifically γ-mercaptopropyltrimethoxysilane, with halogenated polymers[156-158]. The grafting of the organosilanes occurs during processing, and the crosslinking was carried out by immersion in water containing 3% catalyst.

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Another patent[159] mentioned the use of a complex of mercaptoalkoxysilanes with organocadmium or organotin compounds, as crosslinking agents for chlorinated polyethylene. The use of the complex inhibits the hydrolysis of the silane and decreases gel formation.(42% insolubles after 10 days compared with 80% in 2 - 3 days for a graft copolymer containing no complex).

In the above mentioned patents[156-159] the use of additives, such as diamines, are necessary for the grafting of mercaptosilanes. This however seems to increase the sensitivity of the halogenated polymer to degradation, reflected in the fact that the reactions were carried out at temperatures below 100°C.

Blends of PVC with silane grafted polymers have been patented. Tatsuta Electric Wire and Cable[160] used ethylene vinyl acetate copolymers modified with vinylalkoxysilanes to crosslink PVC. A mixture of PVC with silane - grafted chlorinated polyethylene[161] has also been described, and a blend of PVC with butyl acrylate-γ-methacryloxypropyltrimethoxy silane - methyl methacrylate copolymer has been patented[162].

With respect to crosslinking of PVC with organosilane there are a few references in the literature. Hearn et al[163] studied the crosslinking of plasticized PVC with aminosilane, specifically 3(2-amino-ethylamino) -propyltrimetoxysilane, following two processing routes,

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roll milling followed by compression moulding and extrusion. The gel content of the samples after compression moulding and before immersion was up to 50 -54%. This result suggested that premature crosslinking occurred and some degradation, indicated by the deep orange sample obtained. These samples were stabilized with a barium/cadmium compound.

On the other hand when the extrusion process was used at $180^{\circ}C$, the gel content after extrusion and before immersion was 0% and increase up to nearly 60% after immersion, although some discolouration was present. The effects of incorporation of tin catalyst and also calcium carbonate were investigated in the extruded compounds .It was found that the catalyst incorporation resulted in variable gel content and that the filler interfered in the crosslinking process. The extruded formulations were lead stabilized.

Ryningen et al[164,165] reported a new process to avoid the degradation problems observed by Hearn et al[163]. Ryningen mentioned that due to the high reactivity of the amino groups the thermal stability of PVC is seriously affected as well as premature crosslinking occurring. According to them these problems can be overcome by first modifying the PVC that is used in the process. Such a modification is able to both promote the grafting without significantly reducing the thermostability and avoid premature crosslinking. However they do not mention how the modification was made. Instead of using the traditional method to estimate the

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degree of crosslinking (gel content) they used stress relaxation and a good correlation to gel content was found.

Kelner and Schatz[166-168] have also successfully crosslinked PVC by grafting mercapto-alkoxysilanes onto the polymer chains, without degrading the PVC. The grafting of mercaptoalkoxysilanes (MT) on the plasticized and unplasticized PVC was carried out during processing in a Brabender Plasticorder in the presence of lead stabilizers[167]. They reported that the grafting reaction occurred only in the presence of basic lead salts. These stabilizers react with mercaptoalkoxysilanes at laboratory temperature to yield a yellow compound according to eq. 1.37.

$$(PbO_3).PbSO_4.H_2O \quad + \quad 2HS(CH_2)_3Si(OCH_3)_3 \quad \longrightarrow$$

$$[(CH_3O)_3Si(CH_2)_3S]_2Pb.(PbO)_2.PbSO_4.H_2O \quad + \quad H_2O$$

$$(1.37)$$
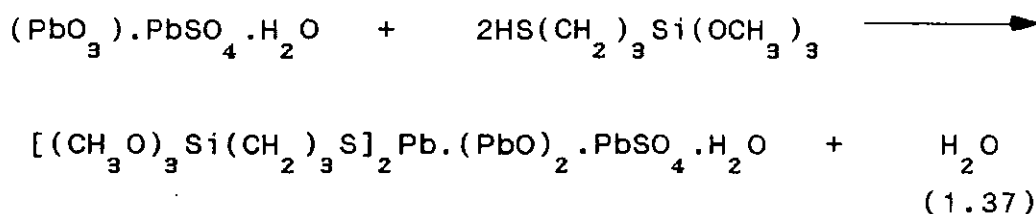
Dissociation of this compound at processing temperatures then leads to the formation of the thiolate anion, which is capable of substituting a chlorine atom in the PVC chain according to eq. 1.38.

$$(CH_3O)_3Si(CH_2)_3S^- \; + \; CH_2-CH \; \xrightarrow[180\,°C]{-Cl} \; CH_2-CH-$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad | $$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad S-(CH_2)_3Si(OCH_3)_3$$

$$(1.38)$$
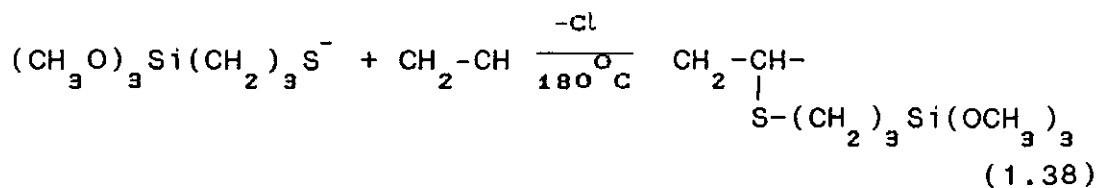
They noticed that grafting with silane occurred only for PbO, and that combination of basic lead stabilizers of PbO with other types of stabilizer did not lead to the grafting reaction in the test period (max. 20 min., $180^{\circ}C$). However, it was stated that by using longer grafting times at $180^{\circ}C$, the reaction could be greatly affected by degradation processes, especially for mixtures without thermal stabilizers. It was also found that the maximum gel content was obtained when 5 phr of MTMS and 5 phr of tribasic lead sulphate were used. The gel content was higher for unplasticized PVC, but for unplasticized PVC the maximum gel formation shifted to lower amounts of stabilizer.

The grafting of mercaptotrietoxy-silane (MTES) was also studied. It was pointed out that it is necessary to use a large amount of MTES in order to attain the same degree of crosslinking as with MTMS. The effect of processing conditions was also reported. The grafting efficiency was higher at high temperatures but if the temperature was higher than $200^{\circ}C$ partial crosslinking was observed. The gel content also increased with increasing blending time, and was used as an indirect method to assess the grafting efficiency. With respect to the type of plasticizer used, they noticed that higher gel contents were attained with plasticizers containing ester groups, and the gel content decreased with increased shielding by higher alkyls.

In a second paper Kelnar and Schätz[168] studied the crosslinking of PVC using different organosilanes, and

the effect of crosslinking conditions. It was found that the crosslinking rate, for samples grafted with mercaptosilanes, was higher for samples catalyzed with dibutyltindilaureate (DBTDL), the rate constant for catalyzed and uncatalyzed reactions differing by two orders of magnitude. On the other hand for PVC grafted with aminosilanes this difference was only one order. They found for PVC grafted with aminotriethoxysilane (ATES) stabilized with organotin stabilizer that this stabilizer catalyzes the crosslinking reaction. The influence of water temperature on crosslinking was also studied. For plasticized PVC it was necessary to use temperatures greater than 50°C; for unplasticized PVC it was pointed out that no crosslinking occurred at temperatures below Tg. Crosslinking also was carried out by atmospheric humidity, but the crosslinking rate was lower in comparison with crosslinking in water; plasticized samples were crosslinked within 30 hrs.in air and 6 hrs. in water. On the other hand unplasticized PVC was crosslinked after approximately 30 days in air compared with 26 hrs in water, this slower rate being due to a lower diffusion of water from the air. They concluded that diffusion of water from the external environment had practically no effect on the crosslinking. The crosslinking reaction apparently occurs through the water contained in the samples. It was found that an increase in water content in the sample produced an increase in the reaction rate.

1.9 ASSESSMENT OF CROSSLINKING.

There are several procedures to evaluate the degree of crosslinking. The most frequent used is to measure the insoluble material (gel content) after Soxhlet extraction with tetrahydrofuran or cyclohexanone, although tetrahydrofuran is preferred for PVC.

Although there are many factors that need consideration when deciding the length of extraction (eg. sample shape, thickness), many authors have reported that more than 12 hours are needed to perform complete extraction with THF[128]. Overnight extraction seems to be the method most widely reported in the literature[31,128,132,168].

Apart from the use of solvent extraction, the use of torque rheometers have been considered. Gonnu and Michel[145] evaluated the reactivity of thiolates as crosslinking agents for PVC. Figure 1.1 shows torque evolution with respect to time. Crosslinking is then characterized by the induction time (ti) which corresponds to the time between gelation peak and the beginning of the upturning torque. The average slope of the curve during the upturning torque was considered as the average crosslinking rate.

It was pointed out that the torque rheometer is not sensitive enough to detect variation of the PVC viscosity when small amounts of crosslinking agent were used and Gonnu and Michel[145] proposed the use of melt rheology,

with separation of viscous and elastic effects. For this, they used a cone and plate rheometer: the elasticity is most affected, and whereas PVC behaves as a liquid at 210°C before crosslinking, it behaves as a gel after crosslinking.

Torque

Gelation peak

Crosslinking peak

Time (min)
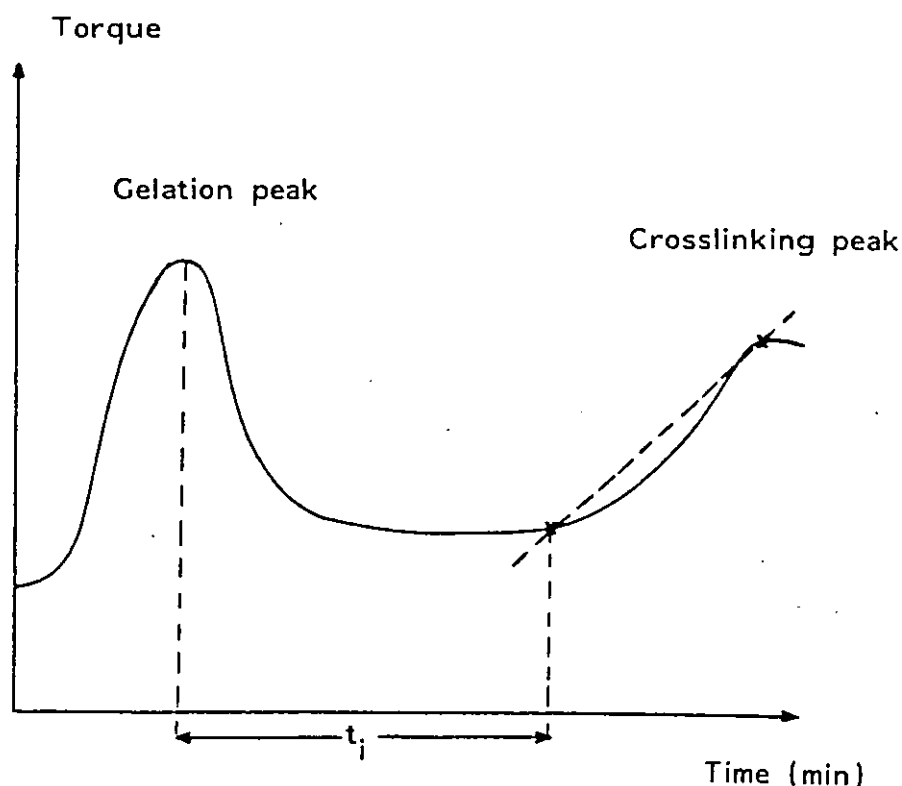
Figure 1.1 Typical curve of crosslinking

Using a similar approach Ghosh et al[143] were able to evaluate the curing characteristics of plasticized PVC crosslinked with EDA. From the Arrhenius plot of Log (crosslinking rate) vs reciprocal of absolute temperature, they calculated an activation energy of 15 Kcal/mol (63 kJ/mol) with is in well agreement with the values obtained by Mori and Nakamura[127] (also using a torque rheometer) for the crosslinking of PVC with

dithioltriazines. In a previous paper Mori and Nakamura[126] found a relation between the torque value and the network chain density and also calculated an Ea of 16.6 Kcal/mol.

Duchacek et al[51,137], in their studies of crosslinking PVC with tetramethylthiuramdisulphide (TMTD) used a Monsanto oscillating disk rheometer to evaluate the crosslinking rate, from the following expression:

$$M - M_{min} = (M_{max} - M_{min}) \cdot (1 - e^{-K(t - ti)})$$

(1.39)

where M_{max} and M_{min} are maximum and minimum torques respectively, K is the rate constant and ti the induction period of the crosslinking reaction. They found rate constants in the range of $0.22 - 1.39 \text{ min}^{-1}$ at $180^{\circ}C$. To evaluate the crosslinking rate of PVC crosslinked with triazines by immersion in water at $90^{\circ}C$, Mori and Jando[133] utilized the crosslink density; they obtained a rate constant of 0.023 min^{-1} at $90^{\circ}C$ and an activation energy of 55.5 kJ/mol.

The quantification of gel content versus time has also provide a useful way to measure rate constants for the crosslinking reaction. Kumar et al[169] reported a kinetic study of the crosslinking of polyethylene and ethylene propylene rubber with vinylalkoxysilanes. In this study it was found that both catalyst concentration and moisture have a great influence on the crosslinking rate. An increase in both produce an increase in reaction rate. They reported an activation energy of 65 kJ/mol.

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Recently, Kelnar and Schatz[168] carried out a study of the crosslinking of PVC with organosilanes; they characterized the rate of the crosslinking reaction using the slope of the straight line of a plot of the logarithm of relative gel content $[(G_{\infty} - G)/(G_{\infty} - G_0)]$ versus time where G_{∞} is the maximum gel content, G_0 initial gel gel content and G is gel content at time t. The slope was termed the rate constant. The results obtained have been discussed in section 1.8.2.2.

Ryningen and Dahl[165] utilized stress relaxation to evaluate the degree of crosslinking. They found a good correlation with gel content; they pointed out that this method is quick and reliable.

1.9.1. SWELLING OF NETWORK STRUCTURE.

Polymers are diluted by solvents when the polymer - solvent interaction leads to an decreased free energy of mixing. However, complete mixing cannot occur in polymer networks. As the network is swollen by the solvent the network junctions and chains are forced apart to accommodate the ever increasing volume fraction of solvent. The resulting strained conformations result in a retroactive force which tends to bring the network chains into more probable conformations. As the volume fraction of solvent increases, so do the retractive forces. Eventually the entropy of dilution and the retractive network forces balance and a state of equilibrium is achieved, as explained by Flory[170].

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The extent of swelling is inversely proportional to the density of crosslinks in the network and is highly dependent on the solvent and the temperature. Swelling at equilibrium is thus commonly used to investigate network polymers. This relationship is quantitatively expressed by the Flory – Rehner equation[171].

$$- [\ln (1 - Vr) + Vr + \varkappa Vr^2] \, Mc = \rho \, Vs \, Vr^{1/3}$$

$$(1.40)$$

where Vr is the equilibrium volume fraction of the polymer in the swollen gel, ρ the polymer density, $\varkappa$ is the Flory-Huggins interaction parameter, Vs the molecular volume of the solvent, and Mc is the number average molecular weight between crosslinks. Vr is defined as $1/q$ where q is the swelling ratio; sometimes the swelling value q is sufficient to give a measure of the crosslink density.

1.9.2. MECHANICAL ANALYSIS OF NETWORKS.

Measurement of the modulus of elasticity is another method to determine the crosslink density and their relationship is expressed by the well known formula of the kinetic theory of elasticity, in its simplest form

$$\sigma = R \, T \, V \, (\lambda - 1/\lambda^2) \qquad (1.41)$$

in which V is the number of crosslinks per volume; λ is the extension ratio and σ is the modulus, R is the gas constant and T the absolute temperature. According to

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this equation the modulus at a certain extension ratio and at a given temperature can only be increased by increasing V, the crosslink density.

1.10 THE EFFECT OF CROSSLINKING ON PROPERTIES.

As mentioned in section 1.8, crosslinking is one way to minimize certain drawbacks that PVC possesses. Bowmer et al[172-173] in their studies of crosslinking of PVC by irradiation, reported that a sample containing 93 % of gel had an increased ultimate tensile strength (UTS) and a decreased elongation at break.

The tensile properties of crosslinked PVC with dithiols have also been evaluated by Mori and Nakamura[118] who reported that the EDA immersion remarkably improves the mechanical properties of the PVC. They concluded that crosslinking by reagents with flexible structure and long molecular chains causes high tensile strength and low brittle temperature, and that crosslinking by reagents with short molecular chains gives high yield strength and high heat distortion temperature.

Mori and Nakamura[135] in their study of crosslinking of rigid PVC with dithiols found that an increase in crosslink density produces an increase in tensile strength (as normal for vulcanized rubbers) and a decrease in Young's modulus and yield strength

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(commonly these properties tend to increase with increasing crosslinking density); also the elongation at break increased with increased crosslinking density. They concluded that this abnormal behaviour is due to the plasticizing effect of the soft crosslinkage introduced and this plasticizing effect is beneficial to the tensile strength, elongation at break, impact strength and brittle temperature. Similar findings have also been reported[145] elsewhere.

For PVC foams crosslinked with dithiol triazines Mori etal.[128] reported that mechanical properties at room temperature were hardly improved, compared with those of uncrosslinked foam. Compression set, and dimensional stability at elevated temperatures can be improved by crosslinking.

The mechanical properties at room temperature for PVC fibres crosslinked with dithiol triazines were studied by Jando and Mori[134] .They found that both tensile strength and elongation at break decreased over 40 % gel content and modulus increased. The heat distortion temperature increased in the case of fibres having at least 75 % gel content. It was pointed out that below the Tg of uncrosslinked PVC, there is only a small difference between crosslinked and uncrosslinked PVC, but above the Tg this difference increases. From loss modulus versus temperature curves they determined the Tg for crosslinked PVC, finding that Tg increased sharply when the gel content became higher than 40 % . This increase was more than 30°C.

The mechanical properties of plasticized PVC crosslinked with TMTD have also been reported[174]. It was found that both tensile strength and elongation at break showed a maximum after 2 minutes of curing time when low levels of TMTD where used (1 and 2 phr); however when more than 3 phr of TMTD were used both properties showed a decrease. This behaviour suggested that some degradation took place at higher TMTD levels.

Gonnu and Michel[145] compared the mechanical properties of uncrosslinked and crosslinked PVC at different temperatures, using either a static test such as a creep or tensile test or a dynamic test in the elastic domain. They found that the rheological behaviour of PVC was strongly modified, particularly the elasticity; the normal PVC behaves as a liquid at $210^{o}C$, and as a gel after crosslinking. Constant values of $\tan\delta$ lower than 1 were obtained for samples with 15 and 30 % of gel content. The creep resistance was also improved even at low level of crosslinking (13% gel content); between $60^{o}C$ and $80^{o}C$ the deformation was halved, and the improvement increased as the temperature was raised. Finally it was concluded that chemical crosslinking leads to the existence of two interpenetrating networks, a physical one and a covalent one, which govern the mechanical properties.

The same authors noticed that tensile strength and elongation at break improved, mainly above $80^{o}C$. The improvement began from room temperature for samples with

100% gel content. But if the gel content was lower than 100%, the improvement of tensile strength was not observed below 80°C. If the gel fraction is lower than 100% the mechanical properties at room temperature are governed mainly by the physical network. The covalent network improves the properties only if the temperature rises above 80°C and melting of the physical network begins. To improve mechanical properties of crosslinked PVC at room temperature, the density of the covalent network must be higher than the density of the physical network; such a situation appears when gel formation reaches 100%.

Ghosh et al[143] also found that the mechanical properties of PVC crosslinked with EDA were hardly improved at room temperature.

The effect of crosslinking on mechanical properties has also been followed by measuring penetration resistance. Hjertberg and Dahl[175] found for PVC crosslinked with dithioltriazines, that the penetration (softening point) increased as the gel content increased, and even with low levels of gel (12%) an improvement in the interval 60-100°C was observed. This improvement was ascribed to annealing (since the samples were crosslinked at 90°C). A further penetration region was observed at about 130°C due to the melting of crystallites formed by annealing. A highly crosslinked material showed another transition at 180-200°C. No further penetration occurred above 200°C indicating the presence of a relatively dense and strong temperature-independent network

connected via covalent bonds. The thermal characteristics were also studied using DSC. Three endotherms appeared and were considered to result from annealing at three different temperatures, storing at room temperature, crosslinking and processing. They found that the second endotherm is displaced towards higher temperatures in crosslinked PVC; also that the endotherm is not influenced by annealing time for non crosslinked PVC , but became sharper and the peak shifted towards higher temperatures. They explained that the introduction of crosslinks tends to reduce the chain mobility in the amorphous phase, causing an increase in the temperature necessary to melt the crystallites. They also concluded that the penetration properties are results of two networks, one physical with crystallites as crosslinks and one chemical based on covalent bonds.

The mechanical properties of crosslinked PVC with aminosilanes were studied by Hearn et al[163] who reported that crosslinking did not improve the UTS and elongation at break at room temperature, significantly. These properties were highly improved when the tensile properties were measured at 130°C.

Dow Corning[153] reported in one patent that the tensile strength of PVC crosslinked with silanes measured at 120°C increased after crosslinking, and even before crosslinking had higher values than normal PVC.

Ryningen and Dahl[164], in their study of PVC crosslinked with organosilanes reported that the mechanical properties at room temperature are very little influenced by the crosslinking but at temperatures higher than 90°C the improvement in UTS is quite dramatic and the difference between uncrosslinked and crosslinked PVC increases with the temperature. The penetration resistance measured by thermomechanical analysis, showed that the crosslinked sample retained the mechanical properties much better as the temperature rose.

The mechanical properties of PVC crosslinked with mercaptosilanes are reported by Kelnar and Schatz[167] who mentioned that PVC containing 70 phr of plasticizer showed an increase in tensile strength and a decrease in elongation at 20°C and 120°C when the gel content increased. The temperature dependence of the strength and elongation have also been reported for samples containing 50 phr of plasticizer at three different gel contents. It was found that the strength decreases with increasing temperature and increases with gel content; at temperatures below 80°C the elongation decreases with increasing crosslinking, but at temperature above 80°C, the more crosslinked samples have higher elongation and the dependence is similar to that for the tensile strength. A similar trend was observed for unplasticized PVC.

The penetration resistance was also evaluated. It was pointed out that this method is useful to characterize the degree of crosslinking as well as the processability

of the material. Grafted PVC was used to study the effect of storage time. It was found that PVC grafted with mercaptosilanes showed 100% deformation above 200°C even at 21 days of storage; on the contrary PVC grafted with aminosilane exhibited an incomplete deformation, connected with the gel formation after grafting. It was also found for PVC grafted with either amino or mercaptosilanes, that there was a shift in the beginning of deformation, to higher temperatures, compared to samples without silane; Kelnar and Schätz[167] ascribed this to a certain degree of hardening of the mixture in the presence of silanes.

1.11 CHARACTERIZATION OF CROSSLINKED POLYMERS.

The use of spectroscopic techniques for the analysis of polymer networks has received little attention in the literature, the majority of this analysis being for thermoset resins, phenolics and epoxies[176].

Nevertheless, some approaches to such investigation have been reported.

Frank[177] used IR spectroscopy to investigate the radiation crosslinking of polyethylene. Nakamura and Mori[118] utilized IR spectroscopy to characterize the gel formed after crosslinking of PVC with dithiols. They assigned four bands in the region of 1020-1115 cm^{-1} to an ether linkage indicating that PVC had reacted. In their

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investigation of the crosslinking PVC with dithioltriazines[126], IR spectroscopy was also used. Mori and Nakamura found this technique quite useful to elucidate the crosslink structure; the results of the model reactions and the infrared spectrum showed that the chemical structure of the crosslinking is the 2 - dibutylamino - 4,6 - dithiol (s - substituted) s - triazine linkage. Recently Jando and Mori[133] came to the same conclusion, using FTIR.

Silane modified polyethylene has been characterized using infrared spectroscopy. Bullen et al[178] followed the crosslinking formation, Si - O - Si through a band that appeared at 1025 cm^{-1}. They also observed the formation of a silanol band at 3690 cm^{-1} after the hydrolysis of the methoxy group. The peak absorbances were normalized using the absorbance band at 3600 cm^{-1}; this is a combination band of the Raman active CH_2 asymmetric stretch and the infrared active CH_2 rock vibration of polyethylene.

Hjertberg et el[179] studied the crosslinking reaction of an ethylene vinyltrimethoxy silane (EVS) copolymer. The kinetics were followed by determination of the content of different structures (Si - OCH_3, Si - OH and Si - O - Si) using FTIR. The absorption indices for these structures were calculated using the overtone of CH_2 bending at 2020 cm^{-1} as internal standard. It was stated that the structures gave characteristic peak absorbances as follows: Si-OCH_3, 800, 1090cm^{-1}[180,181]; Si - OH free, 3691 cm^{-1}[181]; Si - OH hydrogen bonded,

3549, 3431 cm$^{-1(182)}$; Si $-$ O $-$ Si, 1030 cm$^{-1(180-181)}$.
The authors pointed out that it was difficult to quantify
the Si $-$ O $-$ Si since it appears as a shoulder on the
large band due to the Si $-$ O band in Si $-$ OCH₃. However,
they were successful in elucidating these structures and
mentioned that, as expected, the Si $-$ OCH₃ tends to
disappear very rapidly first, then gradually slows down
and becomes constant after about 50 hours of immersion.
At the same time an increase in the content of Si $-$ OH
was observed, during the first 15 hours. Thereafter this
became constant, suggesting that silanol groups were
consumed at the same rate as they were formed.
Consistently, a strong increase in the absorption index
of Si $-$ O $-$ Si was observed. The formation of Si $-$ O $-$ Si
continued even when a maximum gel content was reached.
They concluded that some molecules already part of the
network form even more crosslinks.

Kumar et al[169] studied the graft copolymerization
of vinylsilanes onto polyethylene during reactive
processing; the graft copolymer was characterized by IR
spectroscopy using the absorbance band at 1090 cm^{-1}.

Palmlöf et al[183] studied the crosslinking of
ethylene vinylsilane copolymers. The crosslinking
reaction was followed by determination of the gel
content and by analyzing the structural changes using
FTIR; they used the band at 1030 cm^{-1} characteristic of
the Si $-$ O $-$ Si bond. The overall reaction was also

followed quantitatively by Size Exclusion Chromatography (SEC) of the soluble part. The molecular weight (Mw) increased rapidly even at very low levels of gel; at higher gel content the Mw value drops drastically.

1.12 AIMS OF THE PROJECT

From the literature survey carried out some crosslinking systems for PVC have been identified. The methods discussed so far have some drawbacks. For example, radiation crosslinking is an expensive system and the rate of samples which can be crosslinked is limited due to the low penetration of radiation. Some chemical systems were also considered. However, may have the disadvantage that the crosslinking is promoted thermally and it is difficult to separate the grafting from the crosslinking process.

The organosilane technology, commercially used for polyethylene looks like a good possibility for PVC. It was therfore decided that , the aim of the project was the enhancement of PVC properties by means of chemical crosslinking with aminoalkoxy silanes which can be grafted onto the PVC during processing and subsequently crosslinked.

The work was divided into three main goals:
* First, to develop a process in which the aminosilane can be grafted onto the PVC without gel formation.
* Second, to study the crosslinking process and
* Third , to characterize the grafted and crosslinked polymer.

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CHAPTER 2

EXPERIMENTAL TECHNIQUES

2.1 MATERIALS.

2.1.1. PVC POLYMER.

Two commercial grade suspension PVChomopolymers were used. These were Corvic S71/102 supplied by ICI Ltd., U.K. and Primex 250 supplied by Primex S.A. México. The main characteristics of the polymers are presented in Table 2.1.

TABLE 2.1

Properties of PVC polymers

	Corvic	Primex
K value (Fikentscher)	71	71
Molecular weight Mw[a]	121000	120500
Molecular weight Mn[a]	71000	70500

[a] Estimated by GPC

2.1.2. PLASTICIZER.

Two plasticizers were used in this study : Dioctyl phthalate (DOP) and diisooctyl phthalate (DIOP). The plasticizers were provided by Primex, México and Ciba-Geigy, U.K. respectively.

2.1.3. STABILIZER.

Three different kind of thermal stabilizers were used. Table 2.2 presents the characteristics of the stabilizers.

TABLE 2.2

Stabilizers used

Code	Chemical name
TBLS	Tribasic Lead Stearate
DBLS	Dibasic Lead Stearate
Ba/Cd/Zn	Metal carboxylates
T486*	Dioctyltinthioglycolate ester/ monooctyltinthioglycolate mix.
T192*	Dibutyltinthioglycolate ester
T55*	Dibutyltin carboxylate
TPP	Triphenyl phosphite

*Stabilizers supplied by Akzo Chemicals.

2.1.4. CROSSLINKING AGENT.

The crosslinking agent used was an aminosilane, (Z-6020) N-(2-aminoethyl)-3-aminopropyltrimethoxy silane, supplied by Dow Corning.

2.1.5. CATALYST

The catalyst used was dibutyltin dilaurate, TL.

2.1.6. OTHER ADDITIVES.

Other additives include calcium stearate, which was used as external lubricant.

2.2 SAMPLE PREPARATION.

2.2.1. CROSSLINKABLE FORMULATIONS.

The formulations used to study the effect of different levels of crosslinking agent and different thermal stabilizers types appear in Tables 2.3 and 2.4.

TABLE 2.3

Formulations used to study the effect of different levels of Z-6020.

Form.	0	1	2	3	4	5	6
PVC	100	100	100	100	100	100	100
DOP	50	50	50	50	50	50	50
TBLS	4	4	4	4	4	4	4
DBLS	2	2	2	2	2	2	2
Z 6020	0	1	2	3	4	5	6

Table 2.5 shows the formulations used to evaluate the effect of the processing variables, milling and compression moulding time on crosslinking.

TABLE 2.4

Formulations used to study the effect of stabilizer type

Formulations	1	2	3	4	5	6
PVC	100	100	100	100	100	100
DOP	50	50	50	50	50	50
TBLS	4	4	4	–	–	5
DBLS	2	2	2	–	–	3
Z-6020	–	2	5	2	2	2
Ba/Cd/Zn	–	–	–	4	–	–
TPP	–	–	–	1	–	–
T 831	–	–	–	–	1.5	–

TABLE 2.5

Formulations used to evaluate the effect of processing
conditions.

Formulations	0	1	2
PVC	100	100	100
DIOP	50	50	50
TBLS	4	4	4
DBLS	2	2	2
Z 6020	0	2	5

Table 2.6 shows the formulations used to evaluate the
performance of different tin stabilizers. This part of
the work was undertaken to select the stabilizer which
produced less degradation problems and a formulation with
no gel formation after processing. In some of these
formulations a lubricant was also added to evaluate its
effect on both thermal stability and lubricity.

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TABLE 2.6

Formulations used to study different thermal stabilizers

Formulation	1	2	3	4	5	6	7	8
PVC(Corvic)	100	100	100	100	100	100	100	100
DIOP	50	50	50	50	50	50	50	50
Z 6020	2	2	2	2	2	2	2	2
T 155	3	-	-	-	-	-	-	-
T 184	-	3	3	-	-	-	-	-
T 192	-	-	-	-	3	3	3	3
T 486	-	-	-	3	-	-	-	-
CaSt	-	-	1	-	-	1	2	3

2.2.1.1. DRY BLENDING.

Two different techniques were used for preparing the dry blends.

a) Dry blends were prepared in a Z blade type mixing chamber of 300 ml of capacity, attached to a Brabender torque rheometer, at 67 rpm and 90°C. The PVC, the stabilizer and lubricant were introduced and preheated for 3 minutes, after which the plasticizer plus crosslinking agent were added. The formulations that appear in Tables 2.3 and 2.4 were prepared with this method.

b) Dry blends were prepared in a Fielder high speed mixer, at 3000 rpm, as follows: with the temperature at 70°C, the PVC, stabilizer and lubricant were introduced and preheated. When the temperature reached 90°C, after

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aproximately 5 min, the plasticizer plus the crosslinking agent were added and the ingredients allowed to mix until they reached $120^{o}C$, at which point the mix was discharged and cooled. The formulations that appear on Tables 2.5 to 2.9 were prepared with this method.

When the stabilizers used were liquids (Sn and Ba/Cd/Zn), they were added with the plasticizer.

This experimental section is divided according to the two first sections that will be discussed in the result sections.

2.2.1.2. MIXING AND MOULDING.

Two different fusion processes were used for sample preparation:

a) Dry blends were processed in a roller type blade mixing chamber of 70 ml capacity, attached to a Brabender torque rheometer, at 65 rpm, and $125^{o}C$. The dry blends were fused for 1.5 min., compression moulded at $170^{o}C$ and 8.0 MPa for 1.5min., and then cooled while still in the mould. Formulations produced are listed in Tables 2.3 and 2.4.

b) Dry blends were roll milled at 125 and $140^{o}C$ for different time periods, from 1 to 10 minutes. The milled sheets were then pressed for different time periods from 2 to 10 minutes at 180° C. Formulations produced are listed in table 2.5.

2.2.2. EXTRUSION EXPERIMENTS.

The extrusion was carried out using a single screw extruder (Killion 100) with a screw diameter of 25 mm operated at 65 rpm. The following temperature profile was used. The extruder was fitted with a slit die (dimensions 1mm x 120mm).

zone 1 $150^{\circ}C$
zone 2 $160^{\circ}C$
zone 3 $160^{\circ}C$
die $150^{\circ}C$.

The purpose of the extrusion experiments was to obtain a formulation with zero gel content after processing and to have an extrusion process without degradation problems. For this, several extrusion trials were made, the different factors studied being:

-The effect of two different stabilizers. For this the formulations that appear in table 2.7 were selected. After extrusion the samples were crosslinked in hot water ($80^{\circ}C$) containing 5% v/v of catalyst and the mechanical properties and gel content evaluated. During the extrusion experiment the extruder power consumption was also measured.

-The effect of the tin stabilizer /crosslinking agent ratio. The stabilizer concentration varied from 1 to 5 phr and the crosslinking agent varied from 1 to 5 phr. Formulations 1 - 6 in Table 2.8.

-The effect of different lubricant levels. The
lubricant studied was calcium stearate and its
concentration was 1 - 2 phr.

-The effect of incorporating the catalyst in the
formulation. Formulation 3, Table 2.8.

-And finally one formulation, formulation 3 table
2.8, was selected to study the effect of reprocessing.
For this the dry blend was extruded to obtain pellets and
then the pellets used to obtain a sheet . The gel
contents of all this formulations were also evaluated.

TABLE 2.7

Formulations used to carry out the extrusion experiments
to study different thermal stabilizers

Formulation	1	2	3	4
PVC	100	100	100	100
DOP	50	50	50	50
TBLS	4	4	4	4
DBLS	2	2	2	2
Z-6020	-	2	-	2
T 831	-	-	1.5	1.5

TABLE 2.8

Formulations used to carry out the extrusion experiments to study the effect of stabilizer/crosslinking agent ratio.

Formulations	1	2	3	4	5	6	7
PVC (Primex)	100	100	100	100	100	100	100
DOP	50	50	50	50	50	50	50
T 192	1	2	3	5	3	3	3
Z 6020	2	2	2	2	1	5	2
CaSt	1	1	1	1	1	1	2

TABLE 2.9

Formulations used to carry out the extrusion experiments

FORMULATIONS	1	2	3	4
PVC	100	100	100	100
DOP	50	50	50	50
Z 6020	2	2	2	2
T 192	3	3	–	–
TL	–	5	–	5
CaSt	1	1	–	–
One Pack	–	–	3	3

2.3 CROSSLINKING CONDITIONS.

The crosslinking was effected by immersing the samples in hot water (80°C) containing the catalyst, the immersion time varying from 0 to 8 hrs. These conditions were used to crosslink the formulations from section 2.2.2.

The following crosslinking variables were investigated. For this an extruded formulation was chosen. (Formulation 4, Table 2.8.)

-Catalyst concentration

-The catalyst concentration varied from 0 - 20 %, whereas the temperature and immersion time were kept constant at 80°C and 4 hrs. respectively.

Immersion time

The immersion time varied from 1 - 18 hrs.; the temperature and catalyst concentration were kept constant at 80°C and 10 % respectively.

Immersion temperature

This was varied from room temperature to 90°C, while the immersion time and catalyst concentration were kept at 4 hrs. and 5 % respectively.

Pressure

An autoclave was used in order to have a higher temperature and a high pressure to increase the crosslinking rate. For this the next experiment were carried out.

The samples were placed in an Erlenmeyer flask containing the catalyst solution (5% catalyst concentration). The immersion time and temperature were varied as follows:

RUN	TEMP (^{o}C)	TIME (min)
1	115	10
2	121	10
3	127	10
4	127	20
5	127	40
6	127	60
7	115	40
8	121	40
9	127	40

-Moisture content.

Three different environments were selected to evaluate the effect of water content. The moisture content was varied by keeping the samples in water, normal air , and in a desicator.

2.4 MECHANICAL PROPERTY DETERMINATIONS

2.4.1. TENSILE PROPERTIES.

The tensile properties were measured at room temperature and 130°C using an Instron tensometer, and a rate of stretching of 50mm/min. Tensile strength and elongation were determined at the point of rupture. Dumbell specimens were cut using a BS003 A-2 die cutter.

2.4.2. THERMOMECHANICAL ANALYSIS.

A Du Pont TMA was used to determine the softening point of the uncrosslinked and crosslinked samples. The penetration of an indentor into the sample was used to determine the softening point (SP).

SP were determined on samples approximately 2 mm thick, the temperature was scanned from room temperature to 220°C, at $10\,^\circ$C/min, and the load weight upon the indentor was 10 g.

2.5 ANALYSIS.

2.5.1. GEL CONTENT DETERMINATION.

The gel content was determined by Soxhlet extraction for 20 hrs with tetrahydrofuran. The remaining swollen gel was dried in a vacuum oven at 60°C for at least 20 hr. The percentage of THF insoluble material (gel %) is obtained from the ratio of the weight of the dried gel to

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the weight of the original sample, the plasticizer being excluded.

2.5.2. EQUILIBRIUM SWELLING.

The number average molecular weight between crosslinks (Mc) was determined using the Flory-Rehner equation[171], the determination being made on the gel after removal of soluble material as described above. Mc was calculated using the following equation.

$$-[\ln(1-Vr) + Vr + \varkappa Vr^2] = \rho VoMc^{-1}Vr^{1/3}$$

where

$\varkappa$ = is the polymer - solvent interaction parameter

ρ = is the density of PVC

Vo = is the molar volume of solvent

Vr = is the volume fraction of PVC in the swollen gel

The samples were swollen in methyl ethyl ketone for 7 days at room temperature. The swollen (Ws) and deswollen weights (Wd) were used to calculate the volume fraction of PVC (Vr) in the network swollen to equilibrium.

2.5.3. MOLECULAR WEIGHT DETERMINATION.

Gel permeation chromatography was used for determination of molecular weight distribution (MWD). To carry out this study the formulations that appear in table 2.10 were selected. The dry blends were roll milled

at 165°C for different periods of time, from 1 to 10 minutes. After milling 10 mg of PVC were dissolved in THF and analyzed. A KNAUER HPLC pump was used to produce a flow rate of 1 ml/min at 25°C. Tetrahydrofuran was used as solvent. The column was a Styragel column with a pore size of 10 μm. The eluted solvent is monitored using a refractive index detector. To calculate molecular weight averages, a BBC computer program devoloped in Bradford University was used. The calibration for linear PVC was obtained via the universal calibration curve. The k constant for polystyrene and polyvinylchloride are 1.6 x 10^{-5} and 1.5 x 10^{-5} m^3/kg and the a values 0.71 and 0.77 respectively.

Molecular weights were also measured on the soluble fraction of the crosslinked polymer after Soxhlet extraction.

TABLE 2.10

Formulations used for the determination of molecular weights.

PVC	100
DIOP	50
T 192	3
Z 6020	1, 2,3,4,5
Ca St	1

2.5.4. INFRARED SPECTROSCOPY.

A Matson 3000 FTIR spectrometer was used to characterize the grafted and crosslinked polymer. All the samples used in this study , were first Soxhlet extracted with ether for 24 hrs, to eliminate the plasticizer and the unreacted silane, followed by THF Soxhlet extraction. The soluble fraction obtained were precipitated with methanol, dissolved in THF and precipitated again. Finally a cast film was obtained from the soluble fraction. This film was ether extracted for 20 hrs. to eliminate any THF that could be present, and placed in a vacuum oven at 60°C for 1 hr. With this procedure it was assured that all the solvent and unreacted silane was eliminated.

The gel fraction was also analyzed after being ether extracted.

2.5.5. THERMAL STABILITY.

Different formulations (formulations table 2.4) were selected to evaluate their thermal stability in a Brabender Plastograph. The temperature used was 180°C, rotor speed 65 rpm and charge 65 grams of material. This test is very helpful to evaluate both the stabilizer performance and the crosslinking rate. The increase in torque is an indication that a more rigid structure is being formed. The change in colour of the samples was also followed.

To select the tin stabilizer able to produce less degradation problems and a formulation with no gel formation after processing, the formulations that appear in table 2.6 were chosen, and at the same time a lubricant was evaluated. Another purpose of this study was to have a formulation without processing problems, i.e. degradation or premature crosslinking. The dry blends were roll milled at two different temperatures, 125 and 145°C. The milled sheets were then compression moulding using a preheated steel mould, at 170°C for 2 minutes using a pressure of 80 kg/cm^2. To evaluate the performance of both stabilizers and lubricants, visual appearance was used and also the gel content was measured. The lubricant performance was evaluated using a roll mill at 145°C, the less the sample stick to the roll, the better its perfomance.

CHAPTER 3
RESULTS AND DISCUSSION
PRELIMINARY INVESTIGATIONS

3.1 INTRODUCTION.

The aim of this part of the project was to develop a crosslinkable formulation for plasticized PVC . For this several factors were studied. The results obtained from the experiments carried out will be discussed under the following headings: effect of formulation variables which include crosslinking agent and stabilizer, and effect of processing conditions on gel formation and mechanical properties.

3.2 EFFECT OF FORMULATION VARIABLES ON CROSSLINKING.

3.2.1. CROSSLINKING AGENT CONCENTRATION.

3.2.1.1. EFFECT ON GEL CONTENT.

Table 3.1 presents the results of gel content of samples containing different levels of aminosilane . We can see, that the gel content, as expected, increased with increasing immersion time and aminosilane concentration. But the increase is more pronounced in the latter case Figures, 3.1 and 3.2

From the Figure 3.1 we can observe that under the processing conditions used (roll milling at 125°C for 3

minutes and pressing for 8 minutes at 180°C) and with a lead stabilizer content of 6, phr the gel content reached a maximum at approximately 5 phr of aminosilane. It was found that even before crosslinking the gel content was high specially if the concentration of crosslinking agent was high. On the other hand it can be seen in Figure 3.2 that by increasing the crosslinking time the increase in gel content was not significant specially when more than 2 phr of aminosilane were used, indicating that even the atmospheric humidity is enough to cause condensation of the grafted silane and produce crosslinking.

These results are in good agreement with those obtained by Kelnar and Schätz[167] using mercaptosilanes. The attainment of high gel contents is desired but not during processing as in this case.

TABLE 3.1

Gel Content(%)of formulations crosslinked at different times , containing different levels of aminosilane.

XLT (hr)	0	0.5	1	2	4	8
Z6020(phr)						
1	12	14	17	24	22	27
2	28	30	32	32	33	36
3	38	39	40	40	42	48
4	44	49	49	50	52	56
5	71	71	74	75	72	76
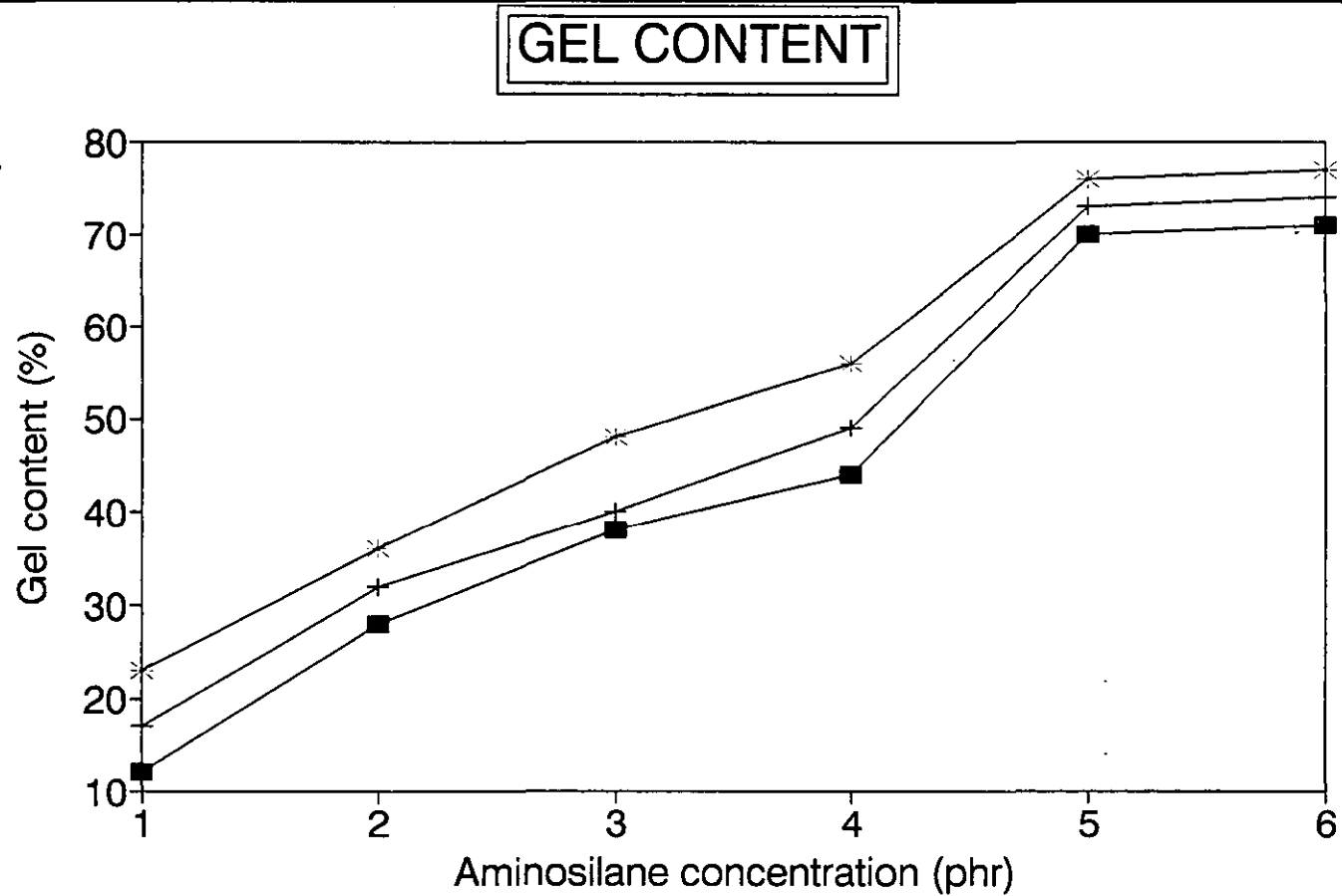
Figure 3.1 Dependence of gel content on aminosilane concentration
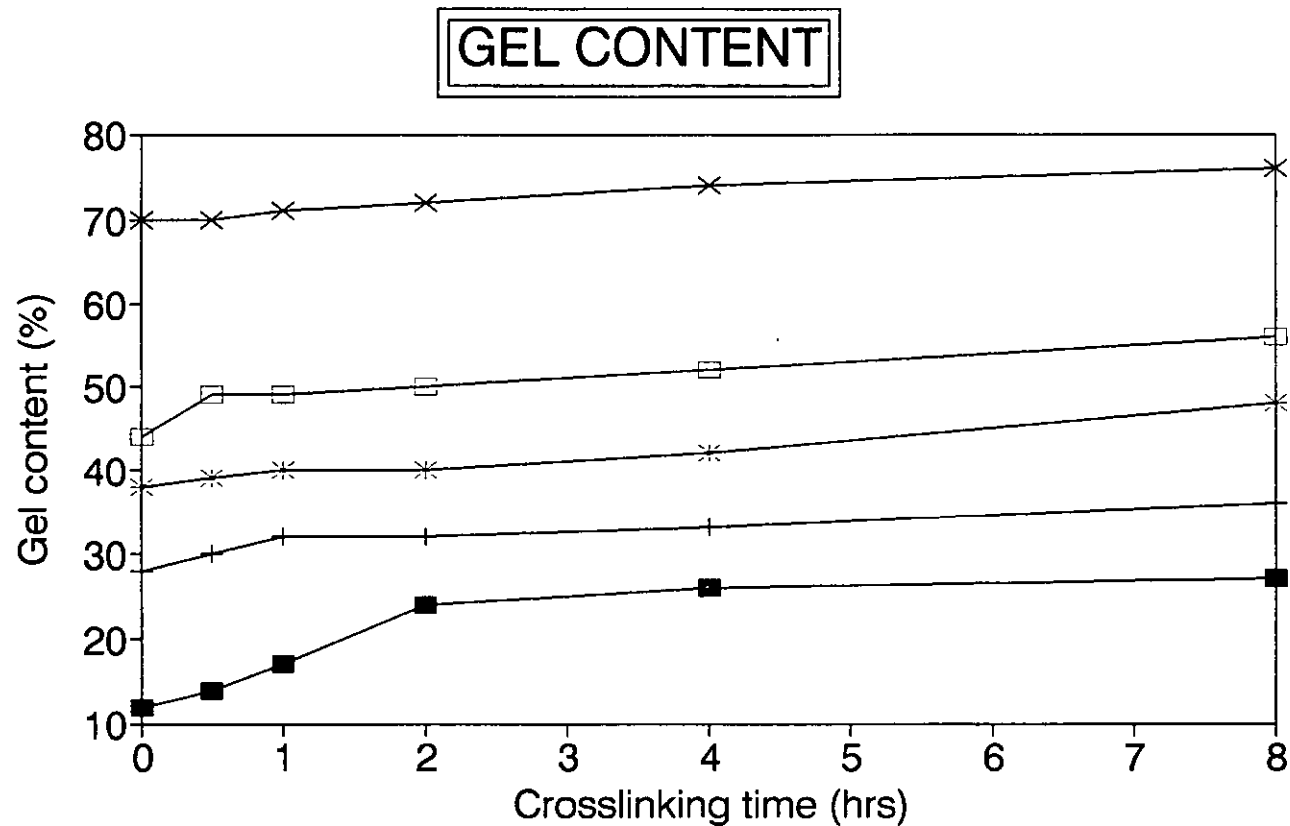
Figure 3.2 Dependence of the gel content on the crosslinking time

- ■ 1 phr z 6020
- + 2 phr z 6020
- ＊ 3 phr z 6020
- □ 4 phr z 6020
- × 5 phr z 6020

3.2.1.2. EFFECT ON MECHANICAL PROPERTIES.

The formulations that appear in Table 2.3 were selected to carry out this study. Figures 3.3 and 3.4 and Tables I.1 and I.2 (Appendix I) show the results of tensile properties measured at room temperature.

We can observe that the tensile strength of samples containing the crosslinking agent is higher than those of the samples without aminosilane, also the tensile strength increases with increasing aminosilane concentration (Figure 3.3). On the other hand the elongation at break decreases with increasing aminosilane concentration (Figure 3.4), as a result of a more rigid structure has been produced.

The results of tensile properties at $130^{\circ}C$, are presented in Tables I.3 and I.4 (Appendix I) and Figures 3.5 and 3.6. One of the reasons, and maybe the principal reason for crosslinking plasticized PVC, is to increase the mechanical properties specially at high temperatures. As expected the tensile strength increases with increasing the crosslinking agent concentration and the immersion time, the elongation showing a similar behavior. This may be understood and interpreted on the basis of two considerations: (i) that a lower gel content (aminosilane concentration), the structure of the network is not yet sufficiently homogeneous and the sample is thus destroyed at low elongations and/or (ii) that this crosslinking system leads to the establishment of relatively flexible crosslinkages.

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Figure 3.3 Dependence of UTS on aminosilane concentration

TENSILE PROPERTIES AT ROOM TEMPERATURE

Figure 3.4 Dependence of the elongation on aminosilane concentration

■ crosslinked 0 hrs   + crosslinked 0.5 hrs   ✳ crosslinked 1 hr

□ crosslinked 2 hrs   ✶ crosslinked 4 hrs   ▲ crosslinked 8 hrs
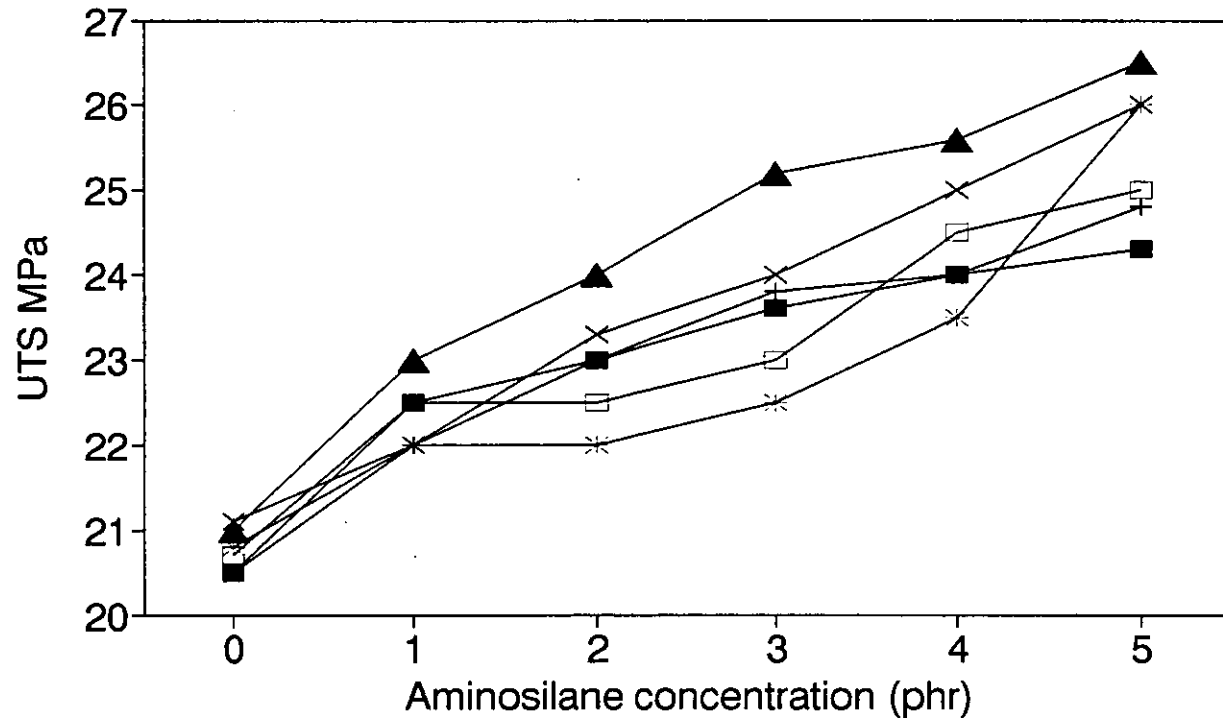
Figure 3.5 Dependence of UTS on aminosilane concentration

—■— crosslinked 0 hrs   —+— crosslinked 0.5 hrs   —*— crosslinked 1 hr

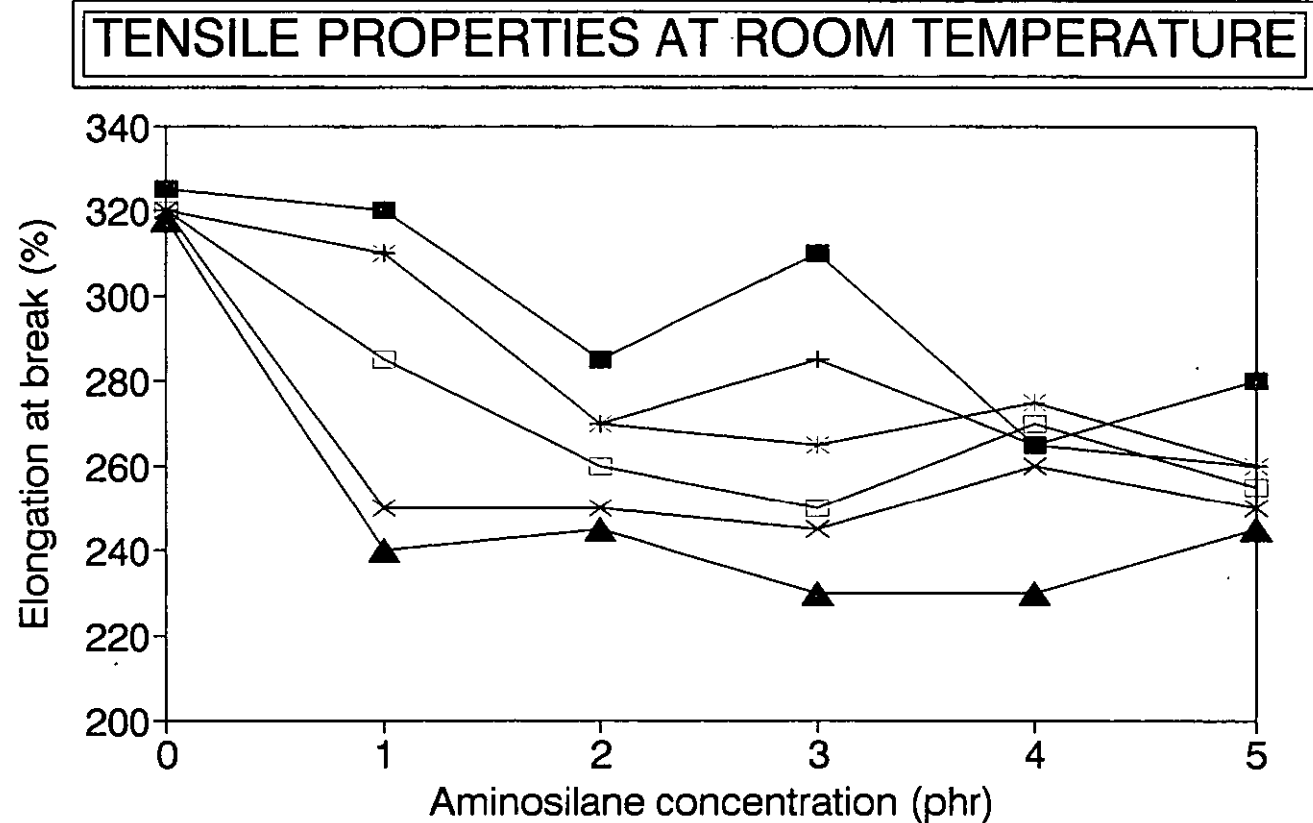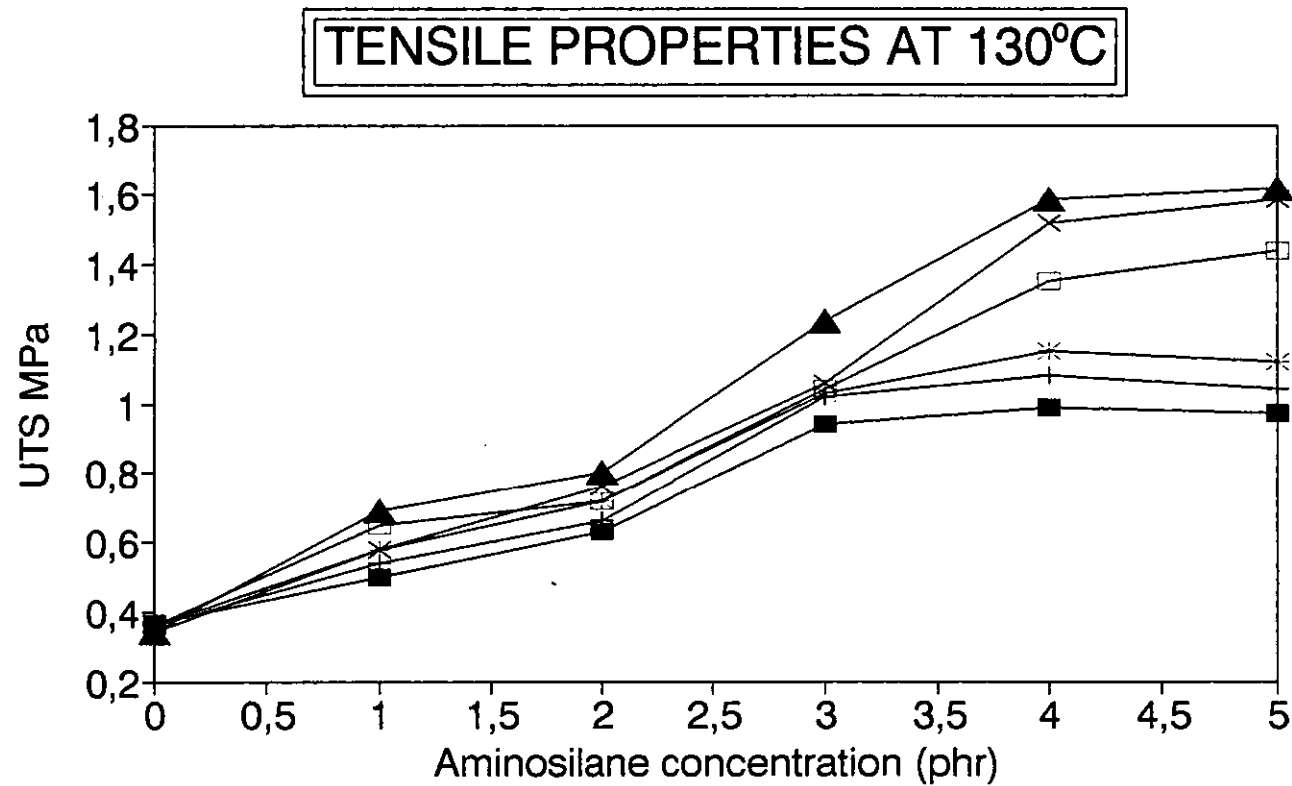—□— crosslinked 2 hrs   —×— crosslinked 4 hrs   —▲— crosslinked 8hrs
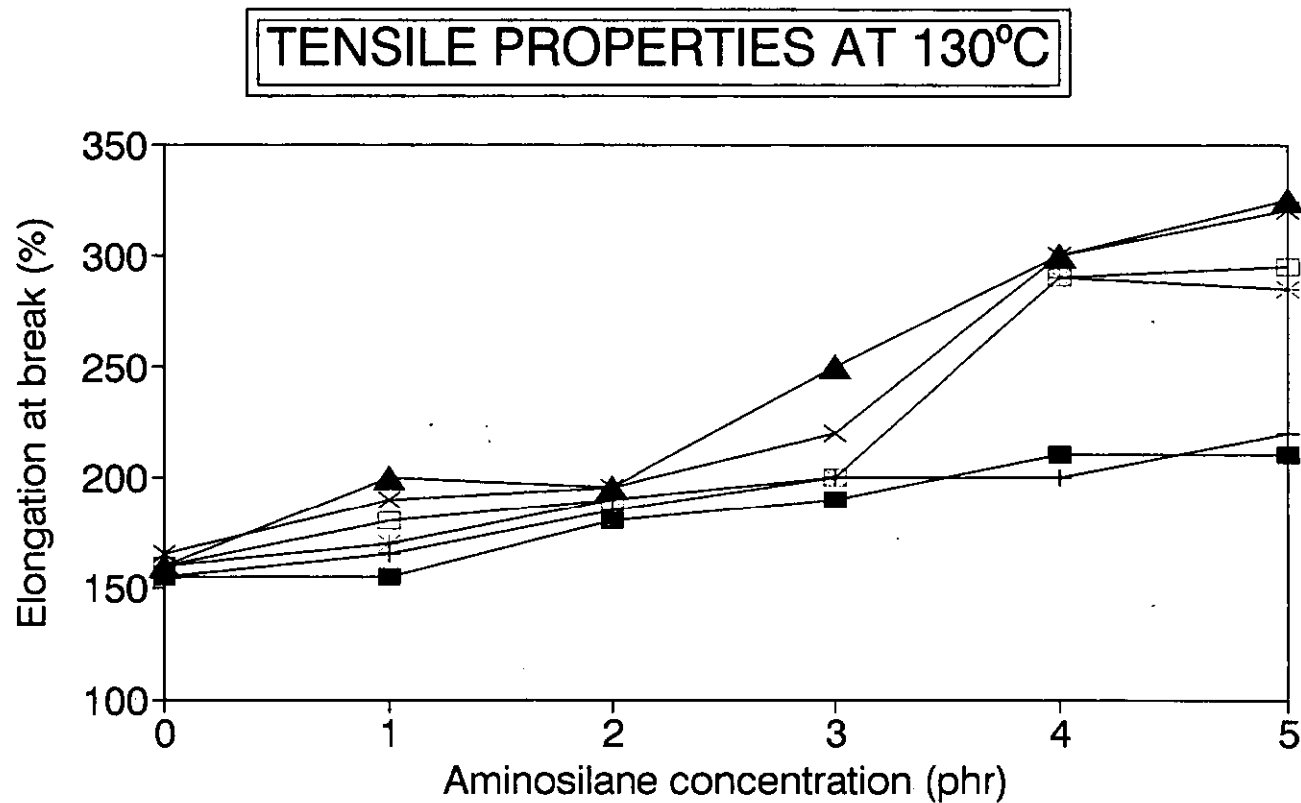
Figure 3.6 Dependence of the elongation on aminosilane concentration

■ crosslinked 0 hrs ┼ crosslinked 0.5 hrs ✳ crosslinked 1 hr
□ crosslinked 2 hrs ✕ crosslinked 4 hrs ▲ crosslinked 8hrs

At higher temperatures, than those used in the tensile experiments, normal PVC presents rubbery flow. The introduction of chemical crosslinks points serve as a permanent network junctures suppressing the flow with the consequent increase in tensile strenght and elongation.

It can be seen that, even when low levels of aminosilane are used is possible to have an improvement in mechanical properties, specially in tensile strength. However the best results, in both the elongation and tensile strength, were obtained when at least 4 phr of aminosilane were used. The tensile strength increased with increasing the crosslinking time, and the elongation reached a maximum after 4 hours.

It can be seen from the dependence of the tensile strength and elongation at break on the gel content (Figure 3.7) that both properties increase with increasing crosslinking. At lower gel contents the network structure is not yet sufficiently homogeneous and the samples therefore fail at lower elongation. This graph is for samples containing different levels of aminosilane (1 - 5 phr) and crosslinked 1 hr.

The Figure 3.8 shows a correlation between gel content and the ultimate tensile strength at high temperatures. This graph is constructed using all the gel content data, irrespective of formulation and processing conditions. It can be seen that the tensile strength increases when the gel content increase, and tend to reach a plateau at about 70 % of gel content.

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3.2.2. EFFECT OF THERMAL STABILIZER TYPE.

To carry out this part of the work the formulations that appear in table 2.4 were chosen.

3.2.2.1. EFFECT ON GEL FORMATION.

Table 3.2 presents the results of gel formation of samples containing 2 phr of aminosilane and different thermal stabilizers. It can be seen in this table that the gel content increases with increasing the crosslinking time but the lead stabilizer produced a high gel content even before immersion. On the other hand both the barium/cadmium/zinc and the tin stabilzer produce less gel formation before crosslinking, but the gel contents after 4 hours of immersion for the compound containing tin stabilizer are similar to those obtained with lead stabilizer.

The tin and metal carboxylates are more effective stabilizers than lead stabilizer, and react with PVC reducing the grafting efficiency of the aminosilane (indirectly measured from the gel content) producing the low gel formation 12-15% after processing. The further increase in gel formation observed is attributed to the catalytic effect of the tin stabilizer.

Figure 3.7 Dependence of the UTS and elongation on the gel content
for samples containing different levels of aminosilanes and crosslinked 1 hr.

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$$Y = 4.75 - 0.13\,X + 9.49^{-3}X^2 - 7.63\ ^{-6}X^3$$
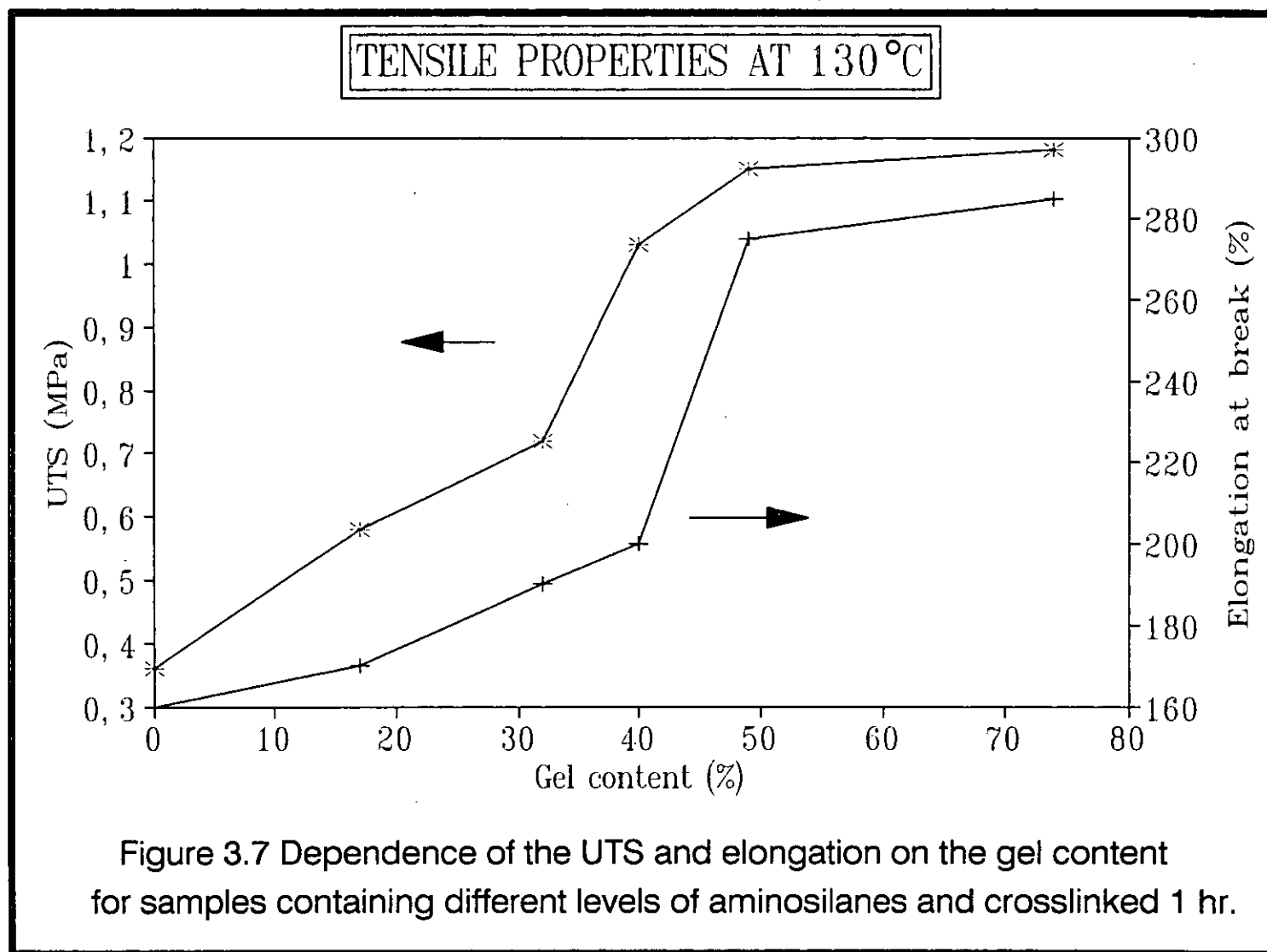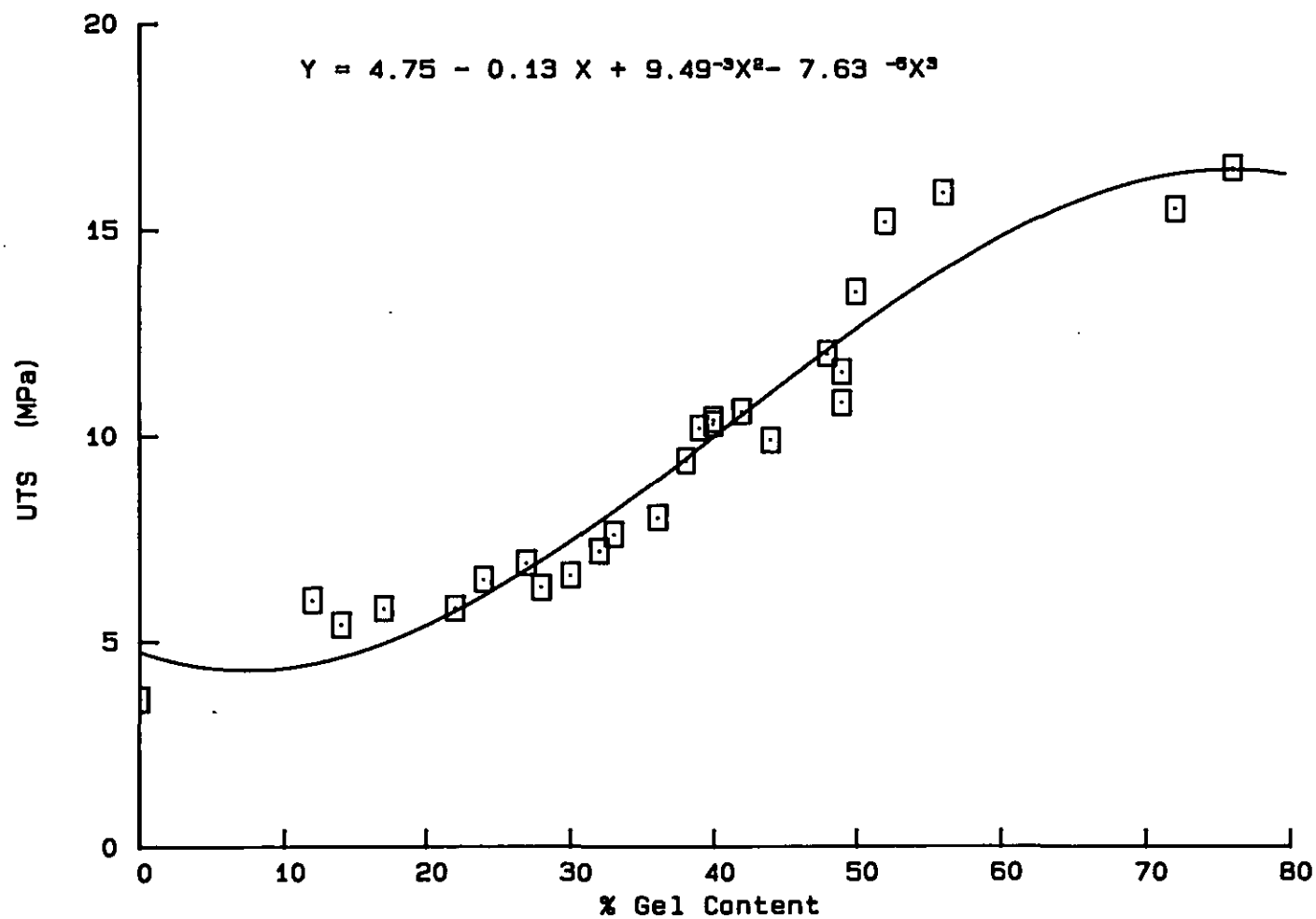
Figure 3.8 Relation between gel content and UTS at 130 C

TABLE 3.2

Gel content of formulations with different thermal stabilizers.

SAMPLE	IMMERSION TIME (hr)		
	0	2	4
Pb 0 Z 6020	0	0	0
Pb 2 Z 6020	30	30	38
Ba/Cd/Zn 2 Z 6020	12	22	28
Sn 2 Z 6020	15	26	36

3.2.2.2. EFFECT ON MECHANICAL PROPERTIES.

Figure 3.9 and Table I.5 (Appendix I) present the results of mechanical properties at room temperature.

It can be seen in Figure 3.9 that the formulation containing lead stabilizer (formulation 2 Table 2.4) shows a slight increase in tensile strength with respect the immersion time, but the difference compared with the sample without silane is marked. The formulation containing Ba/Cd/Zn stabilizer (formulation 4) initially showed low properties, probably due to poor fusion, however, when the sample was immersed, showed an increase in both the elongation and ultimate tensile strength.

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TENSILE PROPERTIES AT ROOM TEMPERATURE

Figure 3.9 Dependence of the UTS on crosslinking time for samples containing 2 phr of Z 6020 and different thermal stabilizers

Pb 0 Z6020 ── Pb ──*── Ba/Cd/Zn ──□── Sn

The sample stabilized with Sn (formulation 5), also showed an increase in properties specially in the ultimate tensile strength.

The other aspect that was evaluated was the colouration of the samples. The formulations containing lead showed an intense yellow colour, the formulations stabilized with Sn and Ba/Cd/Zn had a slightly yellow colour.

From the previous experiment, four formulations were selected to evaluate the tensile properties at $130^{\circ}C$, as well as gel content. The results appear in Figure 3.10 and Table I.6 (Appendix I).

In these tables and in Figure 3.10 it can be seen that the formulation containing lead stabilizer showed a substantial improvement in properties even before immersion, because before immersion the sample has a high gel content.

The sample containing Ba/Cd/Zn showed a slight improvement in properties, but the sample stabilized with Sn showed a significant increase in tensile strength and elongation with increasing immersion time, indicating that the crosslinking reaction was taking place.

The sample stabilized with Sn had a low gel formation before immersion. It is believed that this low value could be because the reactivity of PVC is higher with the stabilizer than with the aminosilane, so the grafting reaction of the aminosilane which takes place is

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TENSILE PROPERTIES AT 130°C
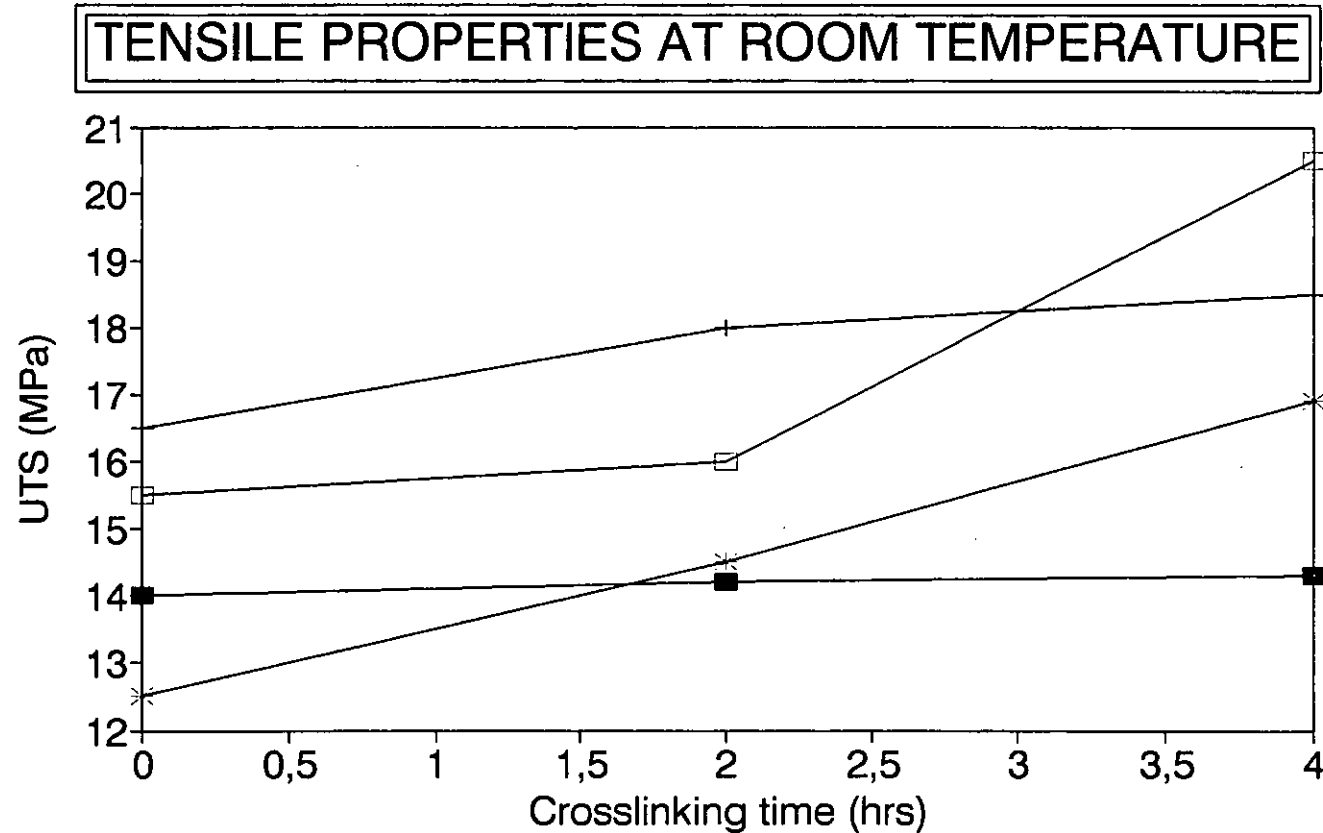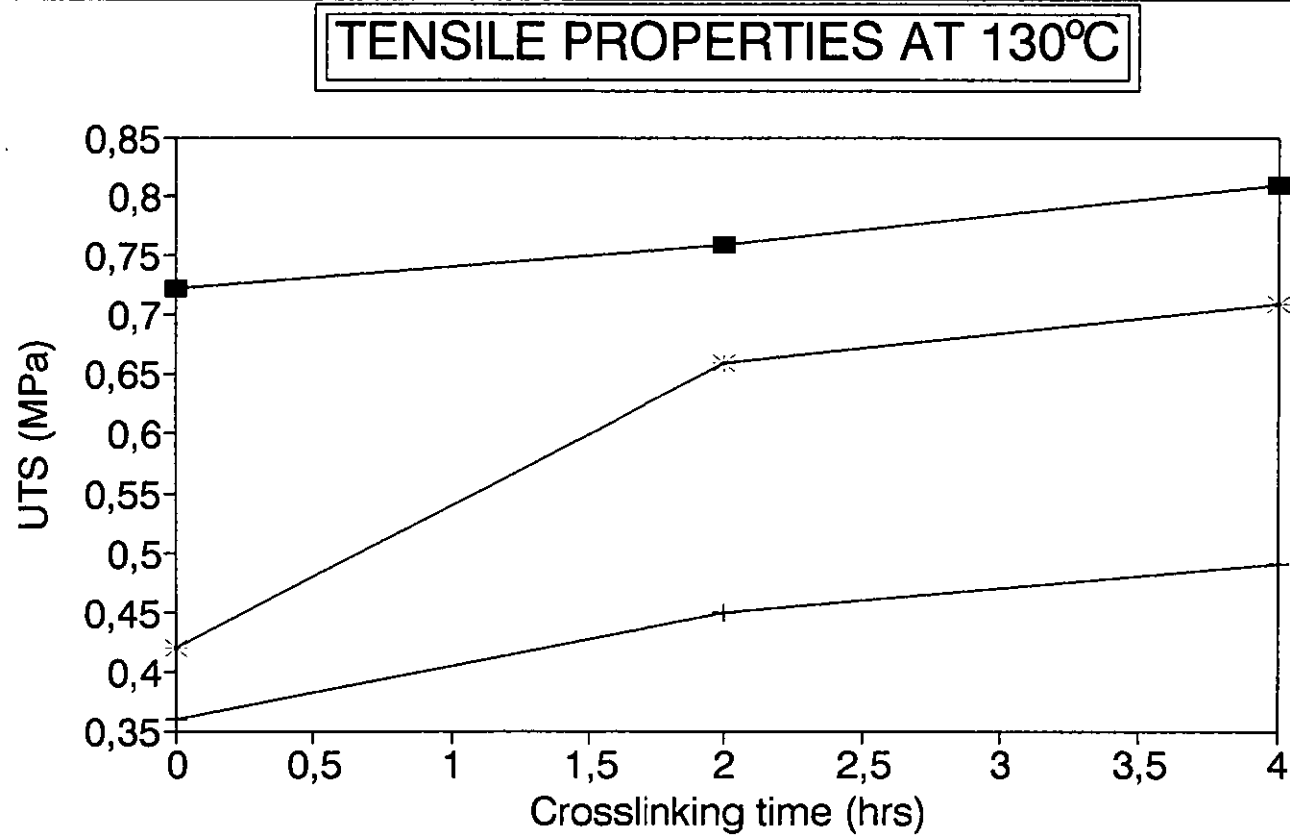
Figure 3.10 Dependence of the UTS on crosslinking time for samples containing 2 phr of Z 6020 and different stabilizers

less extensive. These results could be contradictory because tin compounds are silanol condensation catalysts, but we have to remember that these experiments, i.e., the fusion of the PVC, were carried out in a closed chamber, where possibly the water content is low, avoiding the crosslinking reaction , but after immersion the PVC had high gel content, similar than the obtained with lead stabilizer.

The barium/cadmium/zinc and tin stabilizers look more promising than lead, when 2 phr of aminosilane were used. With these stabilizers is possible to reduce gel formation during processing. Also when lead stabilizer were used some degradation took place and specially when tin stabilizer were used the degradation was less extensive.

In two Dow Corning[153,155] patents it was suggested that lead stabilizers are better for producing high gel content, but according to our results it appears that the tin stabilizers could be a good possibility, because the gel formation is low after processing, and the properties can be improved by immersion in water plus catalyst.

3.2.2.3. THERMAL STABILITY OF COMPOUNDS.

In view of the importance of processing without premature crosslinking and/or degradation, this study was carried out to evaluate under dynamic conditions the effect of different thermal stabilizers and different levels of aminosilane on processing. The formulations that appear on table 2.4 were selected for this purpose.

Table 3.3 presents the results of the dynamic stability test carried out using a Brabender torque rheometer for compounds containing different thermal stabilizers and different levels of aminosilane. The onset of degradation is the time when the torque increases suddenly.

From Figure 3.11 it can be seen that when the aminosilane concentration increases the stability time decreases, or the crosslinking reaction starts earlier. When the lead stabilizer concentration was increased the onset of degradation was slightly delayed. When the lead stabilizers were used, the higher the aminosilane concentration the shorter the period for a controlled processing operation.

When the Ba/Cd/Zn stabilizer was used, the sample was completley black after 12 minutes, and the torque increased slightly (Figure 3.12).

On the other hand, (Figure 3.13), when 1.5 phr of the tin stabilizer was used, the torque did not show an increase, indicating that the crosslinking reaction probably did not occur. However, the colour of the PVC after 25 minutes was black.

When the quantity of tin stabilizer was increased to 3 phr. the torque curve was similar to that in Figure 3.13, but after 33 minutes the PVC was only slightly orange, indicating that the thermal stability had been improved .

Figure 3.11 Thermal stability of samples containing different level of lead stabilizer and aminosilane

Figure 3.12 Thermal stability of samples containing Ba/Cd/Zn
stabilizer and aminosilane

■ Ba/Cd/Zn 4,Z 6020 2

Figure 3.13 Thermal stability of samples containing a Sn
stabilizer and aminosilane
—■— Sn 1.5, Z 6020 2
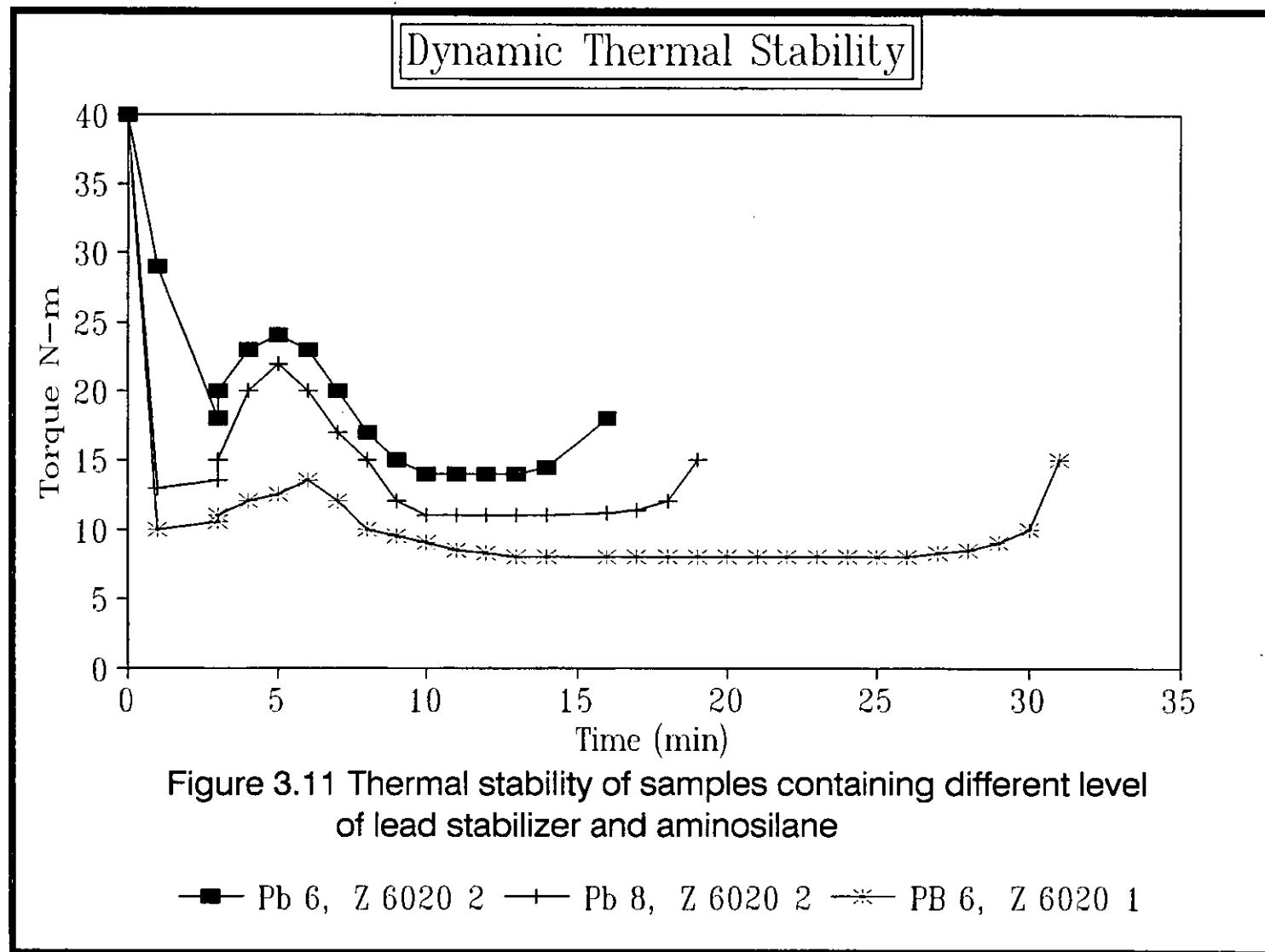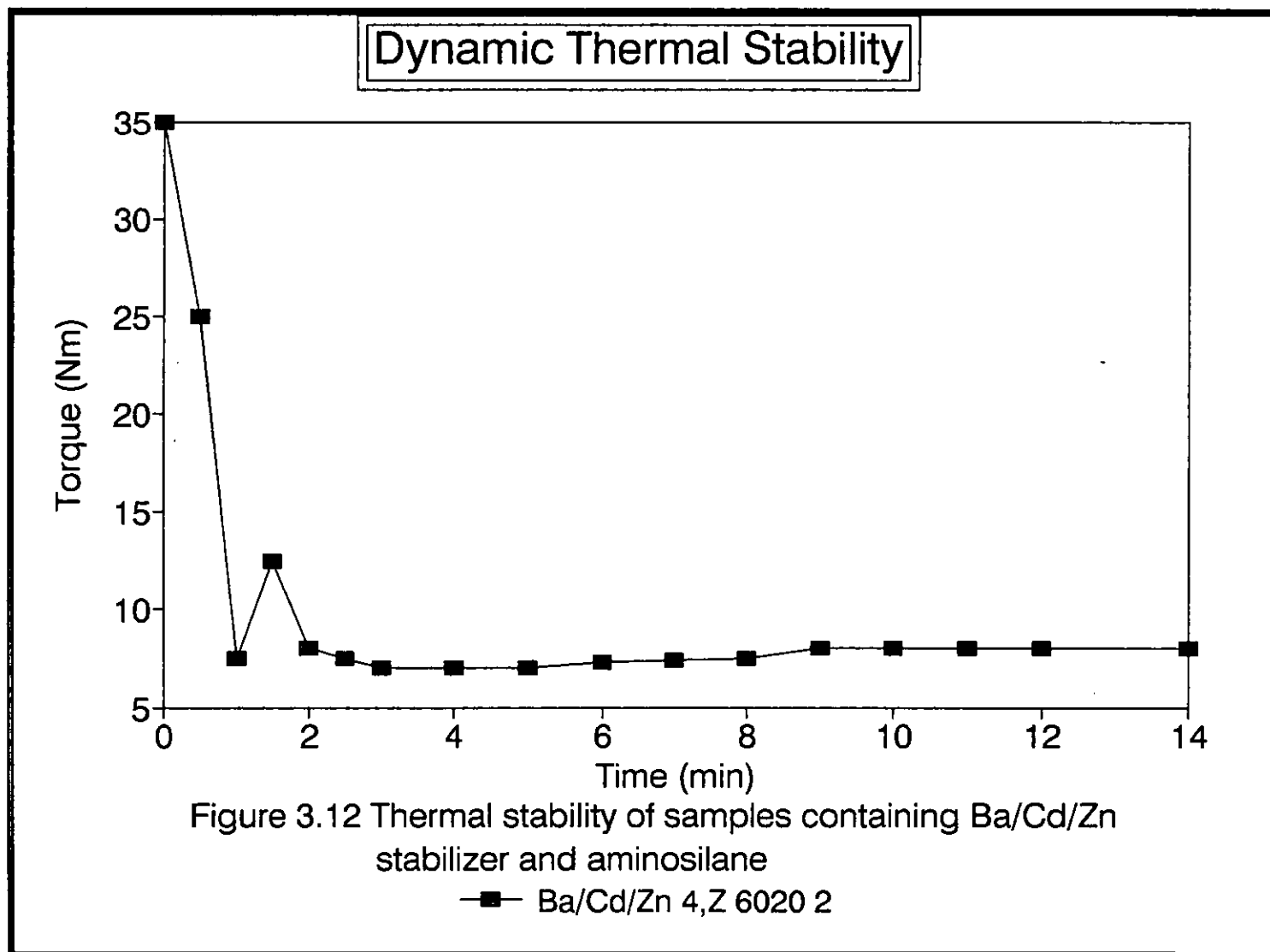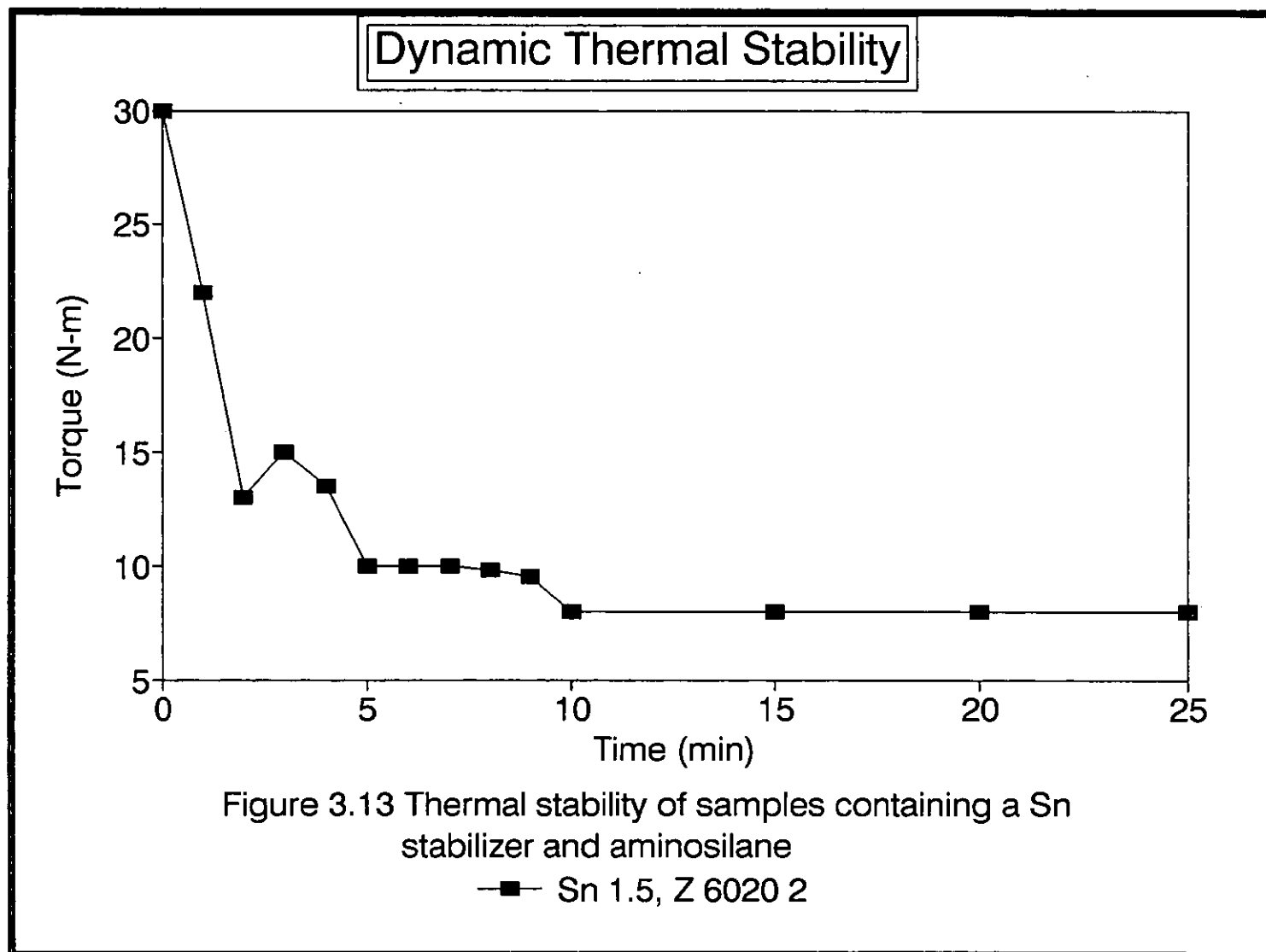
From these results it is seen that, under dynamic test, conditions the lead stabilizer promotes the crosslinking reaction more than the Ba/Cd/Zn and Sn stabilizers. With these latter stabilizers is possible to extend the processing time, but the best results were obtained using a tin stabilizer.

3.2.2.4. SELECTION OF TIN STABILIZER.

From the results of gel formation and thermal stability, it was decided to continue working with tin stabilizers , since they extended processing time without degradation and reduced gel formation, although they still produce some discolouration. The next experiment was conducted in order to find a suitable stabilizer capable of reducing the polymer discolouration. For this, the dry blends (formulations 1,2,4,and 5 from Table 2.6) were roll milled and then compression moulding. It is possible to follow the discolouration by visual appearance after both milling and moulding.

After compression moulding the stabilizer performance was assessed. By comparing the formulations 1,2,4 and 5 from Table 2.6, it is possible to rank the stabilizer performance in the following order of stability:

T 192 > T 184 > T 486 >> T 55

It was seen that formulations (3 and 6) containing calcium steareate (CaSt) lubricant had better colour and

were less degraded, than the formulations without, so this lubricant improves the stability to some extent. When the calcium stearate concentration was increased above 1 phr the stability was not improved further.

When the dry blends were processed on the two roll mill at 145° C they stuck to the roll mill, and when the temperature was reduced to 125° C the problem disappeared. When CaSt was added to the formulation, the processability at 145°C was improved, the sticking problem being avoided. In the formulations containing different levels of CaSt it was not possible to distinguish any differences in colour for the formulations tested.

The formulations containing the stabilizers T 192, T 184 and T 486 did not produce gel and the formulation stabilized with T 55 produced 5-8 % gel after compression moulding. Taking all these facts into account, the stabilizer Stanclere 192 was selected and 1 phr CaSt concentration was added for subsequent work.

The stabilizers containing sulphur in their structure seemed to be the best for avoiding premature crosslinking and degradation. It appears that the more reactive the stabilizer, the more difficult it is for the aminosilane to graft onto the PVC. It is suggested that if we use a highly reactive stabilizer, it will have a competitive grafting reaction with the aminosilane, and thus may delay the grafting reaction of the aminosilane. However there will still be available sites on the PVC molecule to react with the crosslinking agent.

TABLE 3.3

Thermal Stability of formulations containing different thermal stabilizer, and 50 phr of plasticizer.

Formulation		degradation onset (min)	colour
TBLS	4		
DBLS	2	31	Dark orange
Z 6020	1		
TBLS	4		
DBLS	2	15	Dark orange
Z 6020	2		
TBLS	5		
DBLS	3	18	Orange
Z 6020	2	25	Black
BaCdZn	4		
TF	1	12	Black
Z 6020	2		
T 831	1.5	19	Brown
Z 6020	2	30	Black
T 831	3	24	Slightly orange
Z 6020	2	33	Orange
Z 6020	2	8	Black

3.3 EFFECT OF PROCESSING CONDITIONS ON CROSSLINKING.

In order to have a satisfactory crosslinking process it is necessary to control the processing stage and in this way avoid premature crosslinking.

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The samples used in this study were stabilized with lead and contained two different concentration of aminosilane. Table 2.5 shows the formulations.

3.3.1. ROLL MILL MIXING AND COMPRESSION MOULDING.

It is apparent from the Figure 3.14 that the crosslinking reaction occurs during the grafting process on the roll mill. This figure shows the effect of different milling times on gel content for samples containing 5 phr of aminosilane that were roll milled at 125°C and 140°C it can be seen that by increasing the milling time an increase in gel content take place. Figure 3.15 shows that the pressing time also has a notable effect on increasing the gel content. The longer the compression moulding and the the milling time, the higher the gel content of the samples. This suggest that is very important to control the processing conditions in order to avoid premature crosslinking which is undesirable as it occurs during the processing stage.

Table 3.4 present the results of gel content for different milling times for samples containing 2 phr of aminosilane, and Table 3.5 presents the results of gel content for different pressing times for samples that were previously milled at 125°C for 3 and 5 minutes. The values of gel content obtained were lower than those obtained with 5 phr of aminosilane , and again increasing either the milling or pressing time produced an increase in gel formation. Even though a low level of aminosilane was used the samples showed high gel contents.

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TABLE 3.4

Effect of milling time and temperature on gel formation for samples containing 2 phr of aminosilane.

Milling time(min)	$125^{\circ}C$	$140^{\circ}C$
2	5	11
3	12	20
5	15	22
7	18	25
9	20	27
10	22	28

TABLE 3.5

Effect of pressing time on gel content for samples that were milled at two different times

Pressing time(min)	3 min	5 min
0	12	20
2	14	22
4	16	25
8	19	28
10	21	30

Samples with different processing conditions, containing 5 phr of aminosilane (Z-6020) were immersed in the crosslinking emulsion containing 5 percent catalyst for various times. Figures 3.16 and 3.17 show the effect
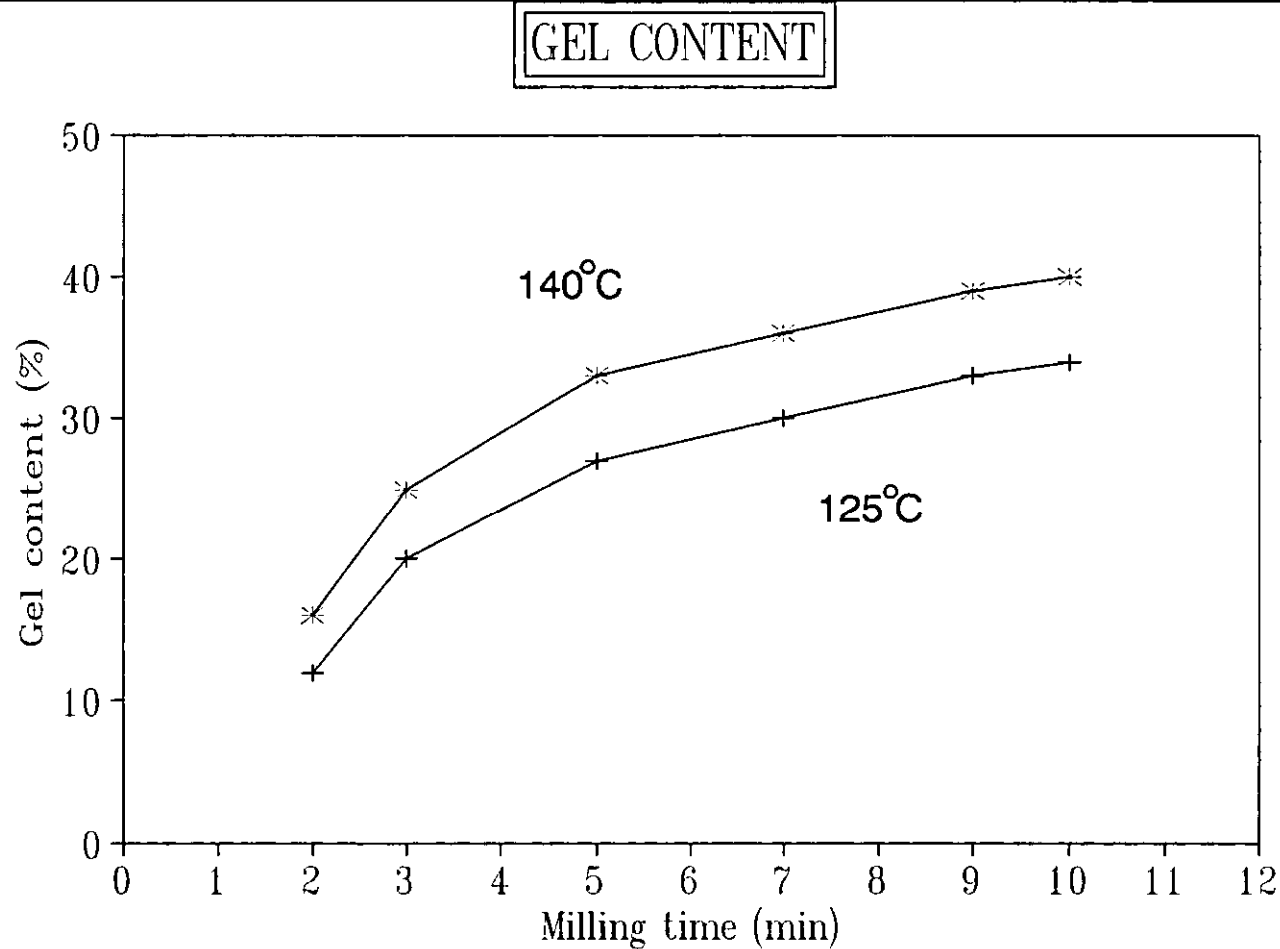
128

Figure 3.14 Dependence of the gel content on milling time
at two different temperatures
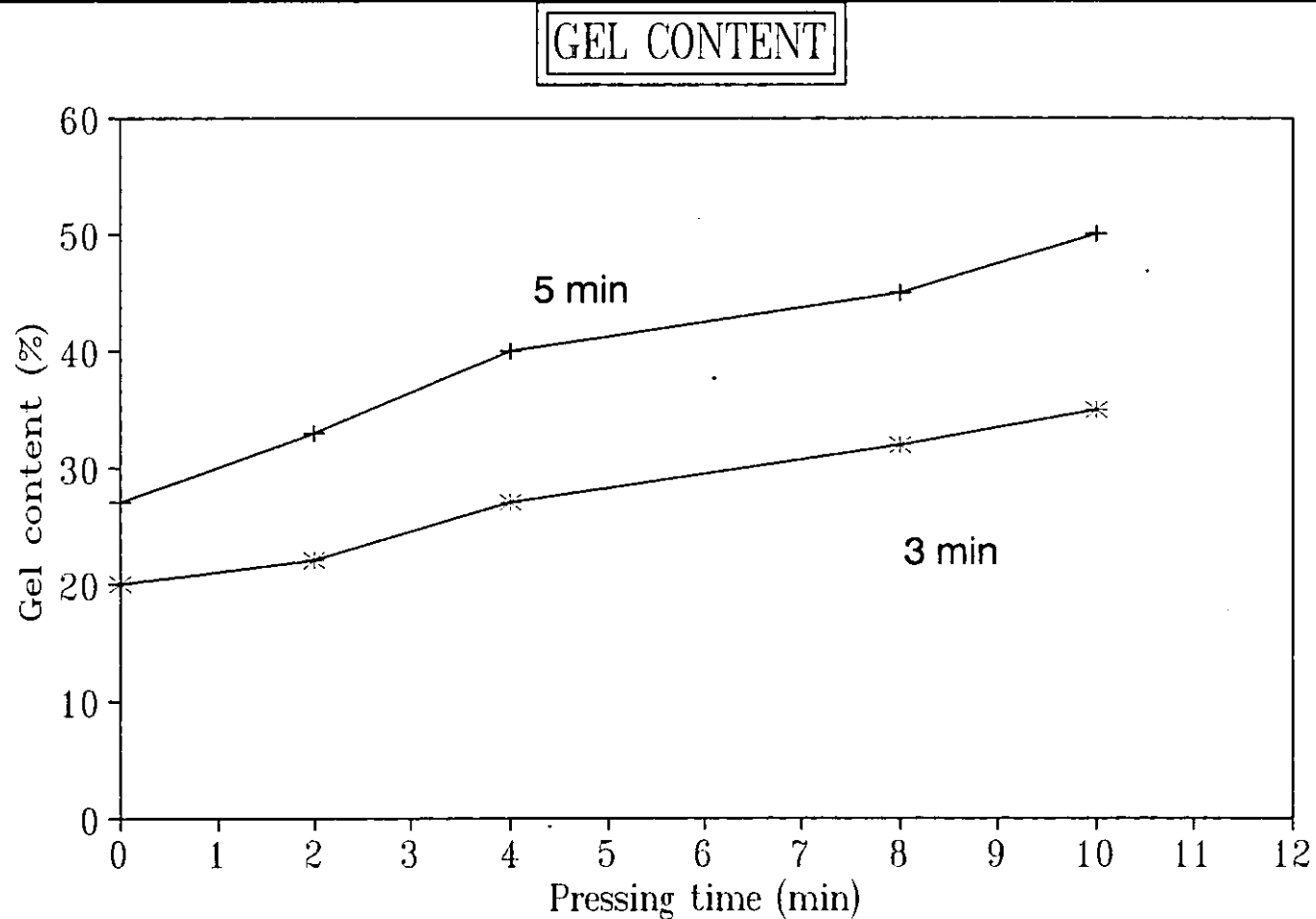
Figure 3.15 Dependence of the gel content on pressing time for samples milled at two different times

of immersion time on the percentage of insoluble material. From the figures it can be seen that the gel content increases on increasing the crosslinking time until it tends to reach an optimum, which is approximatley 4 hours. It is worth mentioning that the thickness of the pressed samples was approximately 2 mm.

Perhaps the most important result obtained from these graphs, is the fact that, before immersion the PVC showed a considerable amount of gel present (27 -45%) depending on the processing time.

From these results it is seen that gel is present after milling and before compression moulding, 20 and 27% for milled samples at 125°C for 3 and 5 minutes respectively. The formation of gel during milling could be due to the fact that there is sufficient atmosphere humidity to cause crosslinking in the grafted PVC, even at low temperatures (125°C).

After compression moulding the milled samples at high temperatures , a further increase in gel content is produced. An increase from 20 to 27% is observed for samples that were milled for 3 minutes and then pressed for 10 minutes. The gel content of samples that were milled for 5 minutes increased up to 50% after pressing for 10 minutes . The longer the milling time the higher the gel formation after the same pressing time. This suggests that by increasing the milling time more aminosilane is grafted onto the PVC and consequently the gel content is higher.
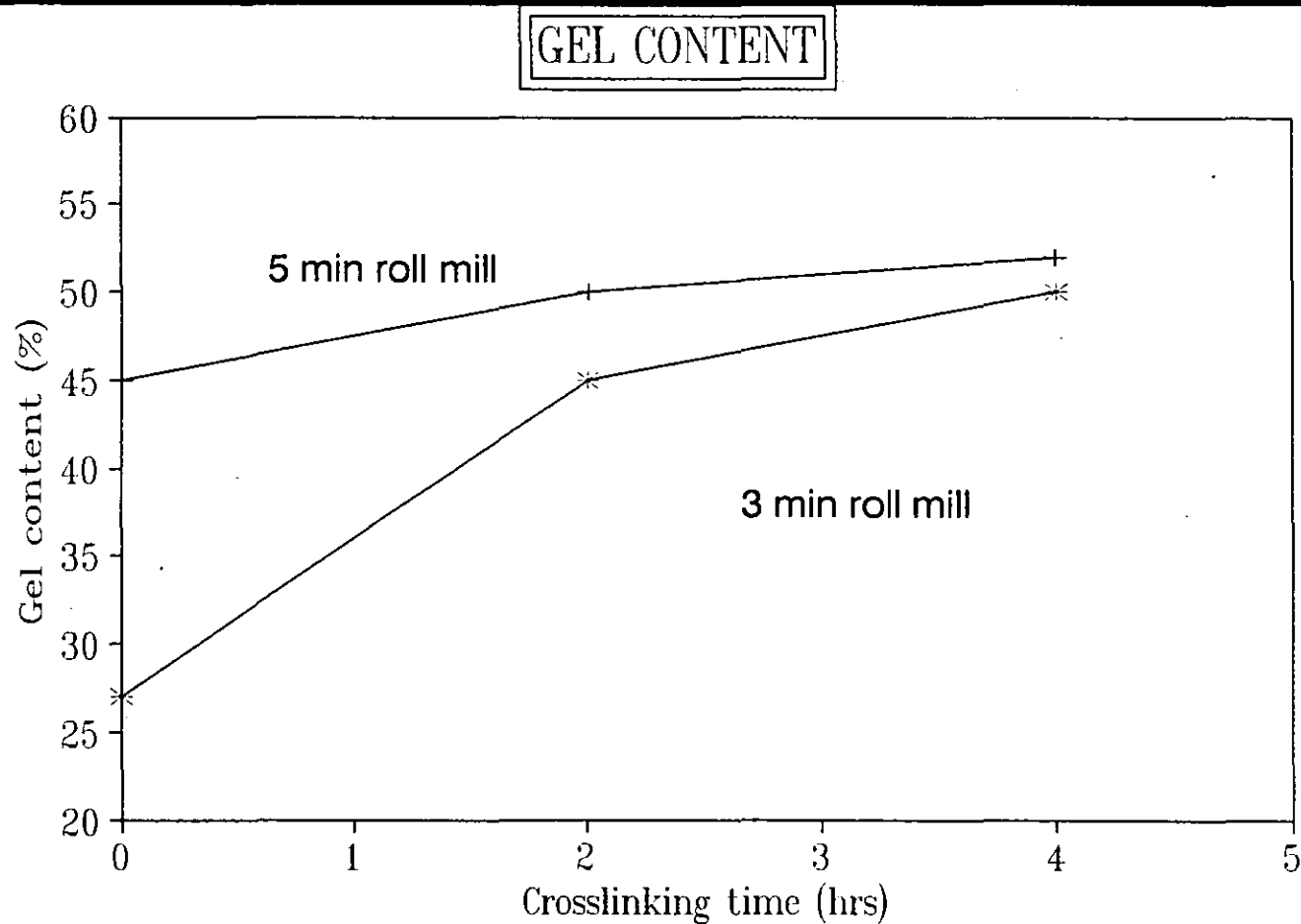
Figure 3.16 Dependence of the gel content on crosslinking time for milled
samples at two different times and pressed 8 minutes
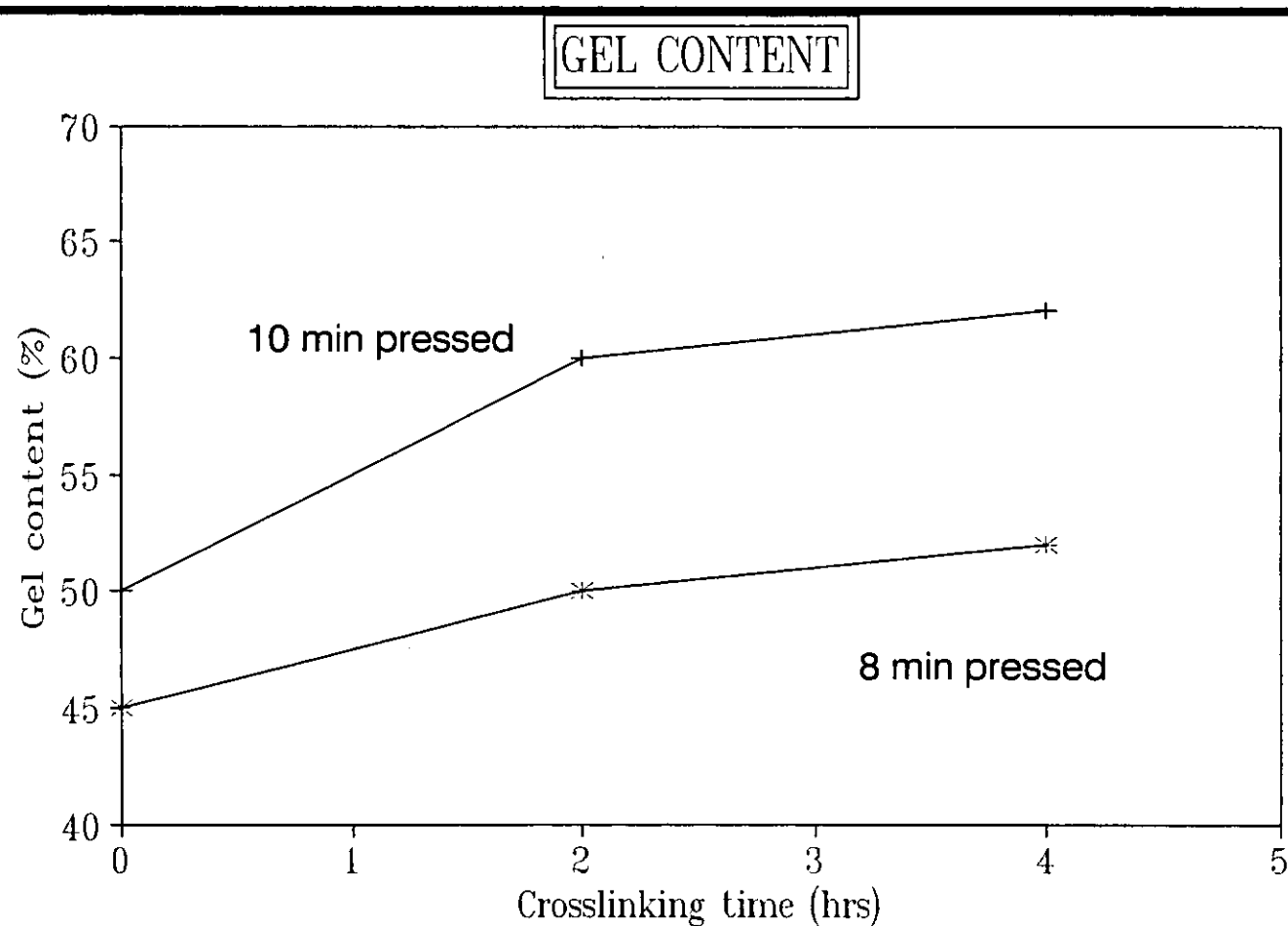
Figure 3.17 Dependence of the gel content on crosslinking time for milled samples 5 min. and pressed at two different times

3.3.2. MECHANICAL AND THERMAL PROPERTIES.

The tensile strength and elongation at break at room temperature of both the uncrosslinked and crosslinked PVC were determined. Table 3.6 shows the results obtained. It can be noticed that there is an increase in the ultimate tensile strength (UTS) for the formulation containing the crosslinking agent and a decrease in elongation. These results support the conclusion that PVC is effectively crosslinked. Nevertheless it was not possible to observe differences between the samples with different crosslinking times.

The softening point, was also measured, and Table 3.6 presents the results obtained. The graphical results are presented in Figures 3.18 and 3.19. Figure 3.18 shows the penetration curve for samples with and without aminosilane that have been milled for 5 minutes and pressed for 10 minutes, and for a sample with aminosilane that only has been milled 5 minutes at 125°C. It can be seen that even before pressing the sample possesses a high softening point (120°C) compared with the formulation without crosslinking agent which has a softening point of 95°C . If we go back to Figure 3.10 we can observe that the sample before pressing showed a gel content of 27-30%. This amount of gel is enough to give a PVC with enhanced properties, but we have to recall that gel formation is undesirable at the processing stage. However it could be a good sign, that it is possible to have an improvement in penetration resistance even at low gel contents.

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On the other hand it is seen (Figure 3.18) that even before immersion the improvement in the penetration resistance is considerable.

PVC with a gel content of 50-60% has a plateau between 120-160°C in the penetration curve, indicating that the material has a higher thermal resistance in this temperature interval (Figure 3.19).

TABLE 3.6

Mechanical properties at room temperature and thermal properties of samples with different processing conditions containing 5 phr of aminosilane.

RMT (min)	CMT (min)	XLT (hr)	UTS MPa	E %	SP C$^\circ$
3	8	0	24	275	150
		2	25	255	165
		4	26	255	163
5	8	0	24	255	156
		2	25	270	166
		4	25	265	165
5	10	0	25	210	160
		2	25	210	160
		4	26	200	165
*5	10	0	20	220	95

*Sample without aminosilane

RMT   Roll Milling time

CMT   Compression Moulding time   SP Softening point.

XLT   Crosslinking time   E Elongation

UTS   Ultimate Tensile Strength
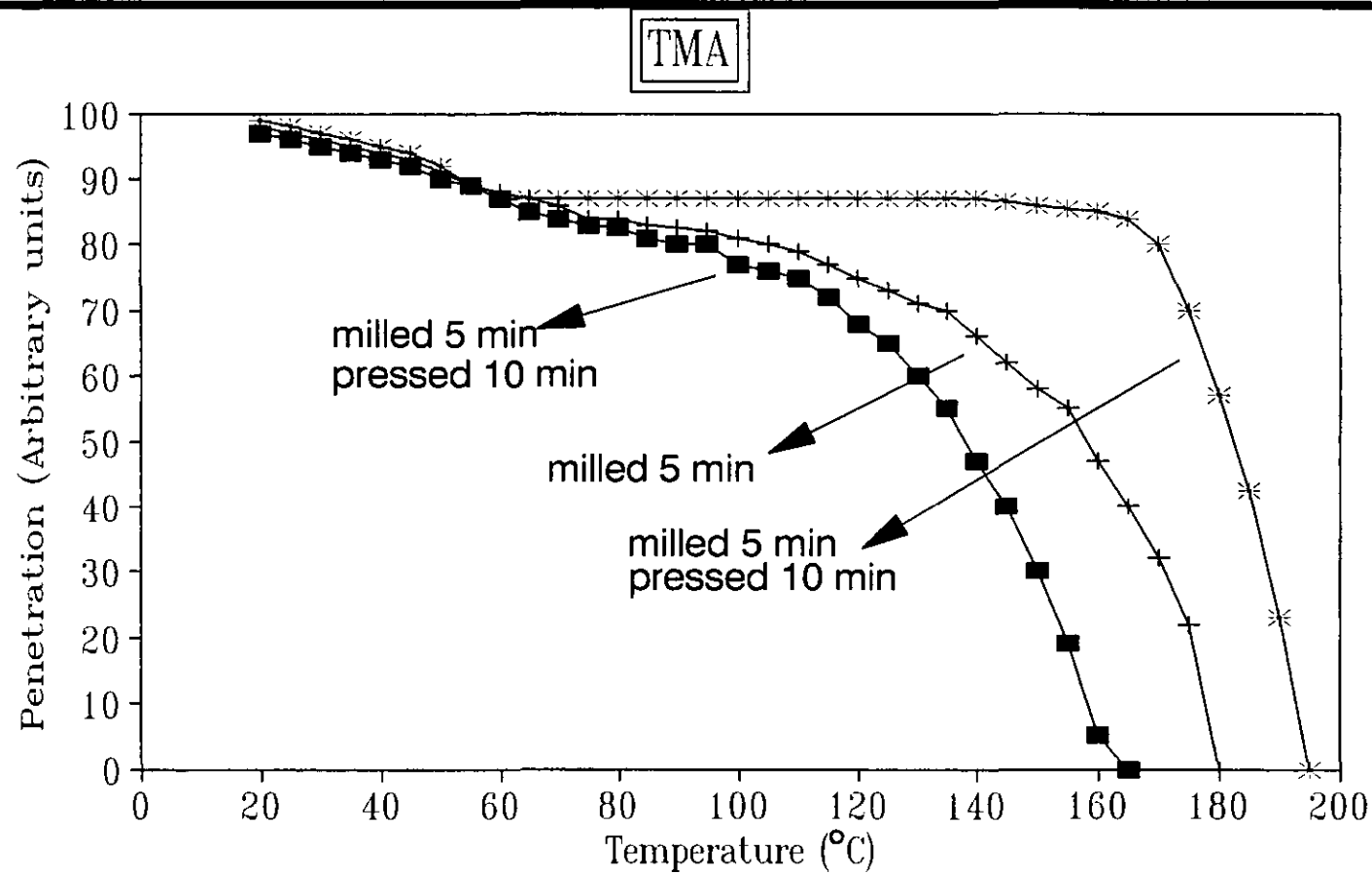
Figure 3.18 Penetration resistance for samples with and without aminosilane before immersion

0 phr Z 6020 —+— 5 phr Z 6020 —※— 5 phr Z 6020

Figure 3.19 Penetration resistance of crosslinked PVC

crosslinked 2 hrs ——×—— crosslinked 4 hrs
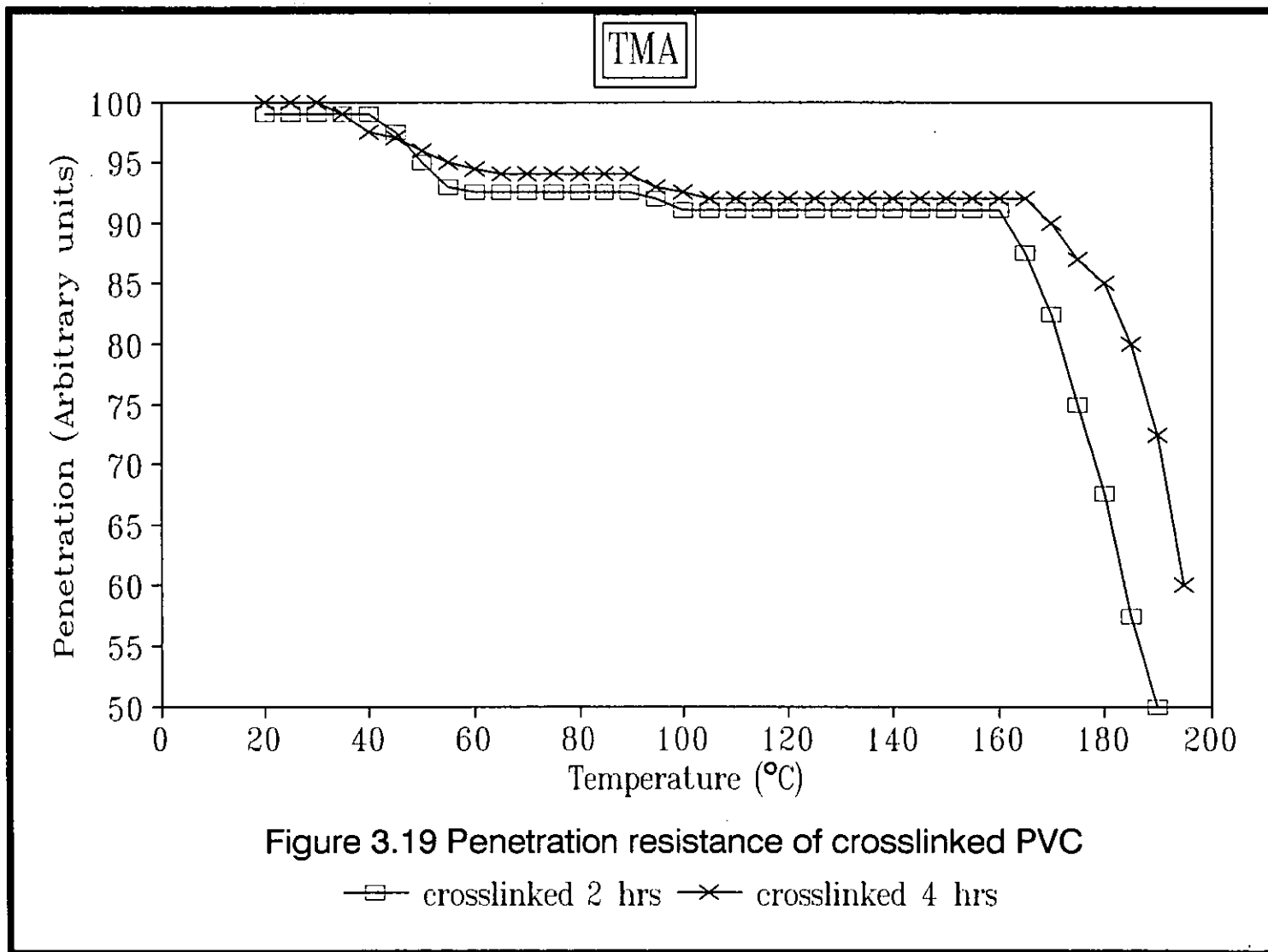
3.4 EFFECT OF PROCESSING AND CROSSLINKING VARIABLES ON MECHANICAL PROPERTIES.

In order to investigate the effect of crosslinking agent concentration, crosslinking time and moulding time, a factorial experimental design 2^3 was selected, (Appendix II). The crosslinking agent concentration varied from 2 to 6 phr, the crosslinking time from 2 to 4 hours and the compression moulding from 5 to 10 minutes.

The treatment combinations in this design are shown in Table 3.7 . By convention the low and high level of each variable are denoted by "-" and "+", respectively. The same Table presents the results of thermomechanical and tensile properties at 130°C. From these results we can analyze the effect of the different variables. Table 3.8 presents the average effect of each variable on properties.

The analysis of results was carried out using the method of Yates.[184] The results of this analysis are presented in Appendix II, as well as the analysis of variance of these data.

The variable that has the most pronounced effect is the crosslinking agent concentration, followed by the crosslinking time and finally the pressing time, so it is very important to have careful control of crosslinking agent concentration. This suggests that it could be possible to control the material properties by controlling the concentration of crosslinking agent.

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TABLE 3.7

Experimental design and results of thermomechanical and tensile properties at 130°C.

RUN	Z6020	XLT	CMT	UTS MPa	%E	SP
1	−	−	−	0.93	190	150
2	+	−	−	1.67	200	160
3	−	+	−	0.96	190	140
4	+	+	−	1.98	200	179
5	−	−	+	0.88	200	135
6	+	−	+	1.40	200	162
7	−	+	+	0.92	170	152
8	+	+	+	1.94	200	184

XLT , CMT, UTS, SP. as in table 3.6.

However , the analysis of variance shows that only the effect of the aminosilane concentration is significant at 5 percent for all the measured properties; the crosslinking time was significant at 5 percent for the softening point and for the UTS , but the compression moulding time had no significant effect.

On the other hand the aminosilane concentration and the crosslinking time showed an interaction for both, the UTS and softening point. The effect of these variables was positive, i.e an increase in these variables produce an increase in UTS and in the softening point. The elongation at break was not modified significantly.

TABLE 3.8

Analysis of the effect of different processing variables on properties.

Effect	UTS	%E	SP
z6020	+0.83	+12.5	+27.0
XLT	+0.225	-7.5	+12.0
CMT	-0.095	-2.5	+1.0

3.5 CONCLUSIONS

Plasticized PVC is readily crosslinked when formulated with an aminosilane. Examination of Table 3.1 and figure 3.1 reveals that PVC compounds becomes more crosslinked when a higher dose of the crosslinking agent is used. However it is worth mentioning that before immersion the samples contained some gel with a further increase of gel occurring upon immersion in water containing the catalyst.

The crosslinking produced an improvement in mechanical properties, specially at high temperature. Both the tensile strength and the elongation a break were improved. This improvement is most clearly observed at high temperatures, because at room temperature there is a cooperation between a physical network, produced by annealing of the crystallites and the covalent network produced purely by chemical crosslinking. As these samples were crosslinked at high temperatures (80°C) , some annealing took place, but as the temperature rises, these crystallite begin to melt, and only the permanent network contributes to improve the properties.

It was possible to establish a relationship between the gel content and the ultimate tensile strength. It was found that there is a unique relationship between UTS at 130°C and the gel content irrespective of processing conditions, with UTS starting to increase sharply around 30% gel content, and reaching a plateau at about 70%.

The investigation of the thermal stability of compounds containing the crosslinking agent, showed that the compounds containing lead stabilizers (TBLS/DBLS) are easily crosslinked during processing, on the contrary compounds containing dibutyl tin mercaptide as stabilizer showed better processability, and less degradation than a a lead based system or a one containing Ba/Cd/Zn carboxylate.

Furthermore, the tin stabilized compound had relatively low gel formation after processing. This fact seems to be contradictory , because tin compounds are reported as silanol condensation catalyst and should promote the crosslinking reaction. However, Tin stabilizer reacts with the PVC molecules reducing the grafting of the aminosilane and indirectly gel formation.

The penetration resistance, which is an important technological property, for instance in cable insulation, is improved by crosslinking, and even low levels of gel (20%) might be enough to give an improvement up to 120°C, which perhaps is important for practical applications.

It was found , under the processing conditions used, that not only the grafting reaction of the aminosilane onto the PVC molecule occurs but also the crosslinking reaction . Even the atmospheric humidity is enough to produce crosslinking.

CHAPTER 4
RESULTS AND DISCUSSION
EXTRUSION STUDIES

4.1 INTRODUCTION.

The main objective of the extrusion experiments was to produce a grafted PVC without gel formation during processing, to avoid or reduce the degradation of the polymer; and subsequently crosslink the grafted PVC in a separate process.

The grafting of the aminosilane was carried out during processing in an extruder. In a preliminary set of experiments two different thermal stabilizers were studied, lead and tin, (formulations Table 2.7). In the second part several factors were studied; tin stabilizer/crosslinking agent ratio, incorporation of lubricants, reprocessing.

4.2 EFFECT OF DIFFERENT THERMAL STABILIZERS.

4.2.1. ON EXTRUSION PARAMETERS.

In order to have a good chemical crosslinking system it is important to have no crosslinking during the processing operation. If this occurs the polymer stops flowing and could cause serious problems. In these experiments the power consumption and the back pressure were measured. (Table 4.1).

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From this table we can observe that the formulation
stabilized with lead produced   a higher   back   pressure
than the formulation stabilized with tin stabilizer.

TABLE 4.1

Extrusion Parameters

	Temp $^{\circ}$ C	Pressure MPa	Current Amperes
Pb 0 Z 6020	171	9.2	3.8
Pb 2 Z 6020	171	12.7	7.1
Sn T 831 0 Z 6020	171	8.4	3.9
Sn T 831 2 Z 6020	171	11.8	5.2

When the   formulations   containing   aminosilane   were
extruded   a   considerable   increase   in   pressure   was
observed. The power consumption also increased   when   the
aminosilane was present,   but   the   increase   was   more
pronounced in the formulation containing lead.

These results suggest that the crosslinking   reaction
is taking place in the extruder, preventing the PVC   from
flowing easily. In another experiment that was run   using
4 phr of aminosilane and   lead   stabilizer,   the   polymer
flow was stopped completely, and it was very difficult to
pull away the screw.

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When chemical crosslinking systems are going to be used extra care must be taken in order to avoid an uncontrollable reaction that could either damage the equipment, or cause alteration of rheological behaviour which might cause flowing defects.

4.2.2. ON GEL CONTENT OF EXTRUDED SAMPLES.

The results of gel evaluation of the extruded samples confirm that some crosslinking took place during extrusion, explaining the increase in both the pressure and amperage.

The results of gel content are presented in Table 4.2. The formulations containing aminosilane produced gel formation before immersion, this being higher when lead stabilizer was used. The increase in gel content after immersion was considerable.

TABLE 4.2

Gel content of extruded samples.

	Immersion time (Hr)	
	0	2
Pb		
0 Z 6020	0	0
2 Z 6020	20	68
Sn		
0 Z 6020	0	0
2 Z6020	12	58

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If we look back to Figure 3.1 in the previous chapter, it is seen that the gel content in the formulation containing 2 phr of aminosilane and stabilized with lead is less than 40%.

The difference in gel content between extruded and compression moulded samples could be explainable, because the thickness of extruded samples is 0.2 mm and the pressed samples were almost 2 mm thick. The crosslinking process by immersion is a diffusion process, so the thicker the sample, the slower the diffusion rate and the lower the gel formation. Another explanation might be that during the extrusion process the shear stresses will be higher than those produced during compression moulding , and consequently more aminosilane is grafted onto the PVC molecule. Although is more probable that is due to diffusion, because the compressed samples also were under stress during milling.

4.2.3. ON MECHANICAL PROPERTIES.

Tensile test specimens were cut from the extruded samples, crosslinked by immersion in hot water (80° C) containing 5% catalyst, and their tensile properties evaluated at 130°C. Tables 4.3 and 4.4 show the results of ultimate tensile strength and elongation at break respectively. It can be seen that the formulations containing aminosilane showed a considerable increase in tensile strength, and the elongation at break was slightly improved with respect to the samples without aminosilane, but with respect the crosslinking time the increase was not significant.

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It is possible to have a formulation with improved properties either by using tin or lead stabilizer, however the formulation stabilized with tin was more easily extruded, although the samples stabilized with tin still produce gel during the processing.

It is worth mentioning that several extrusion experiments were conducted at different temperatures, trying to overcome the premature gel formation. When low temperatures were used the gel formation was reduced or even zero gel formation was obtained with tin stabilizer, but the mechanical properties were too low, due to poor fusion . It is necessary to work at temperatures high enough to produce good fusion and mechanical properties[185] but low enough to reduce or eliminate gel formation.

TABLE 4.3

Ultimate Tensile Strength at 130°C of extruded samples

Immersion Time(hrs)	0	0.25	0.5	1	2
	UTS MPa				
Pb 0 Z 6020	0.36	0.37	0.37	0.37	0.37
Pb 2 Z 6020	0.69	0.7	0.76	0.80	0.83
Sn 0 Z 6020	0.4	0.4	0.41	0.4	0.4
Sn 2 Z 6020	0.77	0.85	0.95	1.0	1.05

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TABLE 4.4

Elongation at break at 130°C for extruded samples

Immersion Time (hrs)	0	0.25	0.5	1	2
			% E		
Pb 0 Z 6020	160	165	160	160	165
6020	185	195	220	245	245
Sn 0 Z 6020	155	160	160	160	160
Sn 2 Z 6020	200	220	230	240	250

4.3. EXTRUSION TRIAL WITH TIN STABILIZERS.

The objective of this study was to obtain a good chemical crosslinking system without gel formation during the extrusion process. For this several factors were studied. From the results of the evaluation of different tin stabilizers the stabilizer T 192 was selected for the next set of experiments. Formulations that appear in Table 2.8 and 2.9 were used.

4.3.1. EFFECT OF STABILIZER/CROSSLINKING AGENT RATIO ON EXTRUSION PARAMETERS AND GEL FORMATION.

Figures 4.1 and 4.2 present the extrusion parameters for samples containing different levels of aminosilane or stabilizer. From Figure 4.1 we can see that at a fixed aminosilane concentration an increase in tin stabilizer produced a decrease in both the extrusion pressure and amperage, this being an indication that, either the

aminosilane grafting reaction or the crosslinking reaction has been reduced. Palmlöf et al.[183], have suggested that the grafting of organosilanes onto ethylene vinyl copolymers produces molecular enlargement - or even crosslinking. Hjertberg et al.[175] have also pointed out that some molecular enlargement takes place when PVC is crosslinked with triazine derivatives.

Even when large quantities of stabilizer were used the extrusion pressure and amperage were higher than those obtained without aminosilane.

From Figure 4.2. it can be seen that as the aminosilane concentration increases the amperage and the extrusion pressure increase. As large quantities of aminosilane are present the grafting onto the PVC molecules is likely to increase.

Table 4.5 shows the results of gel content determination of extruded samples. From this table we can observe that as the ratio of stabilizer/crosslinking agent (T 192/ Z 6020) increases the gel content decreases, also if the Z 6020 concentration is kept constant at 2 phr, and the T 192 concentration increases from 3 to 5 phr the gel content is 0 %. This increase in stabilizer concentration causes a substantial improvement in thermal stability. On the other hand if we keep the stabilizer concentration (3 phr) constant an increase in Z6020 concentration tends to decrease the thermal stability of the system and to produce gel formation after extrusion and before crosslinking in water.
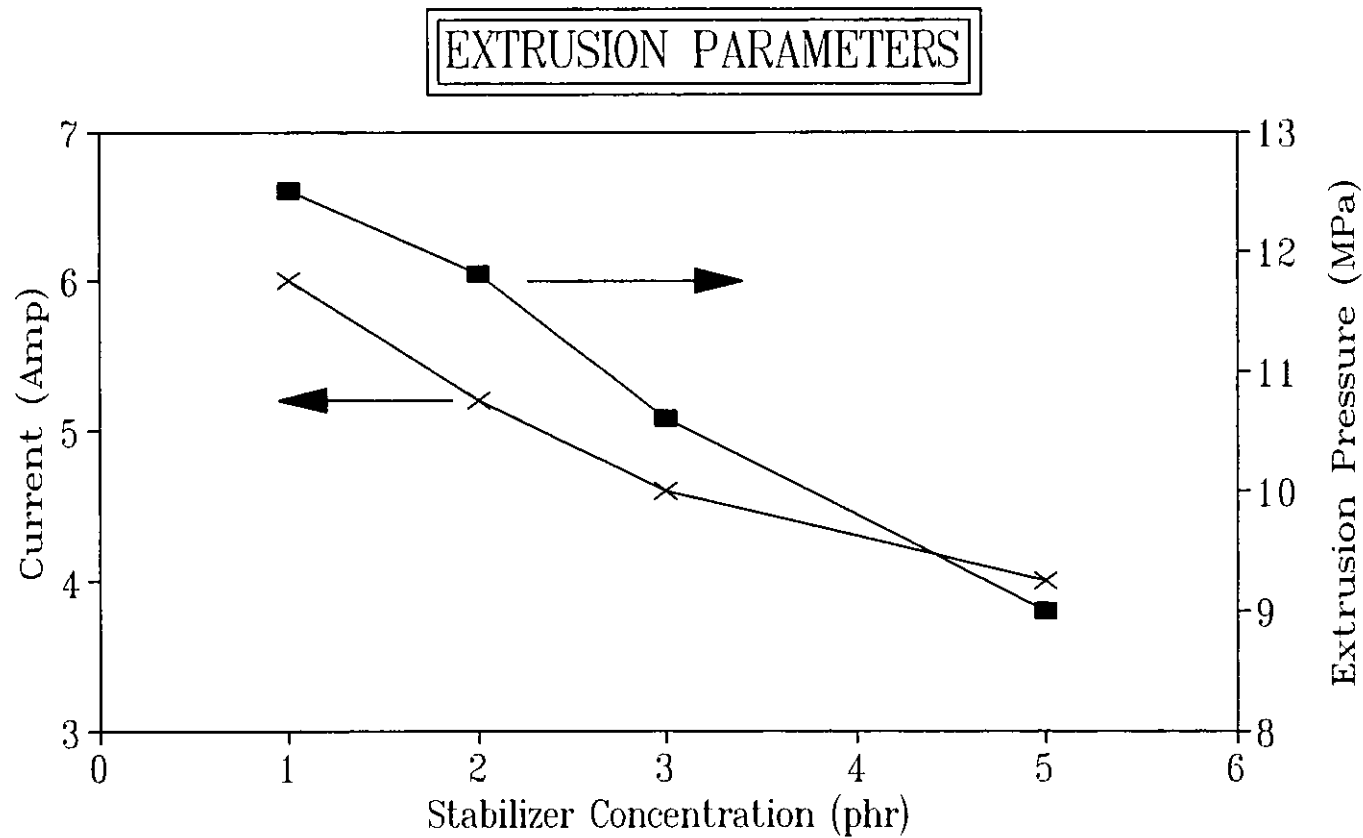
Figure 4.1 Extrusion parameters for a sample containing different
levels of tin stabilizer and 2 phr pf aminosilane
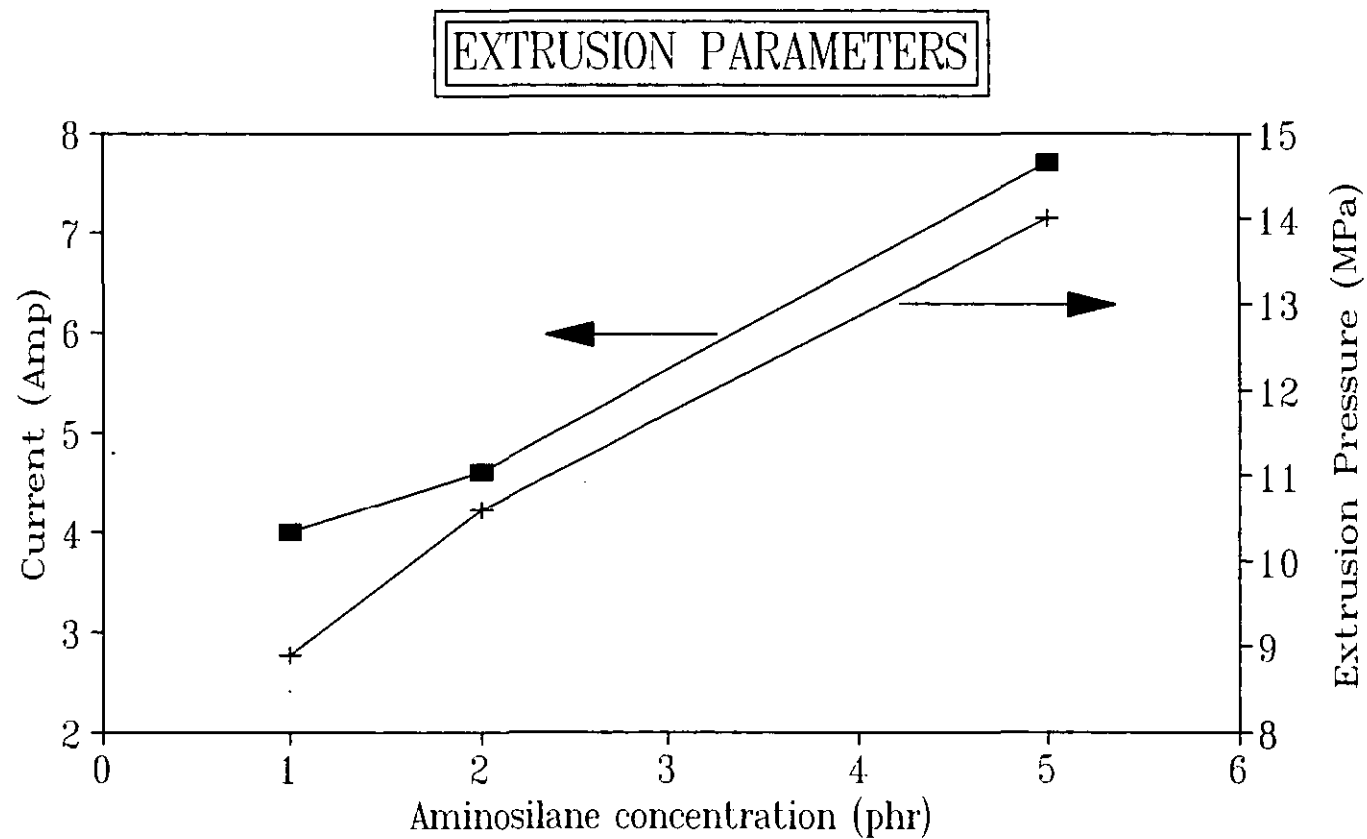
Figure 4.2 Extrusion parameters for samples containing 3 phr of tin stabilizer and different levels of aminosilane

TABLE 4.5

Gel content of extruded samples

Formulation Table 2.8	1	2	3	4	5	6	7
T 192/Z6020 ratio	1/2	2/2	3/2	5/2	3/1	3/5	3/2
Gel Content (%)	<5	<5	0	0	0	10-18	0

The previous gel results confirm that the crosslinking reaction is taking place during the extrusion and the higher the aminosilane concentration and the lower the stabilizer concentration the higher the gel formation . The average molecular weight of the soluble fractions were also measured. Table 4.6 presents the results.

TABLE 4.6

Changes in Molecular Weight Data due to Extrusion

Z 6020 Conc.	$M_n * 10^{-3}$	$M_v * 10^3$	M_v/M_n
1	147	259	1.76
2	161	299	1.85
5	173	335	1.94

From Table 4.6 we can see that both M_v and M_n
increased when the aminosilane concentration increased,
also it can be see that M_v increased relatively more than
M_n. This is what could be expected as larger molecules
have a higher probability of participating in
crosslinking reactions[170]. This results confirm that
some molecular enlargement takes place during processing.
These emphasizes the necessity of avoiding crosslinking
reactions during processing in order to maintain proper
processing properties.

Table 4.7 presents the results of gel content after
crosslinking for 4 hours for formulations containing the
same quantity of Z 6020 (2 phr) and different stabilizers
concentrations.

From this table it can be seen that, when the
concentration of tin stabilizer increased the gel
formation after crosslinking decreased. As mentioned
earlier the tin stabilizer competes with the aminosilane
reducing the grafting efficiency of the aminosilane and
consequently reducing the gel formation. This suggests
that is important to have an adequate
stabilizer/crosslinking agent ratio in order to have an
extrusion process without gel formation, and to have gel
formation after crosslinking.

It is very important to keep the crosslinking agent
concentration as low as possible to avoid gel formation
during extrusion, but to produce enough gel (50-60%)
after crosslinking. With this level of gel a considerable

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improvement in tensile properties is achieved, as reported by Nethsinghe and Gilbert[91], and in the previous chapter Figure 3.8.

On the other hand, as expected, when the aminosilane concentration increased the gel formation increased after crosslinking.

When 5 phr of Z 6020 were used, the extruded sheet contained a lot of bubbles and had a deep yellow colour . When the Z 6020 concentration was reduced to 2 phr the bubble problem disappeared, and a smooth sheet was obtained it still showed a slightly yellow colouration; however it is worth mentioning that the original aminosilane is slightly yellow.

TABLE 4.7

Gel Content of extruded samples containing different levels of stabilizer, before and after crosslinking.

Stabilizer phr	Before Crosslinking	After Crosslinking
1	< 5	28-30
2	< 5	20-25
3	0	18-20
5	0	< 10

Extruded samples containing 3 phr of tin stabilizer (T192) and different quantities of aminosilane were crosslinked at 80° C in water containing 5 % of catalyst. at different periods of time and their mechanical properties evaluated at 130° C. Figures 4.3 and 4.4 show UTS and Elongation at break results respectively. In these two graphs it is again seen, that as the aminosilane concentration and the crosslinking time increase the UTS and elongation also increase. It is interesting to observe in Figure 4.3, that when low level of aminosilane was used (1 phr) the curve seem to reach a plateau after about 4 hours. On the other hand when higher levels were used the UTS continues to increase. On the other hand the elongation tends to reach a plateau after about 4 hours. This behaviour seems reasonable. As crosslinking progresses a more homogeneous network is formed , but when more crosslinking points are introduced a more rigid network will be formed, and consequently it will be unlikely that the elongation will continue increasing.

It appears that when aminosilane is used in formulations containing reactive stabilizers, in this case tin stabilizer, the improvement in properties will be dependent on the ratio of stabilizer/crosslinking agent . The higher the ratio the smaller the improvement in mechanical properties. This is connected with the gel formation and particularly with the competitive grafting reaction during the extrusion process.

Figure 4.3 Dependence of UTS on crosslinking time for extruded samples containing different levels of aminosilane
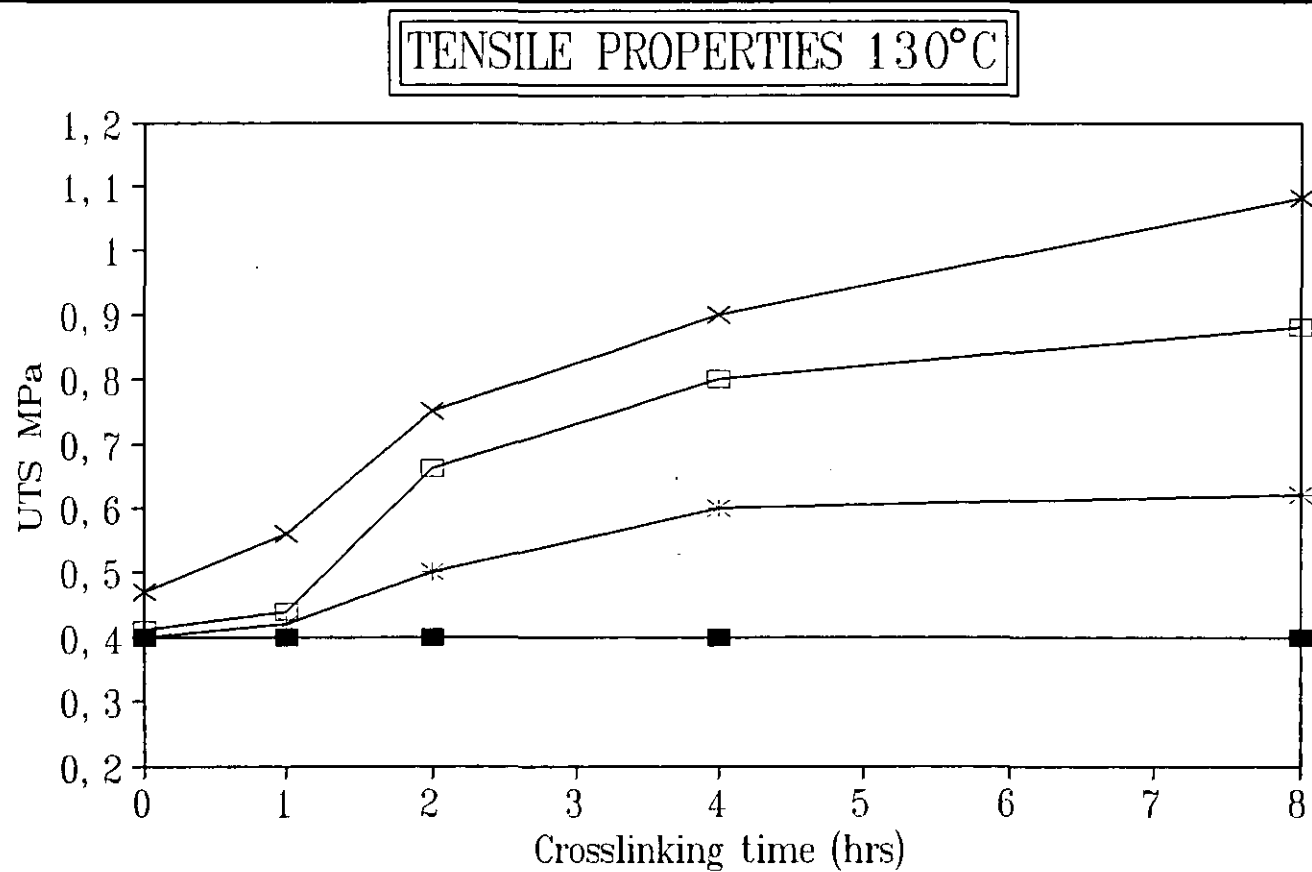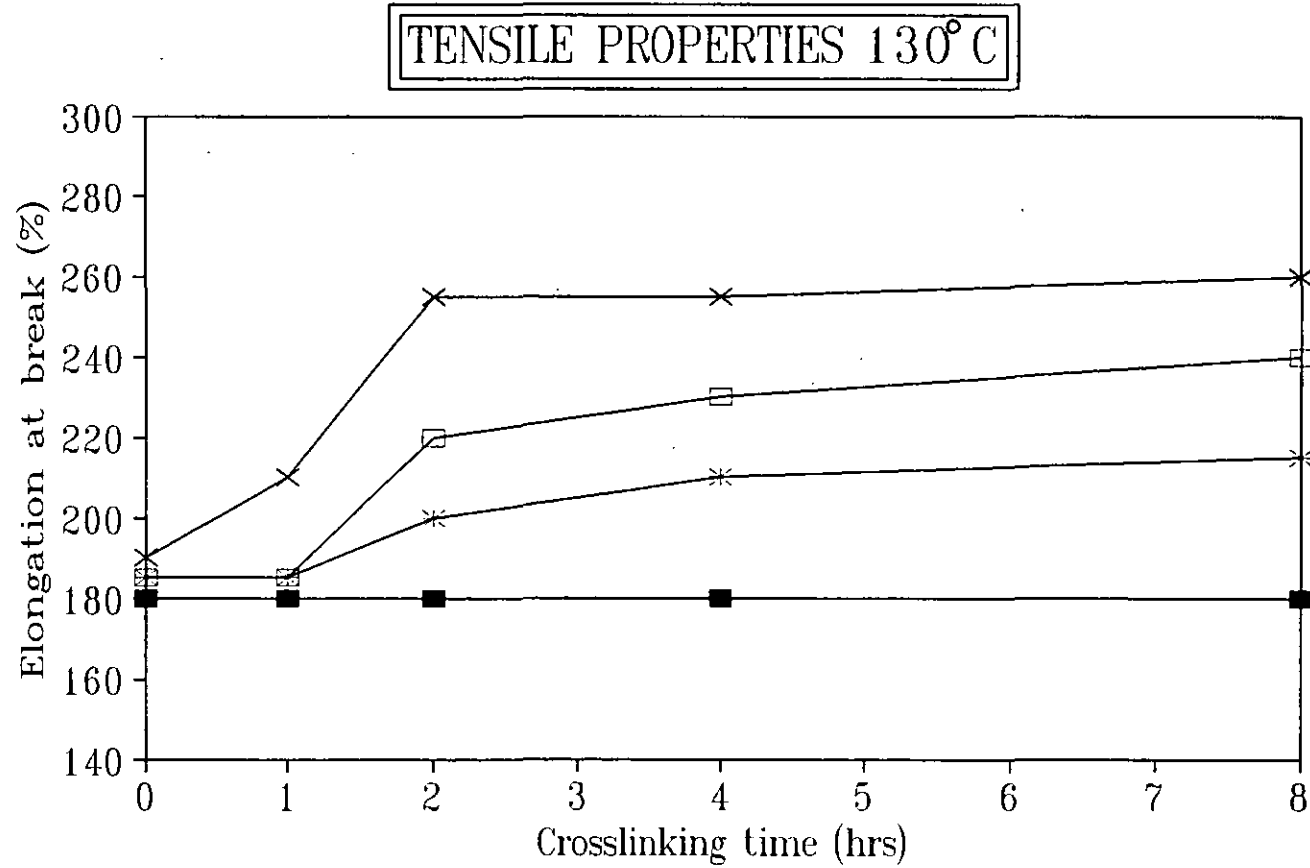
Figure 4.4 Dependence of elongation at break on crosslinking time for extruded samples containing different levels of aminosilane

— ■ — 0 phr Z 6020   —※— 1 phr Z 6020   —⊟— 2 phr Z 6020   —✕— 5 phr Z 6020

4.3.2. EFFECT OF LUBRICANT ON EXTRUSION AND GEL CONTENT.

From the experiments carried out on the roll mill, it was possible to see that is necessary to incorporate CaSt into the formulation to improve the processability. In the extrusion experiments lubricant performance was also evaluated.

It can be seen in Table 4.5, that the formulations containing CaSt (formulations 3 and 7) did not produce gel formation after extrusion.

Comparing the formulations containing 1 and 2 phr of CaSt it was noticed, that the formulation containing 2 phr had some problems during extrusion. When it was fed into the extruder the dry blend slipped in the feed zone and the extruded sheet showed melt fracture; it was not possible to have a constant feeding. On the other hand when 1 phr of CaSt was used a smooth sheet was obtained; the feeding was constant, the slippage was avoided and it was possible to produce a good quality extruded sheet.

4.3.3. EFFECT OF INCORPORATING THE CATALYST INTO THE FORMULATION ON GEL CONTENT.

The primary objective of this study was to evaluate the behaviour of formulations containing the catalyst, and by doing so avoid using it into the crosslinking bath, because the catalyst is insoluble in water and this

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this could cause a non-uniform diffusion process. Formulations from table 2.9 were selected for this study.

Table 4.8 presents the results of gel content. It is seen that is not possible to incorporate the catalyst into the formulation because the crosslinking reaction takes place during extrusion causing flow problems.

TABLE 4.8

Gel Content of extruded samples before crosslinking.

Formulation	1	2 cat.	3	4 cat.
Gel Content (%)	0	5-8	0	< 5

Also a "one pack" containing a tin stabilizer and lubricants was evaluated, again the crosslinking reaction occurred in the extruder.

4.3.4. EFFECT OF REPROCESSING ON GEL CONTENT.

One formulation containing 3 phr of tin stabilizer, 2 phr of aminosilane and 1 phr of CaSt (formulation 3 Table 2.8) was chosen to study the effect of reprocessing. After being extruded twice the formulation did not produce gel. It was therefore possible to have a formulation that can be pelletized and then in a second extrusion process shaped in any desirable form.

4.4 CONCLUSIONS.

It was possible to extrude formulations of plasticized PVC containing a crosslinking agent, although an increase in back pressure and amperage was observed and this increase was more pronounced when a stabilizer system based on lead was used. When a stabilizer system containing tin stabilizer (T 831) was used the increase in both parameters was less intense. The results of gel content of the extruded sheets revealed that during extrusion some gel formation took place causing the increase in pressure and amperage.

The lead stabilizer produced more gel after extrusion than the tin and a further increase in gel content was observed after immersion in water . The crosslinked PVC had better mechanical properties at high temperatures than the uncrosslinked PVC.

The use of a more efficient tin stabilizer permitted extrusion to be carried out without gel formation. The ratio of tin stabilizer/crosslinking agent concentration is an important parameter for controlling the extrusion process. This observation has not been reported before. Kelner and Schätz[167] in their studies of crosslinking PVC with mercaptosilanes using lead stabilizer mentioned that as the stabilizer concentration increased, the gel formation increased. They suggested that this increase in gel content was a consequence of the reaction of the lead stabilizer with the mercaptosilane to produce a more reactive compound. In our studies, using tin stabilizer, it was found that as the stabilizer concentration

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increased the gel formation decreased even though tin compounds are silanol condensation catalysts.

Also it was found that by increasing the aminosilane concentration an increase in gel formation is obtained. However when high levels of aminosilane are used (5 phr) is difficult to control the extrusion process and even during the processing gel is produced.

By using the right combination of tin stabilizer and aminosilane it is possible to have a process without gel formation, even though an increase in pressure and amperage was observed. During extrusion some grafting occurred causing molecular enlargement, causing the increase in both parameters. This was confirmed by GPC.

There are a competitive grafting reactions between the stabilizer and the aminosilane. This was manifested by the decrease in extrusion pressure and amperage when large quantities of stabilizer were used, and by the increase in both parameters when the aminosilane concentration was increased. The gel formation measurements after extrusion corroborated this behaviour.

The use of relatively high extrusion temperatures is necessary in order to have a good fusion level and good mechanical properties. By using low temperatures it is possible to avoid premature gel formation, but with a decrease in mechanical properties.

There is a compromise between tin
stabilizer/aminosilane ratio, and extrusion conditions
(temperature , residence time), in order to have a
successful extrusion process without gel formation , high
gel formation after crosslinking in a subsequent step,
and good mechanical properties.

CHAPTER 5
RESULTS AND DISCUSSION
CROSSLINKING PROCESS

5.1 INTRODUCTION.

Having eliminated the degradation problem during the grafting reaction by choosing the right chemistry, it is important to optimize the crosslinking reaction. This crosslinking reaction takes place in the presence of water and it is accelerated by catalysts like dibutyl-tin-dilaurate.

Although the chemical reaction of hydrolysis and condensation of the crosslinking agent is instantaneous, the speed of the reaction is controlled by the rather slow diffusion of water in the plasticized PVC. This water diffusion rate follows Fick's Law and is strongly dependent on temperature.

To achieve a high crosslinking speed, the extruded PVC has to be placed in warm water or in a steam heated vessel. Practical tests carried out with polyethylene[186] have shown that it is difficult to obtain with precision the time required for crosslinking.

One important point to consider is the achievement of high levels (50-60%) of gel content in order to have good mechanical properties. The following factors have been studied.

5.2 EFFECT OF CATALYST CONCENTRATION ON RATE AND DEGREE OF CROSSLINKING.

To study the effect of the condensation catalyst on crosslinking rate, extruded samples containing 2 phr of aminosilane and 3 phr of tin stabilizer (T 192) were crosslinked for different periods of time. Figure 5.1 shows the results of gel content of samples crosslinked at $80^{\circ}C$ in water and in water containing catalyst. Figure 5.2 presents the crosslinking curves for samples crosslinked under steam at 120° C with and without a condensation catalyst.

The method depicted by Kelnar and Schätz[168] was used to characterize the crosslinking reaction rate. The dependence of the logarithm of relative gel $\ln(G - G/G - G_0)$ on crosslinking time was linear and the slope is termed the "rate constant". Figure 5.3 presents rate plots for the two samples and the rate constant values for crosslinking under various conditions are given in Table 5.1 .

TABLE 5.1

Rate constant of the catalyzed and uncatalyzed crosslinking of plasticized PVC.

Medium	Rate constant (min^{-1})	
	$80^{\circ}C$	$120^{\circ}C$
H_2O	0.0021	0.010
H_2O + Catalyst (5 phr)	0.0026	0.012

It is interesting to note in these figures that the catalyst does not appear to have an important effect on crosslinking rate. It is apparent that the rate constant (Table 5.1) for the crosslinking reaction for samples crosslinked in water and in water plus catalyst at 80°C are about one order of magnitude lower than those obtained when the samples were crosslinked in steam. The effect of increasing the temperature is more obvious.

Narkis et al.[187] and Sen et al.[16] in their studies of silane grafted polyethylene, pointed out that the catalyst is vital to shorten the crosslinking time. Narkis,[187] however, mentioned than even in the absence of catalyst silane grafted polyethylene will crosslink though a much slow rate.

On the other hand, Kelnar and Schätz[168], pointed out that the rate constant for PVC grafted with mercaptosilane was two orders of magnitude lower in presence of catalyst, and for PVC grafted with aminosilane was one order of magnitude lower. They mentioned that the reaction with the aminosilane is more rapid.

The samples used in our study were stabilized with tin stabilizer, which in effect , is a condensation catalyst. The rate constant for this system at 120°C (0.01 min^{-1}) is similar to that obtained by Kelnar (0.0144 min^{-1}) for samples grafted with aminosilane and stabilized with the ester of thioglycolic acid.

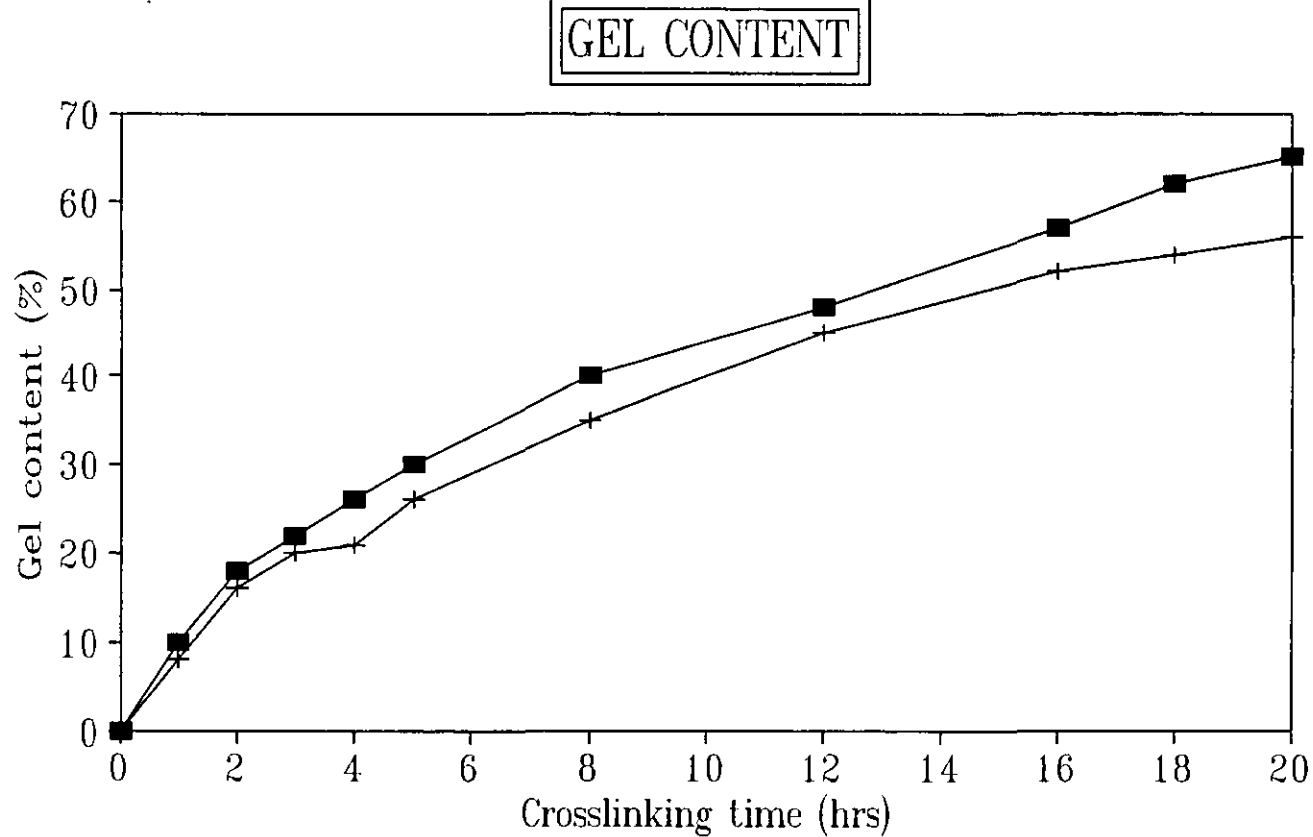Figure 5.1 Dependence of gel content on crosslinkiing time for samples
crosslinked in water and in water plus catalyst at 80 C

H_2O 5 % DBTDL
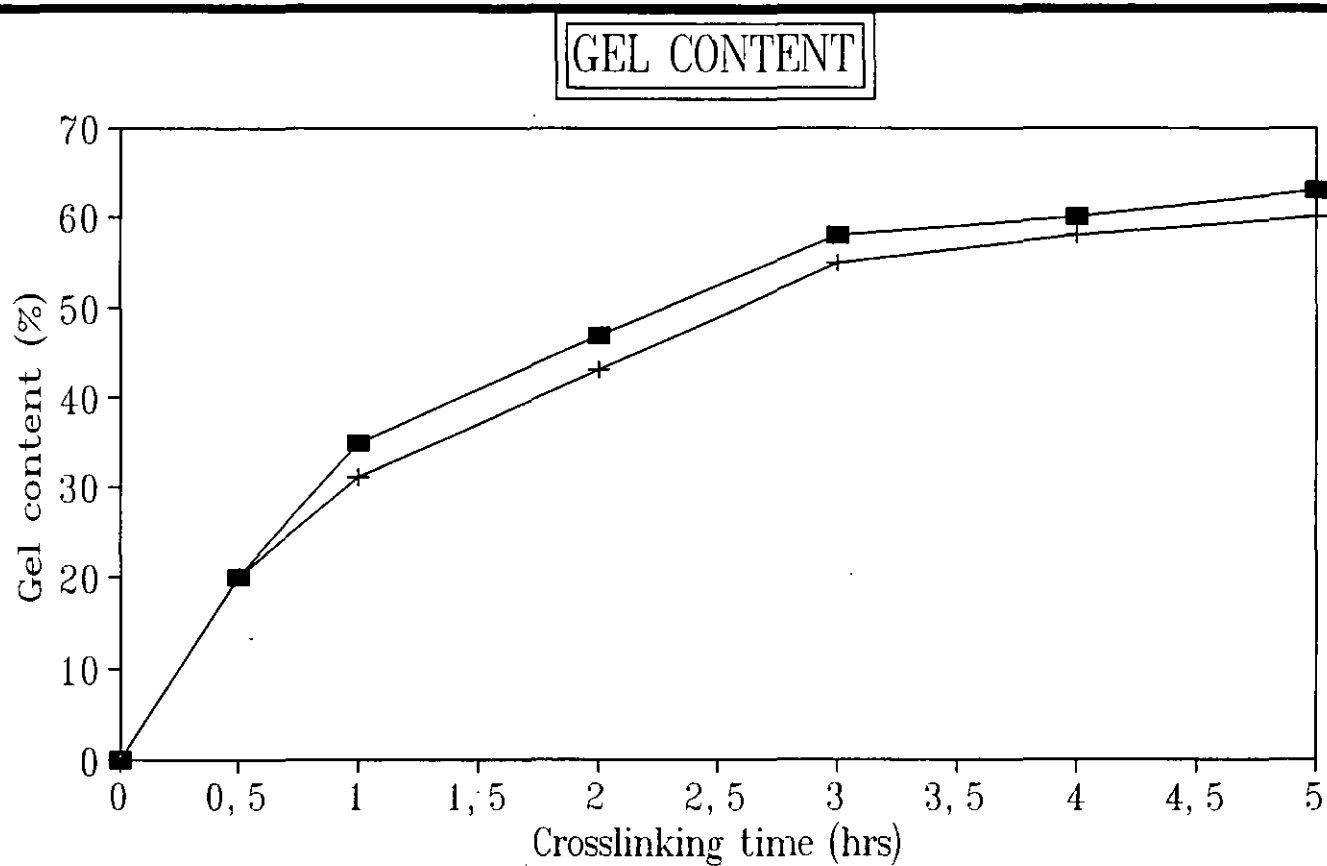
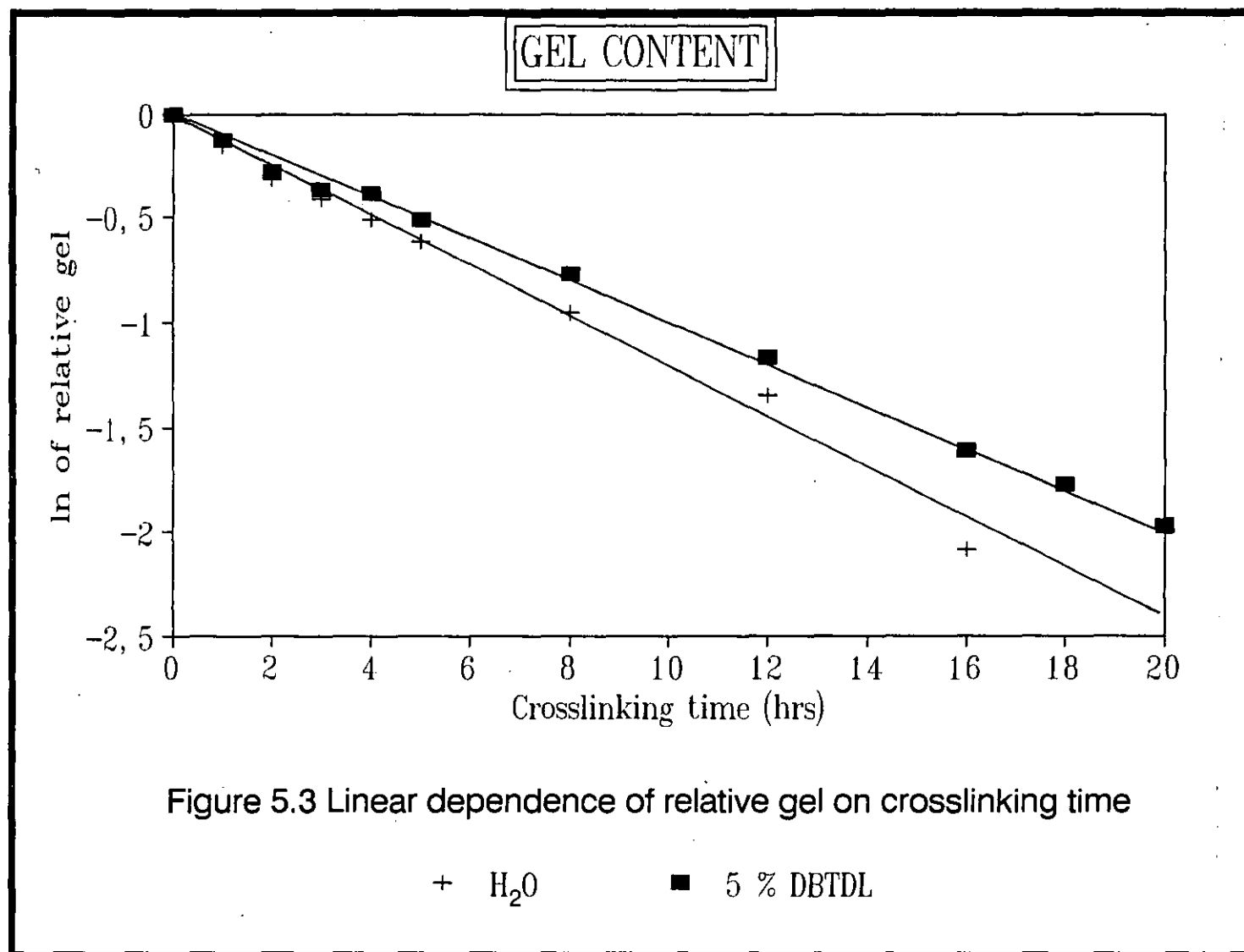Figure 5.2 Dependence of the gel content on crosslinking time for samples crosslinked in steam at 120 C

5.3 EFFECT OF VARIATION OF MOISTURE CONCENTRATION ON RATE AND DEGREE OF CROSSLINKING.
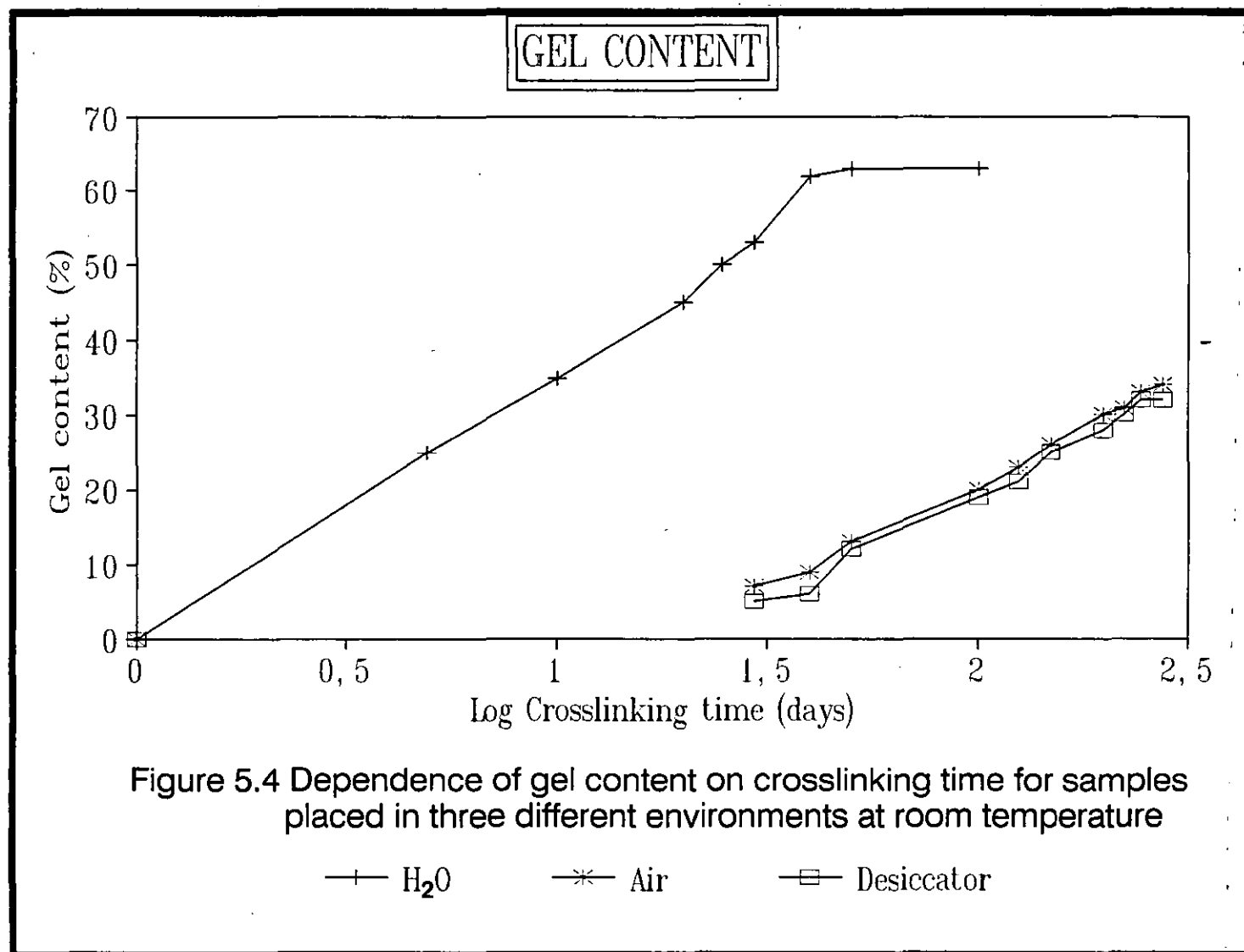
To investigate the effect of moisture content on crosslinking rate, extruded samples were placed in three different environments: water, air, and a desiccator at room temperature. Figure 5.4 shows the crosslinking curves.

It is interesting to note that at room temperature the crosslinking of the samples in air and in the desiccator occurs very slowly . A constant rate value of 1.84×10^{-6} min^{-1} was found for the samples in air , and a constant rate value of 1.79×10^{-6} min^{-1}, was found for the samples in the desiccator. These samples reached a gel content of 35 % after 275 days. On the other hand the samples in water were completely crosslinked after 40 days with a maximum gel content of 63 %. The rate constant value for these samples was 1.14×10^{-4} min^{-1}, which is two order of magnitude higher.

Surprisingly, the crosslinking progress in a dry atmosphere (desiccator at room temperature), is only slightly delayed, and not inhibited, although the rate and degree of crosslinking are lower than when the samples were immersed in water. Only small quantities of water molecules distributed in the grafted PVC are required to produce crosslinking.

Kelnar and Schätz[175], mentioned that diffusion of water from the external environment has practically no effect on the crosslinking. However they showed that the

Figure 5.3 Linear dependence of relative gel on crosslinking time

Figure 5.4 Dependence of gel content on crosslinking time for samples placed in three different environments at room temperature

rate constant obtained during the crosslinking process at 80°C in water and in air were different (almost one order in magnitude).

In our study at room temperature the crosslinking rate was two orders of magnitude higher for the samples immersed in water, and the degree of crosslinking was also higher. These results suggest that the diffusion of water is an important factor to consider in order to increase the crosslinking rate.

The water temperature also has an important influence in shortening the crosslinking time. In the next two sections the influence of water temperature on both the crosslinking rate and diffusion process will be discussed.

5.4 ENERGY OF ACTIVATION FOR CROSSLINKING REACTION.

To determine the activation energy (Ea), crosslinking reactions were carried out at different temperatures (20, 80, 105, and 120°C) in water and in water plus catalyst using a catalyst concentration of 5 phr.

The corresponding gel fraction has been measured against the crosslinking time. Figures 5.5 and 5.6 show that the rate and degree of crosslinking increase with temperature. From the rate constants obtained according the method previously described, Arrhenius plots have been drawn. (Figures 5.7 and 5.8). The linear temperature dependence of the crosslinking reaction is observed in

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both figures, and the energy of activation (Ea) has been calculated as 10.60 and 10.16 kcal/mol for the systems water and water plus catalyst respectively. The lower the energy of activation, the faster the reaction. However in this case the values can be considered equal. The tin stabilizer used, as has been mentioning is a condensation catalyst that is already in the formulation. Extra catalyst in the water bath does not have a significant effect in the rate constants.

5.5 DIFFUSION.

It is necessary to study the water diffusion process in plasticized PVC in order to correlate this with the crosslinking process.

In an attempt to examine the water absorption kinetics, Fickian behaviour for a plane sheet was considered as described by the the well-known equation.[188]

$$\frac{q_t}{q_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp\{-[(2n + 1)\pi/l]^2 Dt\}}{(2n + 1)^2} \quad (1)$$

Where q_∞ represents the water content at equilibrium, q_t represents the water content at time t, D the diffusion coefficient, n is an integer, and l is the thickness.

When t is large D is assumed to be independent of concentration, and equation 1 may be approximated by

$$\frac{q_t}{q_\infty} = 1 - \left(\frac{8}{\pi^2}\right) \exp\left(\frac{\pi^2 \, Dt}{l^2}\right) \tag{2}$$

By plotting $\ln [\, 1 - q_t/q_\infty \,]$ against t, the diffusion coefficient can be evaluated. The approximation for short times

$$\frac{q_t}{q_\infty} = \left(\frac{4}{l}\right) \left(\frac{Dt}{\pi}\right)^{1/2} \tag{3}$$

is also useful. A plot of q_t/q_∞ against $4(t/\pi\, l^2)^{1/2}$ is initially linear and has a slope of $D^{1/2}$

The exact derivation of equation 3 together with a through discussion on all the assumptions required has been given elsewhere[18,9].

This equation can be simplified to

$$\% \text{ of weight change} = 4 \left(\frac{Dt}{\pi\, l}\right)^{1/2} \tag{4}$$

Graphs of % of weight change vs. $t^{1/2}/l$ will provide the diffusion coefficients.

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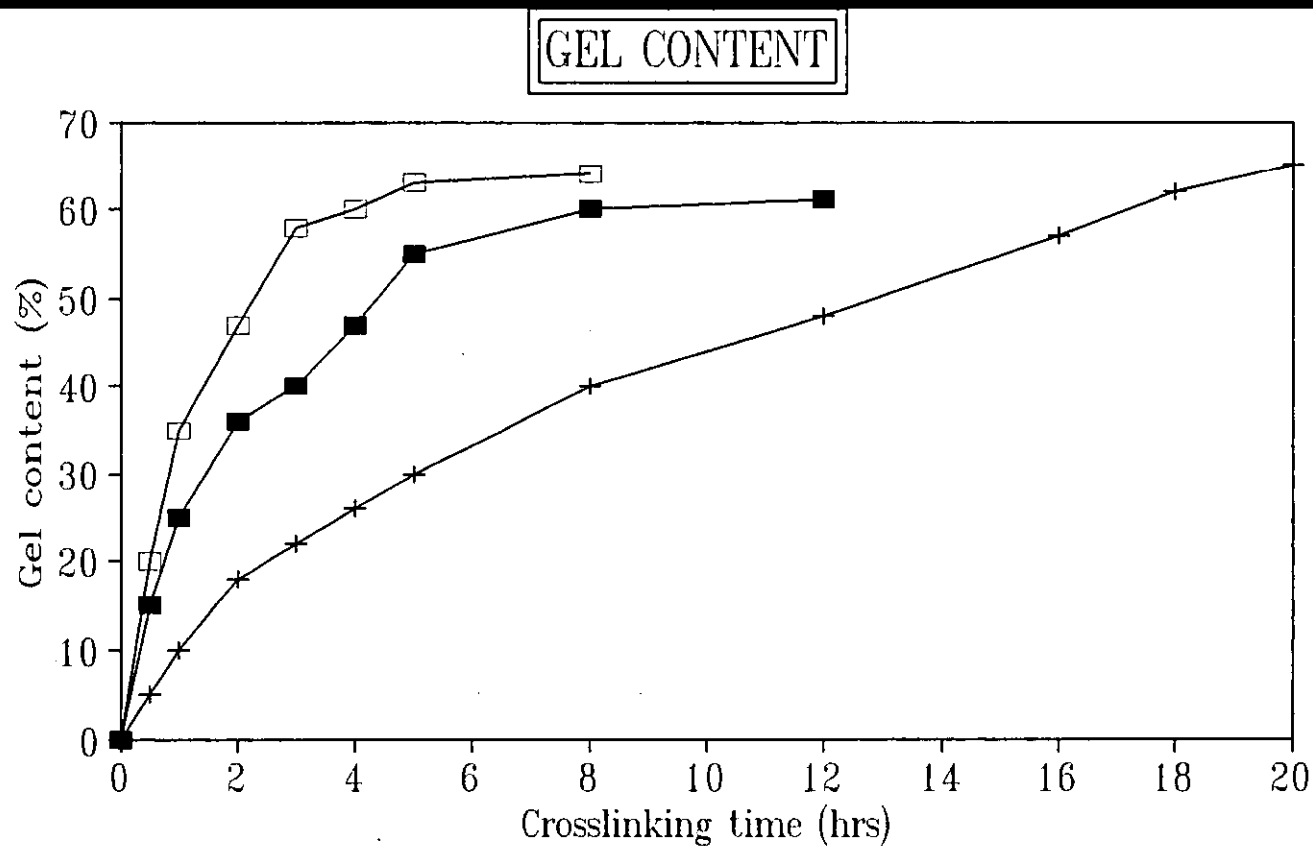Figure 5.5 Dependence of gel content on crosslinking time for samples crosslinked in water plus catalyst at three different temperatures
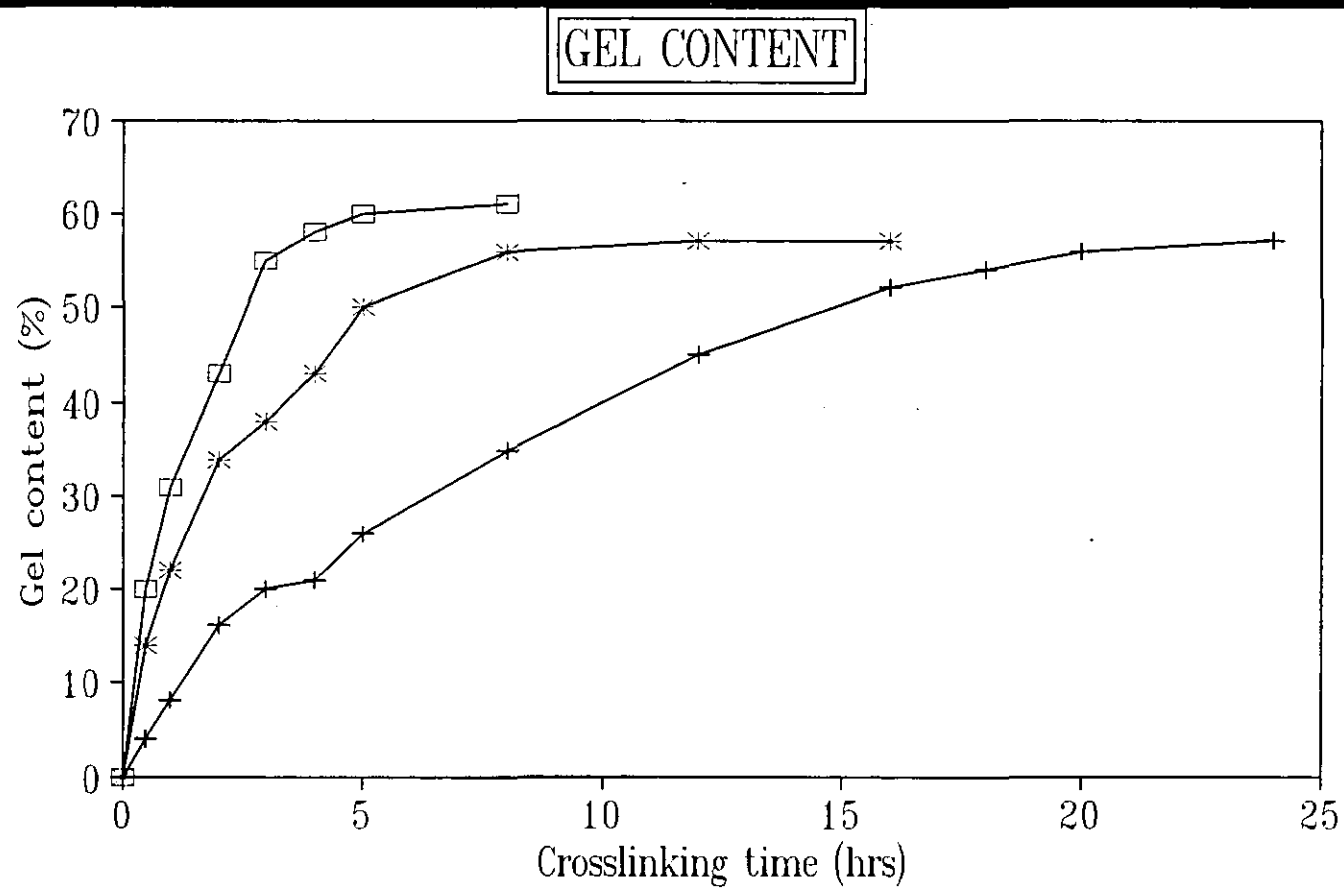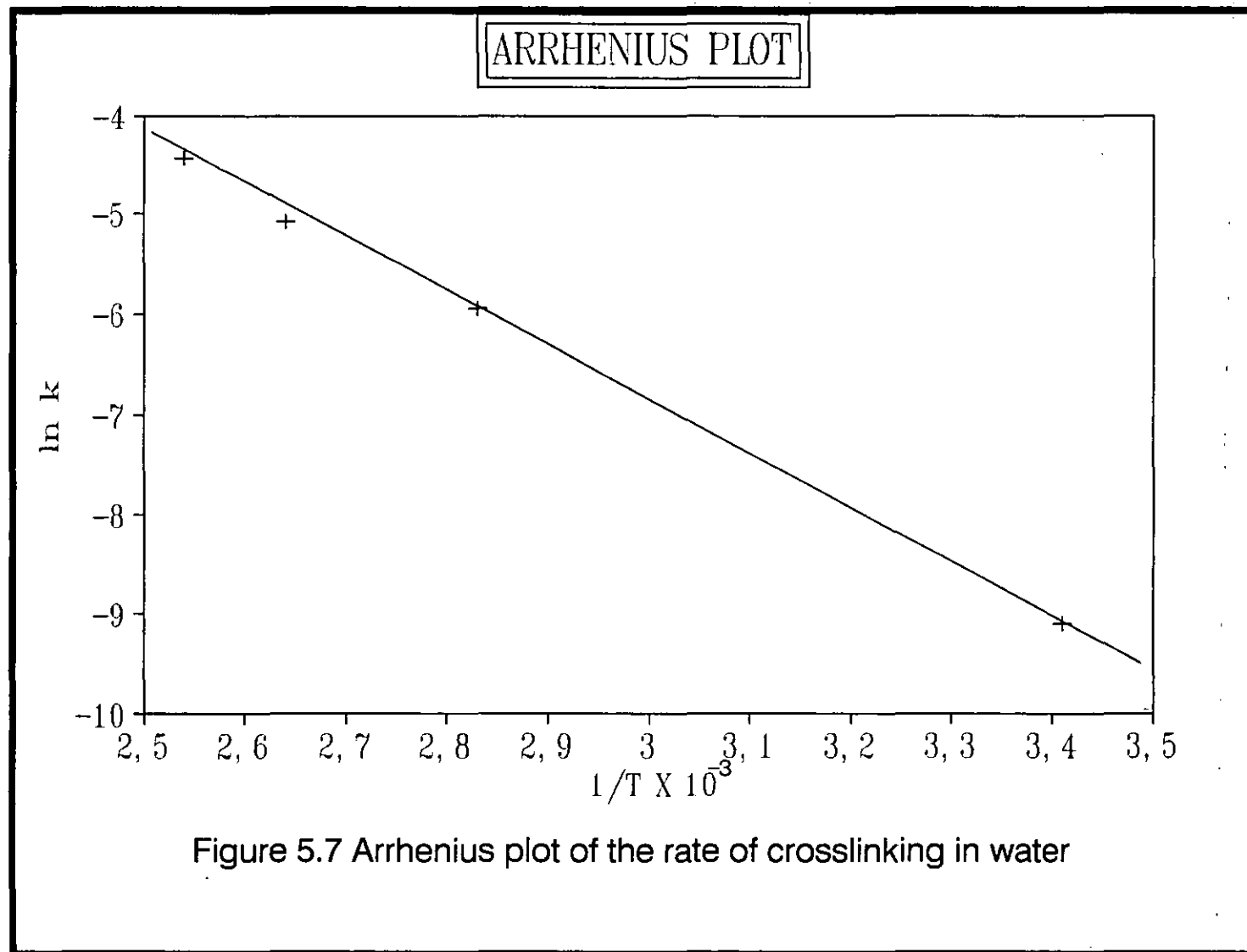
Figure 5.6 Dependence of gel content on crosslinking time for samples crosslinked in water at three different temperatures

—+— 80°C —*— 105°C —□— 120°C

Figure 5.7 Arrhenius plot of the rate of crosslinking in water
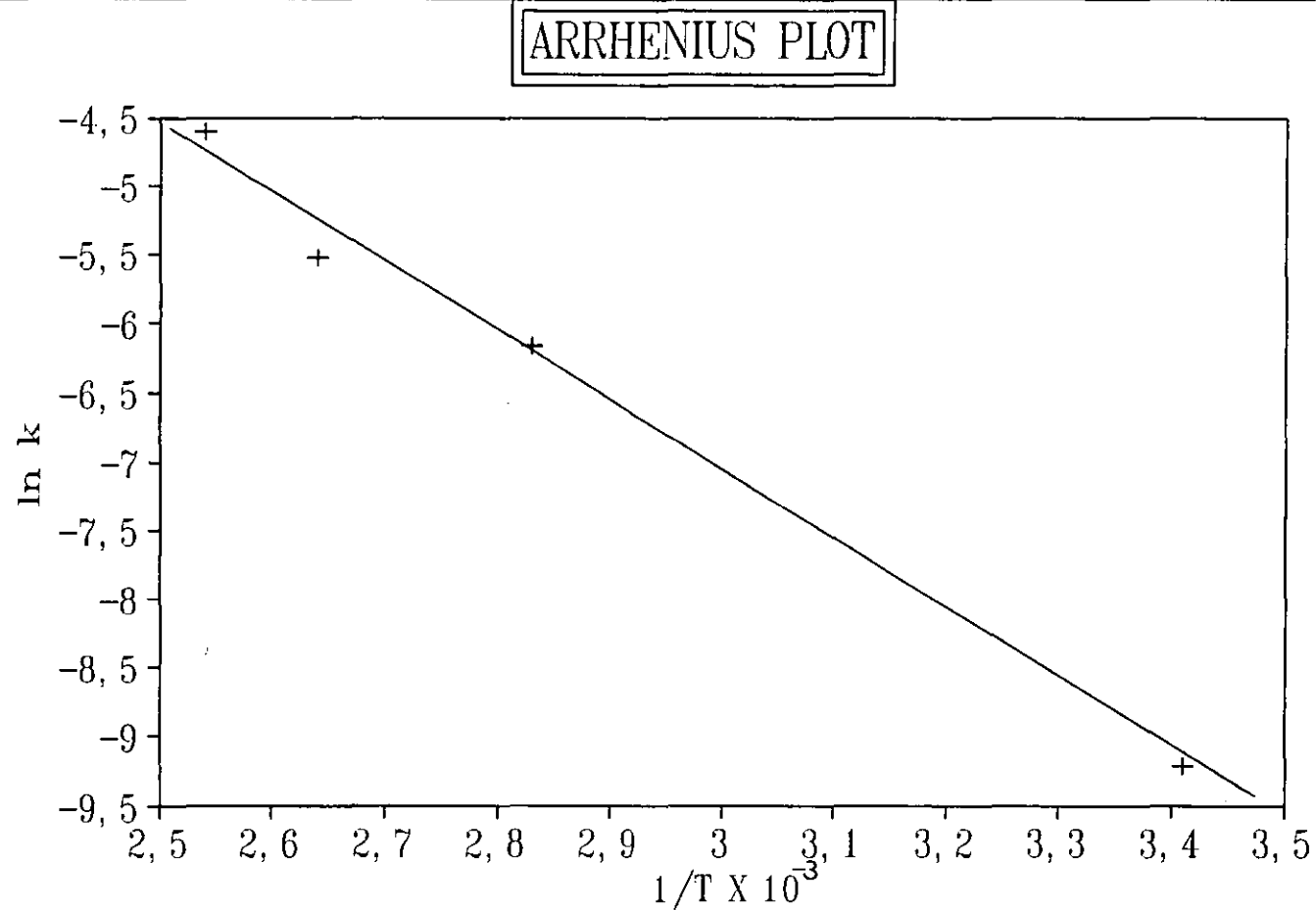
Figure 5.8 Arrhenius plot of the rate of crosslinking in water plus catalyst

It has been pointed out,[190] for plasticizer
migration in PVC, that considerable deviation from the
linearity was evident when the test was conducted for
long times. On the other hand the same author mentioned
that the result obtained during the initial stages are in
accordance with equation 3.

For this study , it was decided to use equation 4
which is a simplification of equation 3 , because it is
of interest that the crosslinking reaction takes place in
the early stages of the diffusion process.

Each of the specimens was immersed in 250 ml of
water . All tests were made at four different
temperatures, 70, 80, 105, and 120° C ($\pm$ 1° C), the last
two experiments being conducted using an autoclave. To
monitor weight changes the samples were removed from the
flask, wiped gently with a tissue and immediately weighed

In Figure 5.9 diffusion curves are presented for the
system immersed in water and in water plus catalyst. From
these figures it can be seen than the samples immersed in
water gained weight, on the contrary the sample immersed
in water and catalyst lost weight, which was unexpected.
To investigate what is taken out from the samples, a
sample of water was taken, the water was evaporated and
the remaining residue was analyzed using FTIR. The FTIR
analysis confirmed that the catalyst extracted some
plasticizer.

Figure 5.9 Diffusion curve for the system immersed in water
and water plus catalyst

■ water   ▲ water + catalyst
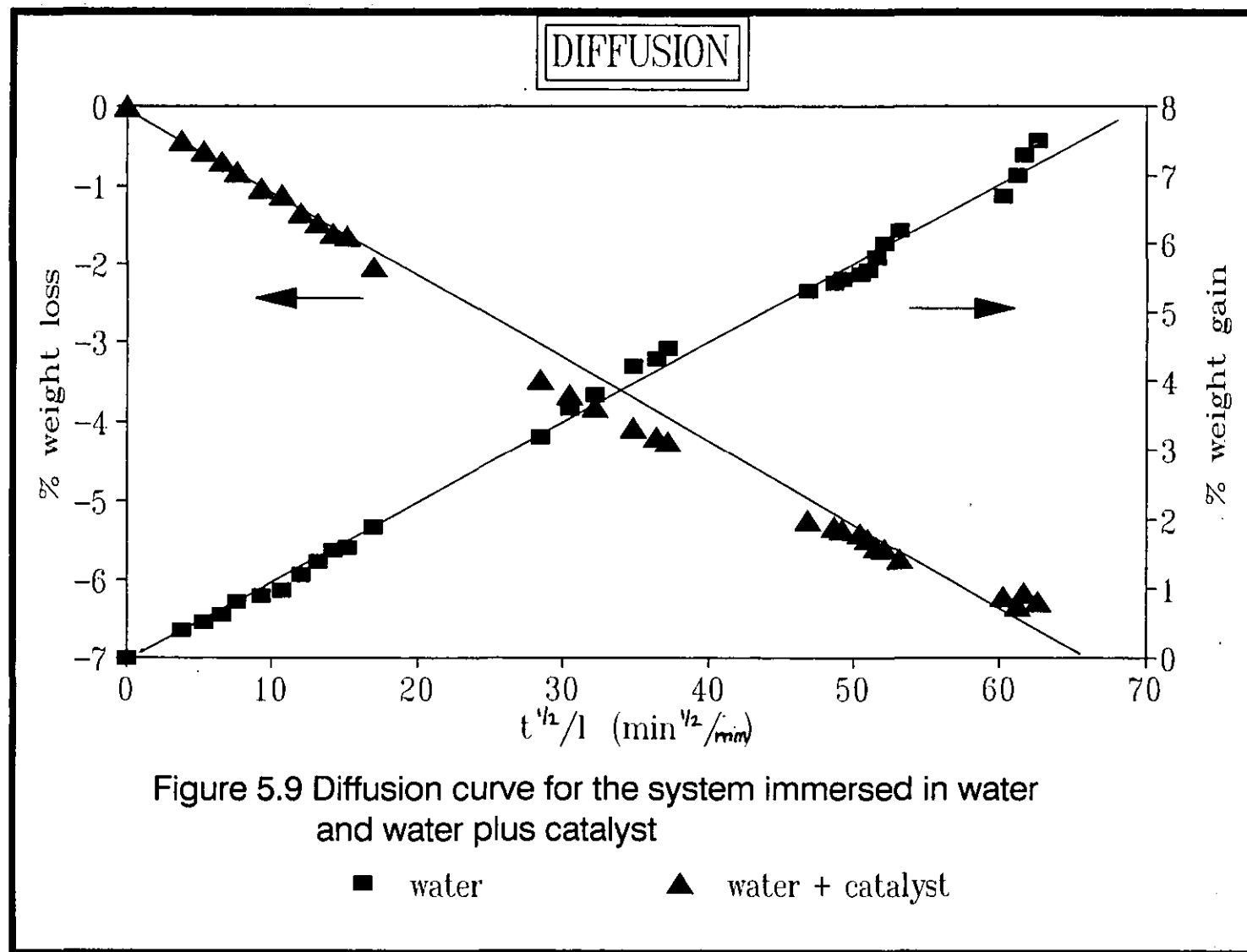
In order to know the amount of water that is absorbed into the plasticized PVC after immersion, the plasticizer content of the samples was evaluated after certain periods of time. The samples immersed in water did not lose plasticizer, but the samples immersed in water and catalyst lost up 15% in some cases. By calculating the amount of plasticizer that was extracted after a series of times it was possible to know the water uptake in the system containing the catalyst.

Figures 5.10 and 5.11 present the diffusion curves for the two systems at four temperatures. As expected, when the temperature increases the water uptake also increases. In these systems the temperature has a marked effect on diffusion. The results presented in Figure 5.11 are the results after correction for plasticizer loss.

However it would be necessary to carry out more experiments on this respect, in order to have a quantitative study of the counterdiffusion process observed in the presence of catalyst. In spite of this counterdiffusion process the water and catalyst are well diffused through the plastic and are capable of producing high gel contents.

The consideration stated above is undoubtedly simplified, ignoring, for instance, boundary layer phenomena, but it may be successfully extended for short term migration studies.

Table 5.2 presents the calculated diffusion coefficients obtained from the previous graphs. The correlation factor of the calculation by the method of least squares was at least 0.98 showing a good accord between the experimental values and theory.

The temperature dependence of D is that corresponding to an activated process obeying a relationship similar to the Arrhenius equation:

$$D = Do \exp \left(-\frac{Ea}{RT} \right)$$

where:

D = diffusion coefficient, Do = pre-exponential factor, Ea = activation energy, R = gas constant, T = temperature Kelvin.

TABLE 5.2

Diffusion coefficients for the system water, and water plus catalyst at four temperatures

Diffusion Coefficient $D \times 10^{6}$ cm^{2}/seg.		
Temperature	Water	Water + Cat.
70° C	0.622	1.01
80° C	2.667	1.39
105°C	6.534	8.00
120°C	27.24	23.3
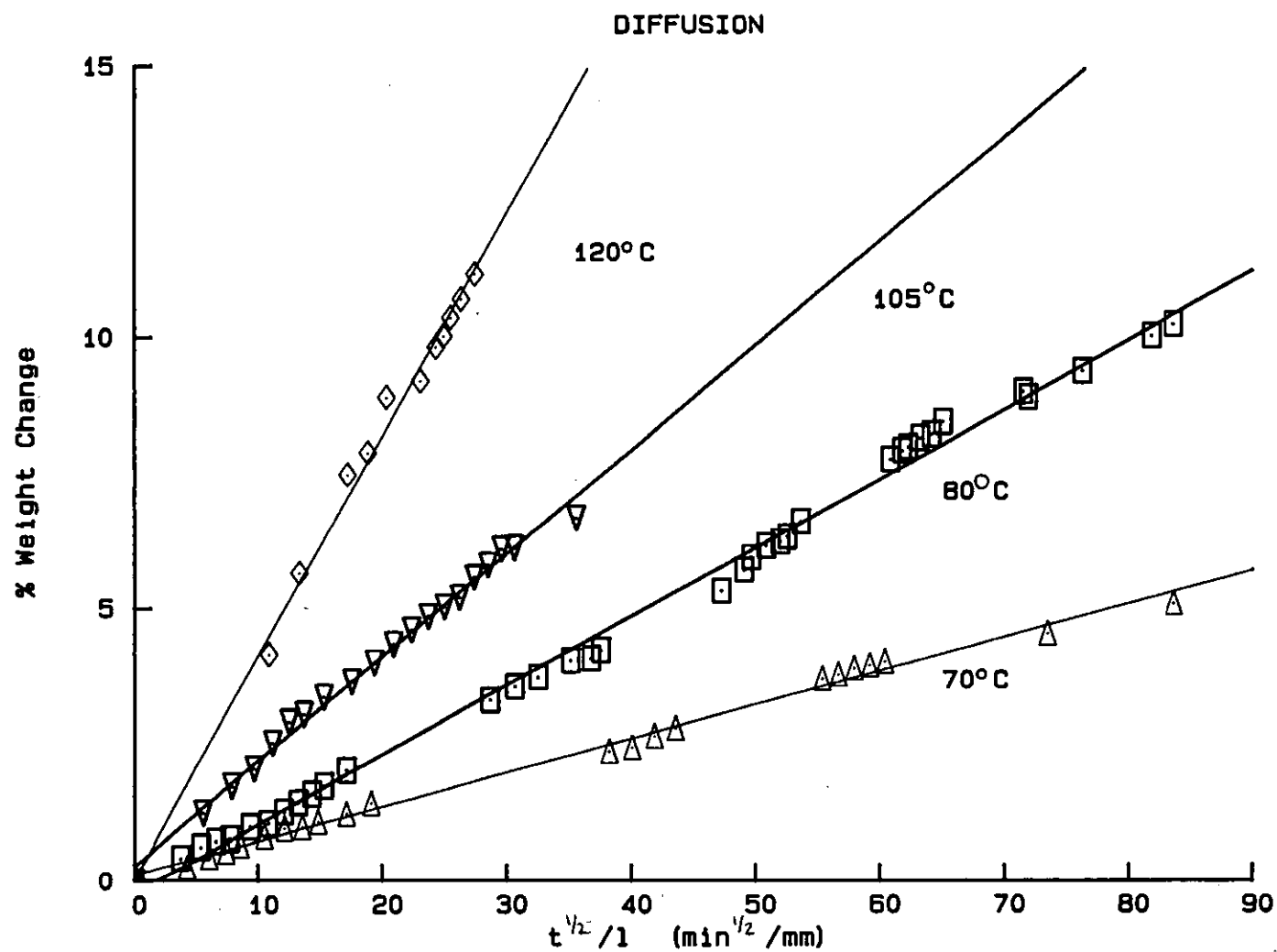
DIFFUSION

Figure 5.10 Diffusion experiments in water at 4 temperatures
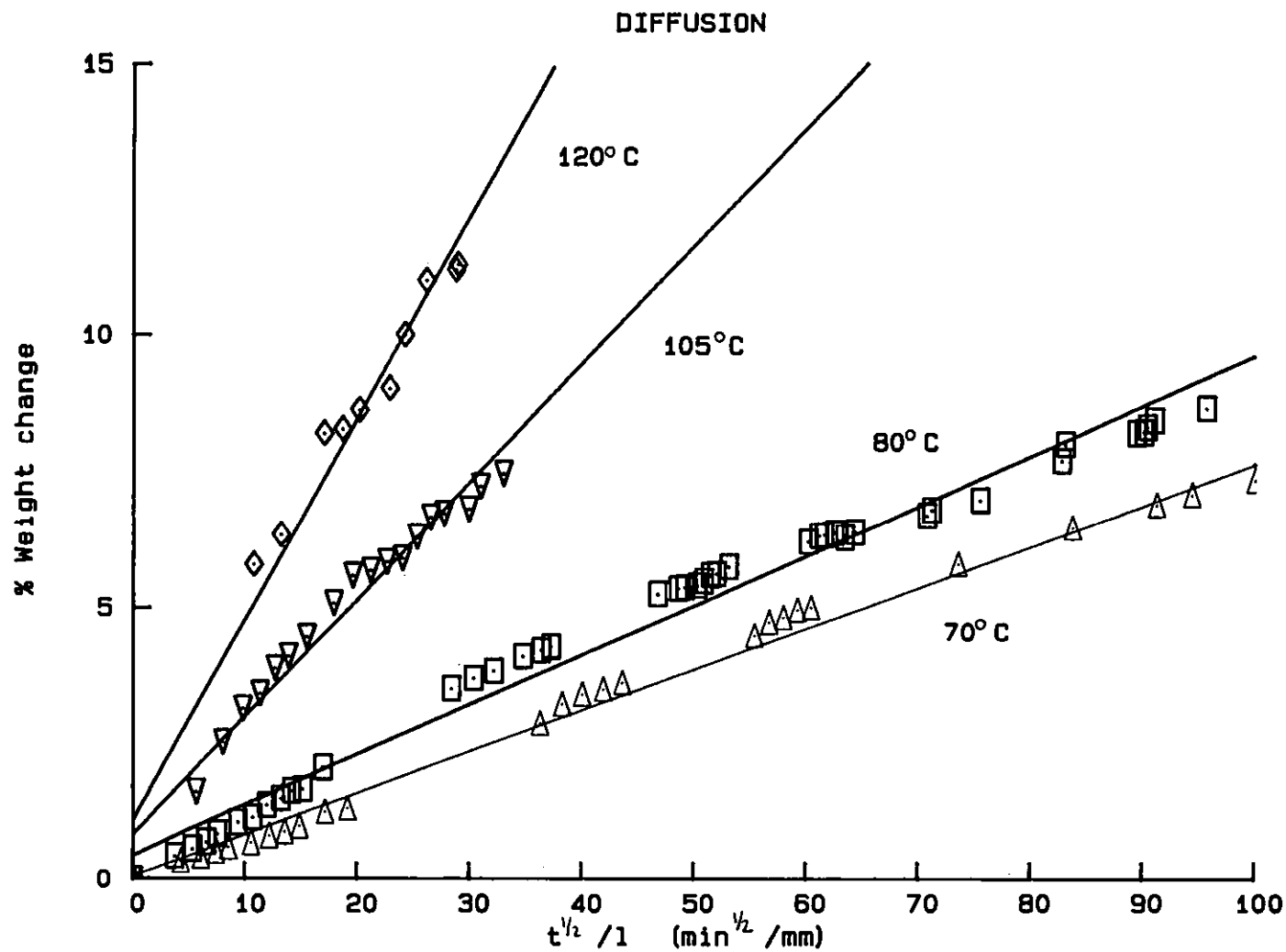
Figure 5.11 Diffusion experiments in water + cat. at 4 temperatures

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These results are presented in Figures 5.12 and 5.13, and are well in accordance with those obtained for systems of migration of plasticizers and stabilizers in PVC[192]. The energies of activation (Ea) for the diffusion process have been calculated as 8.46 kcal/mol and 7.72 kcal/mol for the system in water and water plus catalyst respectively
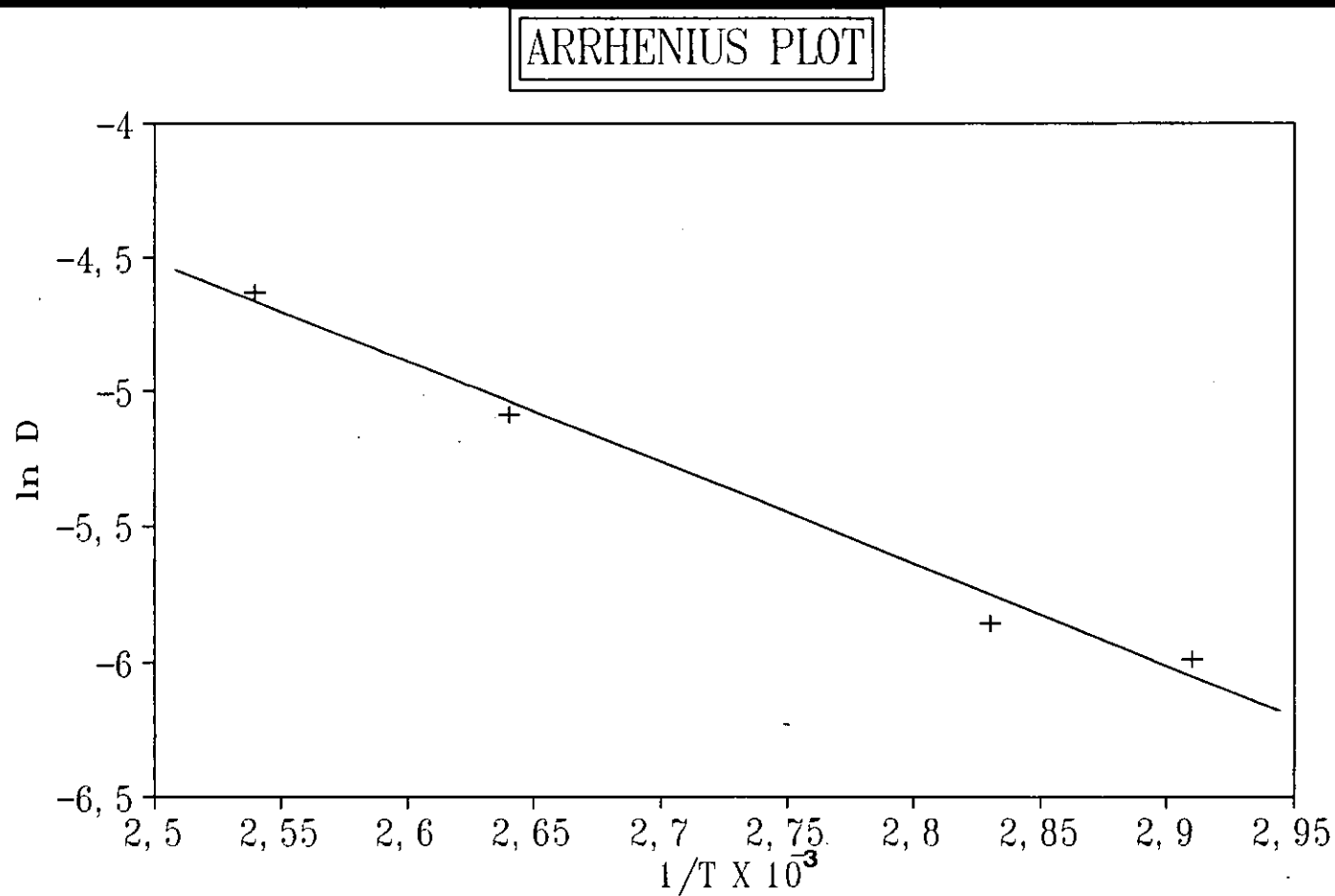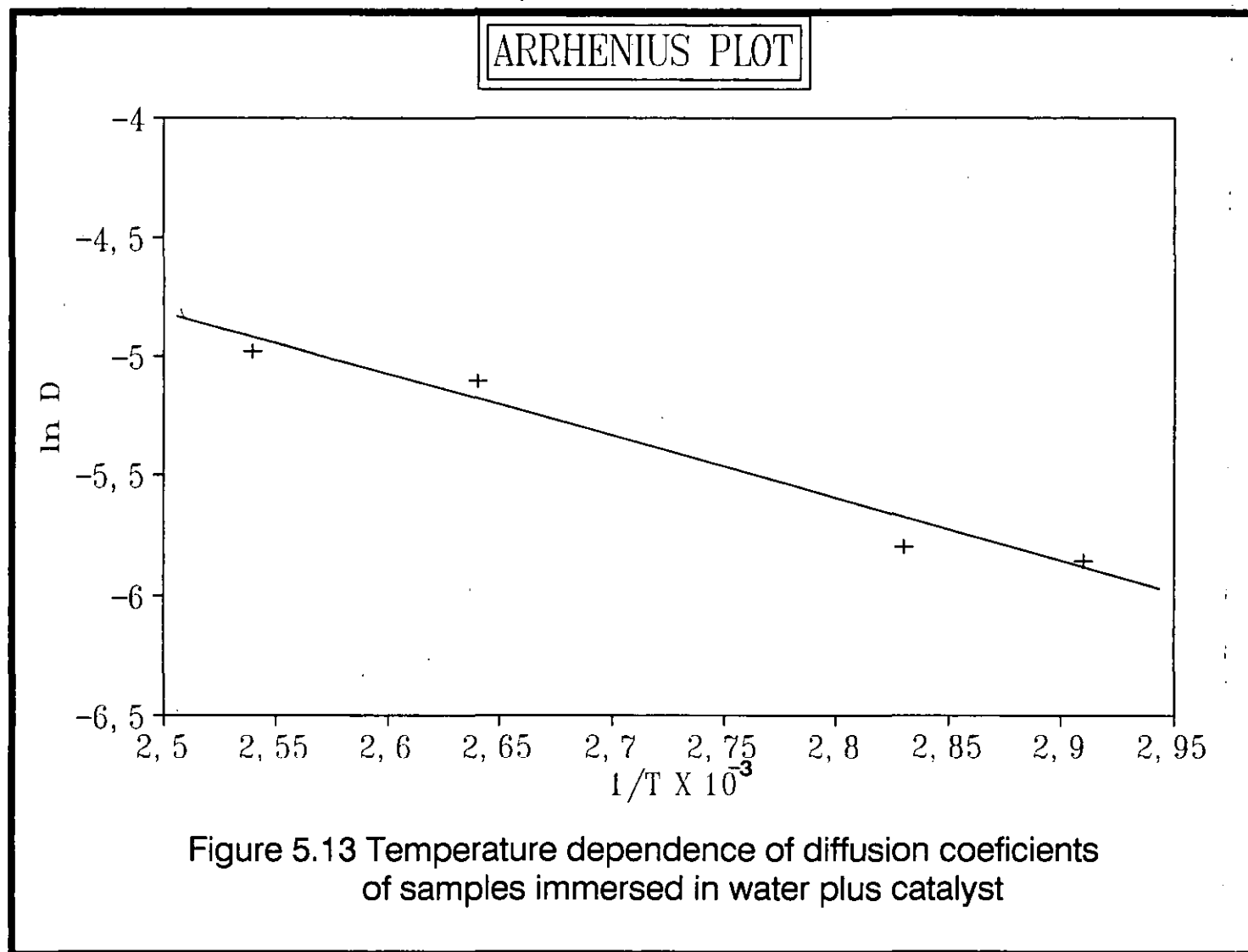
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5.5.1. CORRELATION WITH THE CROSSLINKING PROCESS.

Hochstrasser,[186] suggested the following empirical formula to calculate the crosslinking for polyethylene by using the diffusion coefficient for water.

$$time = \frac{x^2}{RH * D}$$

where x = thickness

      D = Diffusion coefficient

and RH = Relative humidity

If we consider a thickness of 0.6 cm (which is the average thickness of the samples used in this study),and a relative humidity of 1, we can calculate the crosslinking time at different temperatures:

Temperature ($^{\circ}$C)	Crosslinking time (Hrs.)
80	37
105	15
120	3.6

If these results are compared with the experimental data in Figure 5.4, it can be seen that the actual times measured to reach a maximum gel content are very similar to these results. We can observe how the crosslinking time is dramatically reduced as the temperature is increased.

Figure 5.12 Temperature dependence of diffusion coefficients
of samples immersed in water

Figure 5.13 Temperature dependence of diffusion coeficients
of samples immersed in water plus catalyst

5.6 CONCLUSIONS.

It was found that the rate constant for the crosslinking of PVC grafted with aminosilane are similar when the samples are immersed either in water or in water containing catalyst. It is therefore suggested that the organotin stabilizer used acts as a silanol condensation catalyst. It has been reported previously that amino compounds are capable of accelerating the crosslinking reaction.[191] Neither the degree nor the rate of crosslinking are highly influenced by the external catalyst.

The moisture content has a strong influence on the rate and degree of crosslinking. Samples immersed in water at room temperature were fully crosslinked after 40 days. However small quantities of water present in the samples are enough to initiate the crosslinking at room temperature, although the crosslinking rate is very slow and very long periods are required for complete reaction.

The water temperature had a significant effect on both the rate and degree of crosslinking. The higher the temperature, the higher the rate of crosslinking. Energies of activation (Ea) for the crosslinking reaction of 10.60 and 10.16 kcal/mol have been obtained for the systems using water and water plus catalyst, respectively.

It was possible to shorten the crosslinking time from 28 hours to 4-5 hours by increasing the water temperature

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The Ea values are smaller compared to those obtained
with other systems. Jando and Mori[133,134] reported
values of 13.25 kcal/mol for PVC crosslinked with
triazines. Similar values were reported for PVC
crosslinked with ethylenediamine by Ghosh[143]. A rather
higher value of 25.3 kcal/mol has been reported by
Duchacek and Kuta for PVC crosslinked with sulphur
compounds.[137]

A study of diffusion of water into plasticized PVC
during crosslinking was carried out to calculate the
diffusion coefficient. The water transfer into PVC was
found to obey Fick's Law, and the temperature dependence
of the diffusion coefficient could be described by an
Arrhenius equation. The activation energy for the
diffusion process was 8.46 kcal/mol.

There was migration of the plasticizer when the
samples where immersed in water plus catalyst. It was
possible to quantify the migration of plasticizer and
make corrections to calculate the water uptake into the
samples. The water diffusion also followed the Fick's
law, and the temperature dependence of the diffusion
coefficient was described by an Arrhenius relationship.
The activation energy was 7.72 kcal/mol

Using an empirical equation proposed for diffusion of
water in crosslinkable polyethylene,[186] crosslinking
times were obtained. These results are in good agreement
with actual measurements of gel content. We can conclude
in this respect, that the diffusion process has a notable

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influence on the rate and degree of crosslinking for plasticized PVC.

A correlation exists between the energy of activation for diffusion and the crosslinking process.

CHAPTER 6
RESULTS AND DISCUSSION
CHARACTERIZATION

6.1 INTRODUCTION

In this part of the work the aim was to investigate the grafting and crosslinking reactions of plasticized PVC grafted during processing with 3(2-amino-ethylamino)-propyltrimethoxysilane.

The grafting occurs during processing and crosslinking by immersion in water. In the presence of moisture and a condensation catalyst, the alkoxy group of the silane derivatives pendant to the grafted PVC converts to a silanol group and undergoes a condensation reaction to form $-$ Si $-$ O $-$ Si $-$ type network. Both the hydrolysis of alkoxy silanes to silanol and their condensation reactions occur almost instantaneously[147]. The overall mechanism is depicted in scheme 6.1.

In this study the grafting and crosslinking will be followed using FTIR .

As mentioned earlier, some molecular enlargement occurred during the grafting process, so a more detailed study was carried out to investigate the effect of processing, and crosslinking agent concentration on molecular weights.

The crosslink density of the gel will be evaluated.

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SCHEME 6.1

CH_2 CH_2 CH_2 CH_2

CH CH CH

| | |

Cl Cl Cl PVC (I)

+

NH_2 — ⌇⌇⌇⌇ — $Si(OCH_3)_3$ Aminosilane

CH_2 CH_2 CH_2 CH_2

CH CH CH

| | |

Cl NH Cl (II)

⌇

$Si(OCH_3)_3$

x 2

H_2O, catalyst

CH_2 CH_2 CH_2 CH_2

CH CH CH

| | |

Cl NH Cl

⌇

CH_3O — Si — OCH_3

|

O (III)

|

CH_3O — Si — OCH_3

⌇

Cl NH Cl

| | |

CH CH CH

CH_2 CH_2 CH_2 CH_2

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6.2 SPECTROSCOPY ANALYSIS

The purpose of this study is to elucidate how the aminosilane is grafted onto the PVC molecule. For this it was necessary to eliminate any unreacted aminosilane present. After Soxhlet extraction the soluble fraction was precipitated with methanol, dissolved and precipitated and so on until all the unreacted aminosilane was eliminated. FTIR analysis shows that after three precipitations the aminosilane was removed. Also the plasticizer was removed by extensive Soxhlet extraction with diethyl ether.

To follow the grafting and crosslinking reactions, i.e., changes in the contents of structures I - III , the absorption frequencies given in Table 6.1 were used. Figure 6.1 shows the infrared spectrum of normal PVC. Its characteristic bands have been reported by Krimm et al.[193-195]

The insoluble gel was swollen in THF and after three days, the swollen gel was deposited in a glass slide, the solvent was evaporated under an infrared lamp, and the spectrum was obtained Figure 6.2. This spectrum shows some differences compared with the pure PVC: a broad band at 3325 cm^{-1}, a small band at 1662 cm^{-1} and two small shoulders in the region between 1100 and 1020 cm^{-1}. The first band could be associated with the N-H stretching of the grafted aminosilane, or the O-H stretching of the hydrolysed methoxy group of the aminosilane, although is more probable that is associated with hydrogen- bonded

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Figure 6.1
PVC cast film

fig62: gel 3 phr

Figure 6.2
PVC gel

3325.48

1662.74 0.197

1043.56 0.335

Absorbance

Wavenumbers

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silanols as indicated by Smith[181]. The second band could be unsaturation introduced during the grafting process, (it is known that during substitution reactions, also some elimination reaction takes place producing unsaturation) and the third band could be associated with the formation of siloxane bonds (Si-O-Si) introduced during the crosslinking.

TABLE 6.1

Absorption frequencies used to follow the grafting and crosslinking reactions.

Structure	Frequency (cm^{-1})	Ref.
NH2 stretch.	3280	
NH	3320	
-Si-OCH3	800 (1090)	180,181
-Si-OH		
free	3691	181
hydrogen bonded	3549 (3431)	182
-Si-O-Si-	1020-1100	180,181
CH2-N scissoring	1473	

The infrared spectra of the gel and recovered soluble fraction are presented in Figure 6.3 . It can be seen that the gel spectrum has several bands in the region of 1660 cm^{-1}. Additionally the Si-O-Si crosslinks are concentrated in the gel (1040 cm^{-1}) as would be expected.

On the other hand the soluble fraction does not show a band at 1660 cm^{-1} . This result proves that unsaturations sites (as revealed by the appearance of the bands at 1660 cm^{-1}) are concentrated in the gel, rather than in the soluble fraction, and are related to the Si-O-Si structure.

The first stage of silane crosslink formation is hydrolysis to form an intermediate silanol. We have tried to follow the hydrolysis using the disappearance of the bands at 800 and 1090 cm^{-1} and the appearance of the band at 3549 (3431) cm^{-1} but these bands were very weak in intensity so it was difficult to make quantitative measurments. Smith[180] mentioned that the methoxy group also has a characteristic absorption band at 1250 cm^{-1} but in PVC this band overlaps the C-H bending mode. Bullen et al [178] and Hjertberg et al.[179] were able to follow these reactions in polyethylene and ethylene vinyl silanes copolymers respectively. In their studies they used commercial silane grafted copolymers. In our study we prepared the grafted material during processing, so it is likely that hydrolysis of methoxy groups occurred during processing and due to this it was not possible to find methoxy groups in the grafted PVC.

To have a quantitative estimate of the structure formed during the grafting and crosslinking process a baseline was traced on the infrared spectrum and the absorption intensities of some bands of interest were measured. The substitution reaction displaced chlorine atoms , and consequently a decrease in the absorption

fig63: gel 3 phr

Figure 6.3

PVC sol
fraction

PVC gel

Absorbence

Wavenumbers

bands due to the C-Cl should be observed. Also the bands
due to Si-O-Si and Si-O-(CH$_3$) should increase. Absorption
index for peaks arising for the structures presented in
Table 6.2 were calculated using the absorption of C-C at
1105 cm^{-1} as internal standard. The same table also lists
the characteristic configurational and conformational
isomers associated with the C-Cl group frequencies
according to Krimm et al[193,194], Pohl and Hummel[196]
and Robinson et al.[197]

TABLE 6.2

Absorption frequencies used to estimate the degree
of sustitution in grafted and crosslinked PVC

Structure	Frequency cm^{-1}	Config.	Conf.	Type of C-Cl
C-Cl	615	s	*tttt*	S HH
C-Cl	637	s	*tttt*	S'HH
C-Cl	692	i	*tgtgtg*	S HC
Si-O-Si	1030			
Si-O-CH3	1024			
C-H2	1427			

S = syndiotactic   i = isotactic

Absorption indices for the C-Cl structure and Si-O-Si
of the polymer before crosslinking are presented in
Figure 6.4 . It can be seen that as the crosslinking
agent concentration increases the C-Cl structure tends
to decrease as a result of the reaction with the
aminosilane. On the other hand, the Si-OCH$_3$ increases.
The bands in the region between 1100 and 1000 cm^{-1} may

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either be due to Si-O-CH$_3$ or Si-O-Si , because it is difficult to distinguish between the absorption frequencies of these two groups as indicated by Smith.[181]

A similar trend was observed for the crosslinked polymer as shown in Figure 6.5. The grafted polymer is very nearly crosslinked, as indicated by the quasi-quantitative transformation from the grafted to crosslinked structures, although it was not possible to demonstrate by direct measurements of the amount of the structure Si-O-CH$_3$ and Si-O-Si, which are associated to the grafted and crosslinked polymers respectively. However infrared analysis of the soluble fraction after Soxhlet extraction with THF did not show the characteristic bands of siloxanes. From this we can say that almost all the grafted polymer is participating in the crosslinking reaction.

The absorption indices of the other C-Cl structures were also analysed. Figures 6.6 and 6.7 present the results for the grafted and crosslinked polymers respectively. It is interesting to observe in both figures that the C-Cl band at 637 cm^{-1} tends to decrease (this was also observed with the band at 615 cm^{-1}) while the band at 692 cm^{-1} remained almost constant. The bands at 615 and 637 cm^{-1} are associated with a syndiotactic configuration and *tttt* conformation. According to these results it is suggested that the syndiotactic sequences preferently react during the grafting reaction and the isotactic sequences associated with the absorption at 692 cm^{-1} almost remain unmodified. It is reasonable to

Figure 6.4 Absorption index for the C-Cl and Si-OCH
bands of the grafted polymer

Figure 6.5 Absorption index for the C-Cl and Si-O-Si
bands of the gel fraction

propose this mechanism since the steric hindrance is lower in the syndiotactic configuration. However is necessary to recall that the carbon-chlorine stretching region in the vibrational spectrum does not offer a practical route to have a quantitative estimation of tacticity. In order to have a quantitative measurement of tacticity and to know exactly which structures are taking place during the grafting reaction an NMR study would be necessary.

As discussed earlier an absorbance band appears at 1660 cm^{-1} apparently associated with double bonds introduced during the grafting process. If an elimination reaction is taking place according to the Schem 6.3 some CH$_2$ groups would disappear. Figure 6.8 presents the absorption index of the C-H$_2$ bending at 1427 cm^{-1}. It can be seen than this band tends to decrease as the aminosilane concentration increases.

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Figure 6.6 Absorption index for the C-Cl bands
of the grafted polymer

▲ C-Cl at 637 cm^{-1} ✳ C-Cl at 692 cm^{-1}

Figure 6.7 Absorption index for the C-Cl bands
of the crosslinked polymer

—+— C–Cl at 637 cm^{-1} —*— C–Cl at 692 cm^{-1}

Figure 6.8 Absorption index of CH_2 band
of the grafted polymer

6.3 GEL PERMEATION CHROMATOGRAPHY

To detect molecular enlargement during processing, changes in the molecular weight distribution (MWD) were followed by GPC. The samples were stabilized with 3 phr of tin stabilizer and were roll milled at $145^{\circ}C$ for different periods of time. The GPC analysis showed, that extensive molecular enlargement occurred. This is demostrated in Table 6.3 for samples containing 3 phr of aminosilane. The results for samples containing 1 and 2 phr of aminosilane are presented in Table III.1 and III.2 in Appendix III.

TABLE 6.3

Changes in molecular weight due to milling at $145^{\circ}C$. for a sample containing 3 phr of aminosilane.

milling time (min)	Mw * 10^{-5}	Mn * 10^{-5}	Mw/Mn
1	3.29	1.5	2.18
2	3.47	1.83	1.89
3	3.31	1.74	2.03
5	2.89	1.49	1.94
8	2.59	1.35	1.35

Figures 6.9 and 6.10 present the results of Mw and Mn respectively. It can be seen that as the aminosilane concentration increase the Mw increases. This is what would be expected as larger molecules have a higher

probability   of   participating   in   crosslinking

reactions[170]. It is interesting to note also that Mn

increases as much as 120% without formation of gel.

Also it can be noticed that when 1 phr of aminosilane

is used, Mw and Mn always increased as the milling time

increased. When 2 phr were used a maximum in both Mw and

Mn was observed after 5 minutes and when 3 phr were used

the maximum was reached at 2 minutes. This maximum, and

then decrease in molecular weight could be associated to

either chain rupture due to degradation or formation of

gel. The first mechanism is unlikely to occur, because

PVC does not degrade by chain rupture. To verify the

second mechanism the milled sample containing 3 phr of

aminosilane was Soxhlet extracted and this maximum was

shown to be associated with the formation of gel.

The large increase in Mn suggests that, besides the

normal random reaction with normal PVC units, a more

specific reaction favouring low molecular weight polymer

could be taking place. The observed increase in molecular

weight and the decrease in Mw/Mn (Table III.1 Appendix

III) indicates that some terminal groups preferentely

react with the crosslinking agent. On the other hand the

soluble fraction from the crosslinked polymer had a very

low molecular weight.

Hjertberg et al[132], using H-NMR, found for PVC

crosslinked with dithiol triazines that 1-chloro-2-alkene

structures showed a high reactivity towards substitution.

Figure 6.9 Dependence of Mw on milling time for samples containing different levels of aminosilane and tin stabilizer

Figure 6.10 Dependence of Mn on milling time for samples containing different levels of aminosilnane and tin stabilizer

6.4 MOLECULAR WEIGHT BETWEEN CROSSLINKS

After Soxhlet extraction the molecular weight between crosslinks were evaluated for the insoluble fractions. Table 6.4 presents the results of samples crosslinked with different levels of aminosilane.

TABLE 6.4
Molecular weights between crosslinks

Z 6020 concentration (phr)	$Mc * 10^{-3}$ g/mol
1	42.040
2	31.769
3	23.199
4	20.446

As a result of increasing crosslinking agent concentration a decrease in molecular weight between crosslinks is observed, as expected. However this results in principle seem to be high, (the Mn of the pure PVC is 70,000 g/mol) . Also the Mc of these samples seem high compared with the results obtained by Nethsinghe and Gilbert[91] for PVC crosslinked by radiation. However, due to the molecular enlargement detected in the grafted polymer they look quite reasonable. The reaction mechanism with aminosilanes is more specific than that taking place in radiation crosslinking.

6.4. CONCLUSIONS

Infrared analysis proved to be useful for detecting the changes between the original PVC and the gel. The -Si-O-Si- was detected in the region between 1020 and 1090 cm^{-1}. In this region it has also been reported that the structures -Si-O-CH$_3$ and -Si-OH, associated with the grafted and hydrolyzed grafted PVC, are both infrared active, so it was not possible to differentiate between these structures.

The absorption frequencies associated with the CH-Cl vibrational mode, are sensitives enough to detect the reduction in concentration of this structure as a result of the substitution reaction. This decrease, associated with the increase in absorption due to the -Si-O-Si- structure corroborates the propose mechanism showed in scheme 6.1.

The syndiotactic structures seem to be more reactive than the isotactic towars grafting and subsequent crosslinking.

Double bonds produced as a result of secondary reactions were also detected by infrared analysis. These structures were concentrated in the gel and are associated with the crosslinked structure.

A significant molecular enlargement was observed and is associated to long processing times in combination with a highly reactive formulation (high content of aminosilane). This underlines the necessity of a carefully adjusting of the formulation in order to avoid problems during processing. Mw is correlated with material properties which are dependent on mass fraction, i.e., melt viscosity, mechanical properties.

It is suggested that some terminal structures are taking part in the grafting process causing an increase in molecular weight. This is supported by the fact that molecular weight between crosslinks is high for both low (42,040) and high (20,446) crosslinked sample respectively, compared to 70,000 for the normal PVC.

An increase in the crosslink density of the gel was observed as a result of increasing the crosslinking agent concentration.

CHAPTER 7
GENERAL CONCLUSIONS AND
SUGGESTIONS FOR FURTHER WORK

7.1 GENERAL CONCLUSIONS

Plasticized PVC is readily crosslinked when formulated with an aminosilane. Compounds becomes more crosslinked when a higher dose of the crosslinking agent is used.

The crosslinking produced an improvement in mechanical properties, specially at high temperature.

It was possible to establish a relationship between the gel content and the ultimate tensile strength. It was found that there is a unique relationship between UTS at 130°C and the gel content irrespective of processing conditions, with UTS starting to increase sharply around 30% gel content, and reaching a plateau at about 70%.

The investigation of the thermal stability of compounds containing the crosslinking agent, showed that the compounds containing lead stabilizers (TBLS/DBLS) are easily crosslinked during processing; on the contrary compounds containing dibutyl tin mercaptide as stabilizer showed better processability, and less degradation.

The penetration resistance, at elevated temperatures was improved by crosslinking, and even low levels of gel (20%) might be enough to give an improvement up to 120°C.

It was possible to extrude formulations of plasticized PVC containing a crosslinking agent .

The use of a more efficient tin stabilizer permitted extrusion to be carried out without gel formation. The ratio of tin stabilizer/crosslinking agent concentration is an important parameter for controlling the extrusion process. This observation has not been reported before.

There is a compromise between tin stabilizer/aminosilane ratio, and extrusion conditions (temperature , residence time), in order to have a successful extrusion process without gel formation , high gel formation after crosslinking in a subsequent step, and good mechanical properties.

It was found that the rate constant for the crosslinking of PVC grafted with aminosilane are similar when the samples are immersed either in water or in water containing catalyst.

The moisture content has a strong influence on the rate and degree of crosslinking.

The water temperature had a notable effect on both the rate and degree of crosslinking. Energies of activation (Ea) for the crosslinking reaction of 10.60 and 10.16 kcal/mol have been obtained for the systems using water and water plus catalyst, respectively.

It was possible to shorten the crosslinking time from 28 hours to 4-5 hours by increasing the water temperature from 80 to $120^{\circ}C$.

The water transfer into PVC was found to obey Fick's law, and the temperature dependence of the diffusion coefficient could be described by an Arrhenius equation. The activation energy for the diffusion process was 8.46 kcal/mol.

There was plasticizer migration when the samples where immersed in water plus catalyst. It was possible to quantify the migration of plasticizer and make the corrections to calculate the water uptake into the samples. The water diffusion also followed Fick's law, and the temperature dependence of the diffusion coefficient was described by an Arrhenius form. The activation energy was 7.72 kcal/mol

Using an empirical equation proposed for diffusion in crosslinkable polyethylene,[186] crosslinking times were obtained. These results were in good agreement with actual measurements of gel content. We can conclude in this respect, that the diffusion process has a significant influence on the rate and degree of crosslinking for plasticized PVC.

The siloxane type crosslinked structure was detected using infrared spectroscopy. However it was not possible to differentiate between the structures characteristic of the grafted PVC and the structures characteristic of the crosslinked polymer.

Some structures are more reactive towards substitution and subsequent crosslinking, as indicated by the reduction in syndiotactic sequences in the crosslinked polymer.

A large molecular enlargement was detected by GPC analysis and is associated to long processing times in combination with a highly reactive formulation.

Finally the crosslink density in the gel increase as the crosslinking agent concentration increases, although the crosslink density is lower than that reported for PVC crosslinked by electron beam radiation.

7.2 SUGGESTIONS FOR FURTHER WORK

It was found that tin stabilizers compete with the crosslinking agent during the grafting process, making possible to have processing without gel formation, although they are silanol condensation catalysts. A kinetic study is suggested to evaluate the grafting efficiency of the aminosilane. This could be done by thermal analysis, in parallel with elemental analysis.

It was found that certain structures are more susceptible to react during the grafting process. Nevertheless additional examinations would complete this study. The use of NMR is suggested. The objective would be to establish the relationship between degree of conversion and changes in tacticity.

The grafting process was carried out in a single screw extruder using a dry blend with all the ingredients incorporated into it. It would be worth studying the effect of first stabilizing the formulation and then adding the crosslinking agent. This could be done using an extruder with different feed zones.

A high increase in molecular weight during grafting was observed, suggesting that certain terminal groups are more reactive. Again, an NMR study is suggested to elucidate which structures are reacting.

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APPENDIX I

TABLE I.1

Tensile strength at room temperature of formulations containing different levels of Z 6020.

Immersion time(hrs)	0	0.5	1	2	4	8
z 6020 conc. (phr)			UTS MPa			
0	20.5	20.5	20.8	20.7	21.1	21.0
1	22.5	22.0	22.0	22.5	22.0	23.0
2	23.0	23.0	22.0	22.5	23.3	24.0
3	23.6	23.8	22.5	23.0	24.0	25.2
4	24.0	24.0	23.5	24.5	25.0	25.6
5	24.3	24.8	26.0	25.0	26.0	26.5

TABLE I.2

Elongation at break at room temperature of formulations containing different levels of Z 6020.

Immersion time(hrs)	0	0.5	1	2	4	8
z 6020 conc. (phr)			Elongation at break (%)			
0	325	320	320	320	325	315
1	320	310	310	285	250	240
2	285	270	270	260	250	270
3	310	285	265	240	260	230
4	265	265	275	270	260	230
5	280	260	260	255	250	245

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TABLE I.3

Tensile strength at $130°C$ of formulations containing different levels of Z 6020.

Immersion time(hrs)	0	0.5	1	2	4	8
z 6020 conc. (phr)			UTS MPa			
0	0.37	0.36	0.36	0.34	0.34	0.34
1	0.60	0.54	0.58	0.65	0.58	0.69
2	0.63	0.66	0.72	0.72	0.76	0.80
3	0.94	1.02	1.03	1.04	1.06	1.24
4	0.99	1.08	1.15	1.35	1.52	1.59
5	1.06	1.13	1.18	1.44	1.55	1.65

TABLE I.4

Elongation at break at $130°$ C of formulations containing different levels of Z 6020.

Immersion time(hrs)	0	0.5	1	2	4	8
z 6020 conc. (phr)			Elongation at break (%)			
0	155	155	160	165	165	165
1	155	165	170	180	190	200
2	180	185	190	190	195	195
3	190	200	200	200	220	250
4	210	200	275	290	300	300
5	210	220	215	220	220	225

TABLE I.5

Tensile properties at room temperature of formulations containing different stabilizers.

		U T S MPa / % E	
IMMERSION TIME (Hrs)	0	2	4
Formulations			
1 0 Z6020 Pb	14.0 /155	13.7 /145	14.2 /170
2 2 Z6020 Pb	16.5 /180	18.5 /190	18.0 /200
3 5 Z6020 Pb	17.0 /160	19.0 /210	19.0 /210
4 2 Z6020 Ba	12.5 /166	14.5 /290	16.9 /185
5 2 Z6020 Sn	15.5 /180	16.0 /190	20.5 /190
6 2 Z6020 Pb	19.0 /185	19.0 /190	19.5 /200

TABLE I.6

Tensile properties at 130 $^\circ$C formulations with different stabilizers.

		UTS MPa / % E	
IMMERSION TIME (Hrs)	0	2	4
Pb			
0 Z 6020	0.37/ 185	0.34/ 175	0.34/ 165
Pb			
2 Z 6020	0.72/ 160	0.76/ 165	0.81/ 180
Ba/Cd/Zn			
2 Z 6020	0.36/ 200	0.45/ 170	0.49/ 200
Sn			
2 Z 6020	0.42/ 200	0.66/ 210	0.71/ 210

APPENDIX II

ANALYSIS OF VARIANCE FOR FACTORIAL DESIGNS

The method of Yates is a very simple technique for estimating the effects and determining the sum of squares in a 2^k factorial design. To understand this procedure let us consider the results of UTS on table 3.16 .

The treatment combinations are always written down in standard order, and the column labeled "response" contains the corresponding observations (or total of observations) at the treatment combination. The first half of column (1) is obtained by adding the responses of adjacent pairs. The second half of column (1) is obtaining by changing the sign of the first entry in each of the pairs in the response column and adding the adjacent pairs. For example, in column (1) we obtain for the fifth entry 0.74 = -(0.93) + 1.67, for the sixth entry 1.02 = -(0.96) + 1.98, and so on.

Column (2) is obtained from column (1) just as column (1) is obtained from the response column. Column (3) is obtained from column (2) similarly. In general, for a 2^k design would construct k columns of this type. To obtain the estimate of the effect, we divide the entries in column (3) by $n2^{k-1}$ (in this case, $n2^{k-1}$ =8). Finally, the sum of squares for the effects are obtained by squaring the entries in column (3) and dividing by $n2^k$ (in this case, $n2^k$ = 16), n is the levels used in the experiment (in this case n = 2).

TABLE II.1

Yates' Method to calculate the average effect for the UTS.

UTS	MPa response	(1)	(2)	(3)	Effect	Avg. Effect	Sum.of squares
1	0.93	2.6	5.54	10.7	I		
a	1.67	2.94	5.26	3.32	A	0.83	1.361
b	0.96	2.3	1.76	0.9	B	0.225	0.101
ab	1.98	2.86	1.56	0.76	AB	0.19	0.072
c	0.88	0.74	0.34	-0.38	C	-0.095	0.018
ac	1.42	1.02	0.56	-0.2	AC	-0.05	0.005
bc	0.92	0.54	0.28	0.22	BC	0.055	0.006
abc	1.94	1.02	0.48	0.2	ABC	0.05	0.005

TABLE II.2

Analysis of Variance for the UTS results

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Fo
Z 6020 conc.	1.361	1	1.361	136.1^{α}
Cross. time	0.101	1	0.101	10.1^{α}
CMT	0.018	1	0.018	1.8
AB	0.072	1	0.072	7.2^{α}
AC	0.005	1	0.005	0.5
BC	0.006	1	0.006	0.6
ABC	0.005	1	0.005	0.5
Error	0.247	24	0.010	
Total	6.589	31		

α significant at 5 percent. $F_{0.05,1,24} = 4.26$

TABLE II.3

Yates' Method to calculate the average effect for
the Elongation at break.

SP	°C response	(1)	(2)	(3)	Effect	Avg. Effect	Sum.of squares
1	190	390	780	1550	I		
a	200	390	770	50	A	12.5	312.5
b	190	400	20	-30	B	-7.5	112.5
ab	200	370	30	30	AB	7.5	112.5
c	200	10	0	-10	C	-2.5	12.5
ac	200	10	-30	-10	AC	2.5	12.5
bc	170	0	0	-30	BC	-7.5	112.5
abc	200	30	30	30	ABC	7.5	112.5

TABLE II.4

Analysis of Variance for the Elongation results

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Fo
Z 6020 conc.	312.5	1	312.5	1.25
Cross. time	112.5	1	112.5	<1
CMT	12.5	1	12.5	<1
AB	112.5	1	112.5	<1
AC	12.5	1	12.5	<1
BC	112.5	1	112.5	<1
ABC	112.5	1	112.5	<1
Error	6000	24	250	
Total	9150	31		

TABLE II.5

Yates' Method to calculate the average effect for the Softening point

SP °C	response	(1)	(2)	(3)	Effect	Avg. Effect	Sum.of squares
1	150	310	629	1262	I		
a	160	310	633	108	A	27	1458
b	140	297	49	48	B	12	288
ab	179	336	59	34	AB	8.5	144.5
c	135	10	9	4	C	1	2
ac	162	39	39	10	AC	2.5	12.5
bc	152	27	29	30	BC	7.5	112.5
abc	184	32	5	-24	ABC	6	72

TABLE II.6

Analysis of Variance for the Softening points results

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Fo
Z 6020 conc.	1458	1	1458	56.75^{a}
Cross. time	288	1	288	11.21^{a}
CMT	12.5	1	12.5	<1
AB	144.5	1	144.5	5.62^{a}
AC	12.5		12.5	<1
BC	112.5	1	112.5	4.37^{a}
ABC	72	1	72	2.8
Error	411	16	25.69	
Total	6679.5	23		

a significant at 5 percent. $F_{0.05,1,16} = 4.49$

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The "F" for 5% significance and 24 degrees of freedom[189] is 4.26. If the values of Fo are higher than "F" the results are significant.

The "F" for 5% significance and 16 degrees of freedom[183] is 4.49. If the values of Fo are higher than "F" the results are significant.

TABLE III.1

Changes in molecular weight due to milling at 145°C. for a sample containing 1 phr of aminosilane.

milling time (min)	$Mw * 10^{-5}$	$Mn * 10^{-5}$	Mw/Mn
1	2.03	0.91.	2.25
2	2.30	1.08	2.13
3	2.45	1.20	2.04
5	2.47	1.30	1.89
8	2.53	1.46	1.73
10	2.57	1.47	1.74

TABLE III.2

Changes in molecular weight due to milling at 145°C. for a sample containing 2 phr of aminosilane.

milling time (min)	$Mw * 10^{-5}$	$Mn * 10^{-5}$	Mw/Mn
1	2.76	1.39.	1.98
2	2.97	1.50	1.97
3	3.08	1.59	1.94
5	3.30	1.81	1.82
8	3.27	1.83	1.78
10	1.83	1.45	1.98