Modification of Polyvinyl Chloride (PVC)

by

Reactive Processing

by

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(*Department of Chemical Engineering and Applied Chemistry*)

A Thesis Submitted for the Degree of Master of Philosophy

at

THE UNIVERSITY OF ASTON IN BIRMINGHAM

August 1990

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SUMMARY

Chemical binding of two types of vinyl compounds, maleate and acrylate, with PVC was investigated by reactive processing to chemically modify PVC . Dibutyl maleate (DBM), a PVC plasticiser, was used to represent the maleate class of plasticisers. 2-Ethylhexyl acrylate (OA) was used as a representitive of the acryloyl-based plasticisers. It was shown that the extent of binding of DBM tended to 100% in the case of relatively low loading of DBM ($< 1.2 \times 10^{-2}$ *mol·100* g^{-1} *PVC) and that it had another maximum in the higher loading range* ($> 1.5 \times 10^{-1}$ *mol·100* g^{-1} *PVC). More than 90% binding was achieved in the case of very high loadings of OA* ($> 5 \times 10^{-1}$ *mol·100* g^{-1} *PVC). All these results were obtained within 10 minutes under prevailing reaction conditions. The reaction conditions were explored and the studies showed that the extent of binding of DBM depended on the concentration of DBM radicals, the concentration of PVC macro-alkyl radicals, the degree of fusion of PVC and the sequence of processing operations, while the extent of binding of OA especially depended on the radical initiation system. Two mechanisms for the binding reactions of DBM were proposed. One is based on the Diels-Alder reaction, the other is a radical coupling reaction. Which one predominates depends on the concentration of DBM radicals which are formed by radical initiation using radical generators (e.g. peroxides). The binding reaction of OA is thought to involve grafting of OA along the PVC backbones for which the major side-reaction is the homopolymerisation of the OA. The structure-property relationship of the DBM modified PVC systems was also studied. The modified PVC polymers were shown to have built-in plasticisity which was not lost by extraction. It is possible to produce a modified PVC polymer with desired properties by controlling the reaction conditions which determine the chain structure of the modified polymer. It was also shown that the binding conditions led to melt stabilisation of PVC. A DBM-peroxide stabiliser system was shown to be effective in the stabilisation of PVC during closed prosessing with high shear action. It is suggested that stabilisation arises from destruction of the PVC macro-alkyl radicals and inhibition of the formation of unsaturation in PVC.*

Key words: PVC, Vinyl Compound, Reactive Processing, Binding Reaction, Degradation, Stabilisation, Stabiliser

ACKNOWLEDGEMENT

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No word could express my thankful and compunctious feeling to my wife Jin'ai, who had to run our home and bring up our child by herself in China during the unusual two years but always understand and support me. My son Liyu has been looking forward to his five-year-old birthday on 23 August 1990 because he believe that he will live with his father together again from that time. I would like to make my son a birthday present of the thesis, which is a fruit of two years' painstaking work of his parents.

DECLARATION

The work described herein was carried out at the University of Aston in Birmingham between August 1988 and August 1990.

It has been done independently and submitted for no other degrees.

Xing Xianchong

August 1990

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FIGURE

TABLE

SCHEME

CHAPTER 1

INTRODUCTION

Polyvinyl chloride (PVC) has been a marketable product for nearly 60 years.[1] It has been used in a multitude of applications including building, electrical insulation, packaging, floor coverings, foams, coatings and fibre. Nowadays it is one of the most common synthetic resins. The consumption of PVC resin in Western Europe in 1981 was 3.7 X 10^6 tons and was expected to reach 5.1 X 10^6 tons in 1990.[2]

The success of PVC materials in the market largely depends on the ability of PVC to be modified. Although the preparation of PVC was first described in 1872 and the foundation of the PVC industry was laid in 1912, PVC did not become a commercial product, because of serious dehydrochlorination during melt processing of PVC, till 1930' when plasticisers and heat stabilisers for PVC were developed.[1] At present, except for blends of PVC and other polymers, three types of modification technology have been developed. The first is modification during manufacture by introducing co-monomer with different physical or chemical functions, i.e. the copolymerisation of vinyl chloride and co-monomers. The second is the physical modification of PVC by the introduction of additives that can not react with the polymer, e.g. plasticisers, during compounding. The last is the chemical modification of PVC by binding functional agents into PVC chains either in solution or during processing of PVC. Combination of these technologies has given a large number of PVC formulations to meet the processing requirements and various service requirements of PVC materials. This forms an important part of PVC technology and lays a foundation for the applications of PVC polymers.

In spite of its success, the modification technology of PVC today must be further developed because society has set a high demand on synthetic materials involving a combination of economy, environmental impact and effectiveness. The modification technology of PVC must contribute to reducing cost, protecting the environment and human health, and improving the performance of PVC articles[3,4]. At present, the use of toxic additives in PVC is becoming increasingly unacceptable because additives can be readily leached from PVC articles during service and this results in migration into the human environment with potentially serious consequences[5,6] and lower effectiveness of the agents in the polymer[7,8]. The modification of PVC by copolymerisation leads to small scale, speciality manufactures and the products are therefore expensive. The chemical modification of PVC in solution is also not economical and the solvents used may cause pollution.

Potentially the chemical modification of PVC during processing via the reactive processing procedure is one of the most potentially attractive solutions to these problems.

1.1 DEGRADATION OF PVC DURING PROCESSING

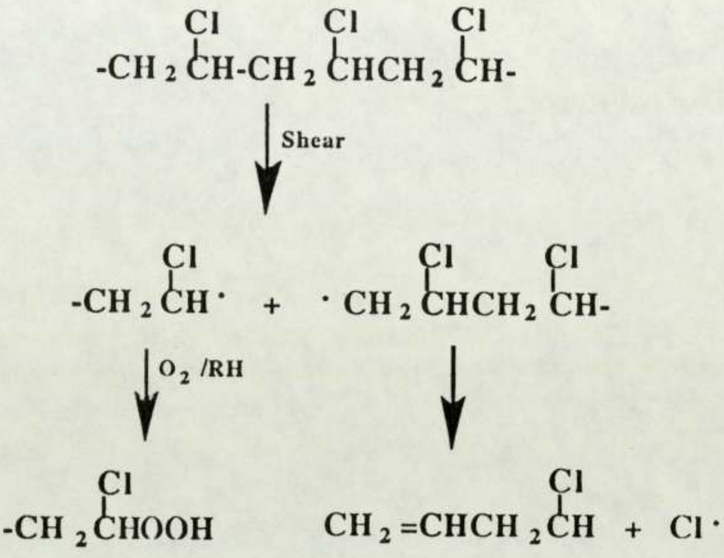
Degradation of PVC during processing is concerned with the practical application of PVC polymer so it has been intensively investigated.[9-15] It is a common observation that PVC is very unstable during melt processing due to the formation of irritating smoke containing HCl and discolouration into red-brown or black products. This has been identified as being due to two interrelated reactions, i.e. dehydrochlorination and development of conjugated polyenes (reaction 1).[9-11]

$$(\text{-CHCl-CH}_2\text{-})_n \longrightarrow n\,\text{HCl} + (\text{-CH=CH-})_n \qquad (1)$$

However, no final conclusion has yet been reached on the mechanism of this degradation process, including the initiation, the action of HCl and the development of the polyenes. A very important factor leading to the different views is the experimental conditions under which the mechanism of degradation of the PVC sample is studied.

1.1.1 Outline of Mechanisms

It is generally accepted[16,17] that normal PVC polymer is much easier to thermally degrade than its lower molecular weight model compounds such as 2,4,6-trichloroheptane. The lower thermal stability of PVC is therefore thought to be initiated by certain structural defects in PVC chains. Initiation under static conditions has been universally considered to be by the structural defects introduced during manufacture and storage of PVC, mainly internal unsaturation[18-28], tertiary chlorine[11,29] and a,ß-unsaturated carbonyl structures[30-33], though which one predominates is still uncertain. Some researchers[11] concluded that the same initiating processes are important in the degradation of PVC during processing, although this view is not widely accepted.[19,34-37,62] The conditions necessary for the processing of PVC involve high temperatures (up to 250 C), lower oxygen content and particularly high shear action, which are very different from those encountered under static conditions. It has been shown [12-14,38] that macroalkyl radicals formed in PVC by high shear action lead to the first step of the "zipper" reaction, and some of these react with oxygen to form hydroperoxides (reaction 2). This scheme can be used to explain experimental observations such as the autocatalytical photodegradation of the processed PVC[39].



(2)

The action of HCl is still confusing. For example, HCl has been reported to accelerate[40-44], retard[45], or have no effect in the absence of oxygen[46-50] or light[47,51]. A radical mechanism has been suggested[54,58] to explain the catalytic effect of HCl particularly under processing conditions[59,60], although most of the mechanisms suggested are ionic[52-54] or molecular[54-57].It has been observed[60-62] that radical-generating redox reactions occur between HCl and hydroperoxide, and, in the case of excess HCl over hydroperoxide, this leads to the formation of additional free radicals which are able to abstract random hydrogen along the PVC chains, especially at allylic positions. The retarding effect of HCl has been explained in terms of an ionic mechanism in which the hydroperoxide is destroyed by HCl in the presence of excess of hydroperoxide so that HCl acts as a stabiliser.[59,60]

Several mechanisms have been suggested to explain how the initiation site develops into polyene sequences. These include radical[51,67], ionic[68-71] and molecular processes[55](Scheme 1.1). Much attention has been focused on an important feature namely the restricted length of the resulting polyene sequences: mean values in the range 6 - 14 have been reported [63-66].

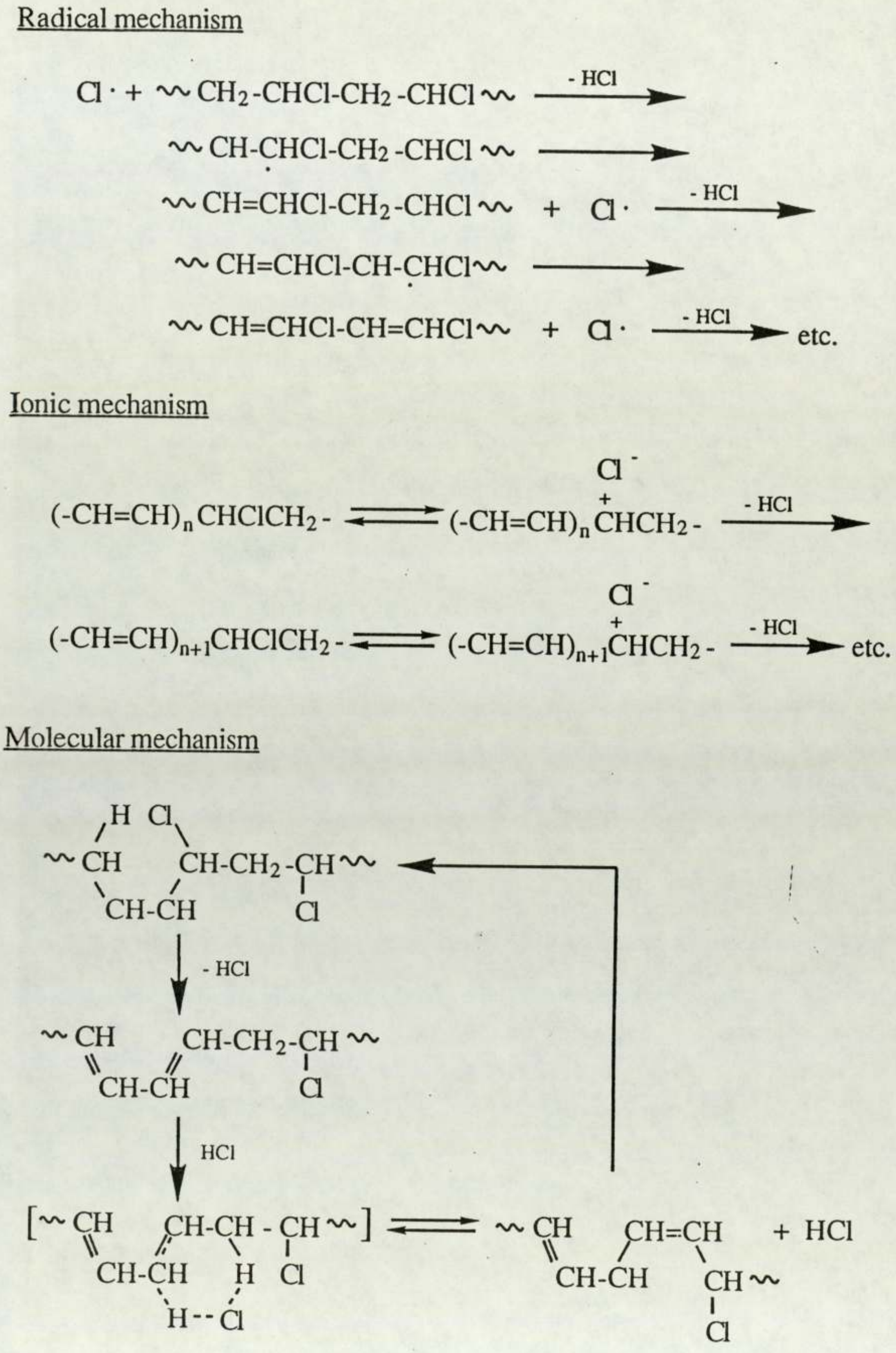
The radical mechanism is most important during processing of PVC especially in presence of oxygen, although the molecular reactions may occur as well. The observations which strongly support the radical mechanism include

(a) the increased rate of dehydrochlorination in the presence of radical generators[48,72] and oxygen[73-77];

(b) the decreased rate of degradation in the presence of radical reaction inhibitors such as hydroquinone[78], polystyrene[79] and other radical traps[80,81];

(c) gel formation in the first stage of processing of PVC[12].

Although HCl catalysis under closed processing conditions may be consistent with a molecular mechanism based on the observation that allylic chlorides with *cis* configuration undergo faster HCl elimination than the corresponding



$$Cl\cdot + \sim CH_2\text{-}CHCl\text{-}CH_2\text{-}CHCl\sim \xrightarrow{-HCl}$$

$$\sim \underset{\cdot}{C}H\text{-}CHCl\text{-}CH_2\text{-}CHCl\sim \longrightarrow$$

$$\sim CH{=}CHCl\text{-}CH_2\text{-}CHCl\sim \; + \; Cl\cdot \xrightarrow{-HCl}$$

$$\sim CH{=}CHCl\text{-}CH\text{-}\underset{\cdot}{C}HCl\sim \longrightarrow$$

$$\sim CH{=}CHCl\text{-}CH{=}CHCl\sim \; + \; Cl\cdot \xrightarrow{-HCl} \text{etc.}$$

$$(\text{-}CH{=}CH)_n CHClCH_2\text{-} \rightleftharpoons (\text{-}CH{=}CH)_n \overset{\overset{Cl^-}{+}}{C}HCH_2\text{-} \xrightarrow{-HCl}$$

$$(\text{-}CH{=}CH)_{n+1} CHClCH_2\text{-} \rightleftharpoons (\text{-}CH{=}CH)_{n+1} \overset{\overset{Cl^-}{+}}{C}HCH_2\text{-} \xrightarrow{-HCl} \text{etc.}$$

Scheme 1.1

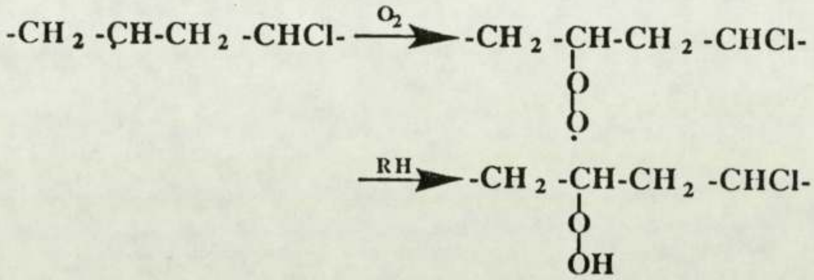
trans isomers[82], the catalytic effect can be explained by the radical generating redox reaction mentioned above[61,62]. The restricted length of the polyene sequences may be caused by many reactions such as random initiation of radicals[83], radical termination[5] or radical chain transfer[67].

The ionic mechanism accounts for the influence of solvent, HCl, and polar additives, as well as the influence of tacticity. Consequently, it provides a plausible explanation in the case of thermal degradation in solution[84-86] or in the presence of polar additives such as acids[87], strong bases[74,88] and some metal salts[75,76,85,89].

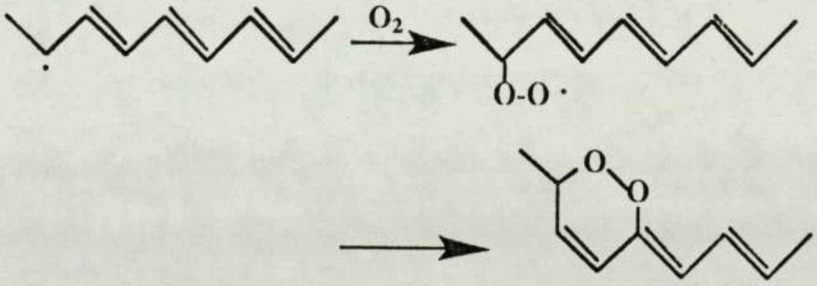
1.1.2 Secondary Reactions

Intermediates formed during degradation of PVC, including radicals, isolated and conjugated double bonds, are of high reactivity so that they can lead to many secondary reactions as well as the development of polyenes. This results in oxidation, crosslinking and chain scission.

Oxidation occurs under the processing conditions of PVC because oxygen dissolves in the PVC or is trapped between the polymer particles even in closed processing[12-14]. Reaction of oxygen with alkyl radicals leads to formation of alkylperoxy radicals and alkylperoxides[12-14,102] (reaction 3), which then carry out further reactions. Radical oxidation of long polyenes[103,104] results in bleaching of degraded PVC[26,73,75,84,90] (reaction 4).

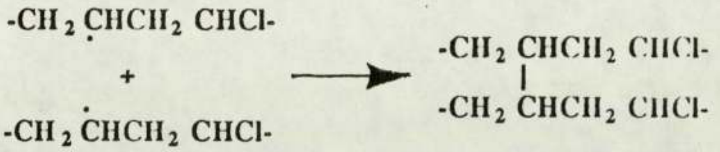


$$-CH_2-\dot{C}H-CH_2-CHCl- \xrightarrow{O_2} -CH_2-\underset{\substack{|\\ O\\ |\\ \dot{O}}}{CH}-CH_2-CHCl- \xrightarrow{RH} -CH_2-\underset{\substack{|\\ O\\ |\\ OH}}{CH}-CH_2-CHCl- \quad (3)$$



(4)

Molecular enlargement is observed in the absence of oxygen at low levels of dehydrochlorination[26] and gel formation occurs at high conversion[26]. This could arise from coupling termination between two macroalkyl radicals[91] (reaction 5) or as a result of Diels-Alder cycloaddition between two polyenes[92-95] (reaction 6). Unstable gel formation is observed after about one minute of closed processing.[12-14] This has been explained by a reaction between alkylperoxy radicals formed mechanochemically and double bonds in PVC[12,97] (reaction 7). If the degradation is performed in oxygen, no molecular enlargement can be observed at low conversion[26] but gel formation can be found at high conversion[74,96]. The crosslinking in this condition has been shown to be through intermolecular Diels-Alder cycloaddition[96].



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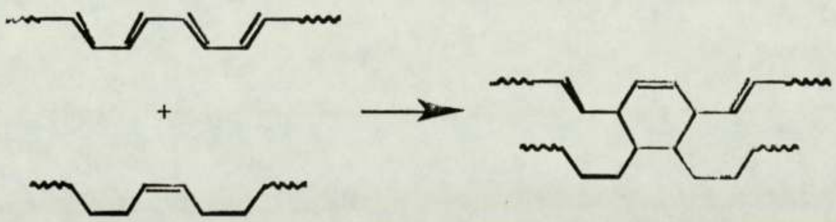

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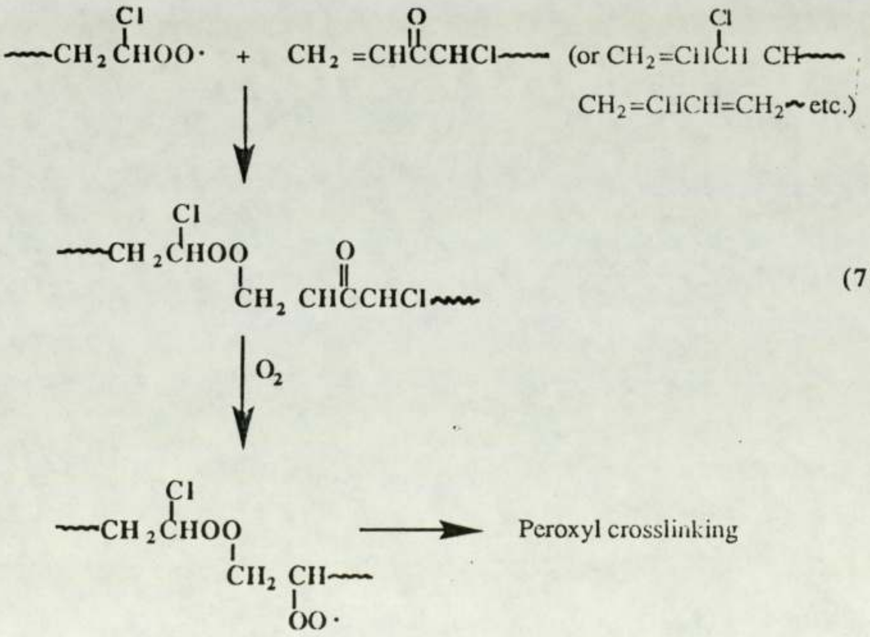
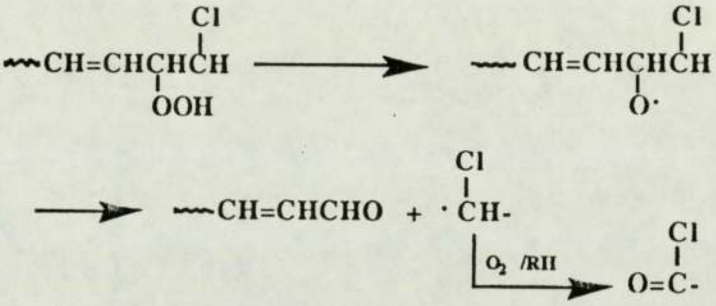


(7)

Chain scission of PVC during processing can be caused by shear force action (reaction 2) or through the thermolysis of alkylperoxides (reaction 8)[98,99]. Benzene evolution, which is found at 180 - 200 C and above[100], has been accounted for by reference to a repeated cyclisation and scission process, starting from 1-chlorovinyl ends (reaction 9)[101].



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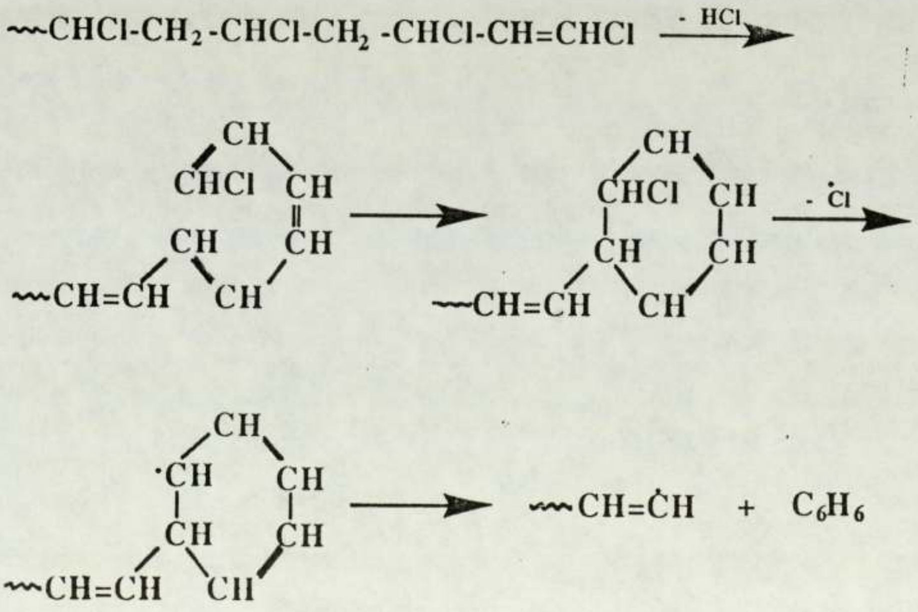


(9)

1.2. PROCESSING PROPERTIES OF PVC

1.2.1 Structure of PVC Particles

Although all the major thermoplastics can exist in powder or granule form the particulate nature of PVC is unique in the extent to which it can influence compounding and processing technology.[105]

A PVC particle is formed during polymerisation and consequent drying.[105,106] The characteristics of the particle e.g. size, size distribution and morphology greatly depend on the polymerisation process. Typical granule sizes of PVC are shown in Table 1.1.[106]

Table 1.1

Polymer Granule Sizes Typical of the Main Polymerisation Processes

Process	*Typical polymer granule size (μm)*	
	Range	Means
Suspension polymerisation	50-250	120-160
Bulk polymerisation	80-200	100-150
Emulsion polymerisation	2-70	Depend on particle size distribution

The granules formed by suspension polymerisation have a substantial degree of sphericity. Viewed in transmitted light, a particle is seen to be surrounded by a dense skin enclosing a porous interior made up of clusters of small primary particles (microgranules) and the associated interstitial voids.[106]

Bulk polymerisation granules are similar to those produced by suspension polymerisation, but they have no outer skin, so that their internal pores are more directly accessible.[106]

The particles of emulsion-produced polymer are somewhat irregular aggregates of highly spherical primary particles (microgranules) of about 1 μm size.[106] There are two types of such polymers in commercial use, i.e. "emulsion polymer" and "paste polymer". The former is normally used in calendering and extrusion formulations because of its more rapid fusion rate, and the latter is commonly used in PVC pastes.[106] It has been noted[107-109] that the size and size distribution characteristics strongly influence paste rheology.

In spite of the differences in particle characteristics, all particles whatever their origin are composed of microgranules.[110,111] A microgranule can be considered as the primary particle made up of PVC chains including crystalline and amorphous phases,[111] although it has been proposed[112,113] that it might be composed of smaller particles of about 100 Å size formed during the initial stages of polymerisation.

1.2.2 Mechanism of Fusion of PVC

When a PVC formulation is processed in equipment such as a Brabender torque rheometer or extruder, PVC particles undergo a transformation from the solid to the melten state. This is a so called fusion process.

A "comminution mechanism" of fusion is widely recognized based on many experiments and practical investigations[111,112,114-122]. According to this mechanism, the fusion process for PVC polymer is a progressive breakdown of the polymer particles involving at least two stages.[106,123]

In the initial stage, the temperature of the PVC particles is rised by the friction and shearing they experience.[106,123] The indications are that temperature is the most important single physical variable controlling the particle/surface friction[124]. When the particles have been heated to a high enough temperature they begin to break down under the shearing and frictional forces, into their constituent microgranules,[106,123] which then become the units of flow[125]. The temperature at which the breakdown proceeds depends on the shear rate.[106] Most investigators regard 160 C as this threshold in a typical extrusion process,[106] but values as low as 90-100 C have been quoted[126]. It is in this stage that the additives in the composition become more intimately dispersed among and onto the microgranules.[106]

The second stage is the breakdown of the microgranules themselves and their merging into a uniform mass.[106] The main mechanisms involved are melting of these primary particles followed by the inter-diffusion of the molecular chains, initially confined within the boundaries of a particle, with those similarly liberated by its neighbours.[106] During this stage further homogenisation between polymer and additives take place. The additives are distributed through the polymer mass from their positions on the surfaces of the microgranules to attain a more uniform stage of dispersion.[106] The processing temperature necessary for reaching this stage is found to be above 190 C for unplasticised PVC.[112,127] It will be influenced by the particle slippage flow behaviour[128,129] and lowered in the presence of plasticisers[106,123,130]. The penetration of plasticisers into the microguanules is recognized as an important factor of the gelation mechanism[106].

If full fusion is reached, the polymer is in a molecular stage of division. The degree of completeness of the breakdown of the microgranules and their inter-merging is the degree of fusion in melt processing.[106] It has been reported[123] that a small amount of crystalline PVC still survives in the PVC melt at safe processing temperatures because of the relatively high melting point of crystalline PVC (265 - 273 C[131-133]).

More recently it has been claimed[134] that the "comminution mechanism" operates only in equipment which subjects the material to very vigorous mechanical working under high shear, such as internal Banbury-type mixers and Brabender torque rheomoters. Otherwise, for what is regarded as less vigorous processing in extruders and on two-roll mills, a "CDFE mechanism" has been proposed[134]; this is said to involve not breakdown but compaction, densification, fusion and elongation of polymer particles, followed directly by melting.

1.3 CHEMICAL MODIFICATION OF PVC

Chemical reactions have been used to modify the character of polymers since the earliest day of polymer chemistry. For example, nitrocellulose and chlorinated rubber have been known for well over a hundred years. Chemical modification has also played an important role in the development of PVC polymers, e.g. chlorinated PVC has been commercially used for a long time.

1.3.1 Objectives of Post-Reaction on PVC

Chemical reactions have been carried out on PVC for a variety of purposes.

In 1970', the primary objectives of chemical modification of PVC were summarized[135] as being

(1) increased solubility in inexpensive solvents;
(2) increased heat-distortion temperature;
(3) increased resistance to hot melt flow;
(4) introduction of ion-exchange capacity;
(5) preparation of polymer structure not otherwise available;
(6) improved stability to light and heat;
(7) improved melt flow.

Today, the objectives will at least additionally include

(8) binding plasticisers and stabilisers in PVC to improve the extraction resistance;
(9) preparation of polymer-bound antioxidant and stabiliser masterbatches;
(10) introduction of controlled biodegradation capacity.

Some of these objectives can be reached by physical modification of additives or by copolymerisation. For example, increased solubility in inexpensive solvents is achieved commercially by copolymerisation.[135] Improved melt flow can be achieved, and normally is, by altering polymerisation conditions.[135] However, post-reactions of PVC are available in those instances in which additives and copolymerisations have failed to yield the desired result. Moreover, the chemical modification of PVC would be a most economical method of property variation if a cost-effective synthesis method using reaction processing procedure could be developed.

1.3.2 Typical Chemical Reactions of PVC

The polymer has been reacted with nucleophlic, electrophilic and free-radical agents. The discussion here will be directed primarily towards structure variation.

1.3.2.1 Chlorination of PVC [135]

Chlorination of PVC can be carried out with either Lewis acid or free-radical catalysis. In case of the former catalyst an elimination-addition mechanism has been suggested. The reaction is reported to be very sensitive to temperature, concentration and time. Chlorine contents up to 64% have been given.[136]

1.3.2.2 The Friedel-Crafts Reaction on PVC [135]

Friedel-Crafts reaction is carried out in the presence of Lewis catalysts which lead to many side reactions such as crosslinking and chain scission. The alkylation of aromatic hydrocarbons with PVC has been studied.[137] It has been shown that the initial alkylation reaction is followed by an intramolecular cyclisation and the extent of degradation increases with increasing aromatic substitution on the chains. In the absence of an aromatic compound the dominant reaction is crosslinking.[137]

1.3.2.3 Reaction of PVC to Give Ion-Exchange Resins [135]

Anion-exchange resins have been prepared by reaction of PVC with amines.[138] The reactions give varying ratios of substitution, dehydrochlorination, crosslinking and chain scission.[138] Thus, aniline reacted with PVC giving a product with about 70% of the introduced amine as primary amine. Low amounts of aromatic amine gave crosslinking.[139] Excess amine gave intramolecular cyclisation but soluble products.[139]

Cation-exchange resins have been prepared from PVC by reaction with chlorosulfonic acid, sulfonyl chloride or sulphur trioxide.[140-142] Sulfonyl chloride groups have also been introduced by reaction of PVC with thiourea, followed by treatment with aqueous chlorine.[143]

1.3.2.4 Reactions of PVC with Unsaturated Compounds

The Diels-Alder reaction of PVC with maleic anhydride and maleate has been reported.[83,144-146] Thus, maleates can react with partially dehydrochlorinated PVC to give modified polymers.[83,144] The amount of dibutyl maleate (DBM) reacting with PVC reaches 20-30% when the reaction is carried out in DBM solution.[83] A DBM modified PVC is also formed by heating PVC in DBM solution.[146]

Diels-Alder adducts formed by the reaction of PVC with conjugated dienes e.g. cyclopentadiene, piperylen, 5-methyl-1,3,6-heptatriene, 1,3,6-octatriene, and methyl sorbate have been reported.[147]

Free-radical initiated nucleophilic substitution of chlorine in PVC by maleate has been reported recently.[83] The reaction of PVC with DBM in DBM solution in the presence of azobiisobutyronitrile (AIBN) can give a plasticiser modified PVC.[83] It has been stated[83] that the bound DBM reaches about 30% of PVC by weight after 10 hours reaction at 90 C.

Graftings of reactive monomers onto PVC to give copolymers have been studied. Many monomers have been used including acrylate[148-153], acrylic acid[149,154,155], styrene[153,156-159], vinyl acetate[160,161], butadiene[153,162,163], acrylonitrile[157,164,165] and ethylene oxide[166]. Thus, ethyl acrylate (EA) has been grafted onto PVC in aqueous emulsion or suspension in the presence of peroxides. [148] The yield increases with increasing temperature and decreased with increasing initial EA-PVC ratio.[148] Grafting of butyl acrylate onto PVC is achieved by exposure to UV irradiation.[149] The yield is greater in the presence of a solvent than that obtained by grafting PVC with the acrylate only.[149]

1.3.2.5 Crosslinking of PVC [135]

PVC can be crosslinked by being irradiated[167] or by reacting with metal oxides or with peroxides and crosslinking agents[168,169].

The effect of gamma radiation depends on reaction conditions. For example, irradiation in air will not give crosslinking[170-172] but irradiation in an inert atmosphere[173] or solvent[174] results in extensive crosslinking. A radical mechanism has been proposed to account for these observations.[175]

UV radiation also leads to crosslinking of PVC. This is more important in the photodegradation and stabilisation of PVC than in chemical modification and has been extensively studied.[176-178]

PVC has been crosslinked chemically with many agents. Thus, 90% gel formation is recorded when PVC is heated with 1,2- benzenedisulfonazide at 150 C.[179] Dithiols and trithiols apparently lead to crosslinking by reaction with unsaturation in PVC.[180] Dicumyl peroxide is found to be less effective in PVC than in polyethylene (PE).[181]

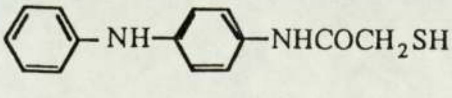
1.3.3 Modification by Reactive Processing

Most of the post-reactions of PVC mentioned above are carried out in solution. This results in higher cost and leads to trouble in separating solvents from products. If modified polymers could be directly obtained during commercial processing via a reactive processing procedure, then chemical modification technology of PVC would be more available in commerce.

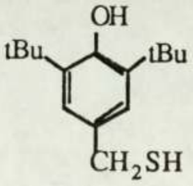
1.3.3.1 Outline of Reactive Processing

Reactive processing in polymer melts is used to describe novel reaction systems in which the "traditional" function of mixers and extruders is executed simultaneously with in-situ modification of the polymer backbones.[182] Modification of polymers by reactive processing normally is via radical initiated chemical reaction in which the radicals are produced by mechanochemical scission of the polymer chains[183], and by radical generators[184,185] if necessary. Available functionalised modifiers which have been used include thiol compounds and vinyl compounds, mainly maleates and acrylates. Applications of reactive processing in preparations of polymer bound antioxidants have been reviewed recently by Scott[183].

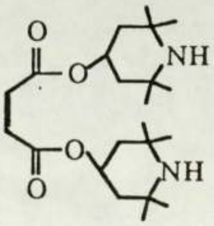
Thiol-based antioxidants have been successfully used to modify polymers during processing in a torque rhoeometer.[186-189] It was found[183] that this process is most successful in the case of polymers containing olefinic unsaturation, although the level of unsaturation does not need to be high. Thus, ethylene propylene diene monomer (EPDM) can react with MADA (I) to give 87% binding in the case of relatively high loadings of MADA (10 g/100 g EPDM).[186] Nitrile-butadiene rubber (NBR) reacts with MADA giving 55% yield and with BHBM (II) giving 62% yield in the case of very high loadings of additives (50 g/100 g NBR).[187] This makes it possible to prepare concentrates which can be used as "masterbatch" additives for other polymers.



(I) MADA



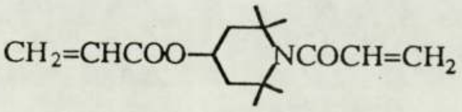
(II) BHBM



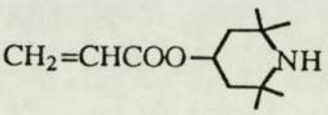
(III) BPM

Bindings of maleate-based antioxidants in polyolofines have been achieved in the presence of a radical generator. Thus, Bis(2,2,6,6-tetramethyl piperidin-4-yl) maleate (BPM) (III) can be reacted with polypropylene (PP) in the presence of dicumyl peroxide to give high levels (up to 90%) of binding under a loading of 5 g/100 g PP (1.27×10^{-2} mol·100 g^{-1}).[184] The adducts from this process have been treated as concentrates of the hindered piperidine in the polymer.[184]

Other concentrates of hindered amines in polymers have been given by reactions of acryloyl-based antioxidants with polyolefines. For example, 1-acryloyl-4- acyloyloxy -2,2,6,6-tetramethyl-piperidine (AATP) (IV) reacts with low density polyethylene (LDPE) in the presence of tert-Bu_2O_2 giving a masterbatch of graft polymer. 2,2,6,6-tetramethyl-4-piperidyl acrylate (AOTP) (V) can be co-reacted with a tris acrylate with PP to give 100% binding.[190]



(IV) AATP



(V) AOTP

The parameters which influence the yield of thiol adducts have been summarized by Scott[183] as follows:

(1) The intrinsic viscosity of the polymer and its change with temperature.

(2) The plasticising effect of the additive, which is in turn dependent on the concentration.

(3) The effect of oxygen, which in very low concentration produces hydroperoxides which lead to high yields of adduct. An excess of oxygen, however, inhibits the free radical chain reaction, unacceptably reduces the viscosity of the polymer by oxidation chain scission and oxidises the thiol antioxidants to products which cannot form adducts with the unsaturation on the polymer.

The extent of binding of BPM has been reported to increase with increasing initiator to additive molar ratio.[184]

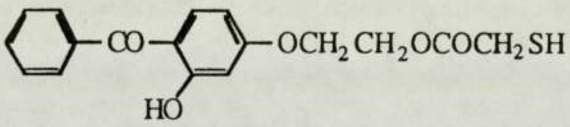
The extent of binding of acryloyl-based hindered piperidines has been reported[182] to be greatly dependent on processing conditions i.e. time, temperature and initiator molar ratio. The latter has been shown to be most important. If the ratio is too low, the concentrate may contain a high proportion of homopolymer of the additive and will become crosslinked and unprocessable. If the ratio is too high, molecular breakdown occurs. The effect of processing time has been investigated based on the torque development. It has been observed that there is an increase in the torque in the first few minutes of processing accompanying increase of binding of the additive: this is considered to be associated with polymerisation or crosslinking. This is followed by a sharp decrease associated with "depolymerisation" to give a bound product. Therefore, as long as processing is continued well past the torque peak, the concentrate can be incorporated in polymers as additive without difficulty.[182]

The concentrates of bound antioxidants have been used as masterbatches in the host or other polymers.[185,191-194] The effectiveness tests of antioxidants, such as the antifatigue test[191], antiozonation[192] and mechanical tests[193,194] in the case of thiol-based antioxidants, and the photoageing test[184,185] with vinyl-based hindered amines antioxidants, have shown[184,185,191-194] that bound antioxidants are at least as effective as "normal" antioxidants but are not lost by extraction.

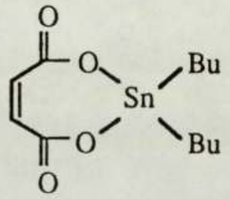
1.3.3.2 Reactive Processing of PVC

A substantial level of binding of thiol-based antioxidants at relatively low loadings with PVC was first reported by Cooray and Scott[195,189] following an investigation of the action mechanisms of thiol-based antioxidants during processing of PVC. In the case of the UV stabiliser EBHPT (VI) ($2.20X10^{-3}$

mol·100 g^{-1} PVC), 100% binding can be achieved within 4 min of processing in the presence of dibutyltin maleate (DBTM) (VII) ($4.48X10^{-3}$ mol·100 g^{-1} PVC) at 170 C.[195,189] The hindered phenol BHBM ($1.30X10^{-3}$ mol·100 g^{-1} PVC) reacts similarly with PVC and becomes 100% bound within 6 min.[195] Adduct formation in this case has been shown to occur through the unsaturation formed in PVC as a result of mechanical shear which leads to the elimination of HCl during the initial stages of processing (reaction 2 and scheme 1.2).[60]

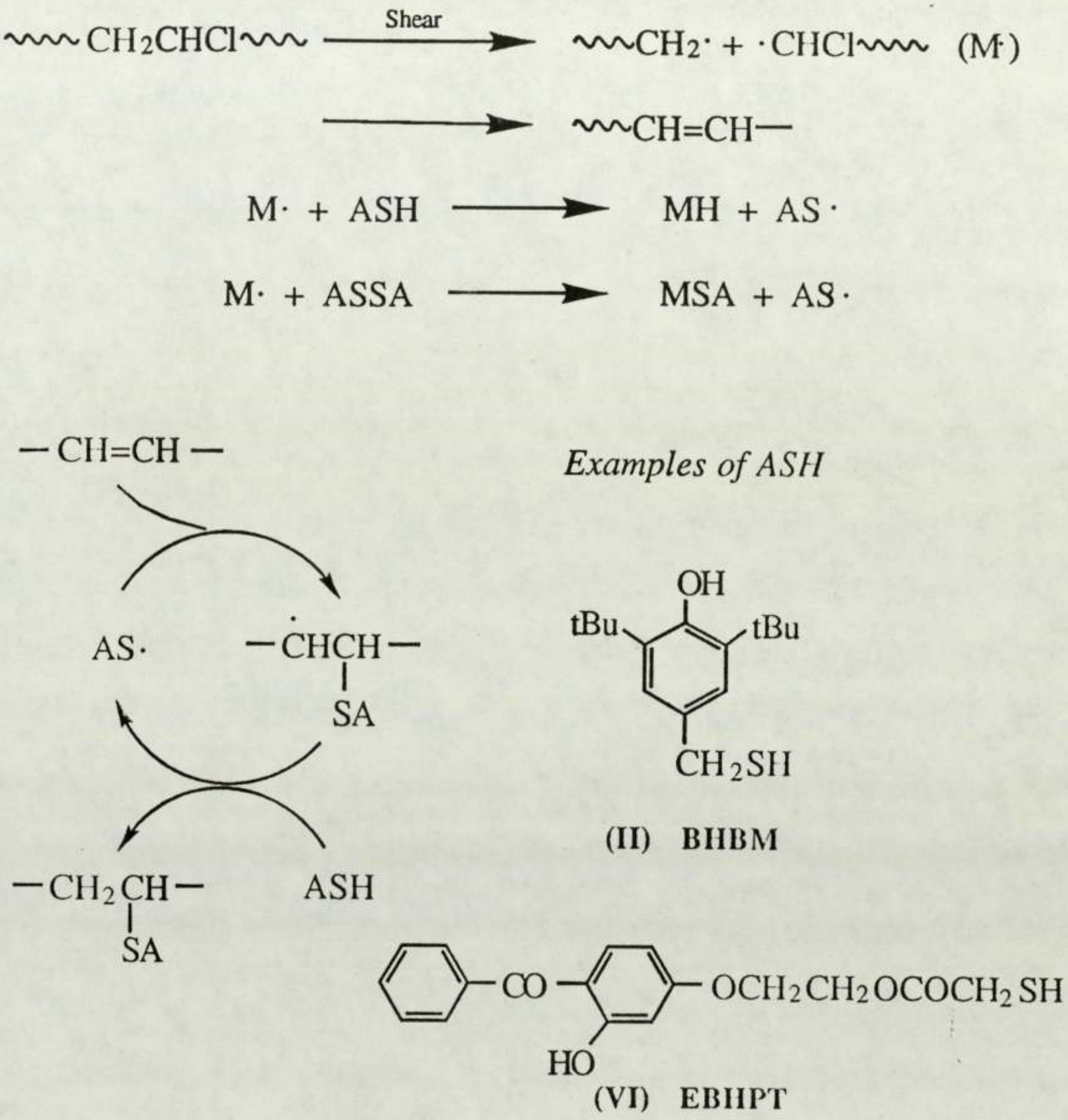


(VI) EBHPT

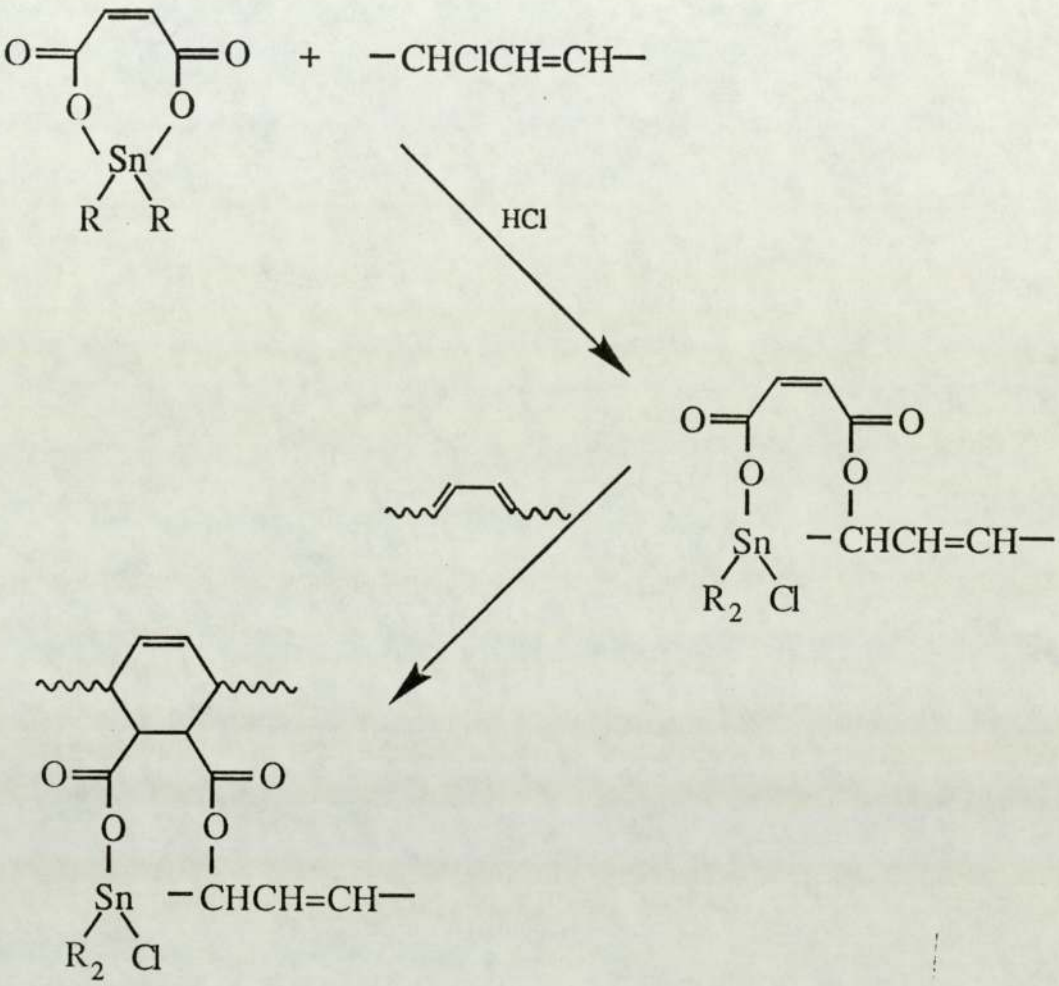


(VII) DBTM

The Diels-Alder reaction of dienophilic-based heat stabilisers, e.g. dialkyltin maleate, with conjugated unsaturation in PVC during processing has been reported to account for the mechanism of PVC melt stabilisation.[60] The reactions proposed in the case of DBTM are shown in scheme 1.3: cyclic adducts would be formed in this process[60]. However, both formation and yield of the adduct has not been reported.



Scheme **1.2** Mechano-initiated addition of thiol-based antioxidants to PVC.[183]



Scheme 1.3 Action mechnism of DBTM on the stabilisation of PVC during processing.[60]

An exception has been found in recent literature[144] which shows that Diels-Alder adducts between partially dehydrochlorinated PVC and a number of maleates (dihexadecyl maleate and dioctadecyl maleate) at a loading of 11.2-17.6 g/100 g PVC can be formed to give a yield of 0.2-1.15%. However, it has been concluded that the use of the Diels-Alder reaction as a means of modifying PVC during processing by grafting-on a suitable dienophile is unlikely to be a viable approach because of the simultaneous degradation of PVC that occurs.[144]

The properties of PVC bound additives have been examined only in a few cases. It has been shown that the combination of bound hindered phenol and tin stabiliser gives exceptional stability in air at 140 C.[189] A combination of BHBM-B and EBHPT-B (where -B indicates polymer-bound) is a very powerful UV stabiliser.[196] Effective melt stabilisation is also achieved with BHBM-B in PVC.[195]

1.4 OVERALL AIM OF THE PROJECT

The modification of PVC by reactive processing is an attractive approach because the application of PVC is much more dependent on the incorporation of additives, especially stabilisers and plasticisers, than is the case for many polymers. However, known additives which become bound during processing of PVC are all stabilisers, e.g. thiol-based antioxidants such as EPHPT and BHBM (see 1.3.3.2). In addition, the binding reactions are all based on low loadings of the additive ($< 1 \times 10^{-2}$ mol·100 g^{-1} PVC) (see 1.3.3.2). Reactive processing procedures which lead to the chemical binding of stabilisers in PVC have also not been studied in any detail this is equally true for other types of additives, especially plasticisers, at higher loadings. Consequently, it is necessary to explore both reaction conditions and mechanisms of reaction of plasticisers and stabilisers in the PVC melt to develop cost-effective reactive processing methods.

It is equally apparent that the effectiveness of bound additives in PVC systems has been studied in only a few cases (see 1.3.3.2). Indeed, the relationships between the processing conditions, structure and properties of additive-bound PVC have not been studied at all. It is therefore neccessary to investigate this subject in order to produce modified PVC polymers with the desired performance characteristics.

Based on above reasoning, the overall aim of the project was to:

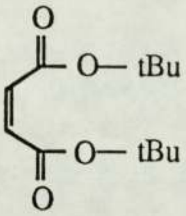
(1) develop reactive processing methods for modifying PVC by binding two types of vinyl compounds, maleate and acrylate, at loadings of additives upto 5×10^{-1} mol·100 g^{-1} PVC; and

(2) study the relationships between processing conditions and the

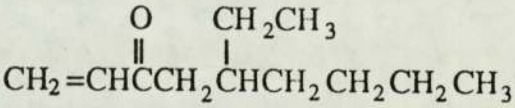
structure and properties of the modified PVC systems.

Dibutyl maleate (DBM) (VIII), a plasticiser of PVC [198], was used to represent the maleate class of plasticisers.

2-Ethylhexyl acrylate (OA) (IX) was used to represent the acryloyl-based plasticiser or stabiliser.



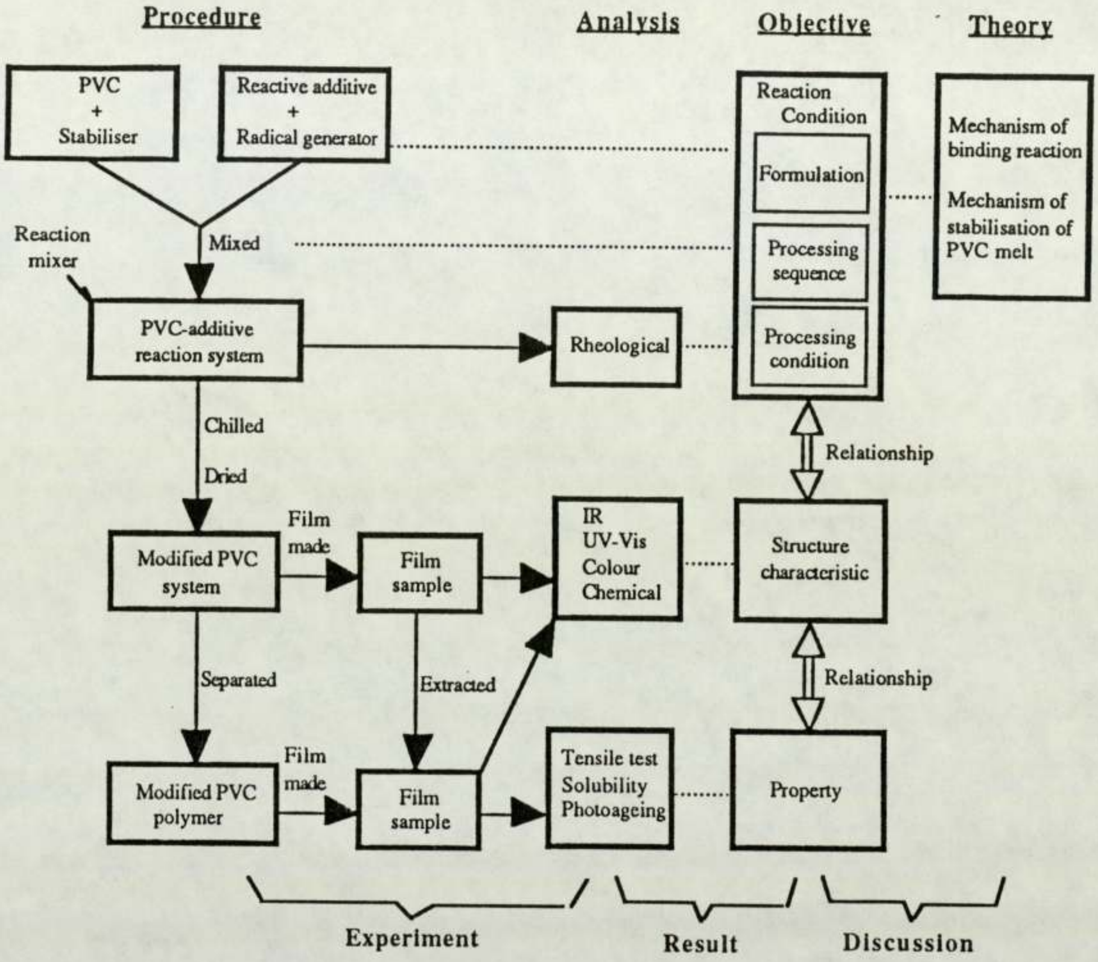
(VIII) DBM



$$CH_2{=}CH\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{CH_2CH_3}{|}}{C}HCH_2CH_2CH_2CH_3$$

(IX) OA

The programme of work is presented in Scheme 1.4.



Scheme 1.4 Outline of this work.

CHAPTER 2

EXPERIMENTS

2.1 MATERIALS

The main chemicals used in the project will be described below. All chemicals were used without additional purifications except where indicated.

PVC resin: was an unstabilised grade, "Corvic"S71/102, from ICI Co. GPC analysis of the polymer provided by the RAPRA Polymer Supply and Characterisations Centre[61] gave the following characteristics:

Mn = 48020, Mw = 119900, Mz = 265200, Mv = 109400,

Mw/Mn = 2.497, Mz/Mn = 5.523.

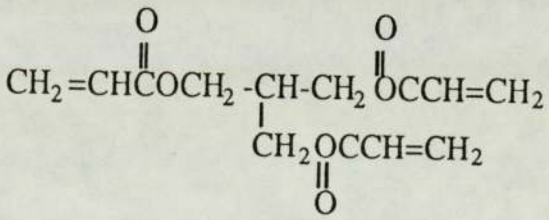
In this work, part of the PVC was stabilised by DBTM to 5.56 X 10^{-3} mol·100 g^{-1} PVC.

Dibutyltin Maleate (DBTM) (VII): was Irgastab T290 as supplied by Giba Geigy. This is known to contain a small proportion of hindered phenolic antioxidant. mp 135 C, bp >200, FW 347.01.

Dibutyl Maleate (DBM) (VIII): purchased from Aldrich Chemicals Co., 99%, bp 281 C, FW 228.29.

2-Ethylhexyl acrylate (OA) (IX): purchased from Aldrich Chemicals Co., 99%, bp 215 - 219 C, FW 184.28.

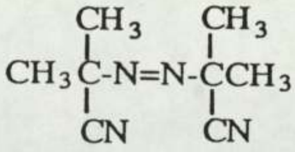
Trimethylolpropantriacrylate (ATM12) (X): purchased from Ancomer LTD. FW 270.



$$CH_2{=}CH\overset{\overset{O}{\|}}{C}OCH_2\text{-}\underset{\underset{CH_2O\underset{\underset{O}{\|}}{C}CH{=}CH_2}{|}}{C}H\text{-}CH_2O\overset{\overset{O}{\|}}{C}CH{=}CH_2$$

(X) ATM12

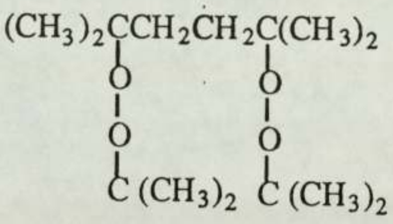
Azobiisobutyronitrile (AIBN) (XI): purchased from Ventron GMBH Ltd., 99%, mp 107 C, FW 162.21.



$$CH_3\overset{CH_3}{\underset{CN}{C}}\text{-}N{=}N\text{-}\overset{CH_3}{\underset{CN}{C}}CH_3$$

(XI) AIBN

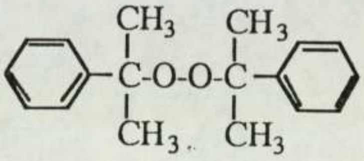
Triganox101 (101) (XII): supplied by Akzo Chemicals Ltd., 99%, FW 290.



$$(CH_3)_2\underset{\substack{|\\O\\|\\O\\|\\C(CH_3)_2}}{C}CH_2CH_2\underset{\substack{|\\O\\|\\O\\|\\C(CH_3)_2}}{C}(CH_3)_2$$

(XII) 101

Dicumyl peroxide (DCP) (XIII): purchased from BDH Chemicals Ltd., 99%, mp 39 - 41 C, FW 270.37.



(XIII) DCP

2.2 REACTIVE PROCESSING

PVC-additive reaction systems were processed in the closed chamber of an internal mixer (RAPRA-Hampden torque rheometer)[61] under different processing conditions. The chamber of the mixer was oil heated and thermally programmed. Reactive processing was carried out in the chamber filled with the reaction system, air being essentially excluded by means of a sealing ram during the processing procedure. The torque values were recorded during processing. The processed product was then rapidly withdrawn, chilled in cold water, dried and stored in sealed plastic bags.

2.3 FILM PREPARATION

2.3.1 Casting of Film

The processed product was cut into small pieces and dissolved in tetrahydrofuran (THF) for 12 hours to give a clear solution. The solution was then carefully poured onto a shiny glass surface and kept in a ventilation cabinet for 2 hours to completely evaporate the solvent. Uniform films with a thickness of about 3×10^{-3} cm were chosen for later analysis.

2.3.2 Compression Moulding of Film

The processed product was cut into small pieces and compressed between stainless steel plates, using PU grade cellophane to separate the polymer from the steel plates, at the available temperature (160 - 180 C) for 90 seconds under a ram pressure of 0 - 5 $Kg \cdot cm^{-2}$; after preheating, the film was further processed at 160 - 180 C for 30 seconds under a ram pressure of 100 $Kg \cdot cm^{-2}$. Uniform films of thickness 3×10^{-2} cm were chosen for analysis and property studies.

2.4 PURIFICATION

2.4.1 Extraction

The film samples were extracted in a Soxhlet extraction unit with refluxing solvent for 24 hours. Hexane, an excellent solvent for DBM [83], was used for the samples of the DBM modified PVC systems. Methanol was used for the samples of the OA modified PVC systems.

2.4.2 Separation (See Scheme 4. 1, P. 152)

5.0 g of processed product in small pieces were refluxed in 200 ml benzene for 3 hours. The refluxed solution was allowed to stand for 0.5 hour and then separated into a soluble part and an insoluble part. The benzene insoluble part was washed by benzene repeatly and then dried in a vacuum drier at 15 C for 24 hours. The purified product was weighed and stored in a sealed plastic bag for later use: this product was shown to be OA bound PVC polymer. The benzene soluble part was precipitated by means of the addition of methanol under agitation. The precipitate was separated and washed by methanol repeatly and then dried in a vacuum drier at 15 C for 24 hours. The product was collected and stored in a sealed plastic bag for later analysis. It was shown to be the homopolymer of OA.

1.0 g of the purified product was refluxed in 100 ml tetrahydrofuran (THF) for 2 hours. The solution was then separated into a soluble part and an insoluble part. The THF insoluble part was washed by THF repeatly and then dried in a vacuum drier at 15 C for 12 hours. The purified product was weighed: this product was regarded as crosslinked bound PVC polymer. The THF soluble part was made into film by means of casting for later analysis. It was regarded as OA grafted PVC copolymer.

2.5 CHEMICAL AND PHYSICAL ANALYSIS

2.5.1 Extent of Binding of Additives to PVC

The extent of binding was determined from carbonyl group absorption at 1734 cm^{-1} in IR spectra contributed by the ester groups of DBM or OA. An internal standard method[201] was used based on A_{1734} / A_{1427} to eliminate the influence of differences in film thickness. The film thickness ranged about $1X10^{-3}$ inch. Calibration curves for DBM and OA were obtained from measurements on a set of PVC films with DBM or OA contents in the concentration range from 0 to 6.00×10^{-1} mol·100 g^{-1} PVC. The measurements were performed by using a Perkin-Elmer 599 Infrared Spectrometer and a Perkin-Elmer 1710 Infrared Fourier Transform Spectrometer.

For DBM modified PVC systems, the extent of binding was calculated from the following equation:

$$E = I_e / I_o$$

in which $I = A_{1730} / A_{1427}$; o and e indicate sample before and after extraction respectively.

For OA modified PVC systems, the extent of binding was calculated from the following equation:

$$E = I_b / I_o$$

in which $I = A_{1730} / A_{1427}$; o indicates unpurified sample; b indicates sample of the OA bound PVC polymer which has been separated from OA modified PVC system by benzene treatment (see 2.4.2).

The conversion of OA was calculated from following equation:

$$C = I_e / I_o$$

in which $I = A_{1730} / A_{1427}$; o and e indicate sample before and after extraction respectively.

2.5.2 Colour Development

Colour formation in the film samples was expressed as the total colour difference related to a calibrated reference film cast from a 5% THF solution of the unprocessed PVC resin. The thickness of the sample was 3 X 10^{-2} cm. Measurements were carried out using a MEECO Colourmaster Model V in transmission. Readings were obtained by using green, red and blue filters and the total colour difference, ΔT, was calculated by the following equation:

$$\Delta T = (\Delta G^2 + \Delta R^2 + \Delta B^2)^{1/2}$$

where ΔG, ΔR and ΔB refer to differences between intrument readings on the test sample and the reference sample using green, red and blue filters respectively.

2.5.3 Unsaturation

2.5.3.1 UV-Vis Spectroscopy Measurement

Conjugated unsaturation was detected from the absorption bands from 260 - 500 nm in UV-Vis spectra[88] by using a Beckman DU-7 Spectrometer.

2.5.3.2 IR Spectroscopy Measurement

Short sequence conjugated unsaturation was measured from the absorbance at 1650 cm^{-1} in IR spectra.[200]

2.4.3.3 Acetic Acid Liberation Method

Monounsaturation was determined by the acetic acid liberation method adapted from Martin [197] by Cooray[61].

0.5 g of film as small pieces was swollen in 75 ml of chloroform for 12 hours in a conical flask with stopper. 4.0 g of acid-free mercuric acetate and 30 ml of methanol were added. After adding 75 ml of saturated aqueous sodium chloride and 100 ml of distilled water, the liberated acetic acid was titrated with 0.1 N sodium hydroxide after 3 hours and the phenolphthalein end point (yellow to pink) determined. Blank runs were also similarly examined for each set of experiments.

2.5.4 Hydroperoxide and Hydroxyl Groups

2.5.4.1 Iodine Liberation Method

Hydroperoxide was detected by the iodine liberation method adapted by Cooray[61].

0.5 g of film as small pieces was swollen in 75 ml of deaerated chloroform for 12 hours in a conical flask with stopper. 1 ml of deaerated glacial actic was added followed by 25 ml of freshly prepared 5% sodium iodide. After allowing the sample to stand in the dark for 4 hours at room temperature, the liberated iodine was titrated with 0.01 N sodium thiosulphate solution. For each set of experiments blank runs were also similarly examined.

2.5.4.2 IR Spectroscopy Measurement

Hydroxyl group was monitored by the IR absorbance at 3420 cm^{-1}.[39]

2.5.5 Molecular Weight and Molecular Weight Distribution

Molecular weight and molecular weight distribution were measured by gel permeation chromatography (GPC) at RAPRA Polymer Supply and

Characterisations Center, Shawbury, Shrewsbury, Shropshire. Tetrahydrofuran (THF) was used as solvent.

2.6 PROPERTY TESTS

2.6.1 Extraction Resistance

The extraction resistance of the DBM modified PVC system was assessed by both extracting samples of film in refluxing hexane and immersing film in hexane at 15 C. The loss of weight of the sample was recorded over set time intervals.

2.6.2 Blooming Resistance

The blooming resistance of the DBM modified PVC systems was determined by exposing the samples of film under UV irradiation in a simulated sunlight cabinet (see 2.6.4). The appearance of the surface of the sample was observed and recorded.

2.6.2 Solubility

0.5 g of film in the form of small pieces was added to 50 ml of tetrahydrofuran, cyclohexanone, chloroform and acetone respectively. Details of the treatment conditions will be given in the results chapters.

2.6.3 Plasticity and Mechanical Properties

Plasticity and mechanical properties were measured by means of a tensile test using a Testometric 500M electrical tensile machine. The readings of load and extension were recorded to give a stress-strain curve. The tangent modulus (M_t) and the elongation to break (E_b) were calculated from the curve; the plasticity was then expressed as an index (PI) from the following equation:

$$PI = E_b / M_t \, .$$

2.6.4 UV Photostability

The UV photostability of the modified PVC polymer was evaluated by photoageing a film sample in a simulated sunlight cabinet. The cabinet consisted of a symmetrical array of 24 fluorescent Type C Phillips actinic blue lamps (05) and 8 Type A2 Westinghouse sunlamps (FS20). The fluorescent blue lamps gave a symmetrical distribution from 300 - 400 nm peaking at 374 nm while the fluorescent sunlamps gave a symmetrical distribution at 280 - 400 nm peaking at 317 nm. A set of four lamps (three actinic and one sunlamp) was replaced sequentially at intervals of 2000 hours.

Variations in colour, unsaturation and hydroxyl group content were monitored during UV irradiation. Changes in tensile properties were also measured during UV irradiation.

Embrittlement time was used as an indicator of the photostability of the sample: this was the time to fracture of the film on bending through an angle of 180°. Each measurement was carried out in triplicate and the accuracy was +/- 5%.

CHAPTER 3

MALEATE MODIFIED PVC SYSTEMS

3.1 CHAPTER LAYOUT

In this chapter, the experimental results for DBM modified PVC systems covering synthesis, structure analysis and physical properties will be presented (**3.2**). The ranges of the formulations and the processing conditions used were as follows:

(a) Formulations:

PVC	100 g
DBTM	2 g (0.0056 mol)
DBM	0 - 70 g (0.30 mol)
Radical generator	0 - 1.0 molar radical to DBM;

(b) Processing conditions:

Temperature	80 - 200 C
Time	1 - 25 min.

In sections **3.2.4** and **3.2.5** the modified PVC samples are analysed and tested and compared with standard PVC samples. Details of the formulation and processing conditions of these samples are showed in Table 3.1.

Table 3.1

PVC and DBM Modified PVC Samples

Sample	*Formulation*				*Processing Condition*		*DBM bound*	
	PVC (g)	DBTM[a]	DBM[a]	RG[b]	Temperature (C)	Time (min)	a	(%)
PVC [c]								
pPVC	100	0.056			145	10		
P50	100	0.056	2.17		145	10	0.15	7
A1	100	0.056	2.17	AIBN(0.01)	145	10	0.15	7
A2	100	0.056	2.17	AIBN(0.30)	145	10	0.15	7
A3	100	0.056	2.17	AIBN(1.00)	145	10	0.15	7
T1	100	0.056	2.17	101[d] (0.01)	145	10	0.15	7
T2	100	0.056	2.17	101[d] (0.30)	145	10	0.67	31
T3	100	0.056	2.17	101[d] (1.00)	145	10	1.12	52

a The unit is Mol·100 g^{-1} PVC (X10).

b Radical generator (Molar radical ratio to DBM).

c Original PVC powder.

d Triganox101.

3.2 EXPERIMENTAL RESULTS

3.2.1 Formation of DBM Modified PVC Polymers during Processing

A series of DBM modified PVC polymers were prepared under the conditions listed for processing and then made into films and extracted in refluxing hexane for 24 hours. The extracted DBM modified PVC films were transparent and colourless and were softer than PVC film. Evidence for the binding of DBM into PVC chains during processing is provided by I.R. spectra shown in Fig.3.1. The extracted modified PVC polymer shows a strong carbonyl peak at 1734 cm^{-1}. When compared with the results for the unextracted modified PVC system, reduction of the carbonyl peak as well as disappearance of the peak at 3030 and 1640 cm^{-1}, which arise from the unsaturation in DBM[199], indicate that the unreacted DBM has been removed.

Because of the relatively low concentration of DBTM in the reaction system, its binding effect was regarded being identical to that of DBM, even though the reactivity of DBTM may be different from that of DBM.

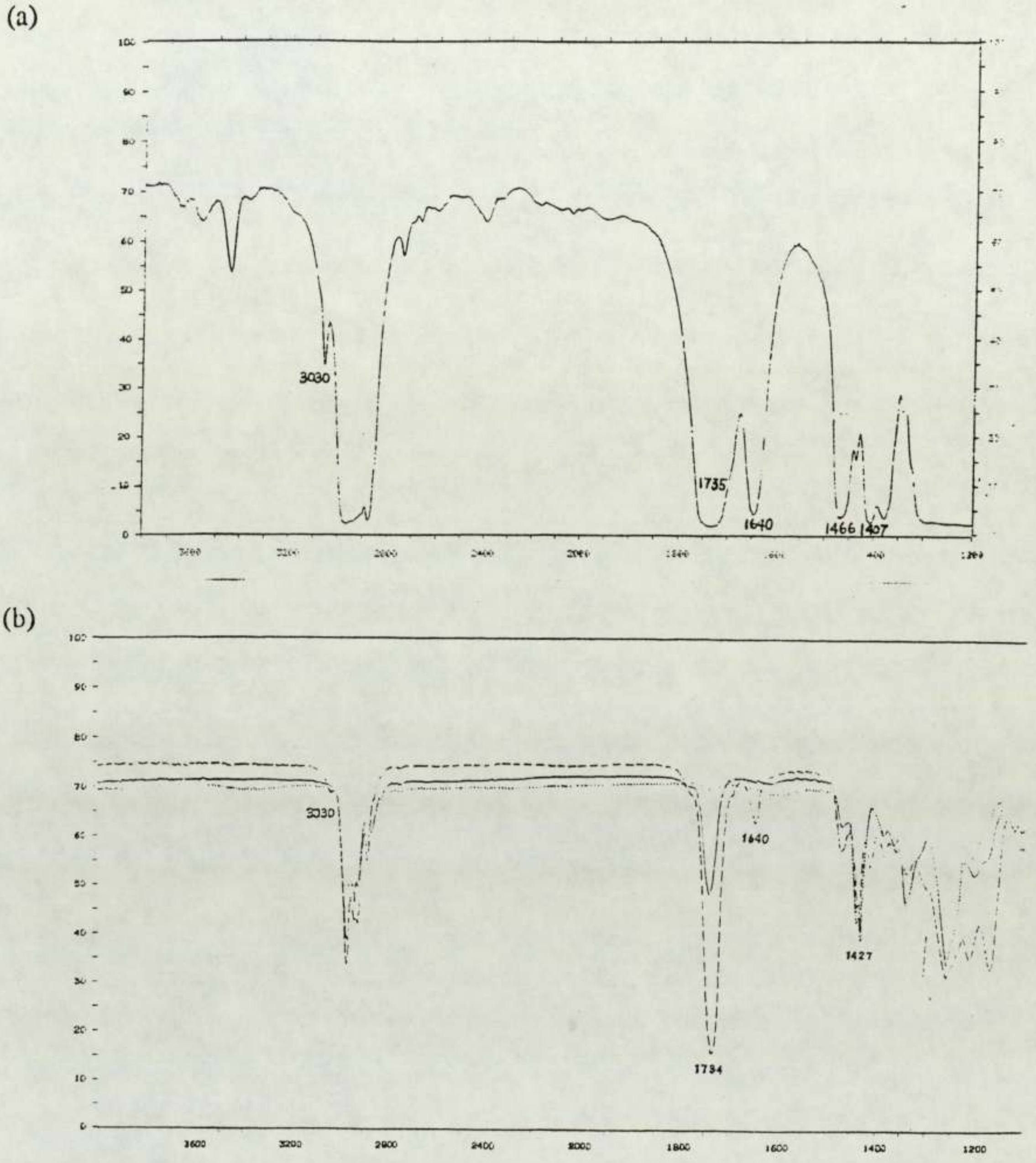


Fig.3.1 IR spectra of DBM, processed PVC and DBM modified PVC system.

(a) DBM

(b) .... pPVC

---------- DBM modified PVC system (unextracted)

_______ DBM modified PVC system (extracted)

For details of the samples, see pPVC and T2 in Table 3.1.

3.2.2 Effects of Reaction Conditions on the Extent of Binding of DBM

3.2.2.1 Effect of Type and Concentration of Radical Generator

The effect of the concentration of the radical generator on the extent of binding of DBM is shown in Fig.3.2. The extent of binding of DBM does not depend on the concentration of AIBN and is at a relatively low level. However, it obviously depends on the concentration of peroxide: binding is relatively low in the case of low concentration (less than 0.05 molar radical ratio to DBM) and rises rapidly with an increase in the concentration of peroxide up to a value of about 0.25 before the gradient decreases somewhat. This result is interesting not only because of the positive relationship between the extent of binding and radical generator concentration but also because of the melt stabilisation of PVC when combined with DBM at higher concentrations of peroxide (up to equimolar radical ratio to DBM) during processing under high shear action. On the other hand, the low initiation effectiveness of AIBN may be due to a cage effect, which will be discussed in detail in **3.3.2.**

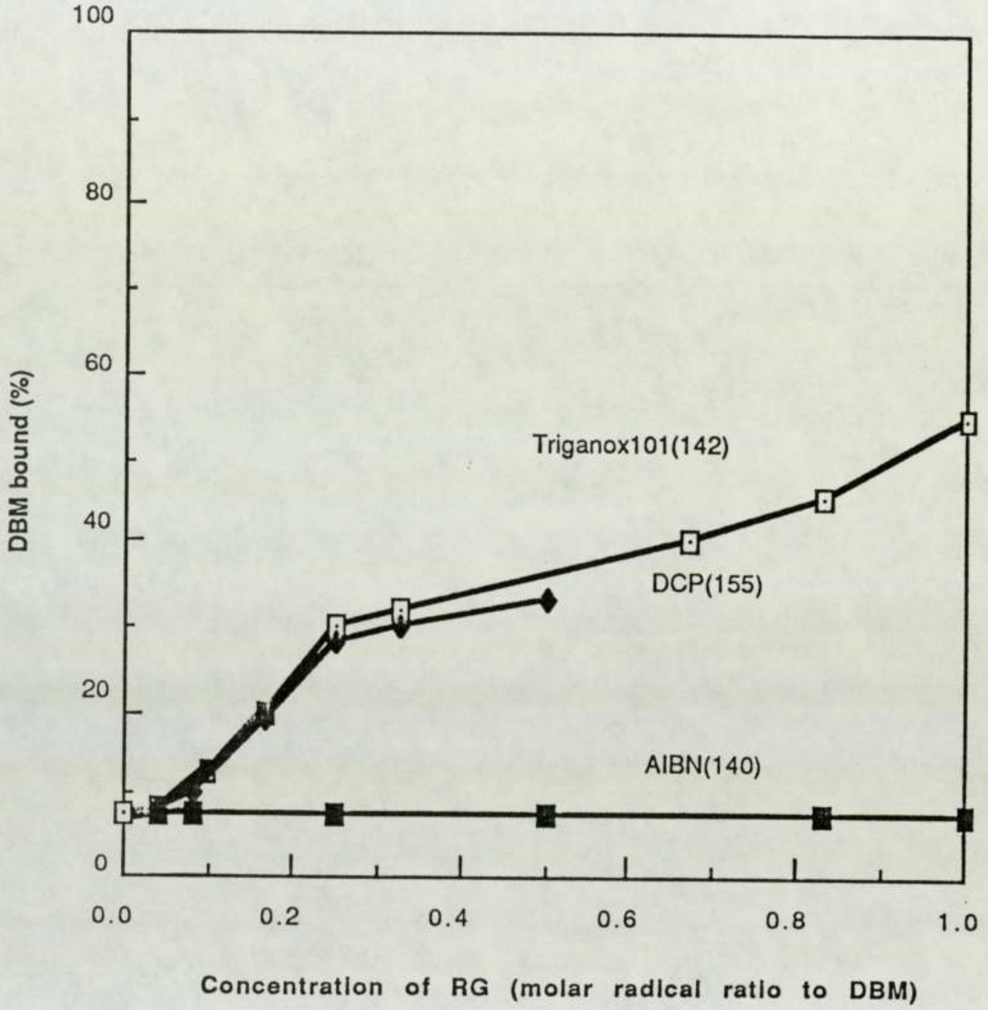


Fig.3.2 Extent of binding of DBM in PVC as a function of radical generator loading in the reaction systems. Numbers in parentheses are processing temperatures (C). In each case the loading of DBM was 2.17 X 10^{-1} mol·100 g^{-1} (50 g/100 g PVC) and the processing time was 10 min.

3.2.2.2 Effect of Loading of DBM

The effect of the loading of DBM on the extent of binding is shown in Fig.3.3. It will be noted that this is related to the type and concentration of radical generator, especially in the case of higher loadings of DBM. The extent of binding of DBM decreases continuously with increasing in loading of DBM when AIBN is used or the concentration of radical generator is low (see Fig.3.2), but it remains at higher levels (around 30 - 55%) when higher concentrations of peroxides are used. The slight peak, if significant, is very similar to that for thiol antioxidant as reported by Ajiboye and Scott[187]. In the case of the lower loadings of DBM (below about 4.0×10^{-2} mol·100 g^{-1} PVC), the extent of binding rises rapidly in each case and tends to 100% when the DBM loading is less than 1.2×10^{-2} mol·100 g^{-1} PVC. It could be inferred that such a high level of binding might have occurred in a PVC formulation stabilised by DBTM (5.56×10^{-3} mol·100 g^{-1} PVC) during processing[195].

On the bases of the relationship between the extent of binding of DBM and both the loading of DBM and concentration of radical generator, two possible mechanisms in binding of DBM to PVC are postulated. These will be discussed in 3.2.4.2.

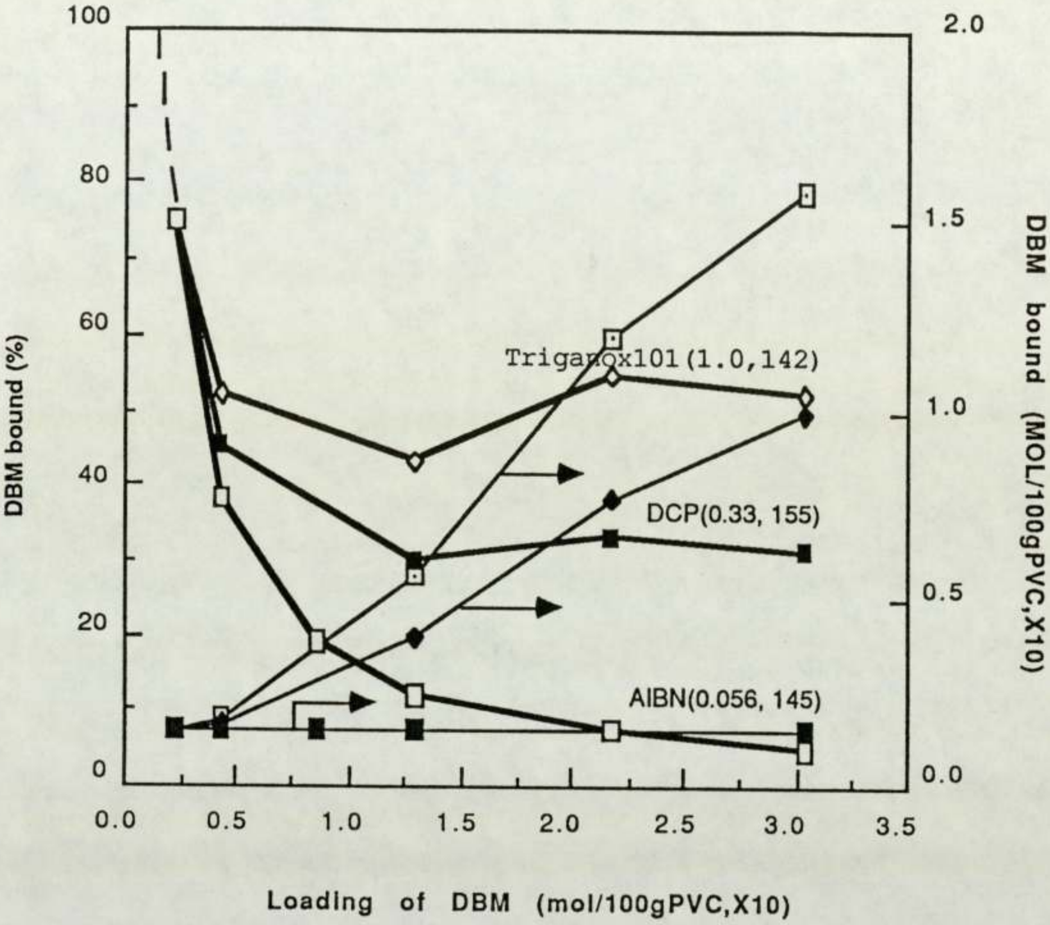


Fig. 3.3 Extent of binding of DBM in PVC as a function of DBM loading in the polymer. Numbers in parentheses are the concentration of radical generator (molar radical ratio to DBM) and processing temperature (C) respectively. In each case the processing time was 10 min.

3.2.2.3 Effect of Processing Temperature

The effect of processing temperature on the extent of binding of DBM is shown in Fig.3.4. In the case of peroxides, similar curves are obtained and these show an increase in the extent of binding of DBM with an increase of processing temperature. However, there is a levelling off at temperatures about 15 - 20 C below the degradation temperature. The extent of binding of DBM in the case of AIBN is shown to be temperature-independent over the range from 80 to 200 C. It should be noted that the processing temperatures here indicated the oil temperature of the mixer, which were above 5 - 10 C higher than the PVC melt temperature.

3.2.2.4 Effect of Processing Time

The effect of processing time on the extent of binding of DBM is shown in Fig.3.5. The extent of binding of DBM rises very rapidly to a plateau after passing the induction period for a particular formulation. Under the prevailing processing conditions, 5 - 10 min was in general enough to complete the binding reaction. The significance of the binding - time relationship will be explained in 3.2.3.

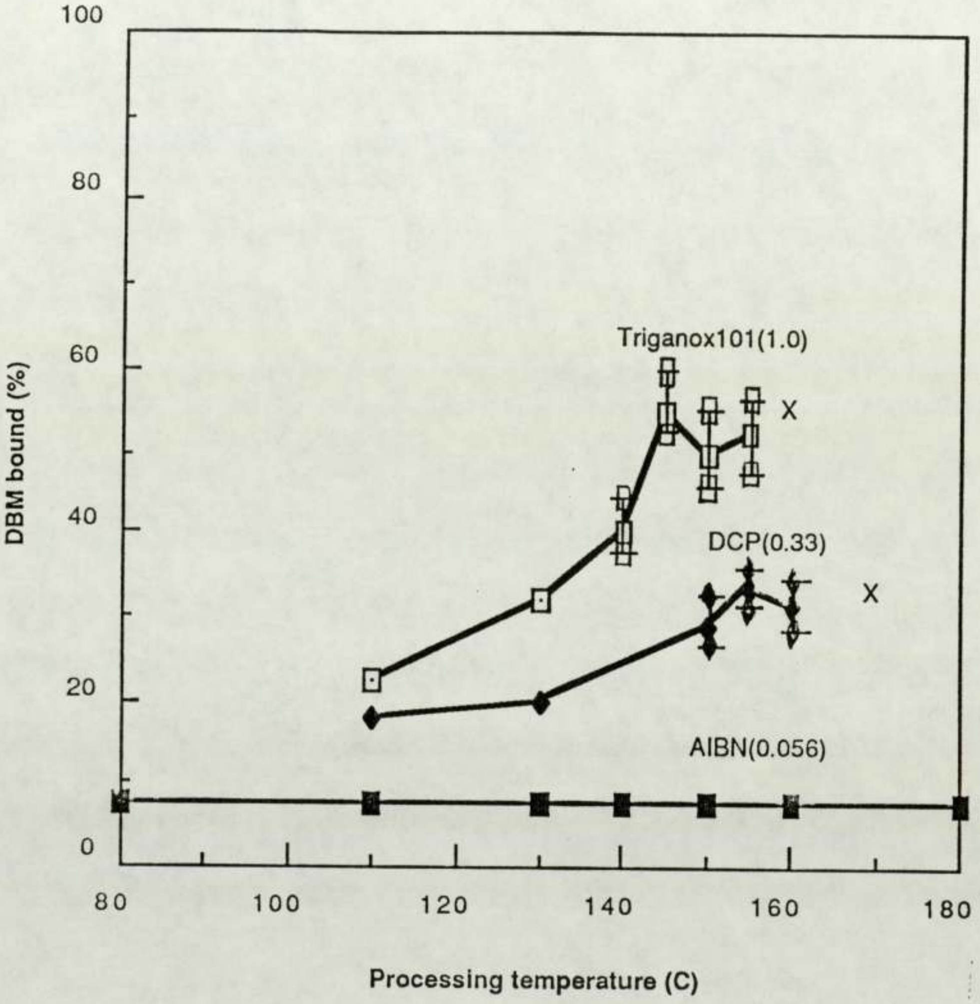


Fig.3.4 Extent of binding of DBM in PVC as a function of processing temperature. Numbers in parentheses are concentration of radical generators (molar radical ratio to DBM). In each case the loading of DBM was 2.17 X 10^{-1} mol·100 g^{-1} and the processing time was 10 min. X indicates degradation.

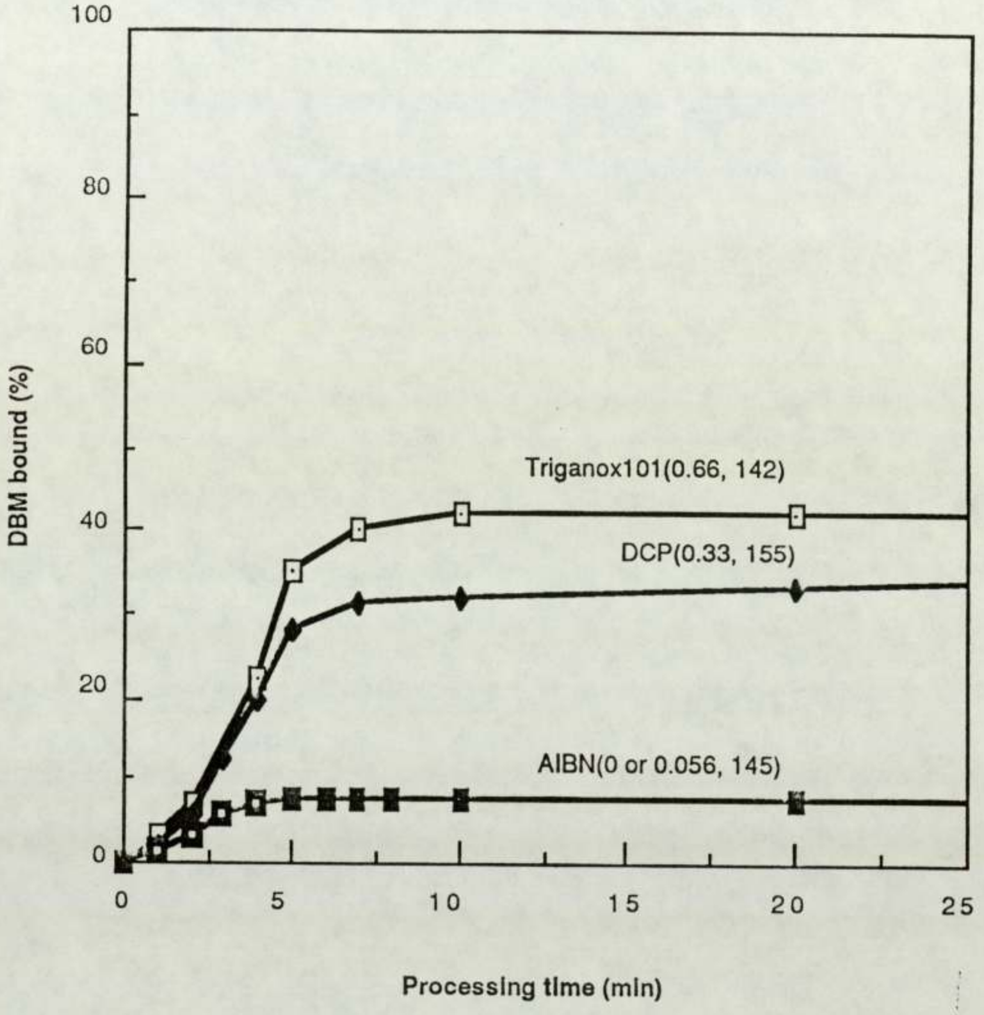


Fig.3.5 Extent of binding of DBM in PVC as a function of processing time. Number in parentheses are concentration of radical generators (molar radical ratio to DBM) and processing temperature (C) respectively. In each case the loading of DBM was 2.17 X 10^{-1} mol·100 g^{-1}.

3.2.2.5 Effect of Shear Force

The effect of shear force on the extent of binding of DBM is shown in Fig.3.6. The extent of binding of DBM does not depend on the shear force for the reaction systems with AIBN whereas it increases with increase of the shear force for the systems with peroxide. These results suggest that binding of DBM relates to the concentration of PVC macro-alkyl radicals in the presence of higher concentrations of peroxide, assuming that a higher shear force really does increase the concentration of PVC macro-alkyl radicals.

3.2.3 Rheological Behaviour of PVC-DBM Reaction Systems during Processing

3.2.3.1 Effects of Processing Temperature and Loading of DBM

Effects of both processing temperature and loading of DBM on the rheological behaviour of PVC during processing are shown in Figs.3.7-3.9. Three stages in the fusion process of PVC during processing can be identified from these figures based on a knowledge of the structure and characteristics of PVC particles (see **1.2**).

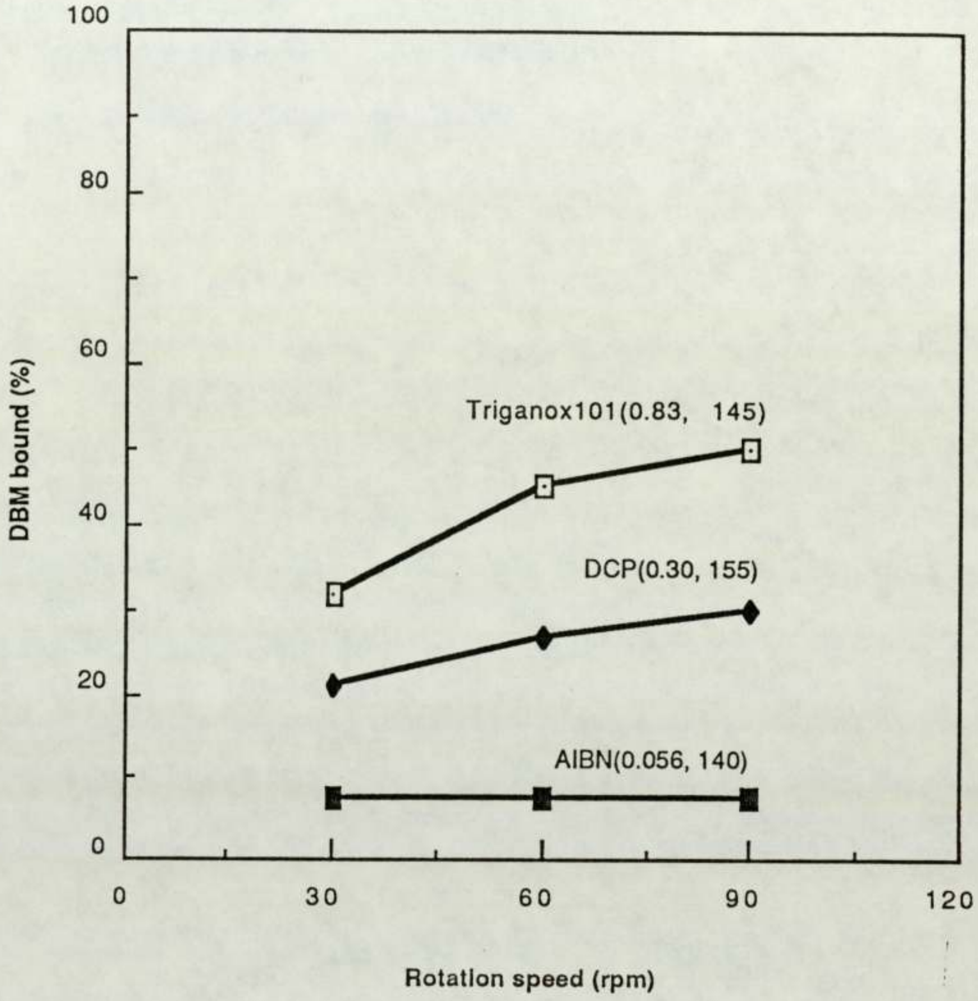


Fig.3.6 Effect of shear force on extent of binding of DBM. Numbers in parentheses are concentration of radical generators (molar radical ratio to DBM) and processing temperature (C) respectively. In each case the loading of DBM was 2.17×10^{-1} mol·100 g^{-1} and the processing time was 10 min.

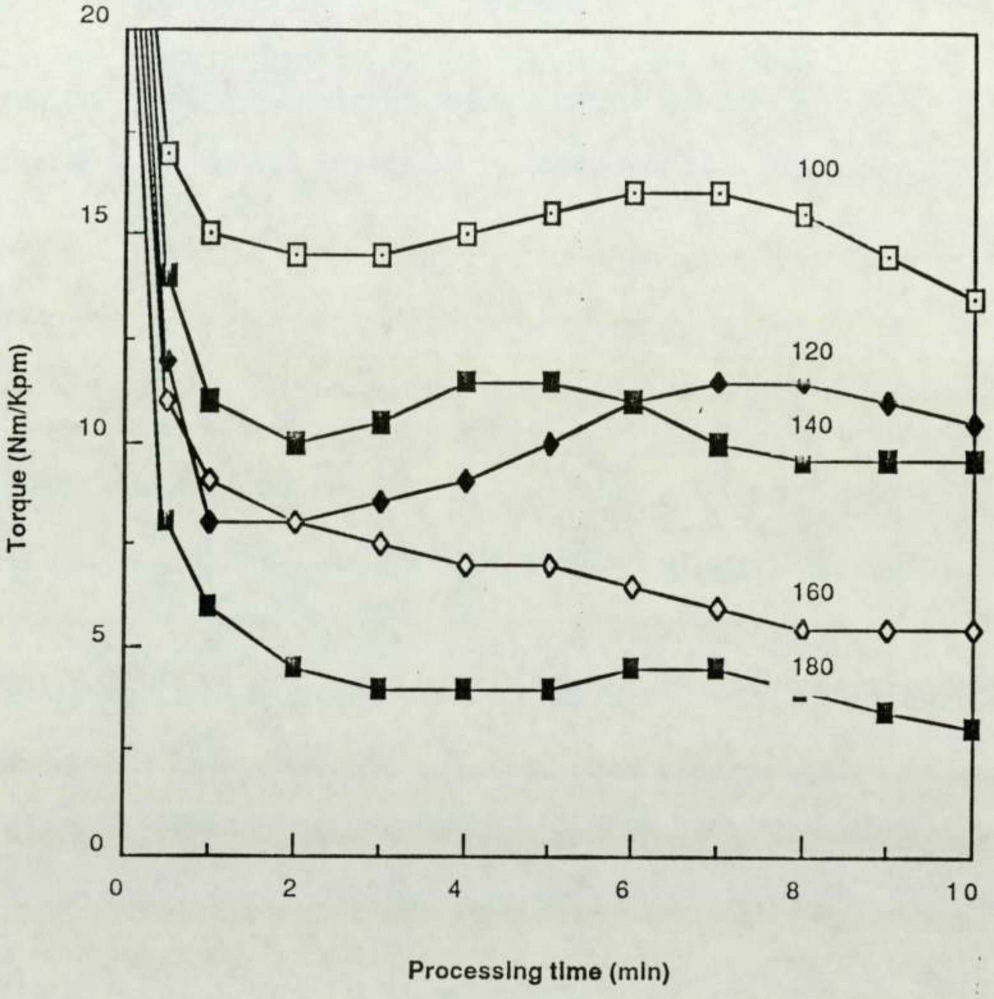


Fig.3.7 Rheological curves of a PVC-DBM reaction system at different processing temperatures. Numbers on curves indicate the processing temperature (C). In each case, the loading of DBM was 2.17×10^{-1} mol·100 g^{-1}, the concentration of AIBN was 0.056 molar radical ratio to DBM and the rotation speed was 60 rpm.

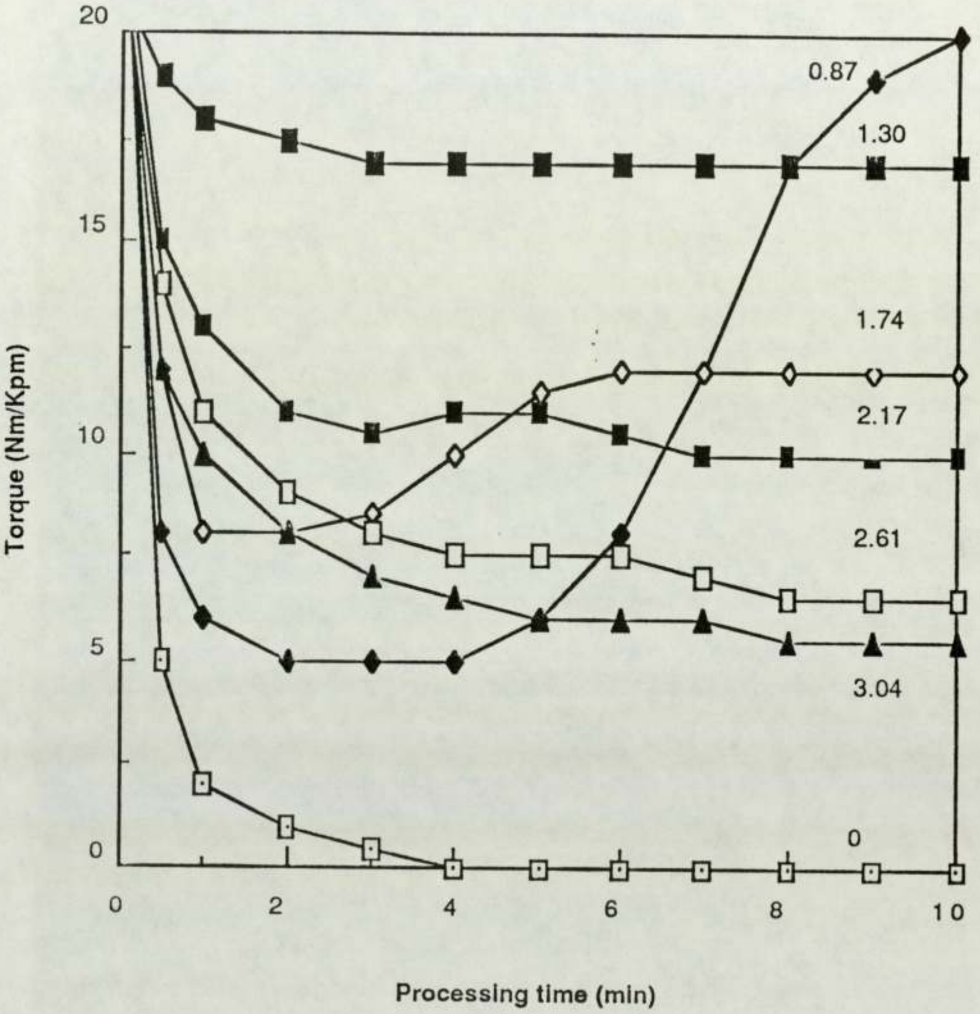


Fig.3.8 Rheological curves of PVC-DBM formulations with different loadings of DBM at 140 C and 50 rpm. Numbers on curves indicate loading of DBM (X10 mol.100g-1). In each case, the concentration of AIBN was 0.056 molar radical ratio to DBM.

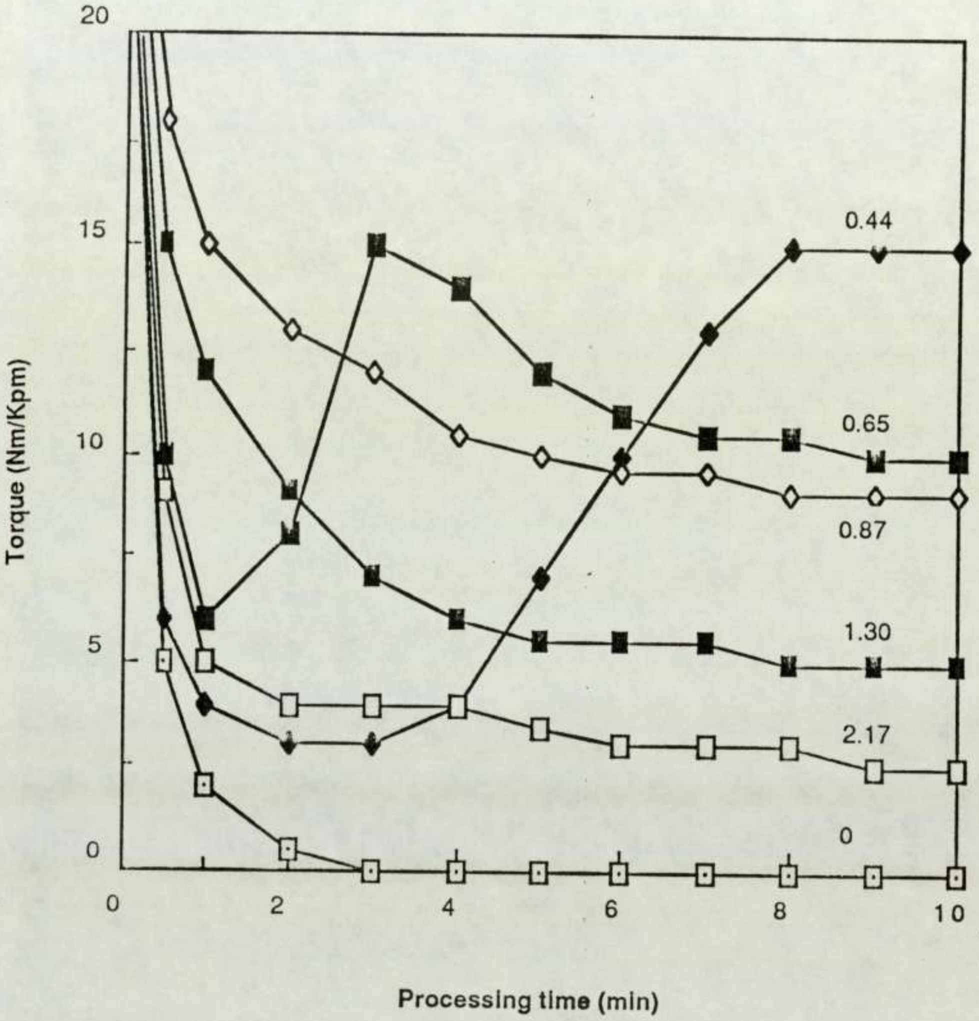


Fig.3.9/43,10 Rheological curves of PVC-DBM formulations with different loadings of DBM at 180 C and 50 rpm. Numbers on curves indicate loading of DBM (X10 mol.100g-1). In each case, the concentration of AIBN was 0.056 molar radical ratio to DBM.

Table 3.2

Fusion Process of PVC during Processing

Stage	*Process*	*State of PVC*	*Appearance of Cooled Product*
I	Absorption of heat and breakdown of PVC particles into micro-granules by high shear and heat.	Solid (as smaller particles).	White powder.
II	Fusion of microgranules. Progress of fusion of amorphous phase in PVC. Completion of fusion of amorphous phase but crystalline phase unaffected. Progress of fusion of part of crystalline phase.	From solid to molten.	Opaque bulk.
III	Shear flow of fused PVC.	Molten state.	Transparent bulk.

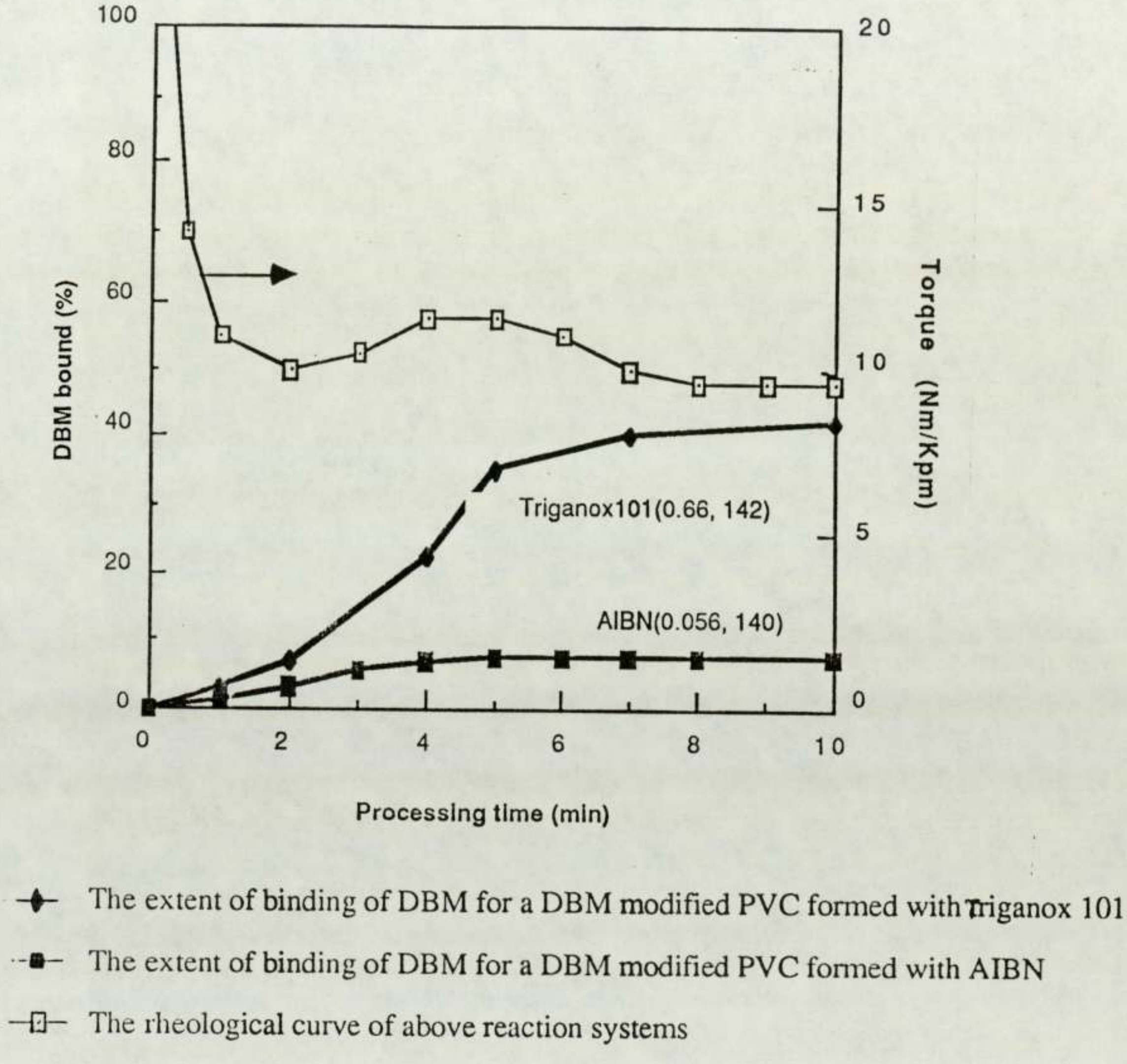


Fig.3.11 Relationships between the extent of binding of DBM and the degree of fusion of PVC in the presence of AIBN or Triganox 101. Numbers in parentheses are concentration of radical generators (molar radical ratio to DBM) and processing temperature (C). In each case the concentration of DBM was 2.17 X 10^{-1} mol·100 g^{-1}.

Figs.3.7-3.9 show that an increase of temperature or an increase in the concentration of DBM shortens the time to gellation, i.e. PVC is easier to fuse. It means that DBM is a good plasticiser and compatible with PVC. Fig.3.11. shows that the extent of binding of DBM reaches a maximum after an induction period for the formulaton with AIBN whereas it increases with a shorter induction period and reaches a maximum after about six minutes for the reaction systems with Triganox101.

3.2.3.2 Effect of Shear Force

The effect of shear force on the fusion process of PVC is shown in Figs.3.12 and 3.13. It is seen that an increase in shear force obviously contributes to the fusion of PVC. For example, as shown in Fig.3.13, the time for completing fusion reduces from about 8 min at 30 rpm to about 5 min at 90 rpm in that case. It means that the binding reaction is completed earlier with a higher shear force (See Fig.3.6). On the other hand, the viscosities of the PVC-DBM reaction systems at different shear forces differ slightly at the later stages. Thus it is suggested that more PVC macro-alkyl radicals

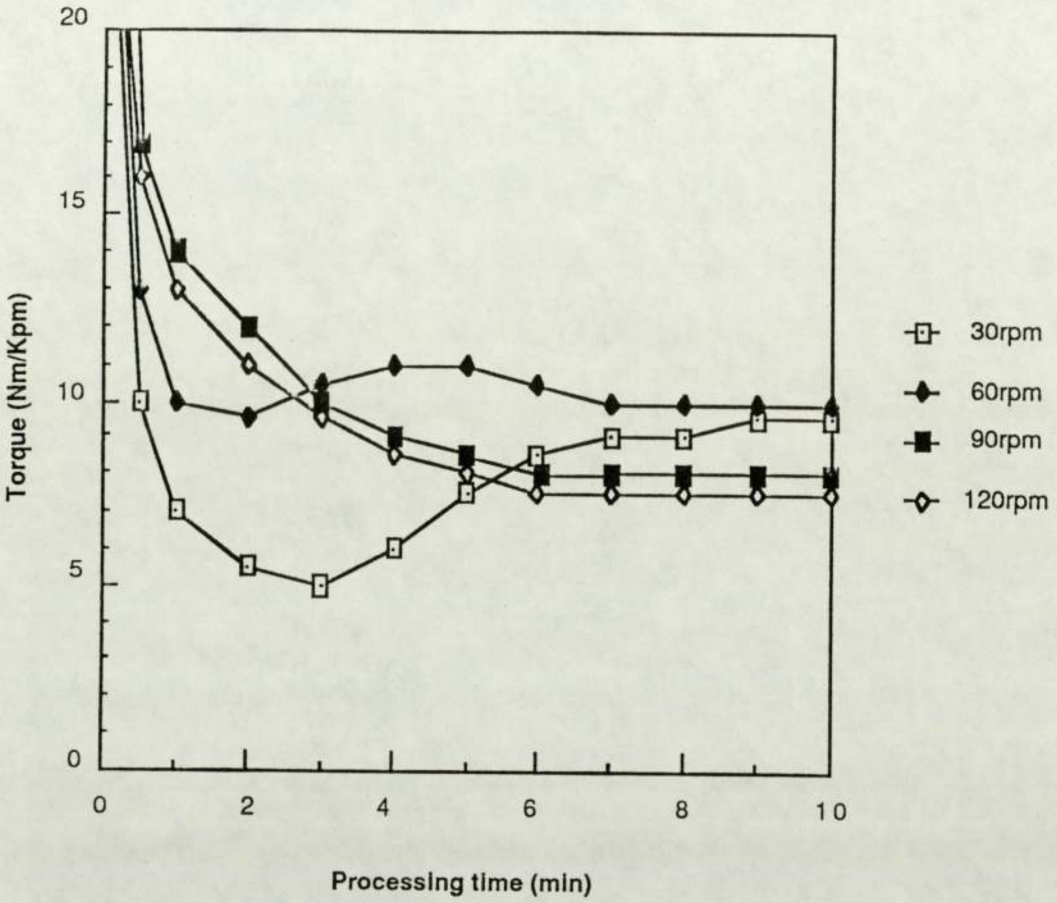


Fig.3.12 Rheological curves of a PVC-DBM reaction system (as Fig.3.7) at different rotational speeds. In each case, processing temperature was 140 C.

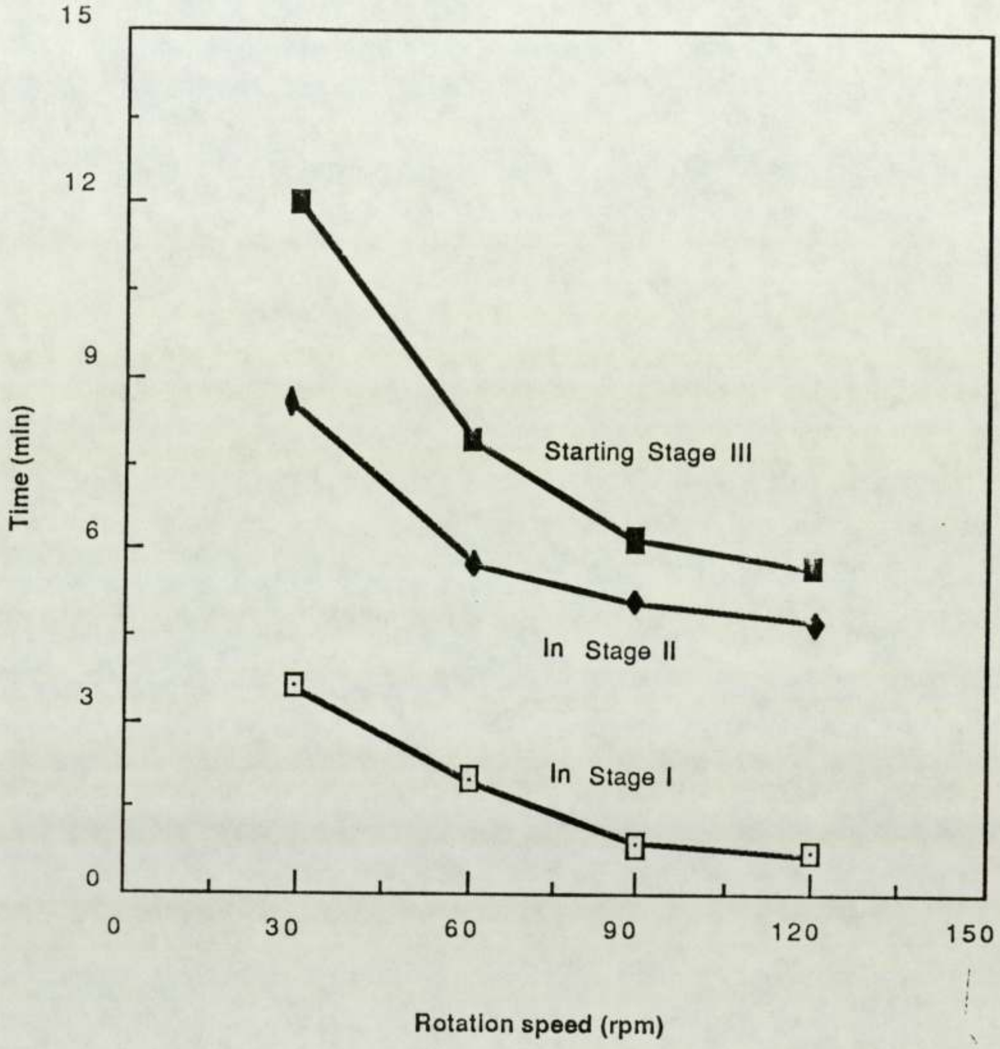


Fig.3.13 Effect of shear force on the time of fusion of PVC. In this case, the loading of DBM was 2.17×10^{-1} mol·100 g^{-1} and the processing temperature was 140 C.

are formed at higher shear forces. The positive relationship between the extent of binding of DBM and shear force (Fig.3.6) might be therefore related to both the time for completing the binding reactions and the concentration of PVC macro-alkyl radicals.

3.2.4 Structure Variation of Processed PVC and Modified Polymer Systems

3.2.4.1 Molecular Weight and Molecular Weight Distribution

GPC graphs of pure PVC, processed PVC and modified PVC systems are shown in Fig.3.14. Comparisons of weight-average molecular weight, polydispersity index, and polydispersity index for the high molecular weight end of these samples are shown in Figs.3.15-17. The molecular weights of the processed PVC and the modified PVC systems are about the same as that of the pure PVC, but the polydispersity index of the processed PVC and the modified PVC systems is lower. At the high molecular weight ends, the polydispersity index of the processed PVC and the modified PVC systems is lower than that of the pure PVC except that of sample T3. These results indicate that chain scission of PVC occurred during processing both in the absence and presence of plasticiser (DBM), which results in the decrease at the high molecular weight end, and that crosslinking of PVC is not predominant under the processing conditions used. The GPC graphs of both

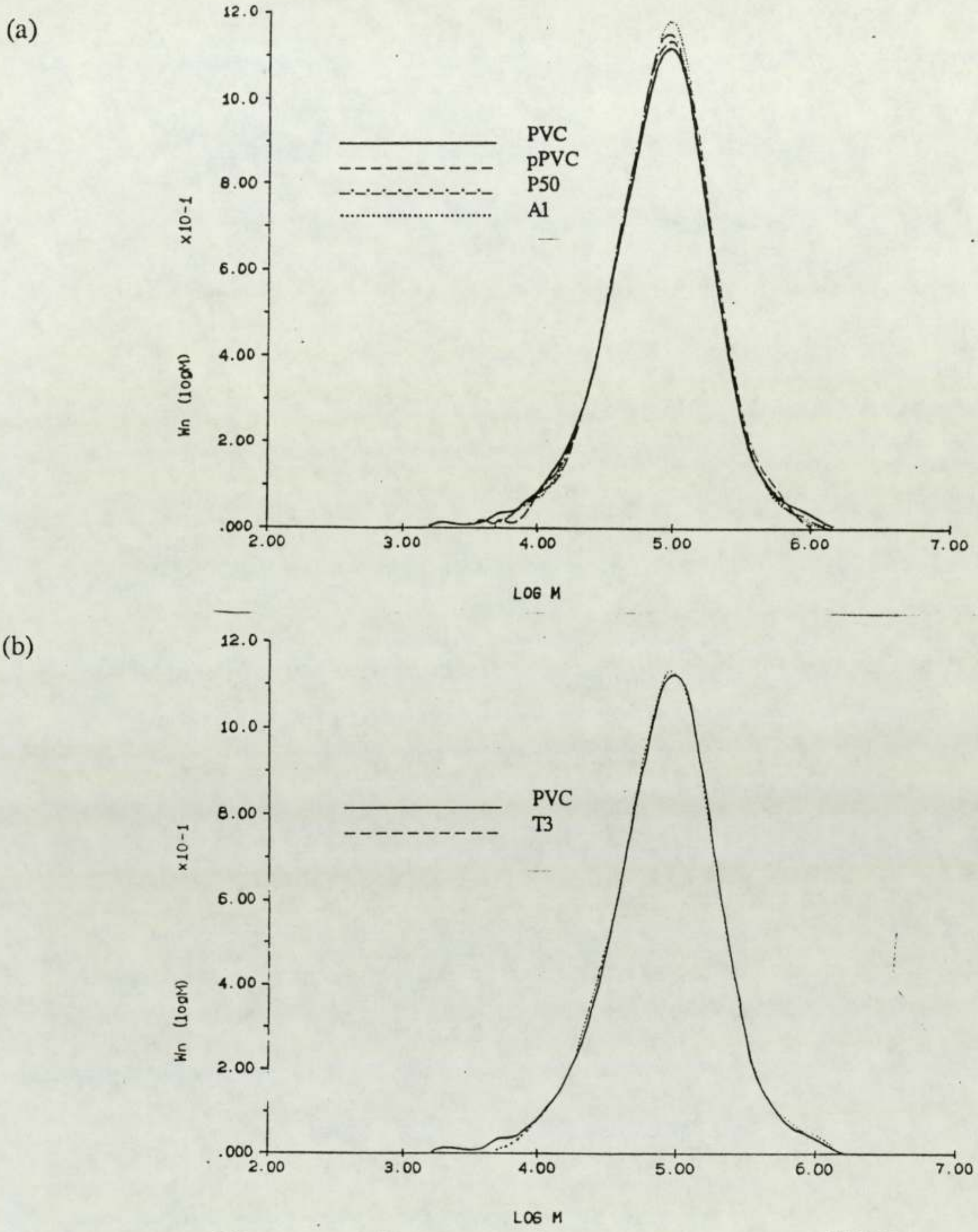


Fig.3.14 GPC graph. For details of the samples see Table 3.1.

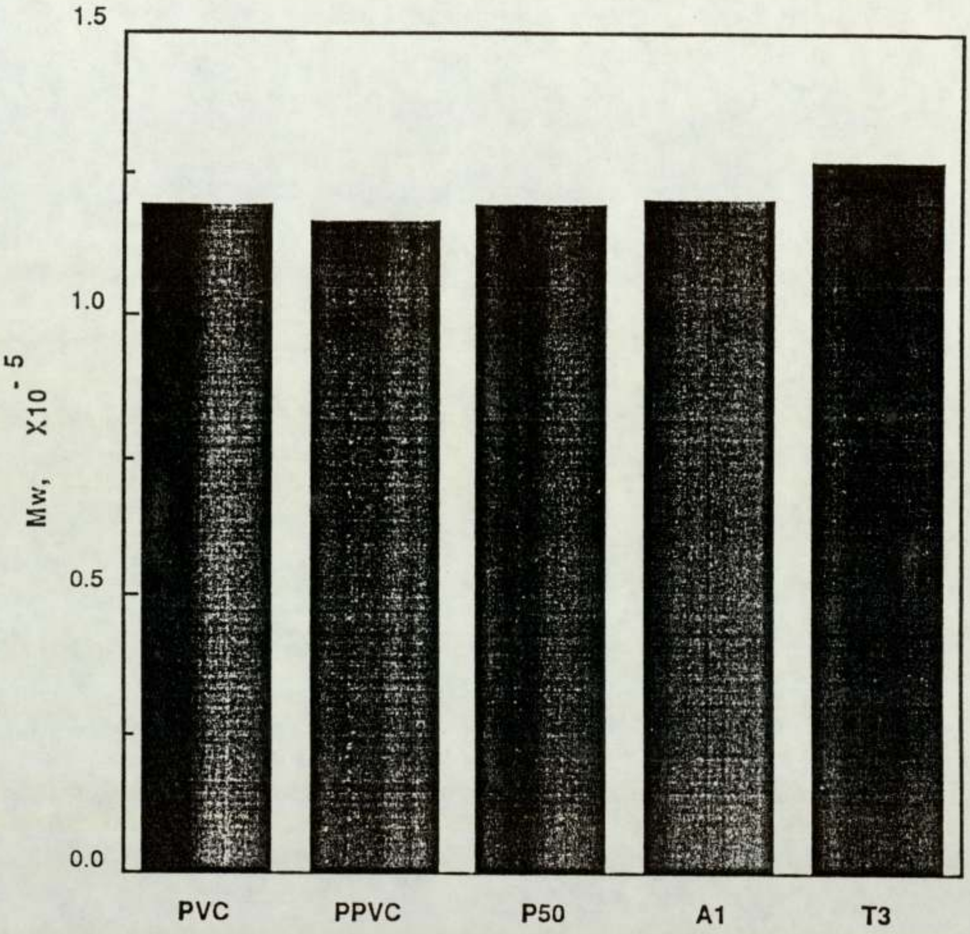


Fig.3.15 Weight-average molecular weight. For details of the samples, see Table 3.1.

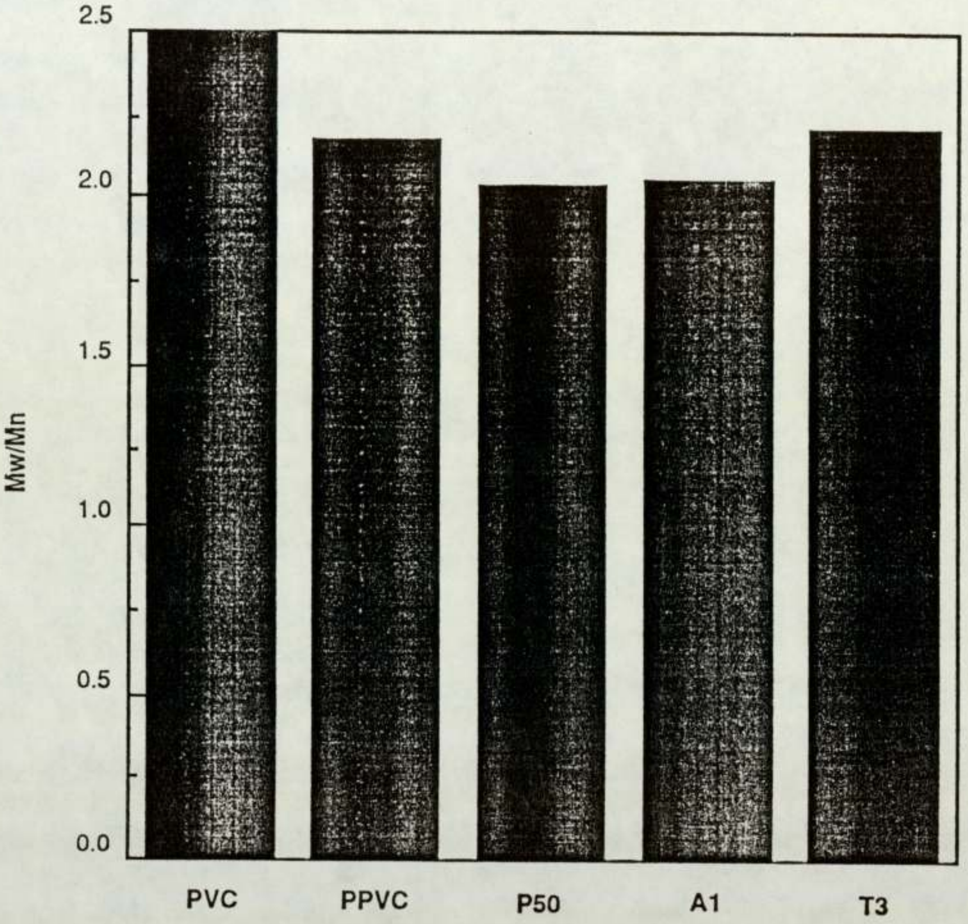


Fig.3.16 Polydispersity index. For details of the samples, see Table 3.1.

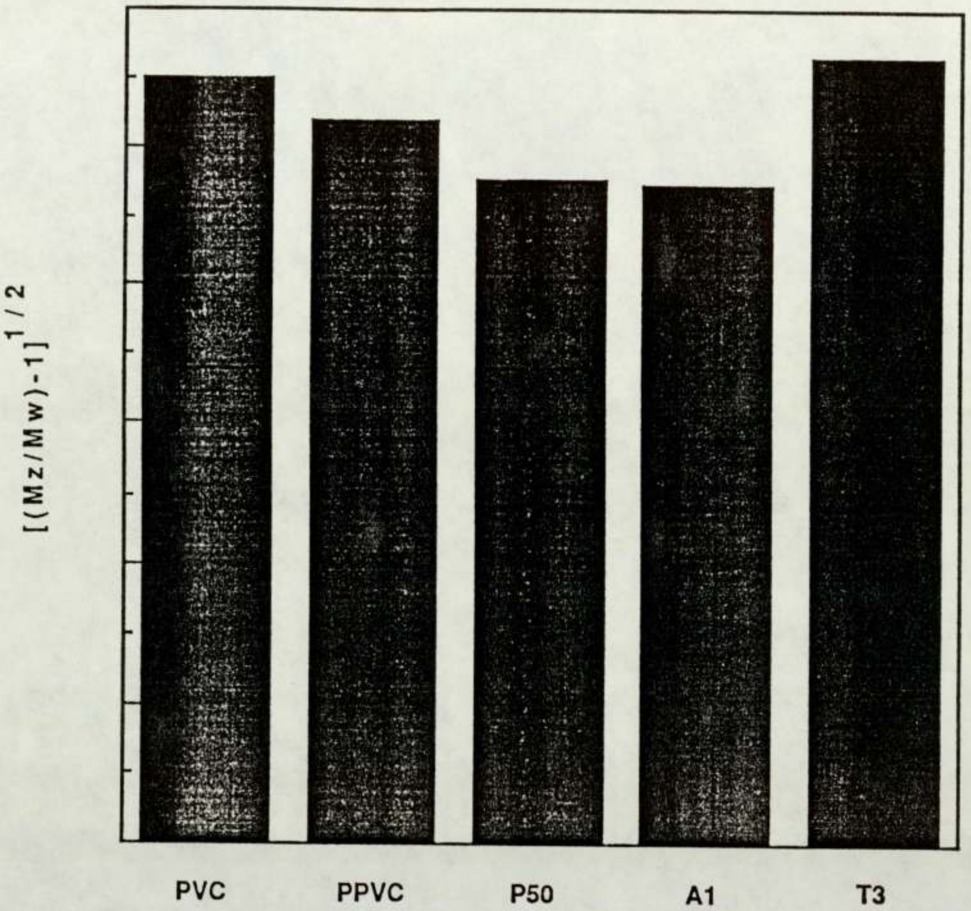


Fig.3.17 Polydispersity index for the high molecular weight end. For details of the samples, see Table 3.1.

T3 and the original PVC are very similar (Fig.3.14(b)). This may be due to crosslinking via double radicals formed by Triganox101 (see scheme 3.4 in 3.3.3), which compensates for the decrease at the high molecular weight end caused by the scission of PVC chains.

3.2.4.2 Unsaturation

IR spectra of two groups of unextracted modified PVC samples obtained with AIBN and Triganox101 are shown in Figs.3.18-19. Absorbances at 1640 cm^{-1} and 3030 cm^{-1} contributed by the unsaturation of DBM can be observed (c.f. Fig.3.1(a)). Effects of the concentration of radical generator absorbance depend on the type of radical generator. In the case of AIBN (Fig.3.18) absorbance only changes slightly with increase in the concentration of AIBN (0.01 - 1.00 molar radical ratio to DBM), being almost the same as that of the sample formed from a system without a radical generator (P50). This indicates that DBM was still retained in the modified PVC systems and that AIBN was not effective under the processing conditions. By contrast absorbance weakened with an increase in the concentration of Triganox101 (Fig.3.19), the trough at 3030 cm^{-1} almost disappearing in the case of the equimolar radical ratio to DBM. This indicates that Triganox101 was highly effective in converting DBM to radicals.

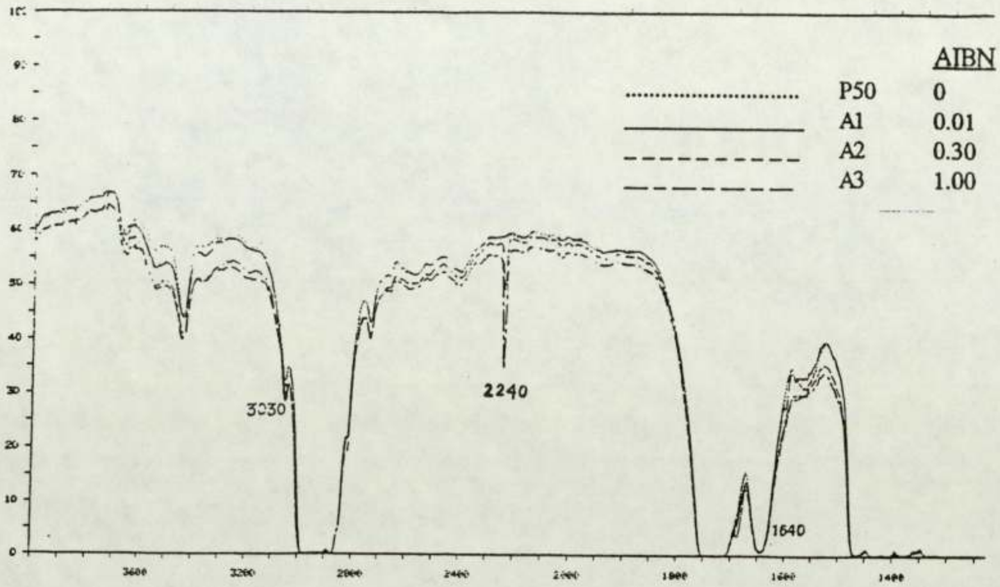


Fig.3.18 Effect of the concentration of AIBN on absorbance at 1640 cm^{-1} and 3030 cm^{-1} in the IR spectra of DBM modified PVC polymers (unextracted). Details of the samples are shown in Table 3.1.

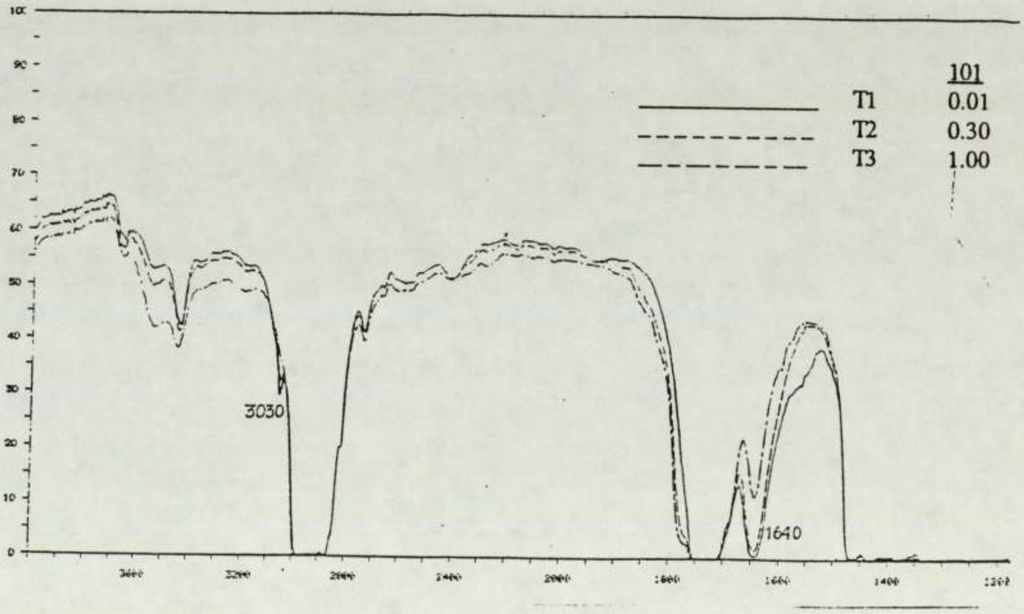


Fig.3.19 Effect of the concentration of Triganox101 on absorbance at 1640 cm^{-1} and 3030 cm^{-1} in the IR spectra of DBM modified PVC polymers (unextracted). Details of the samples are shown in Table 3.1.

The IR spectra of these two groups of modified PVC samples after extraction are shown in Figs.3.20-21. Absorbance at 3030 cm^{-1} disappeared and absorbance at 1640 cm^{-1} almost disappeared, instead of which there was a weak absorbance at 1650 cm^{-1} which may arise from the shorter sequence of conjugated polyenes in the PVC chains (the change of the absorbance at 1650 cm^{-1} during photoageing will be shown in Figs.3.44-45 in **3.2.5**). This indicates that the unreacted DBM had been removed from the modified PVC systems after extraction. Any unsaturation retained in the extracted modified PVC systems could therefore be assocciated with the modified PVC chains themselves.

The effect of the concentration of radical generator on the absorbance at 1650 cm^{-1} is shown in Fig.3.22. The absorbance changes only slightly with an increase in the concentration of both radical generators. UV-vis spectra of DBM, processed PVC and the extracted modified PVC systems are shown in Fig.3.23. The absorption maxima is at 215 nm for DBM but shifts to 241 nm for the modified PVC samples (e.g. P50, A1, A2 and T1) and to 247 nm for T3. No other absorption peaks have been found in the UV-Vis spectra of the modified PVC systems. However, an absorption peak at 280 nm has been found for the processed PVC as well as an absorption maximium at 238 nm, which is contributed by the conjugated double bonds (n = 3) [88] along PVC chains.

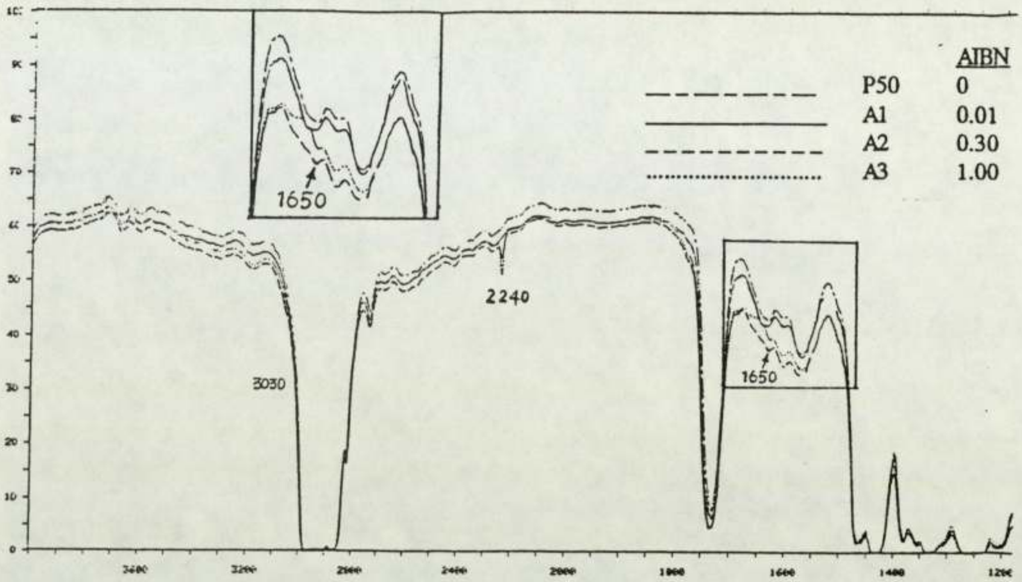


Fig.3.20 Effect of the concentration of AIBN on absorbance at 1650 cm^{-1} and 3030 cm^{-1} in IR spectra of DBM modified PVC polymers (extracted). For details of the samples, see Table 3.1.

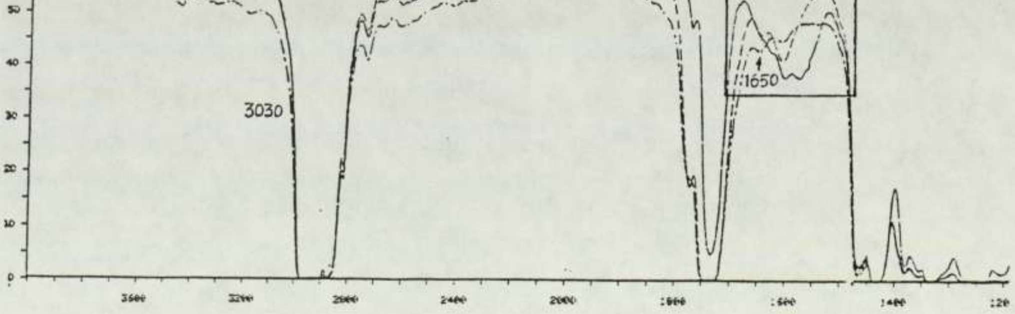


Fig.3.21 Effect of the concentration of Triganox101 on absorbance at 1650 cm^{-1} and 3030 cm^{-1} in IR spectra of DBM modified PVC polymers (extracted). For details of the sample, see Table 3.1.

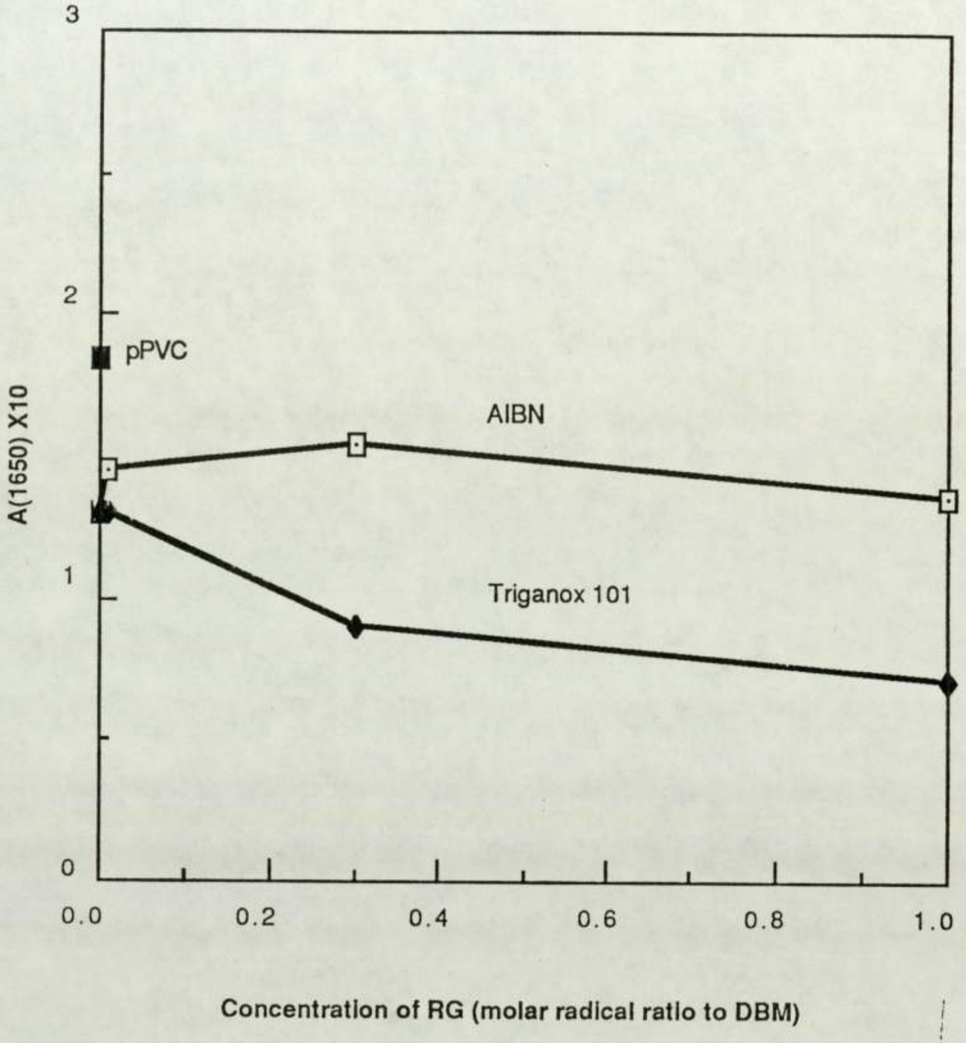


Fig.3.22 Effect of concentration of the radical generators on the absorbance at 1650 cm^{-1} in the IR spectra of the DBM modified PVC polymers (extracted). All film samples here were with same thickness.

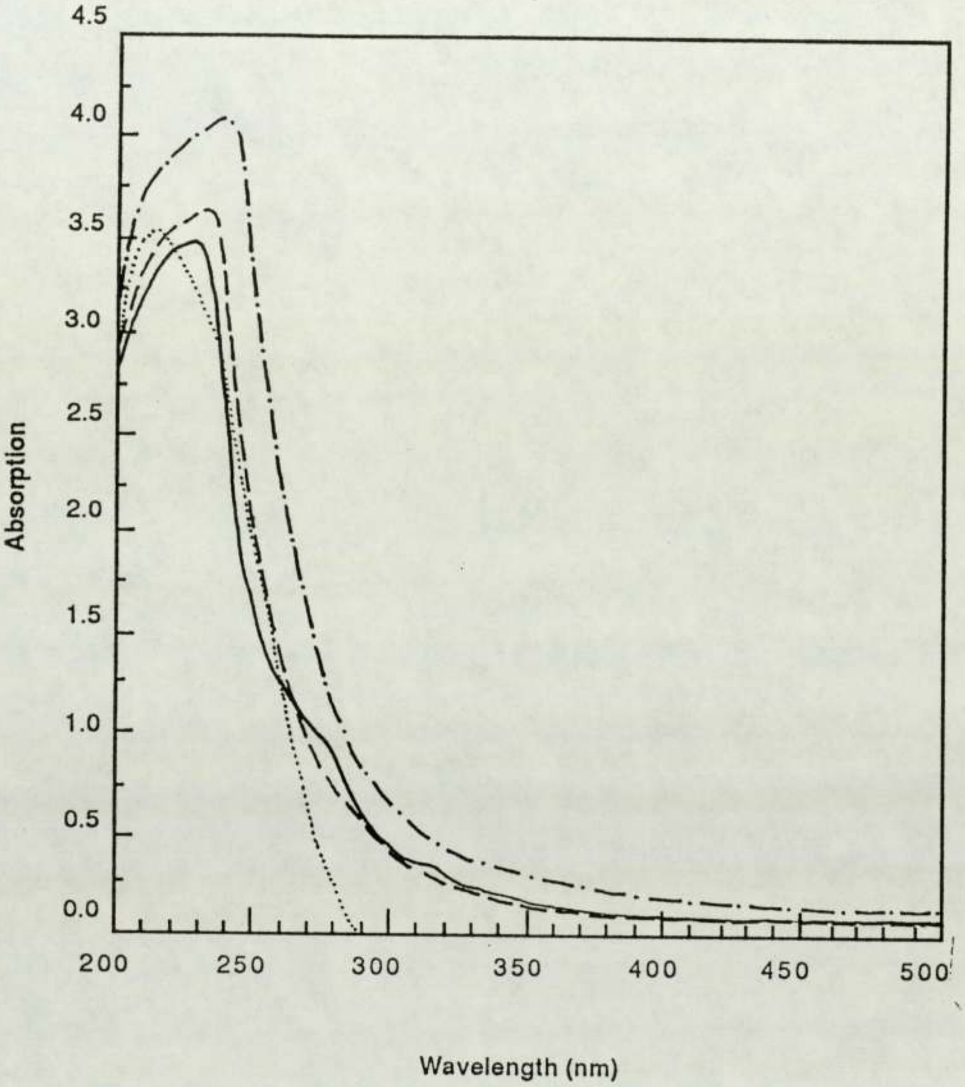


Fig.3.23 UV-vis spectra.

·················· DBM

———————— pPVC

— — — — — — T1

—·—·—·—·- T2

For details of the samples, see Table 3.1.

The monounsaturation recorded by chemical analysis is shown in Fig.3.24. The level of monounsaturation in the processed PVC is higher than that in the modified PVC systems. The level of monounsaturation is almost independent of the concentration of AIBN but it decreases on increasing of the concentration of Triganox101. A relationship between the monounsaturation and the extent of binding of DBM for the modified PVC systems formed using Triganox101 was obtained by combination of Fig.3.24 and Fig.3.2 and is shown in Fig.3.25. It should be noted that the higher the concentration of Triganox101, the lower is the level of monounsaturation and the higher is the extent of binding of DBM. This provides proof that monounsaturation is not contributed by maleate groups but only by the isolated double bonds in PVC.

It is interesting that peroxide seems to play an important role in inhibiting the formation of isolated double bonds in PVC or destroying these double bonds. It has been noted that Triganox101 is highly effective in converting DBM to radicals. The changes in both the extent of binding of DBM and the isolated double bonds in bound products would therefore appear to depend on the concentration of DBM radicals in the reaction system. This point will be further discussed in **3.3**.

3.2.4.3 Peroxide and Hydroxyl Groups

The concentrations of peroxide in processed PVC and the extracted modified PVC systems are shown in Fig.3.26. A measurable amount of peroxide was

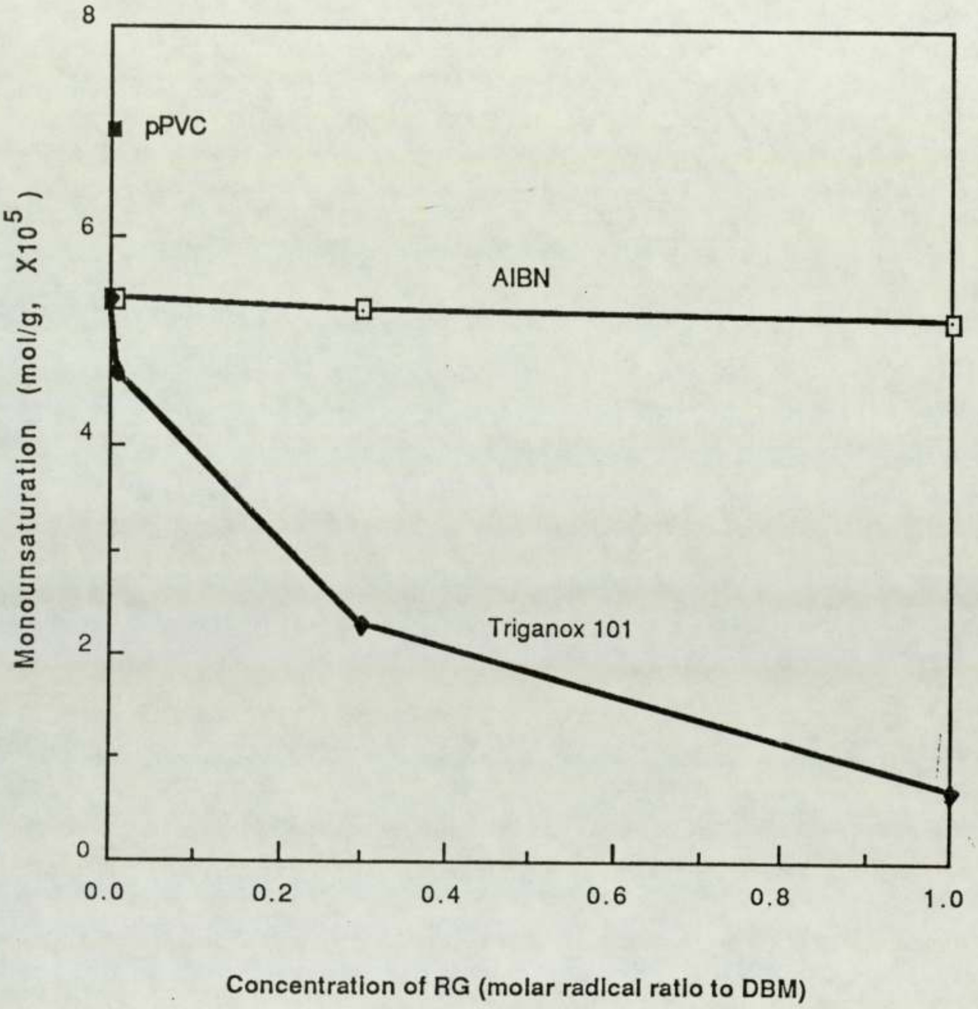


Fig.3.24 Monounsaturation of the extracted modified PVC systems as a function of the concentration of radical generators.

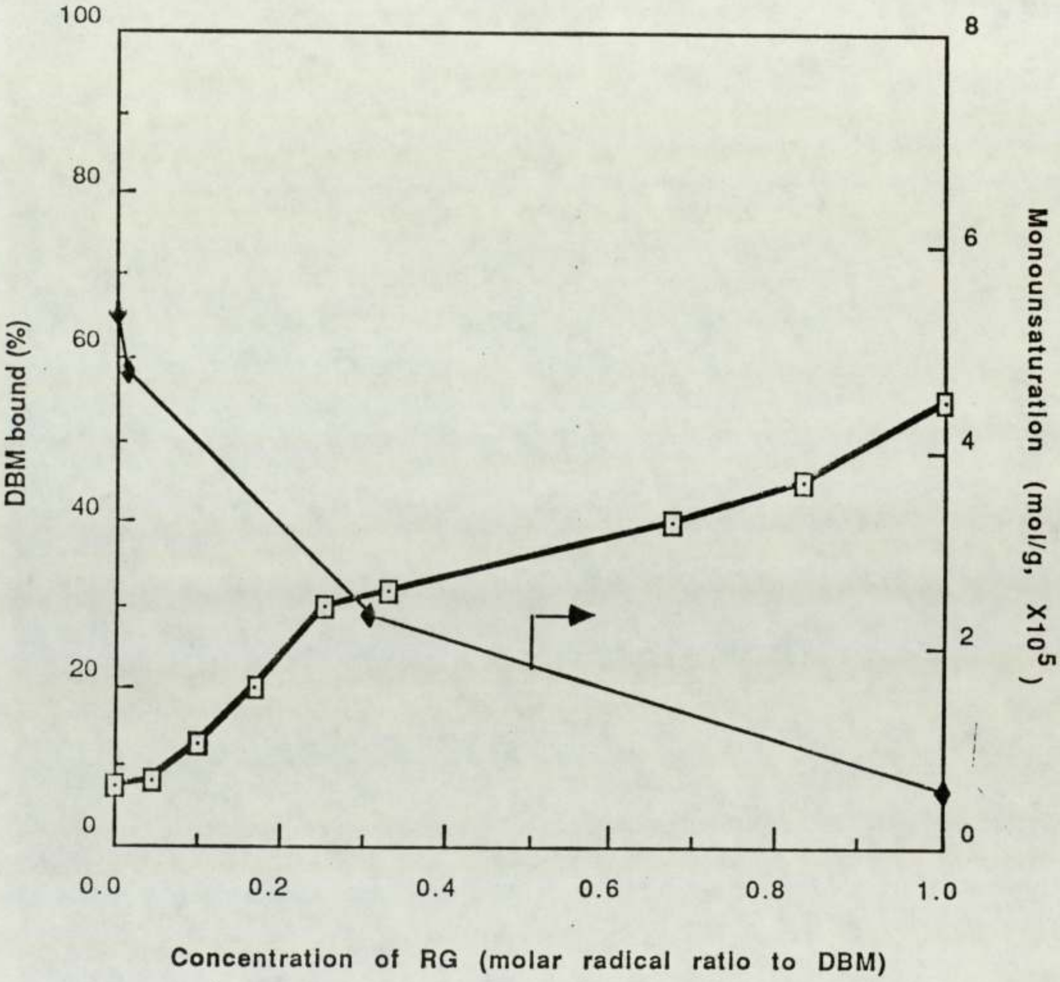


Fig.3.25 Relationship between the monounsaturation and the extent of binding of DBM at various concentrations of Triganox101.

detected in the processed PVC sample. This is in accordance with the result of Cooray and Scott.[60] However, no peroxide could be detected in the modified PVC systems. Perhaps the plasticiser (DBM) played an important role in retarding the formation of the macro-alkyl peroxide and converting the peroxide into hydroxyl groups.

Fig.3.27 shows the level of hydroxyl groups in these samples. It should be noted that the concentration of hydroxyl groups in the modified PVC systems is not higher than that in the processed PVC, even in the case when an equimolar radical ratio of Triganox101 to DBM was used.

3.2.5 Properties of DBM Modified Polymers

3.2.5.1 Extraction Resistance

A series of DBM modified samples were extracted in two ways by refluxing in hexane for 24 hours and by contact with hexane at 15 C for 96 hours. The extraction results are shown in Fig.3.28-29. In all samples the initial loading of DBM was 50% of PVC by weight. The degree of extraction was similar in both cases, but the extraction rate in refluxing hexane was higher. DBM in samples P50 and T1 was almost completely lost after 20 hours' extraction in refluxing hexane or 96 hours immersion in hexane at 15 C, whereas the other modified PVC samples, T2 and T3, retained much more DBM.

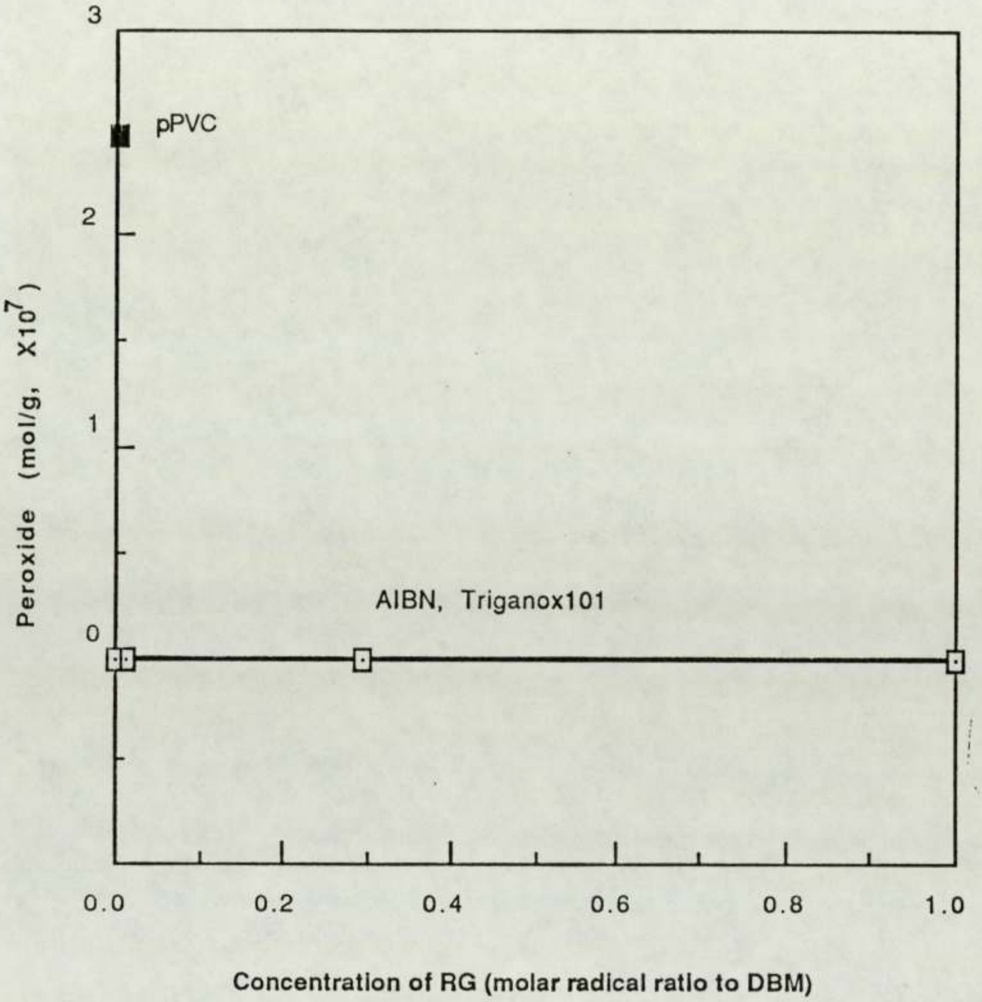


Fig.3.26 Peroxide formation in processed PVC and the extracted modified PVC systems.

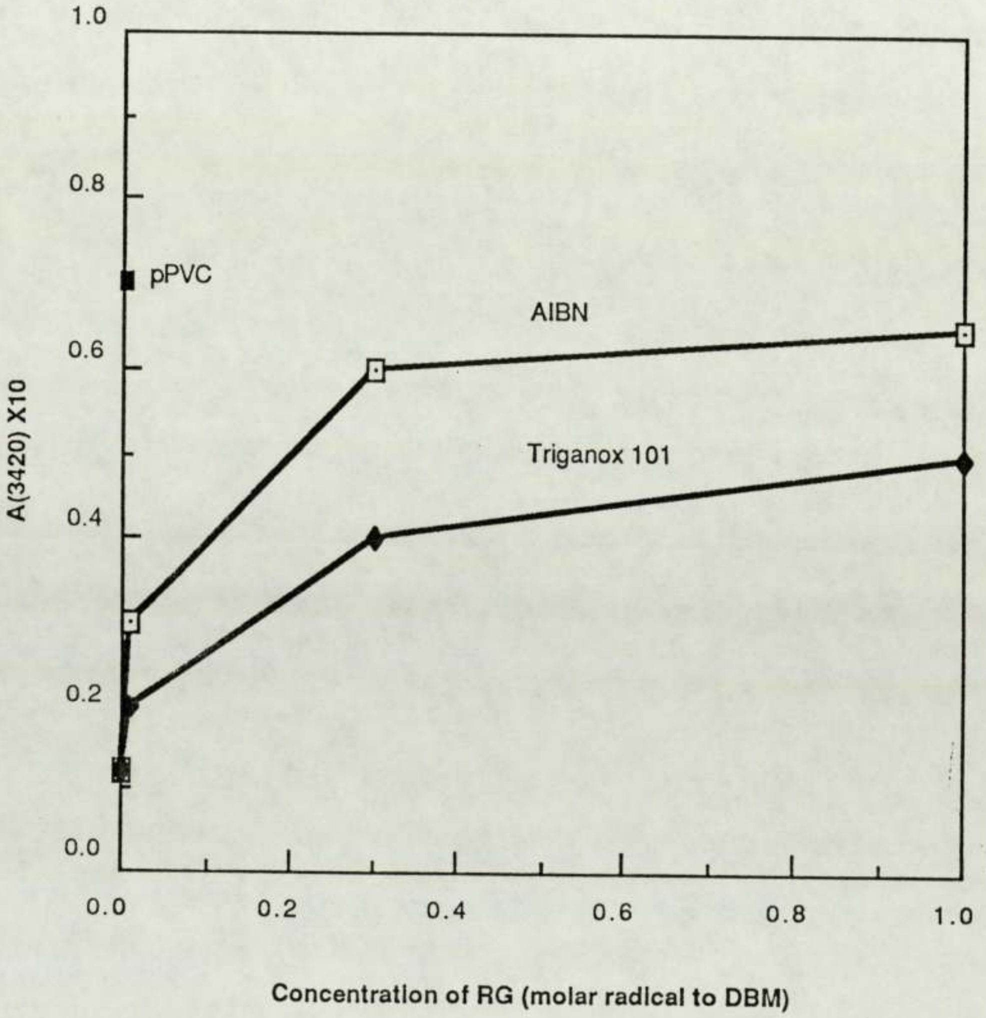


Fig.3.27 Formation of hydroxyl groups in processed PVC and the modified PVC systems.

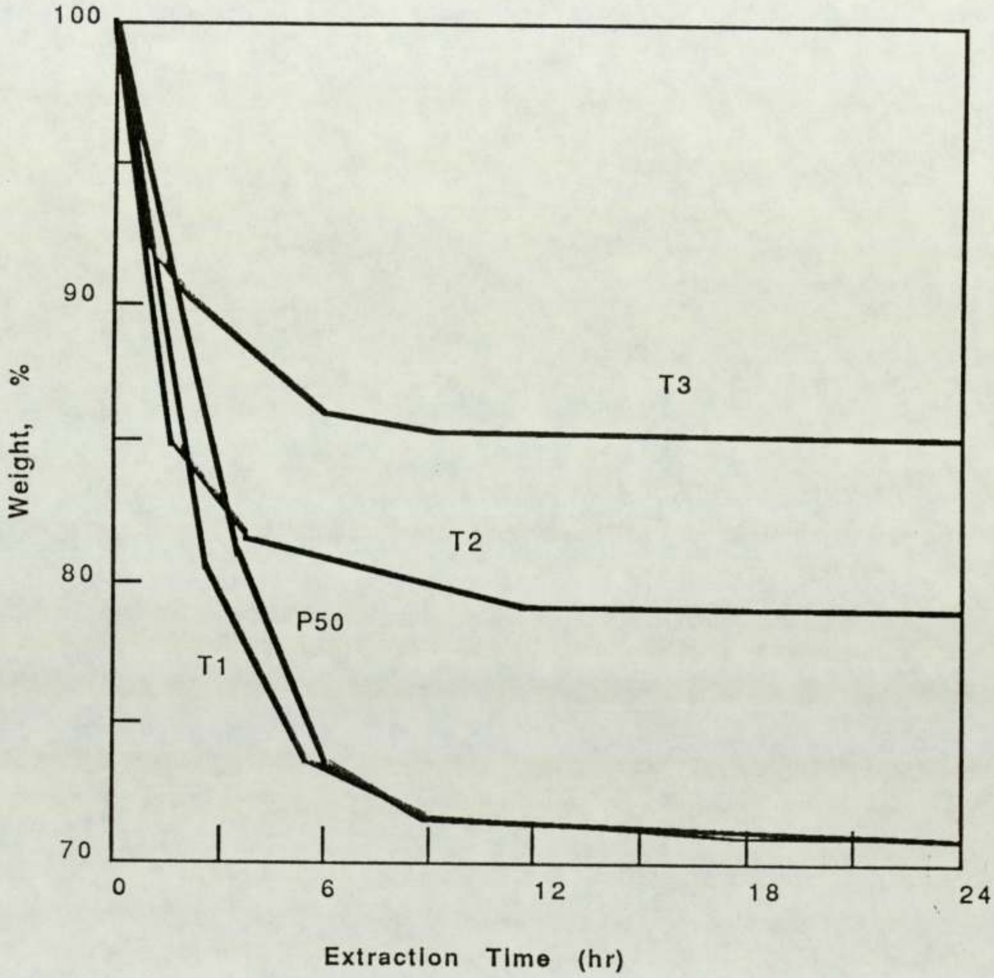


Fig.3.28 Extraction results (in refluxing hexane) of the modified PVC systems and the plasticised PVC with the same initial loading of DBM (50% of PVC by weight).

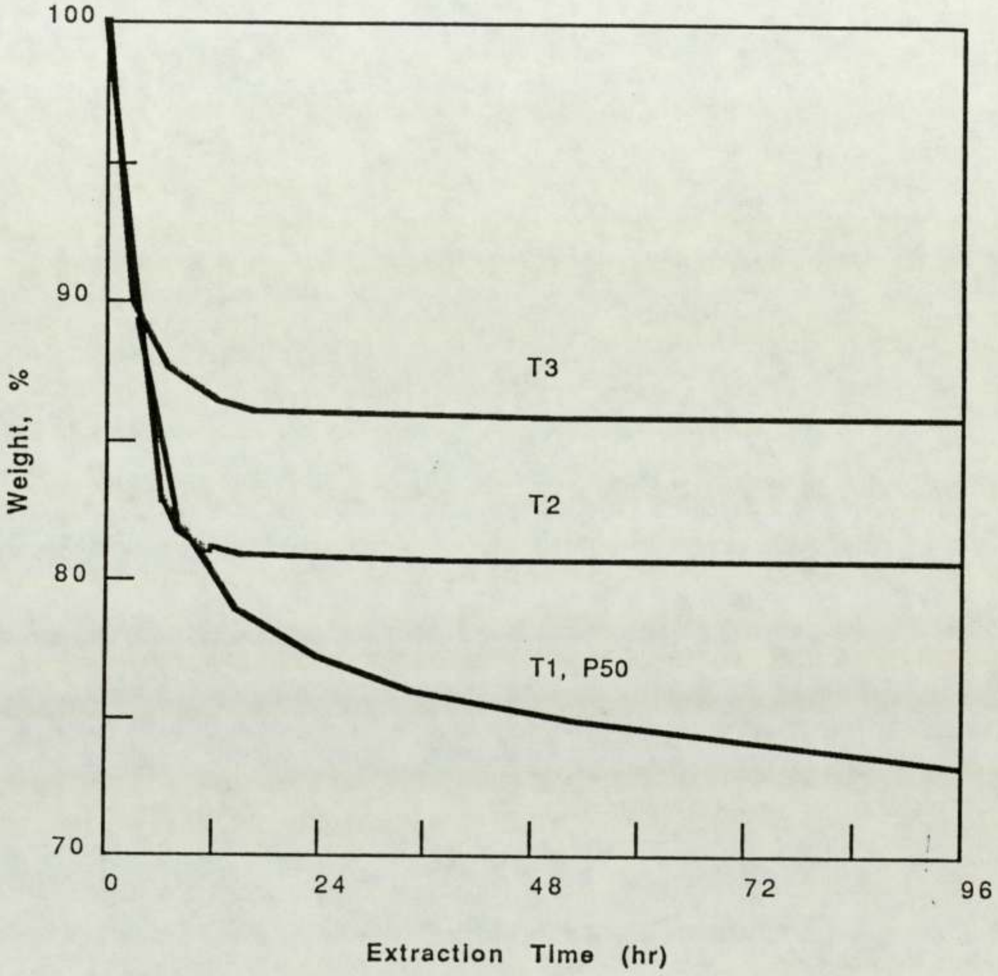


Fig.3.29 Extraction results (in hexane at 15 C) of the modified PVC systems and the plasticised PVC with the same initial loading of DBM (50% of PVC by weight).

3.2.5.2 Blooming Resistance

A modified PVC film sample (T3) and a normally plasticised PVC film sample were exposed under UV irradiation in a sunlight cabinet. The initial loading of DBM was 50% of PVC by weight. It was found that the surface of the plasticised PVC film became grey-white and lost gloss, whereas that of sample T3 remained transparent and retained its gloss till photodegradation was serious.

3.2.5.2 Solubility

The solubility of the processed PVC and the modified PVC systems in various solvents is shown in Table 3.3.

Table 3.3

Solubility of the processed PVC and the modified PVC systems in some organic solvents

Sample	*Solubility* [a]			
	THF[b]	Cyclohexanone[c]	Chloroform[b]	Acetone[d]
pPVC	2	2	3	3
P50	1	1	3	3
A1	1	1	3	3
A2	1	1	3	3
A3	1	1	3	3
T1	1	1	3	3
T2	1	1	3	3
T3	1	1	3	3

a Is ranked in 4 grades: 1. clear solution; 2. unclear solution; 3. swollen; 4. insoluble.

b At 15 C for 12 hours.

c Reflux under agitation for 20 minutes.

d At 15 C for 1 hour.

It can be seen that the solubility of all modified PVC samples was higher than that of the processed PVC.

3.2.5.4 Mechanical Properties and Plasticity

The stress-elongation and associated curves of the processed PVC and the extracted modified PVC samples are shown in Figs.3.30-33. Compared with the figures for the processed PVC, the decrease in tangent modulus and the increase of the elongation for the modified PVC samples indicates that binding of the plasticiser into PVC chains still maintained plasticity. The effects of the concentration of the radical generator on the tangent molulus and the elongation to break are shown in Fig.3.32 and Fig.3.33 respectively. It can been seen that the tangent modulus reduces on increasing the concentration of the radical generator in the case of both AIBN and Triganox101. In contrast, the elongation to break goes through a maximum on changing the concentration of AIBN, whereas it increases on increasing the concentration of Triganox101. The effect of concentration of radical generator on the plasticity, as shown in Fig.3.34, mirrors the results for break elongation. These effects are similar to the effect of the concentration of radical generator on the extent of binding of DBM (see Fig.3.2). Taken together, these results indicate that the plasticity of a modified PVC increases on increasing the extent of binding of the plasticiser and that the radical generator used in the reactive processing is not a significant factor in determining the tensile properties of modified PVC.

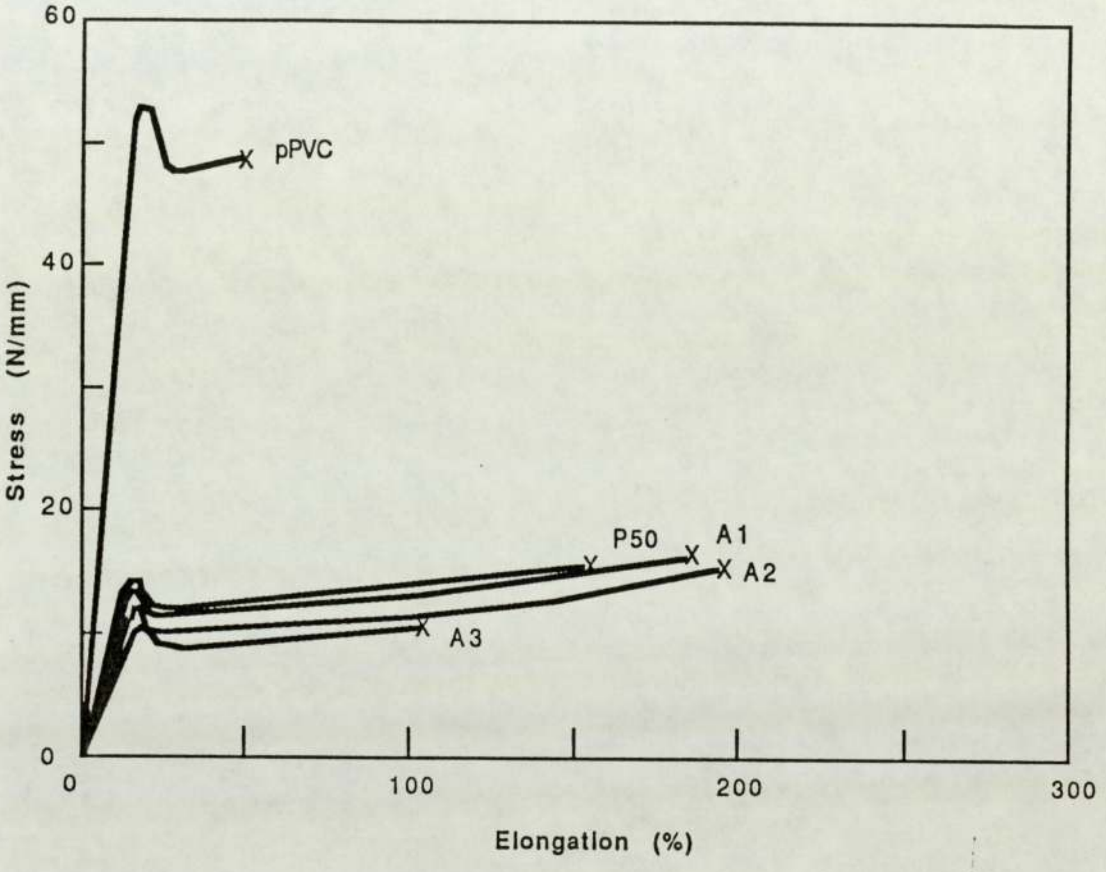


Fig.3.30 Stress-elongation curves of the processed PVC and the extracted modified PVC samples. For details of the samples, see Table 3.1.

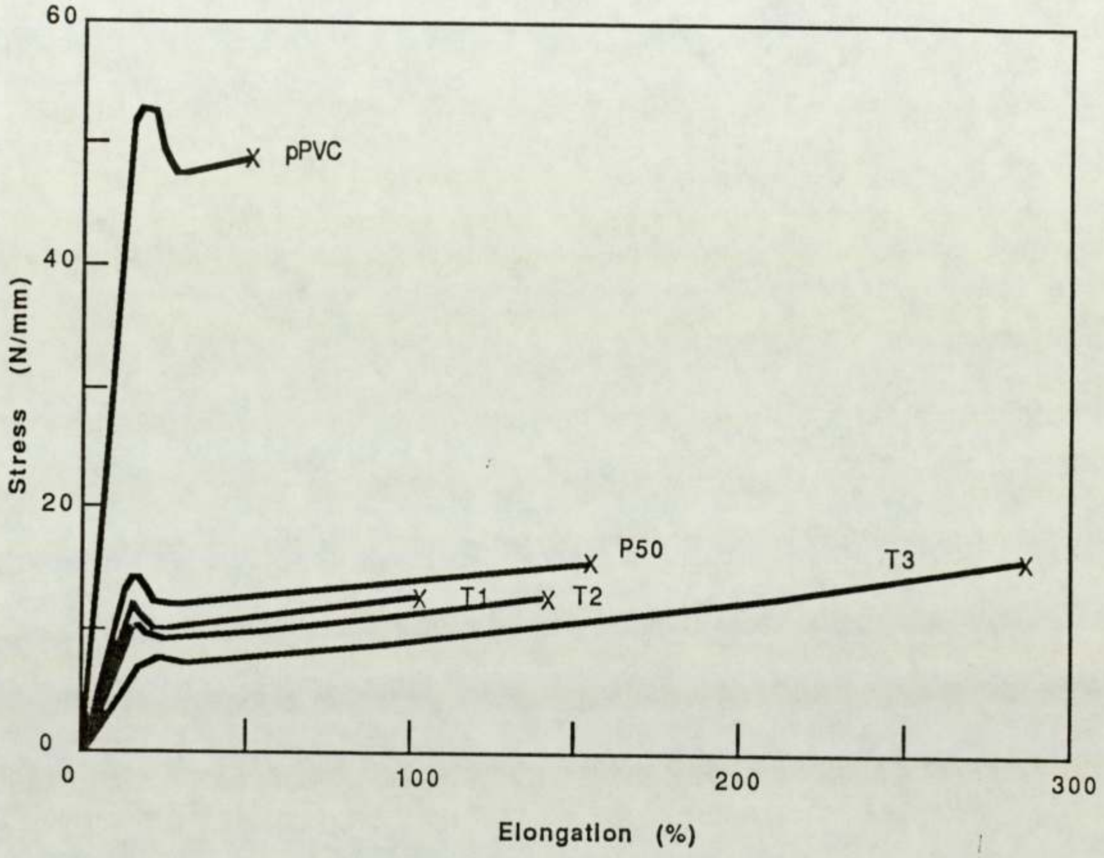


Fig.3.31 Stress-elongation curves of the processed PVC and the extracted modified PVC samples. For details of the samples, see Table 3.1.

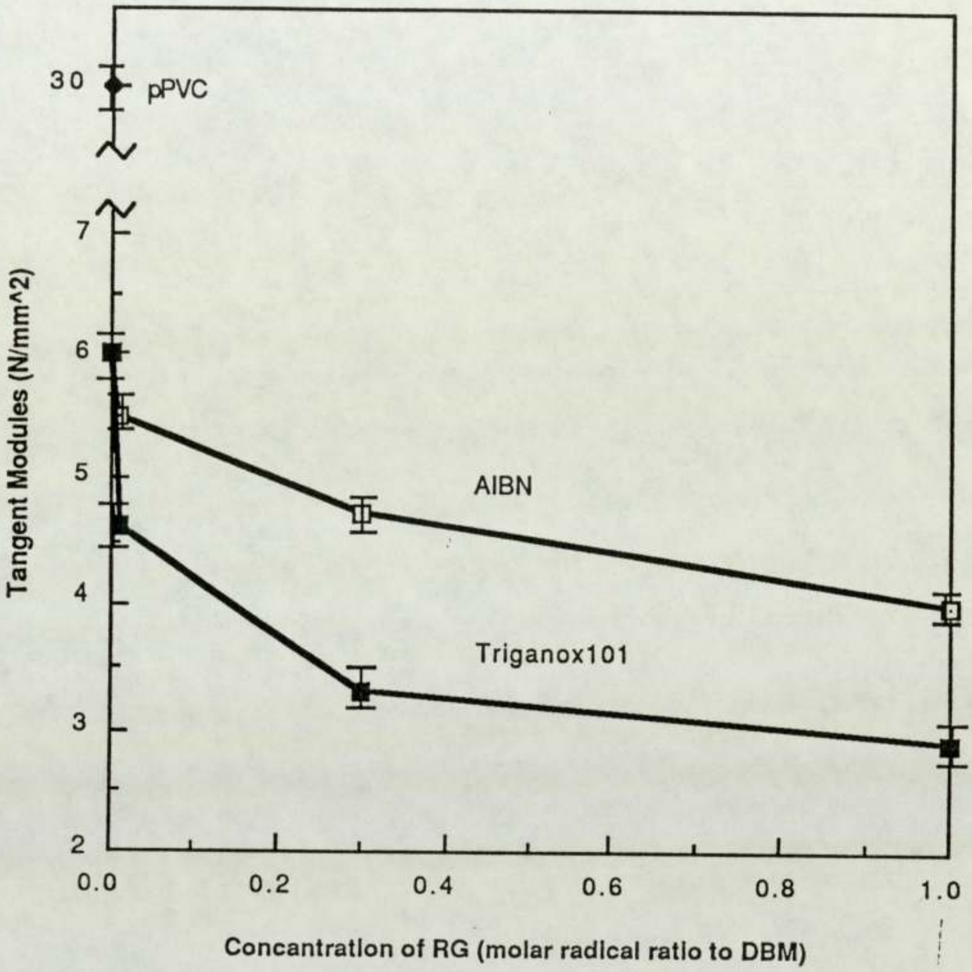


Fig.3.32 Effect of theconcentration of radical generators on the tangent modulus of the extracted modified PVC systems.

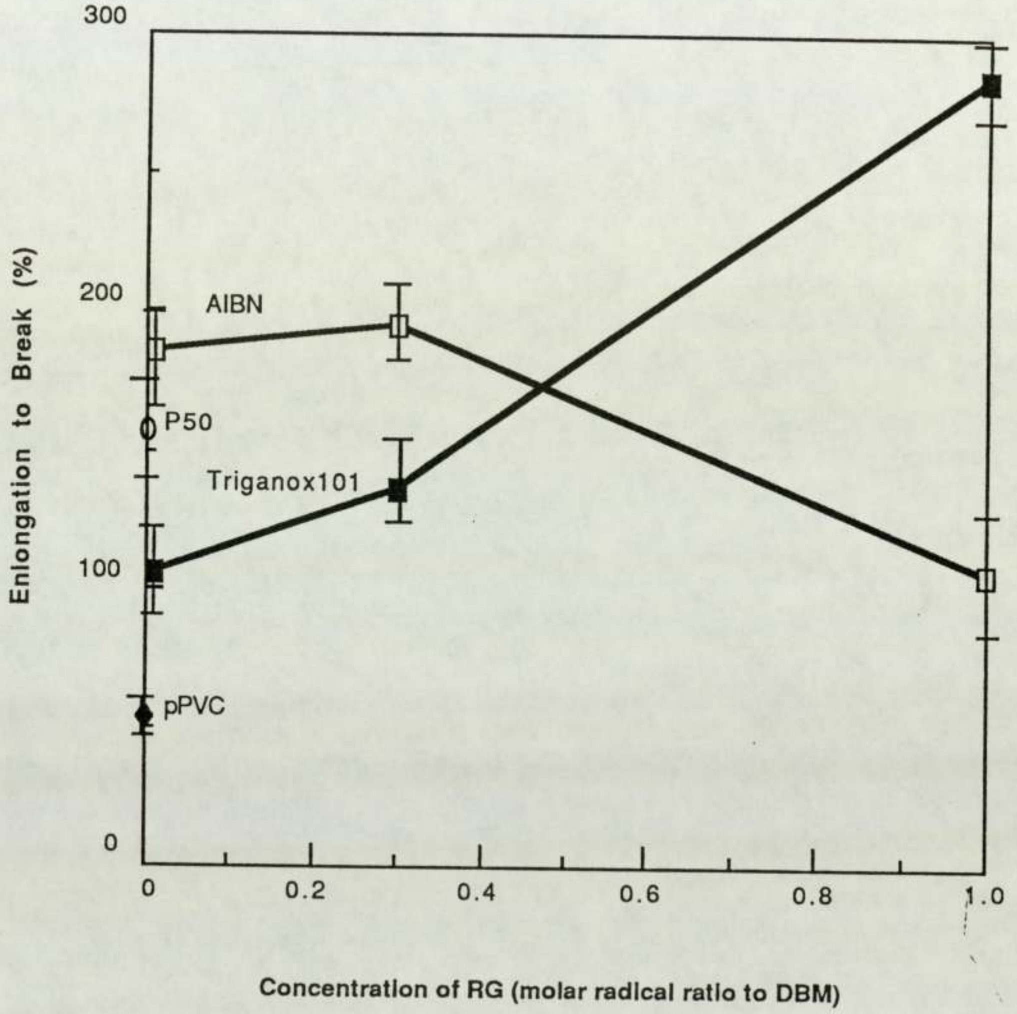


Fig.3.33 Effect of theconcentration of radical generators on the elongation to break of the extracted modified PVC systems.

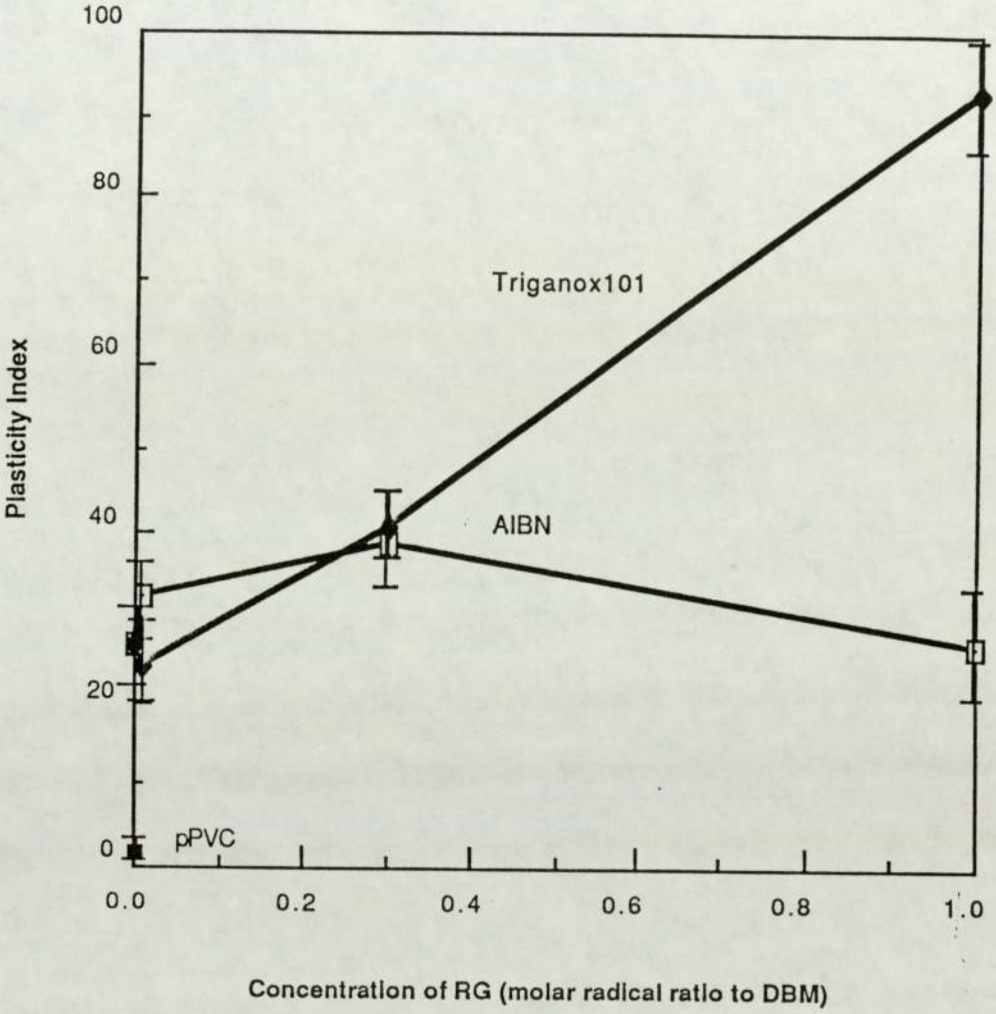


Fig.3.34 Effect of concentration of radical generators on the plasticity of the extracted modified PVC systems.

3.2.5.5 Photoageing Performance

The embrittlement times of the processed PVC and the extracted modified PVC samples under UV irradiation are shown in Table 3.4 and Fig.3.35. It is to be noted that all the modified PVC samples, except T3, have longer embrittlement times than PVC. The modified samples with a relatively lower degree of DBM binding have excellent photostability, and as shown in Fig.3.35, the embrittlement time decreased with increase in the extent of binding of DBM. This may contribute to the structure of the modified PVC systems: this will be discussed in **3.3.5**.

The percentage elongation of these samples during UV irradiation is shown in Fig.3.36. With the processed PVC sample, the elongation increased in the first 200 hours and then decreased rapidly. Sample T3 desplayed a sharp fall even after 100 hours' exposure, whereas other modified PVC samples, e.g. P50 and A1, showed a more gradual decrease.

The discolouration of these samples is shown in Figs.3.37-38. After an induction period the processed PVC discoloured seriously: the sample turned black before it became brittle. However, the modified PVC samples remained transparent and clear after more than 2000 hours of UV irradiation with the exception of sample T3, which developed some small brown spots, but was still transparent when it became brittle.

Table 3.4

Embrittlement Time

sample [a]	*Embittlement Time (hour)*
PVC	690
P50	2190
A1	2140
A2	2190
A3	2120
T1	2070
T2	1150
T3	620

a. For details of the samples, see Table 3.1.

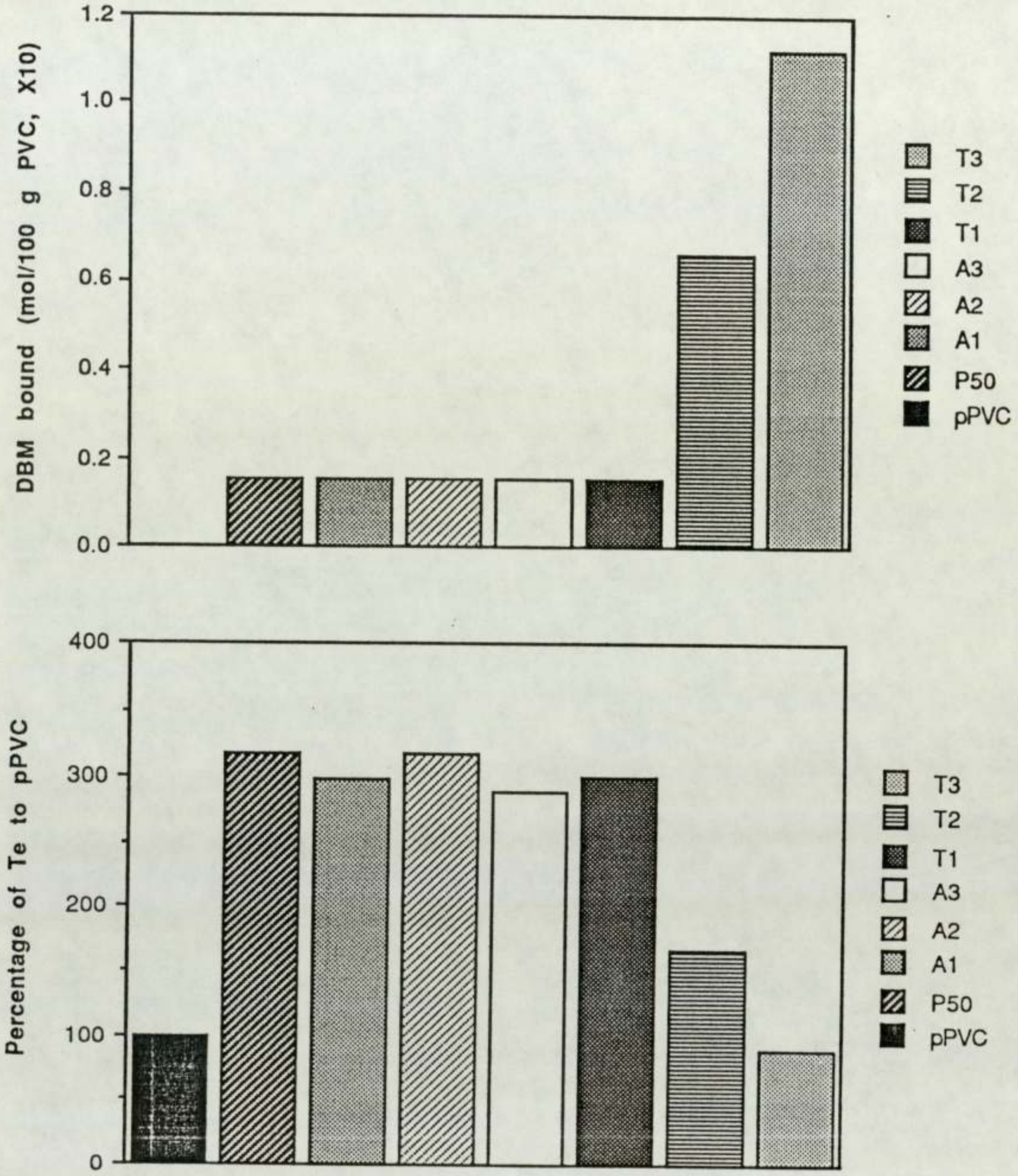


Fig.3.35 Embrittlement time (Te) and extent of binding of DBM. For details of the samples see Table 3.1.

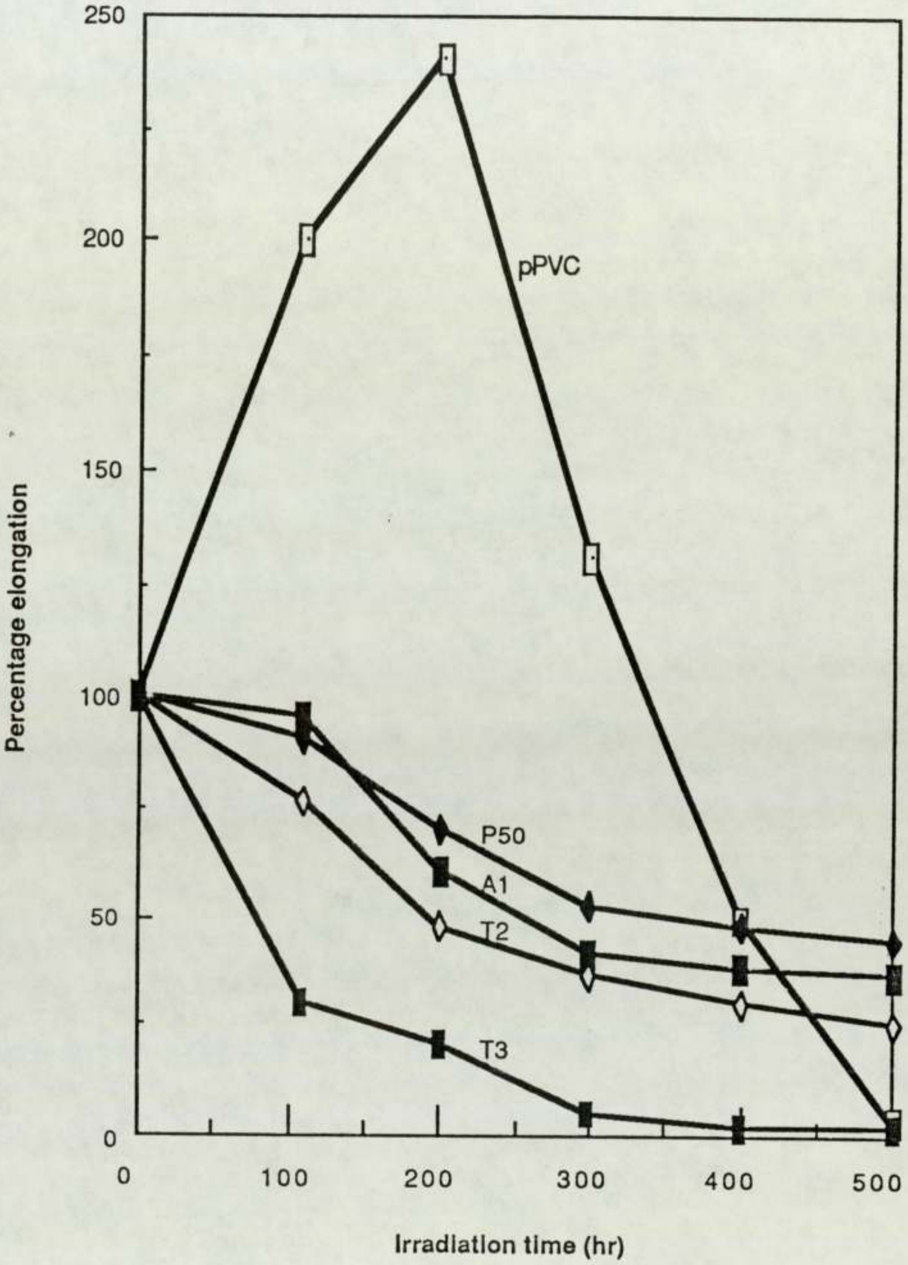


Fig.3.36 Percentage elongation as a function of UV irradiation time for processed PVC and the extracted modified PVC systems.

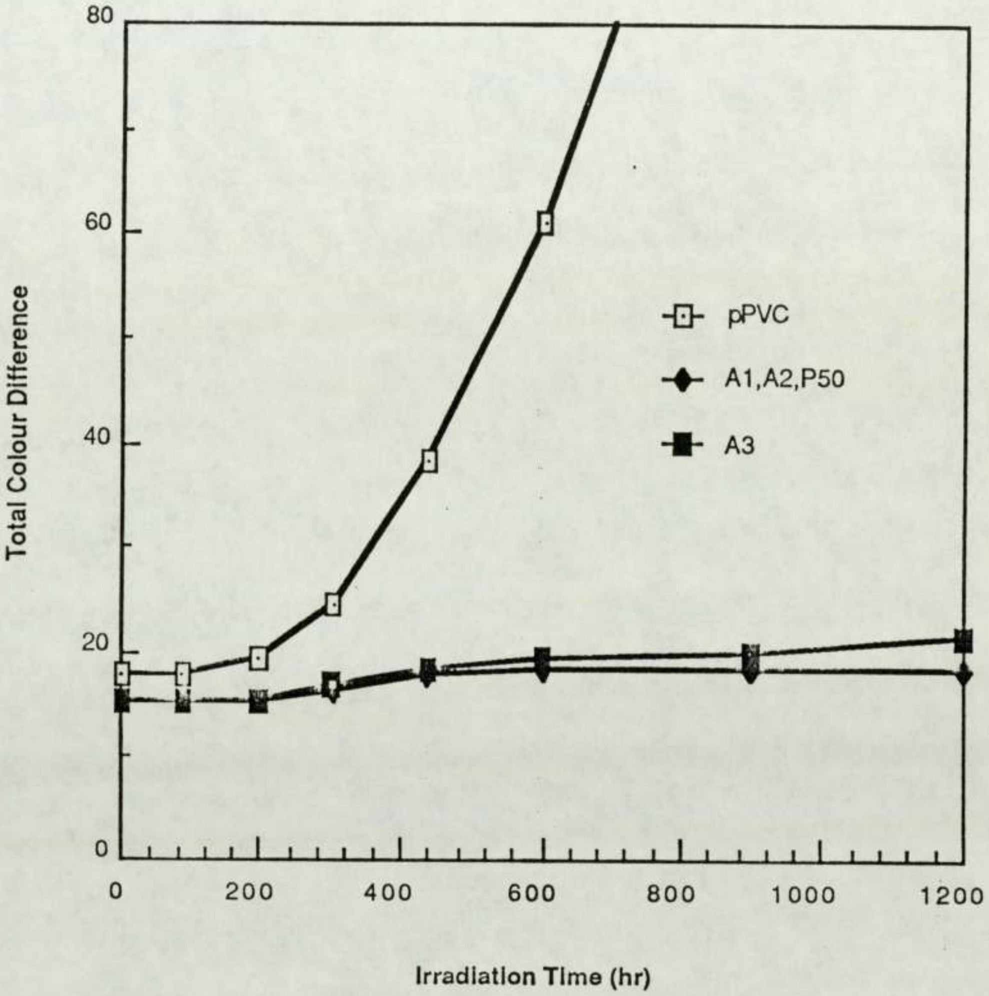


Fig.3.37 Discolouration of processed PVC and the extracted modified PVC systems during UV irradiation. For details of the samples, see Table 3.1.

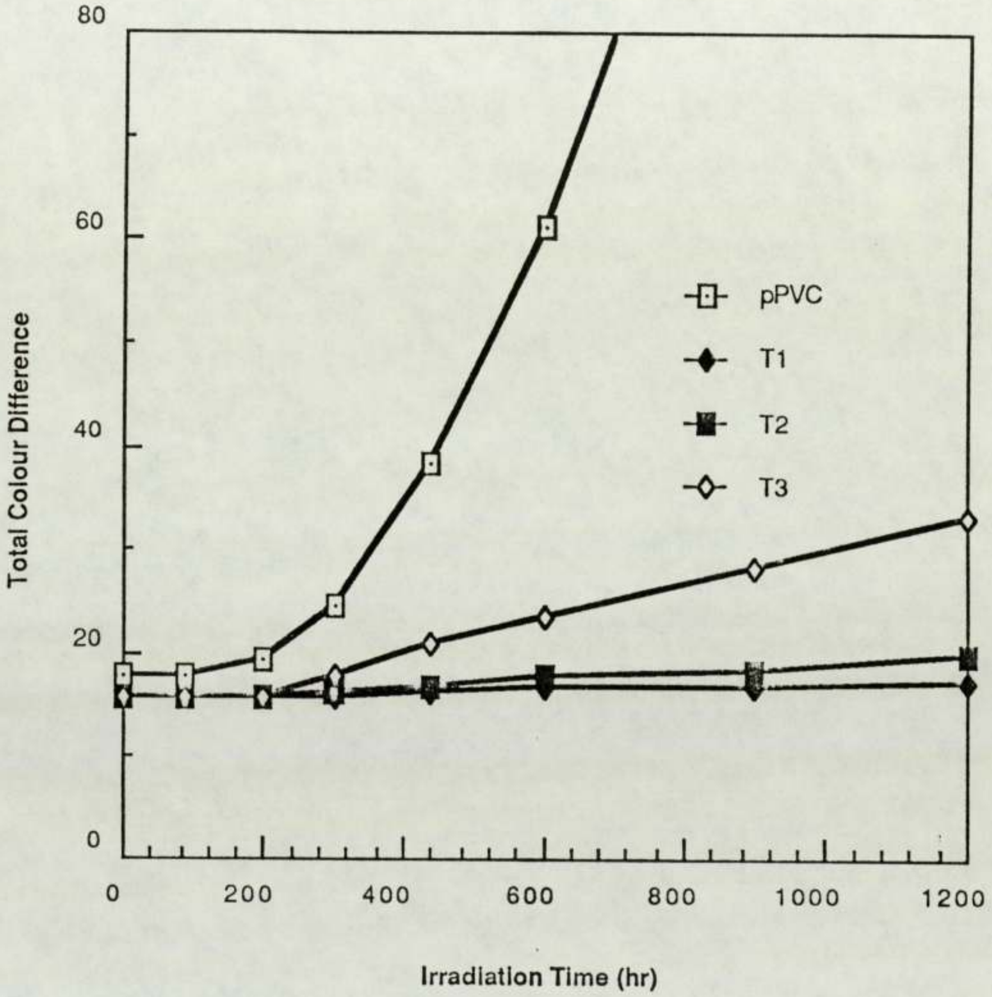


Fig.3.38 Discolouration of processed PVC and the extracted modified PVC systems during UV irradiation. For details of the samples, see Table 3.1.

The structure variations related to photoageing were evaluated by measuring the molecular weight and its distribution (Figs.3.39-40), unsaturation (Figs.3.41-45) and hydroxyl groups (Fig.3.46).

Figs.3.39 and 40 show that the molecular weight increased slightly after 110 hours of UV irradiation in the case of sample P50 but that it decreased for sample T3; again, the molecular weight distribution changed slightly for a sample P50 and clearly increased in the case of sample T3. These results indicate that the photodegradation processes in the case of T3 mainly involved chain scission, but that chain scission was not important for P50.

The UV-Vis spectra of processed PVC, T1 and T3 during UV irradiation are shown in Figs3.41-43. The degree of unsaturation increased rapidly between the period of 200-1000 hours of UV irradiation for the processed PVC. However, unsaturation only increased slightly in the case of sample T1 (Fig.3.42) whereas the results for T3 show similarities with those for pPVC (Fig.3.43). It is noted that the carbonyl absorbance at about 240 nm decreased during the early stages of UV irradiation, especially for sample T3; this trend arise from loss of the carbonyl groups in the side chain via a Norrish I type reaction.

The variations of the IR absorbance at 1650 cm^{-1} of the processed PVC and the extracted modified PVC systems during UV irradiation are shown in Figs3.44 and 45. The absorbance increased steadily during the first 400 hours and then even more rapidly in the case of the processed PVC, whereas it rose rapidly after about 200 hours for sample T3. However, the absorbance showed little change during UV irradiation of more than 1200 hours with samples P50, A1, A2, A3 and T1. These variations can be related to changes in the UV absorbances in the range of 280 - 350 nm (see Figs.3.41-43), which contribute to conjugated double bonds with numbers 3 - 6 [88].

The hydroxyl content variations of the processed PVC and modified PVC polymers during UV irradiation are shown in Figs.3.46-47. Again relatively rapid changes in hydroxyl content were measured following exposure of the processed PVC and sample T3, The hydroxyl content increased much more slowly in the case of samples P50, A1, A2, A3 and T1.

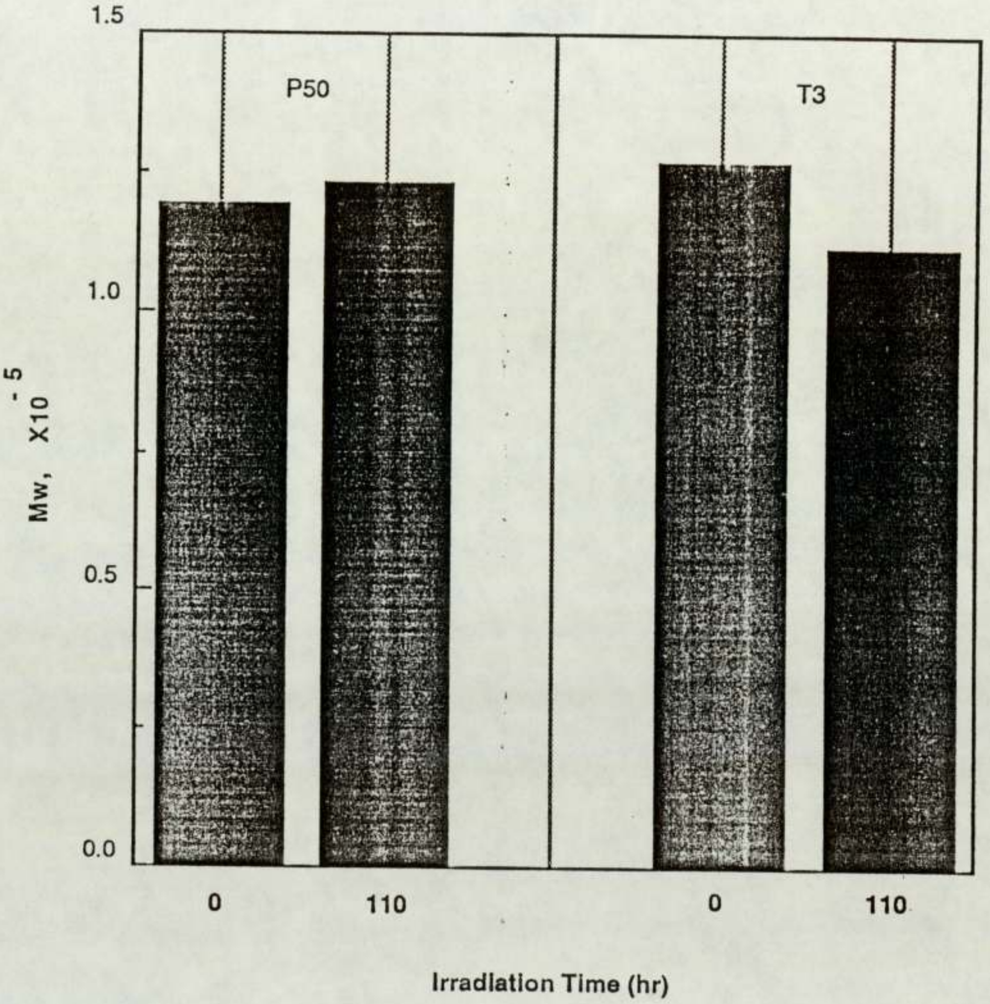


Fig.3.39 Molecular weight variations of DBM modified PVC polymers during UV irradiation. For details of the samples, see Table 3.1.

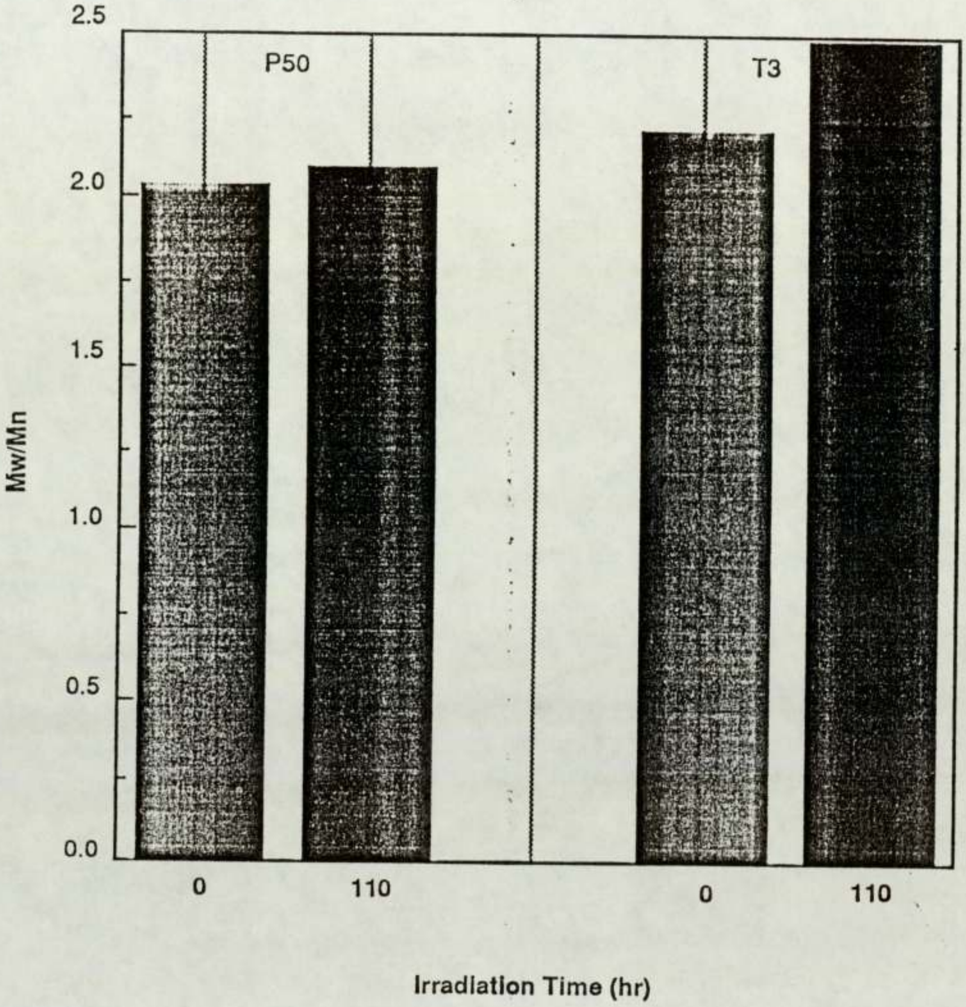


Fig.3.40 Polydispersity index variations of DBM modified PVC polymers during UV irradiation. For details of the samples, see Table 3.1.

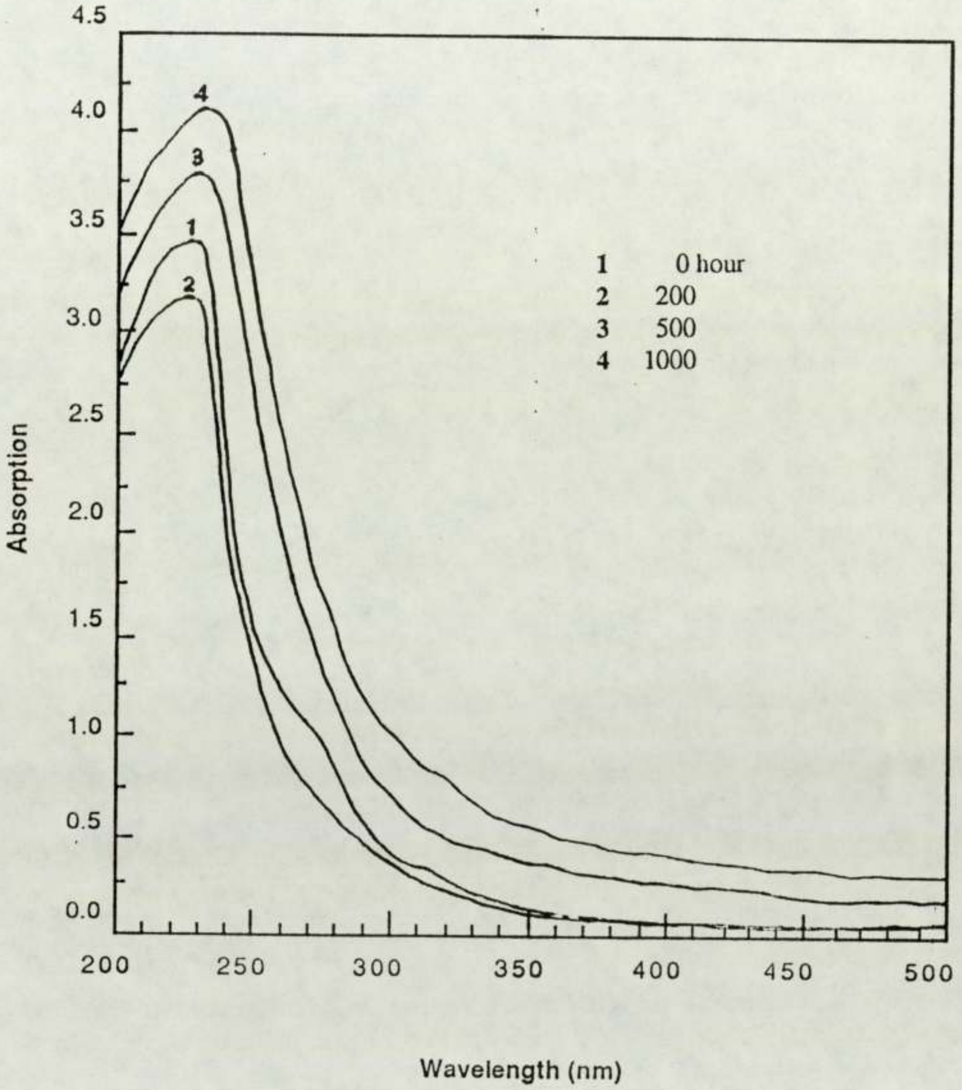


Fig.3.41 Variation of the UV-Vis spectra of the processed PVC during UV irradiation.

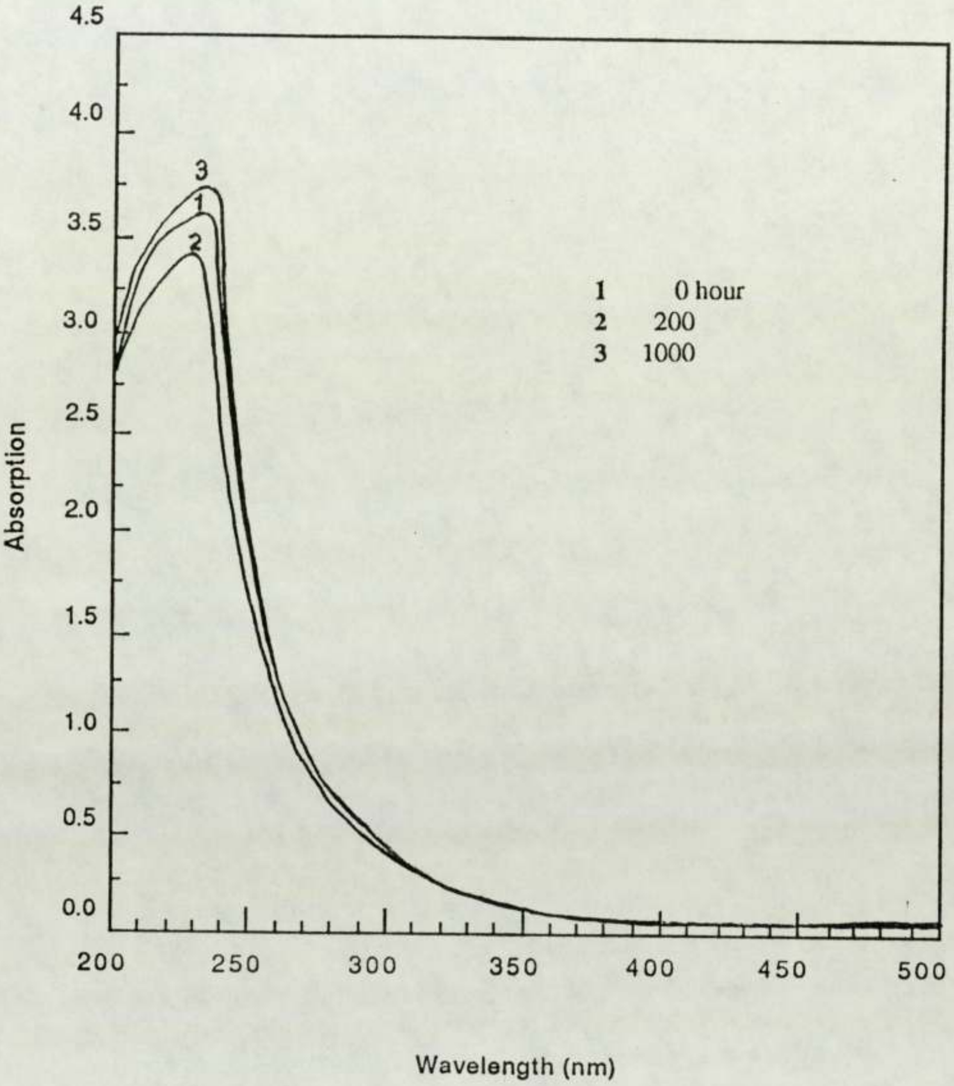


Fig.3.42 Variation of the UV-Vis spectra of an extracted DBM modified PVC sample (T1) during UV irradiation.

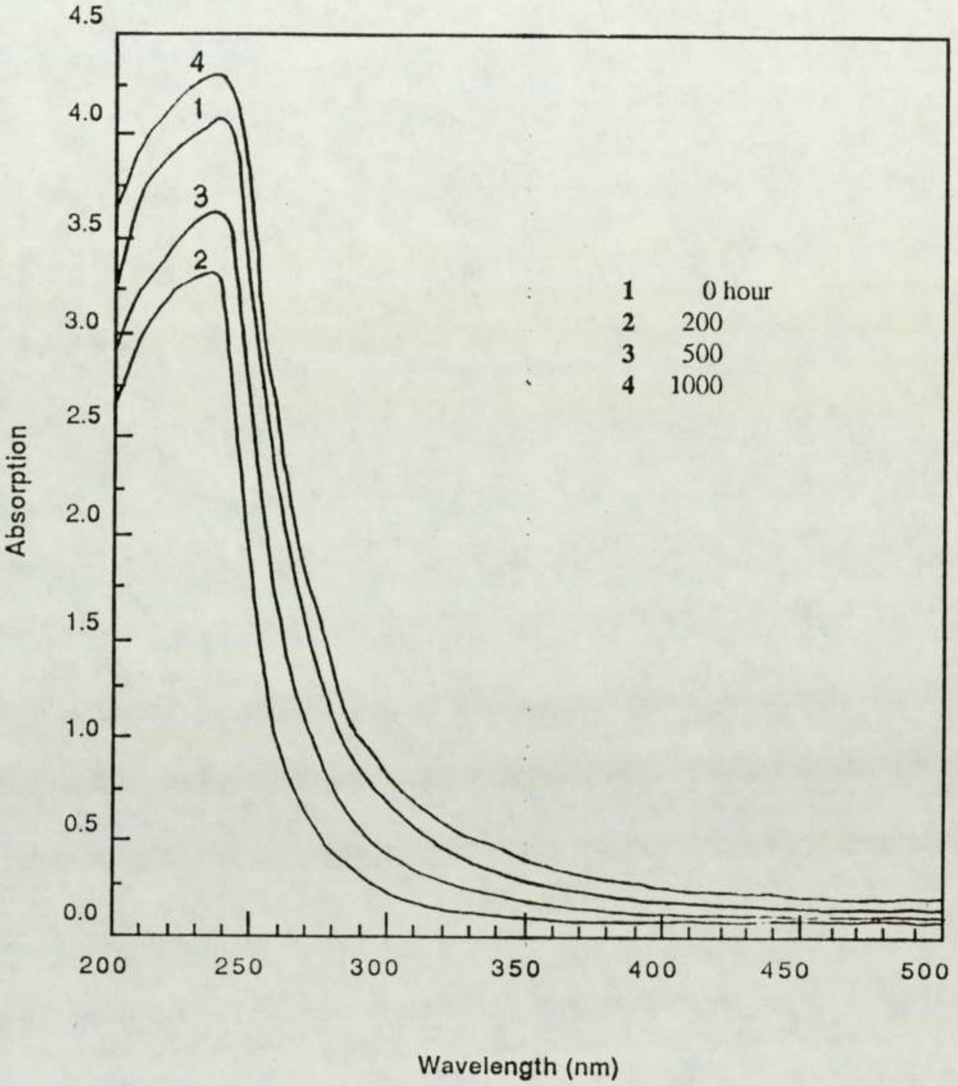


Fig.3.43 variation of the UV-Vis spectra of an extracted DBM modified PVC sample (T3) during UV irradiation.

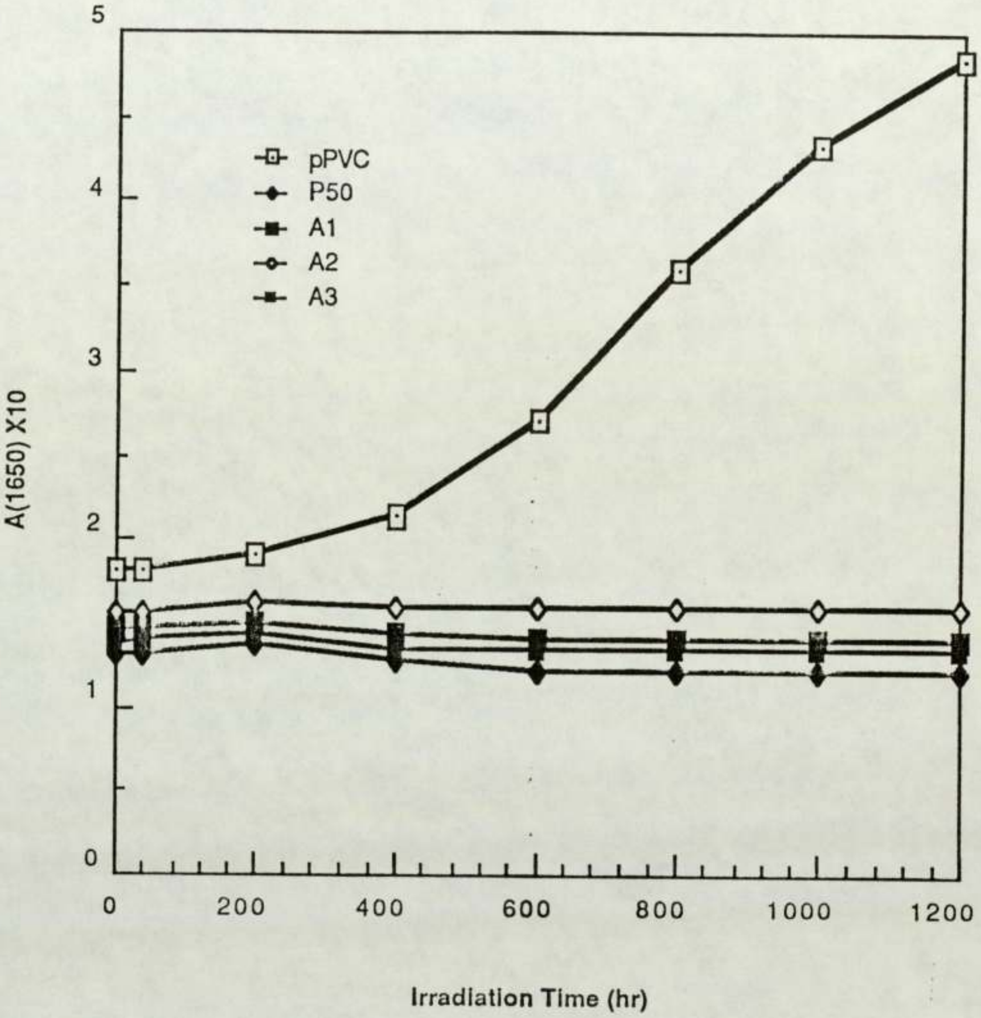


Fig.3.44 Variation of the IR absorbance at 1650 cm^{-1} of processed PVC and the extracted modified PVC systems during UV irradiaion. For details of the samples, see Table 3.1.

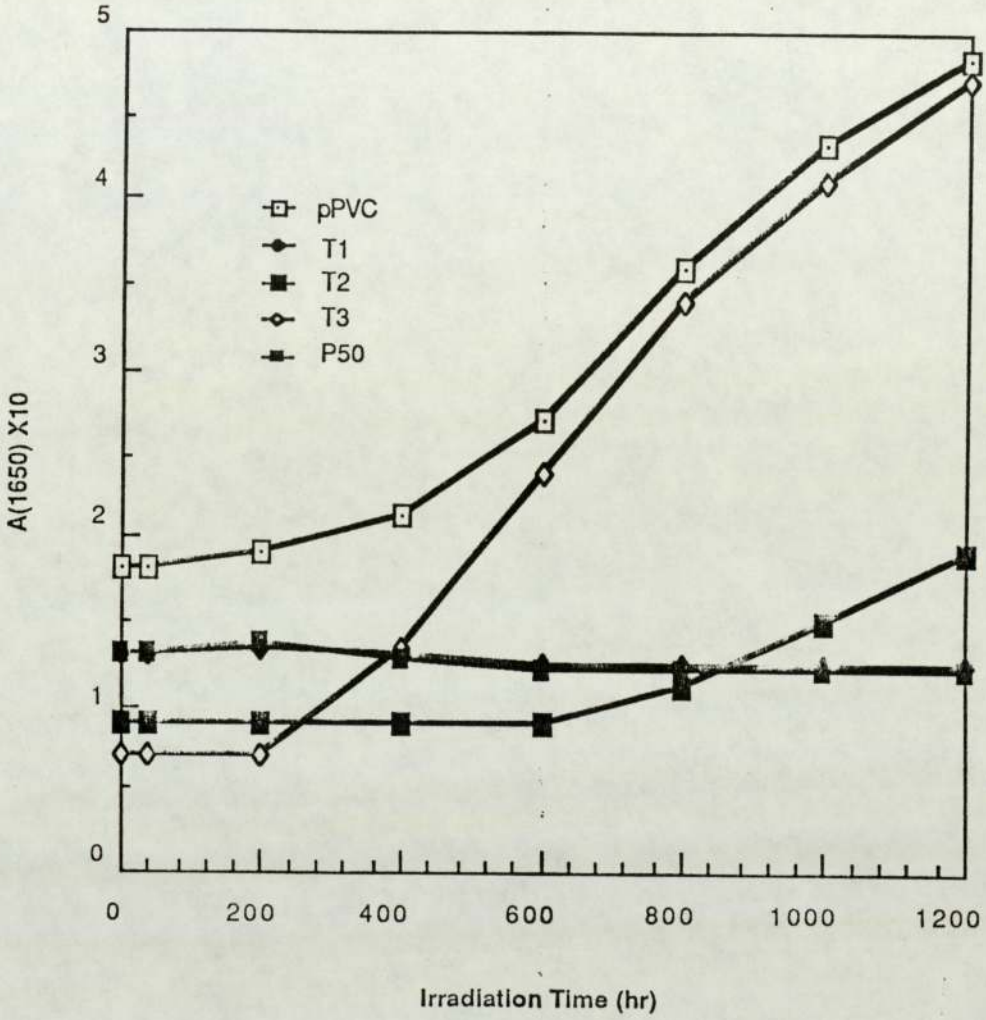


Fig.3.45 Variation of the IR absorbance at 1650 cm^{-1} of the extracted modified PVC systems during UV irradiation. For details of the samples, see Table 3.1.

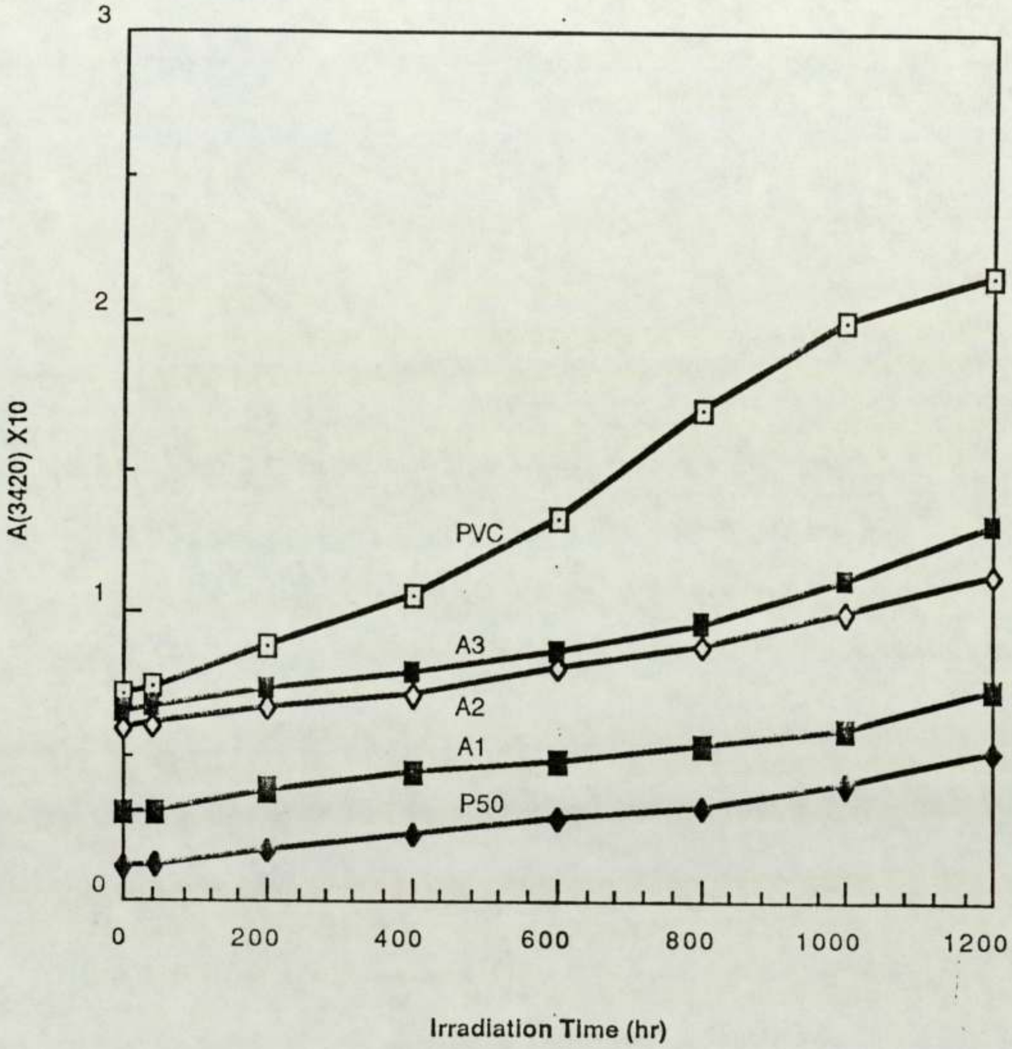


Fig.3.46 Photooxidation of processed PVC and the extracted DBM modified PVC systems. For details of the samples, see Table 3.1.

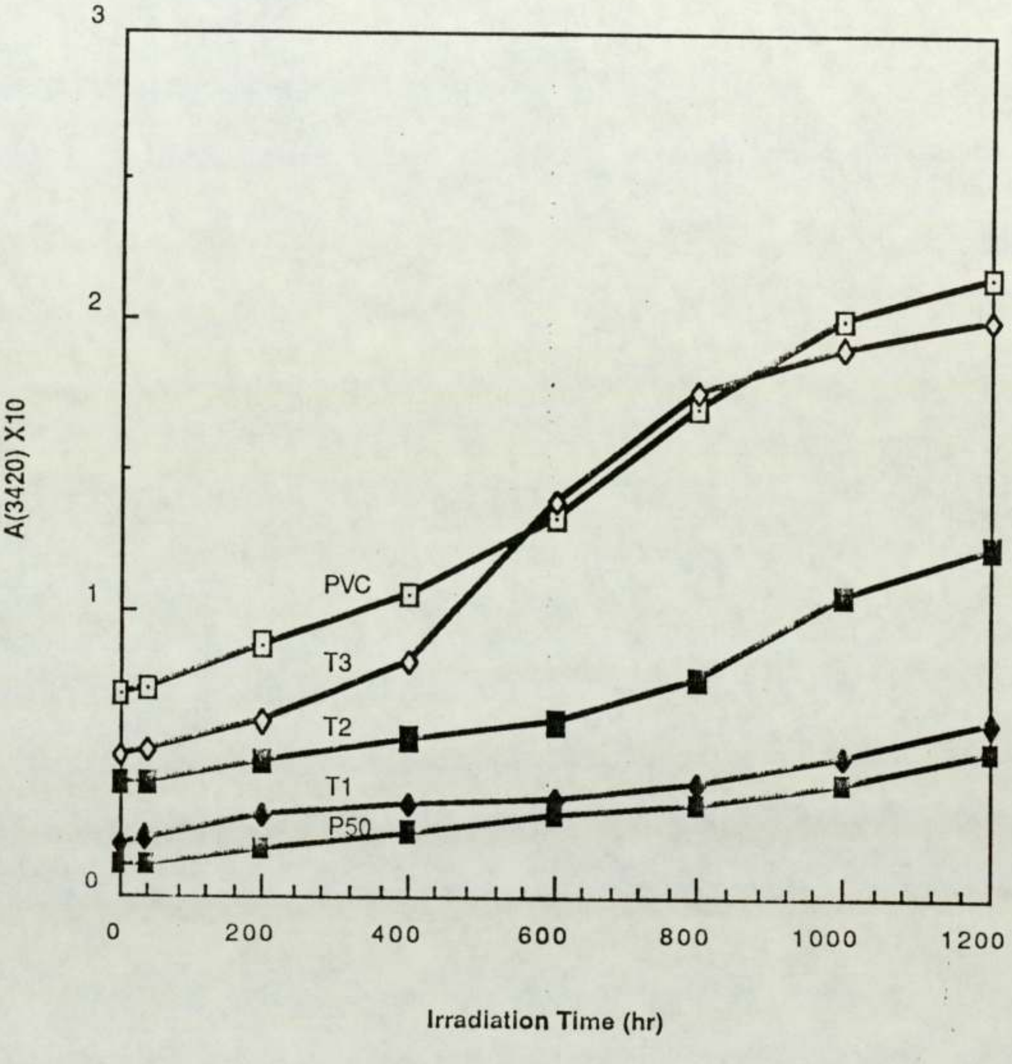


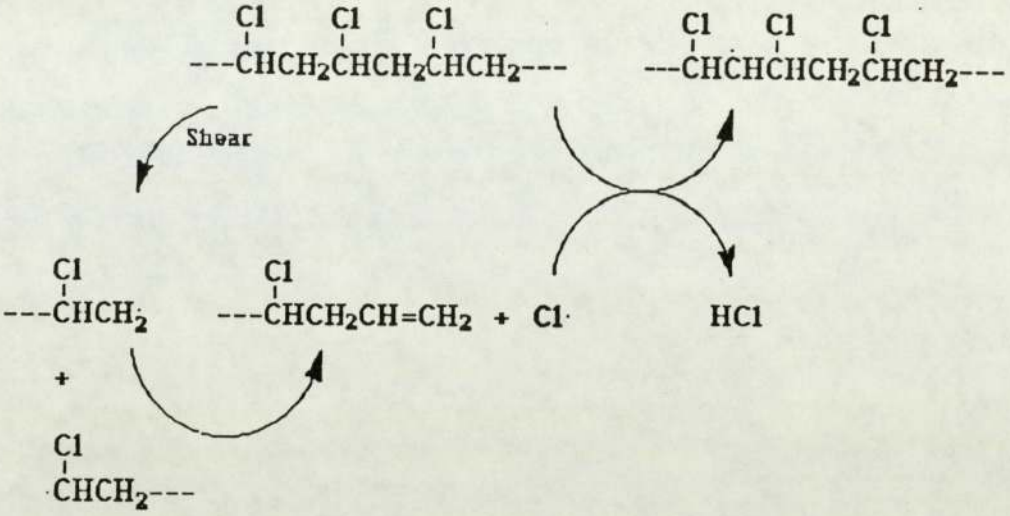
Fig.3.47 Photooxidation of the processed PVC and the extracted DBM modified PVC systems. For details of the samples, see Table 3.1.

3.3 DISCUSSION

3.3.1 Mechanisms for the Binding of DBM with PVC during Processing

It is clear from above results that two different mechanisms for the binding of DBM occur and that they largely depend on the concentration of DBM radicals. In order to understand these two mechanisms, it is necessary to analyse all the main reactions involved in the processing operation.

It is known[12-14,38] that in unplasticised PVC systems the formation of PVC macro-alkyl radicals by shear forces will occur in the first few minutes during processing. In the absence of oxygen, some of the original chain-end radicals will develop into isolated double bonds and form chloride radicals, by which the further formation of macro-alkyl radicals will be initiated. These macro-alkyl radicals will provide the sources of unsaturation in PVC by subsequent reactions, mainly dehydrochlorination. The GPC results from this work suggest that this process also happens in plasticised PVC systems (see *3.2.4.1*). It is shown in Scheme3.1.

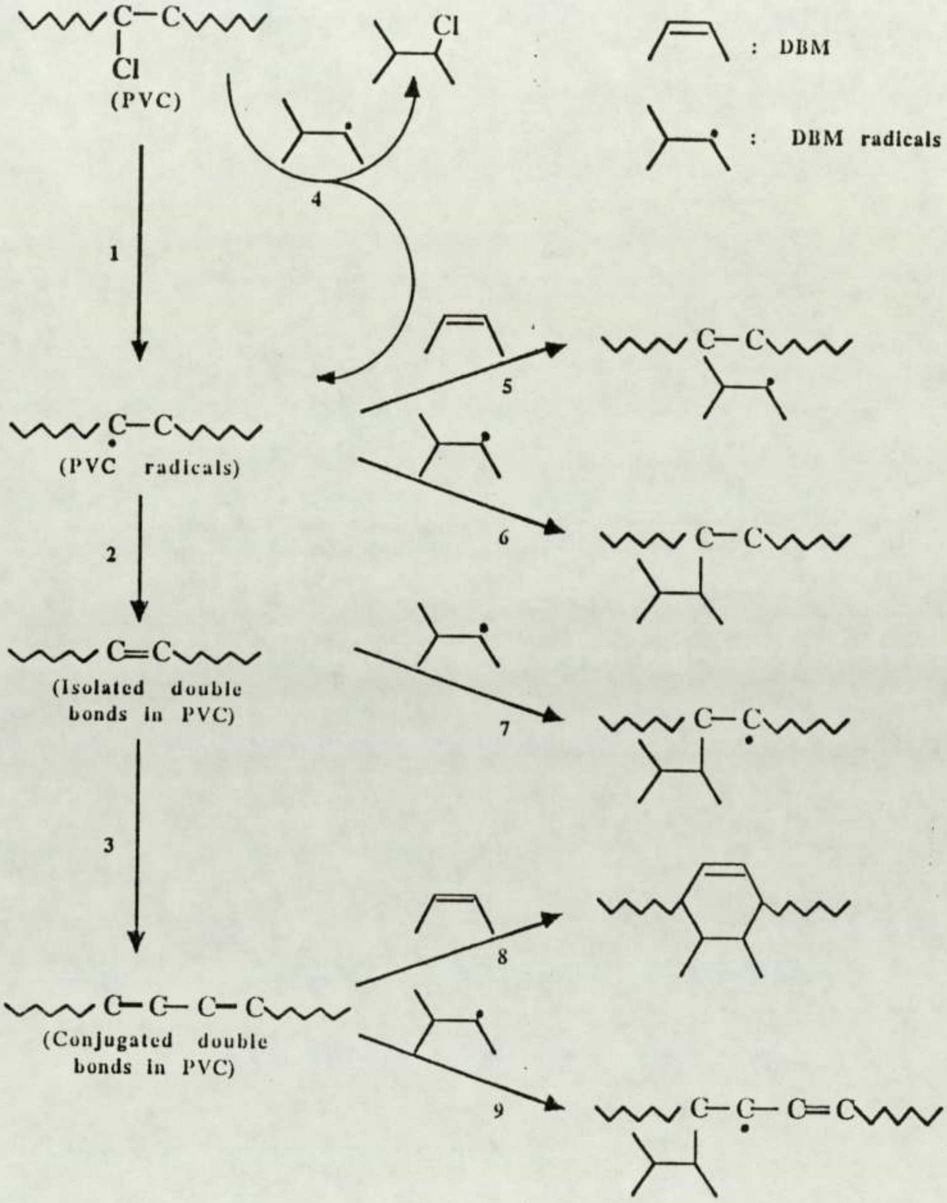


Scheme3.1 Formation of PVC macro-alkyl radicals under the influence of high shear during closed processing.

Undoubtedly, the radical mechanism will be the dominant one in dehydrochlorination of PVC under the influence of high shear. The macro-alkyl radicals will change into isolated double bonds and then develop into conjugated double bonds accompanied by the alternate formation of chlorine radicals and hydrogen chloride in the case of an unstabilised system.

When DBM and a radical generator are incorporated into PVC, it is mainly the DBM and DBM radicals, initiated by the radical generator, that will react with intermediates formed during the degradation of PVC. Possible reactions are shown in Scheme3.2.

If part of the DBM changes into DBM radicals, the concentration of



Scheme3.2 Possible reactions of DBM and DBM radicals with PVC and varied intermediates during PVC degradation.

loaded DBM ($[DBM]_L$) will consist of DBM radicals ($[DBM\cdot]$) and residual DBM ($[DBM]_R$):

$$[DBM]_L = [DBM\cdot] + [DBM]_R,$$

then the proportion of DBM radicals is $[DBM\cdot]/[DBM]_L$ and the proportion of residual DBM is $[DBM]_R/[DBM]_L$.

In the case of a high $[DBM]_R/[DBM]_L$ ratio, the reactions mainly occurring would be Reactions **5** and **8** in Scheme3.2. Reaction **8** is a Diels-Alder reaction which has been confirmed in maleic acid derivative-PVC reaction systems[144]. Reaction **5** is a binding reaction of DBM with PVC by a radical mechanism which competes with Reaction **2**, a development from PVC macro-alkyl radicals to unsaturation. It has been suggested[83] that Reaction 5 is easier than **2**, but this can not convincingly explain why the extent of binding of DBM was experimentally much lower than the theoretical one by this mechanism. Results in the author's work have not provided evidence to support the predominance of reaction **5** in the binding reaction. On the contrary, an increase in the loading of DBM does not contribute to the binding in the case of higher $[DBM]_R/[DBM]_L$ ratio (Curve AIBN in Fig.3.3). Moreover, monounsaturation was detected all modified PVC products after extraction (Curve AIBN in Fig.3.24). These indicate that Reactions **2** and **8** are more important because Reaction **5** is not fast enough to inhibit the formation of isolated double bonds in PVC through Reaction **2**. It is therefore suggested that Reaction **8**, i.e. a Diels-Alder reaction, is predominant in the binding of DBM with PVC in the case of a lower proportion of DBM radicals.

In the case of high $[DBM\cdot]/[DBM]_L$ ratio, the main reactions should be Reactions **4**, **6**, **7** and **9**. Reaction **4** leads to a decrease of $[DBM\cdot]$ and a increase of PVC macro-alkyl radicals. Reaction **6** is a radical coupling reaction between DBM radicals and PVC macro-alkyl radicals, which competes with Reaction **2**. The finding that the monounsaturation almost disappears from a bound product formed from a reaction system with an equimolar radical ratio of Triganox101 to DBM (Fig.3.24) proves that Reaction **6** is faster than Reaction **2** under these conditions. Thus the development of unsaturation in PVC is effectively inhibited. Reactions **7** and **9** may possibly also be occurring; they contribute to the binding of DBM with PVC, but the probability of both of them taking place would be in inverse proportion to that of Reaction **6**.

It is therefore suggested that Reaction **6**, a radical coupling reaction between DBM radicals and PVC chain radicals, is predominant in the binding of DBM with PVC in the case of a high proportion of DBM radicals.

3.3.2 Approaches to Increasing the Extent of Binding of DBM

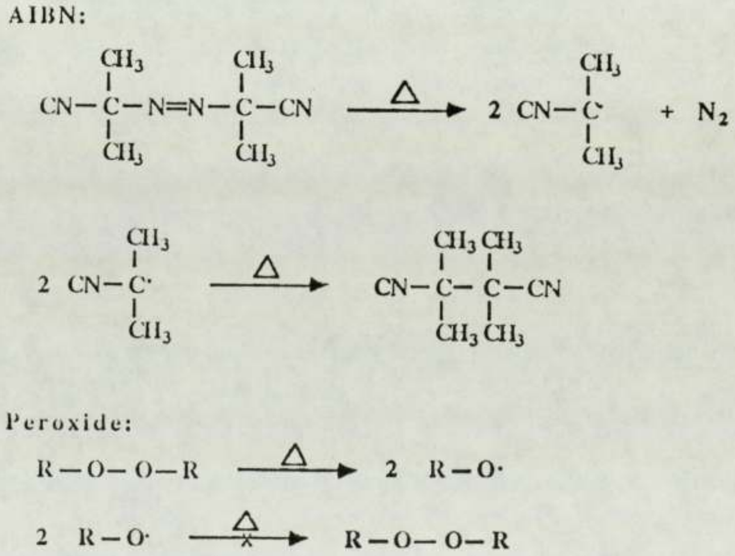
Four main factors may influence the extent of binding of DBM based on the analysis of the mechanisms of the binding. They include:

a. Concentration of DBM Radicals.

There are two ways of describing the concentration of DBM radicals. One is relative concentration, i.e. the proportion of DBM radicals in loaded DBM ($[DBM\cdot]/[DBM]_L$); the other is absolute concentration, i.e. the ratio of DBM radicals to PVC ($[DBM\cdot]$). Fig.3.2 and Fig.3.3 respectively show the effects of the relative and absolute concentration of DBM radicals on the extent of binding of DBM.

The binding mechanism is mainly determined by the relative concentration of DBM, as shown in **3.3.1**. The fact, as shown in Fig.3.2, that lowering the concentration of Triganox101, lowers the extent of binding of DBM suggests that the radical coupling mechanism (Reaction **6** in Scheme 3.2) is more effective in improving the extent of binding of DBM than the Diels-Alder reaction. Therefore, it is important to see how to increase $[DBM\cdot]/[DBM]_L$ to ensure that the radical coupling mechanism predominantes.

One of the most effective ways to form DBM radicals is to use a radical generator (RG). Triganox101 has been shown to be a highly effective RG for DBM (see 3.4 and Fig.3.2) whereas AIBN was much less effective (Fig.3.2). This may be due to a recombination of the radicals produced from AIBN as a result of a cage effect[202],such recombination reactions are less likely in the case of peroxides e.g. Triganox101 or DCP (Scheme3.3).



Scheme3.3 Decomposition and recombination of AIBN and peroxides.

Therefore, peroxide is more available as a radical generator in the binding of DBM with PVC during processing.

On the other hand, the absolute concentration of DBM radicals can be adjusted by controlling the loading of DBM and radical generator. In this context, reference should be made to Fig. 3.3.

b. Concentration of PVC Macro-alkyl Radicals.

An increase in the concentration of PVC macro-alkyl radicals contributes to the binding of DBM with PVC either by the radical coupling reaction or by the Diels-Alder reaction (Scheme3.2). The experimental results (Figs.3.4, 3.6 and 3.12) indicate that increasing both processing temperature and shear force is an effective way of increasing the concentration of PVC macro-alkyl radicals as well as increasing the effectiveness of the radical generator and consequent DBM radicals (Reactions **4**, **7** and **9** in Scheme3.2).

c. Collision Frequency between Reactive Substances.

The higher the collision frequency between reactive substances, the larger is the probability of the binding reaction taking place. Two important factors affecting collision frequency in the processing operation are the compatibility between PVC and DBM and mixing efficiency on the micro-scale. DBM has been shown to be a good plasticiser to PVC (Figs. 3.8 and 3.9) so that it should be compatible well with PVC. The extent of mixing at the molecular level will depend on the degree of fusion of PVC as well as on the mechanical means employed. The binding results show that good mixing is likely to be achieved when the rheological curve of a PVC-DBM reaction system includes a stage **III** segment (Fig.3.11). The rheological curves as shown in Figs. 3.7-3.9 could therefore be useful to in determining the most suitable processing conditions.

d. Sequential Formation of DBM Radicals and PVC Macro-alkyl Radicals.

A feature of reactive processing is the change with time of both the physical and chemical properties of the reacting mixture, including its ability to absorb heat, changes of state and viscosity. Manipulation of both the operational sequence and processing conditions might, therefore, be used to control binding, especially for a PVC reaction system. For example, if the DBM radicals are allowed to form at a high level just before the formation of PVC macro-alkyl radicals, then the coupling reaction between DBM radicals and PVC macro-alkyl radicals would dominate ; whereas a contrary order of formation of DBM radicals would lead to a rapid dehydrochlorination of PVC followed by the Diels-Alder reaction.

Some of the options are listed below:

1. All ingredients are premixed and then fed into the reaction mixer for processing.
2. DBM and the radical generator are premixed and then mixed with

b. The limitation of the Diels-Alder Reaction between DBM and the conjugated double bonds in PVC.

The Diels-Alder reaction is mainly responsible for binding in the case of a very low proportion of DBM radicals: Fig.3.5 reveals that the extent of binding of DBM is indeed limited by this mechanism. Based on the experimental fact that the extent of binding of DBM reaches a certain level and never increases with processing time till the degradation of PVC becomes serious, it is suggested that the Diels-Alder reaction occurs at an early stage of processing and inhibits formation of conjugated double bonds in the PVC.

On the other hand, *physically*, the liquid state of DBM limits a higher loading of DBM to PVC (more than 3.5×10^{-1} mol·100 g^{-1} PVC) when operating the reaction mixer used by the author. If a higher loading of DBM were acceptable the extent of binding of DBM might increase (see also Fig.3.3). Perhaps modifications to the processing equipment could contribute to the solution of this problem.

3.3.4 Melt Stabilisation of PVC through theBinding Reaction

Unstabilised PVC is very unstable and dehydrochlorination and *b. The limitation of the Diels-Alder Reaction between DBM and the conjugated double bonds in PVC.*

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3.3.4 Melt Stabilisation of PVC through theBinding Reaction

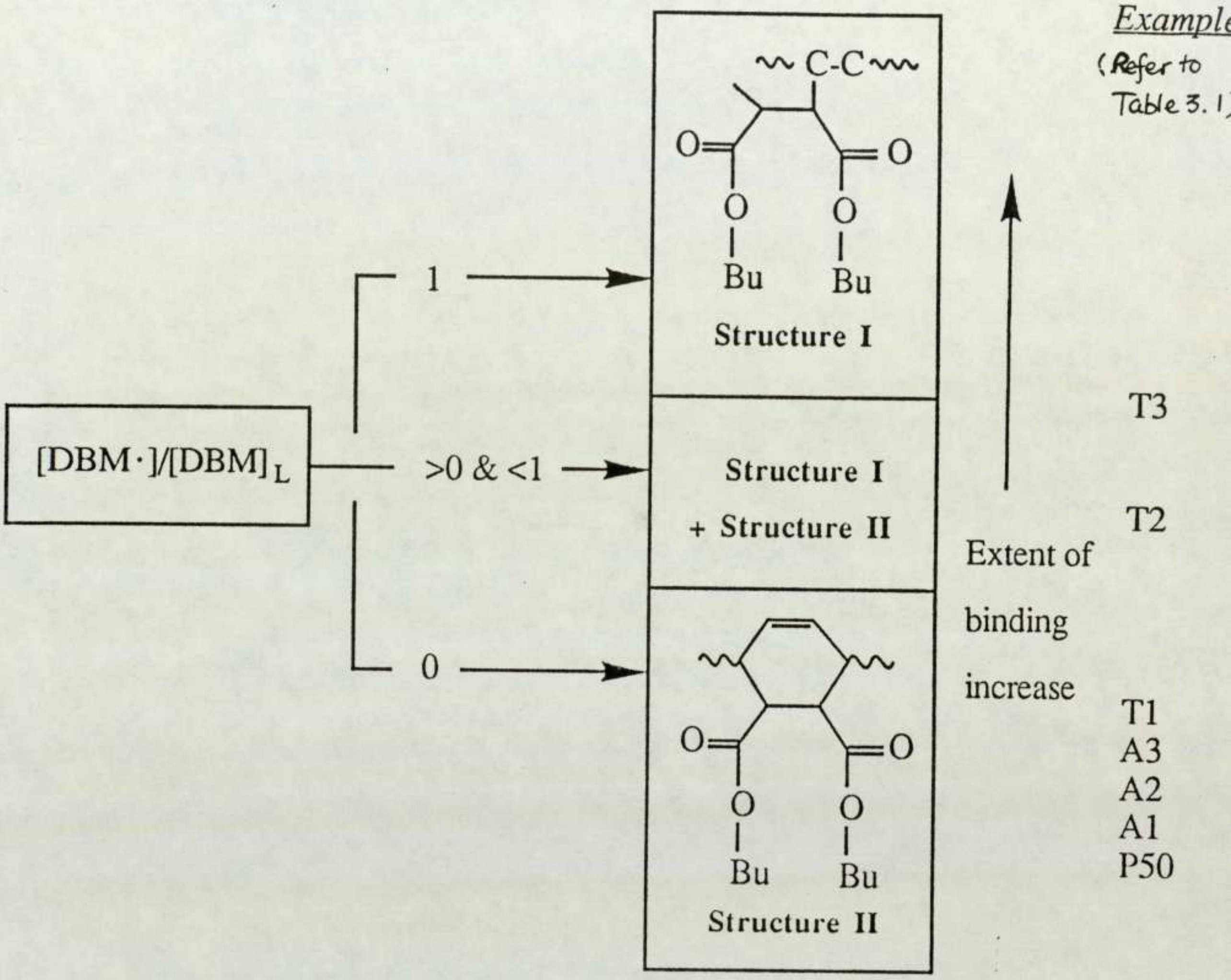
Unstabilised PVC is very unstable and dehydrochlorination and discolouration would nomally be very serious in the processing conditions used in this work, i.e. relatively high temperature and high shear action. The heat stabiliser used by the author was DBTM which is considered to be effective only during the later stage of PVC degradation during processing because it cannot destroy the radicals in the system and cannot inhibit the formation of isolated double bonds in PVC or react with these double bonds[60]. Even so, successful processing has been carried out in this work to give stable, modified PVC polymers without dehydrochlorination and discolouration.This suggests that the binding reaction of DBM with PVC actually leads to melt stabilisation of the PVC, a view which is also given support from the analysis of the mechanisms of binding as shown in **3.1**. The two mechanisms put forward to account for the binding may play a part in the stabilisation of PVC by DBM. One mechanism involving a Diels-Alder reaction could reduce the conjugated double bonds along PVC chains; the other mechanism involving radical coupling reactions between DBM radicals and PVC macro-alkyl radicals or chlorine radicals could cause destruction of the PVC macro-alkyl radicals and inhibit the formation of unsaturation in PVC. To date, melt stabilisation of PVC by the combination of a peroxide and a maleic ester has not been reported, althought stabilisation using a combination of peroxide and a metal salt has been known for a long time[204,205]. Finally, it should be noted that the DBM-peroxide stabiliser system in this work has been studied only under closed processing conditions. It has been shown to be highly effective in providing melt stabilisation of PVC during processing at high shear.

3.3.5 Structure/Property Relationships of DBM Modified PVC Polymers

3.3.5.1 The Relationship between Chain Structure and Reaction Conditions

Because of the two mechanisms for the binding of DBM with PVC, there are two types of basic chain structure in the modified PVC as shown in 3.3.1 besides the normal PVC chain structure. One is the pendant structure (structure I in Scheme 3.5) and the other is the cyclic structure (structure II in Scheme 3.5). Which one is predominant depends on the proportion of DBM radicals, i.e. $[DBM\cdot]/[DBM]_L$ (see 3.3.1). The effect of $[DBM\cdot]/[DBM]_L$ on the bound structure is also shown in Scheme 3.5.

In the modified PVC samples investigated (see Table 3.1), the samples formed from reaction systems containing very low concentrations of DBM radical, e.g. P50, A1, A2, A3 and T1 (see Figs.3.18-19) can be expected to contain structure II, whereas samples formed from systems containing very high concentrations of DBM radicals (T3) can be expected contain



Scheme 3.5 The effect of the proportion of DBM radical in a reaction system on the structure of the DBM modified PVC polymers.

mainly structure I. Other samples formed from systems with moderate concentrations of DBM radicals (e.g. T2) should contain both structure I and II.

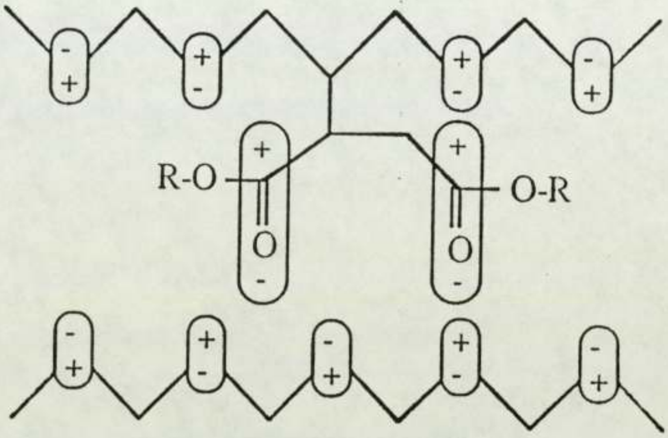
3.3.5.2 Plasticity and the Mechanism of Plasticisation

The improvement in the extraction resistance of the modified PVC (see 3.2.5.1) is due to the binding of the plasticiser into the PVC chains. The results on elongation (Figs.3.30-34) indicate that the bound, plasticisable groups are still effective in the plasticisation of PVC. The DBM modified PVC polymers can therefore be treated as self-plasticised PVC polymers. The mechanism for the plasticisation may be based on dipole attraction[206], in which case the action of structure I is a screen type and that of structure II is a hinge type[206](Scheme 3.6).

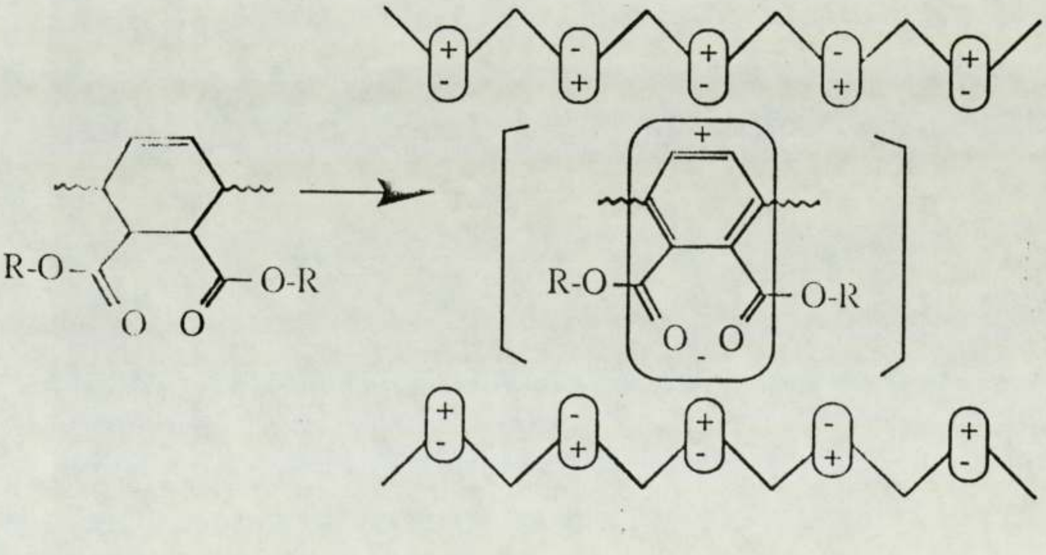
3.3.5.3 Photoageing Performance and the Mechanism of Photoageing

The mechanism of photoageing may be different for the processed PVC, the modified PVC with structure I and the modifed PVC with structure II.

For the processed PVC, the author's results support the view that the combination of unsaturation and peroxides initiates the photooxidation of PVC[39](Scheme 3.7). The important final products are polyenes

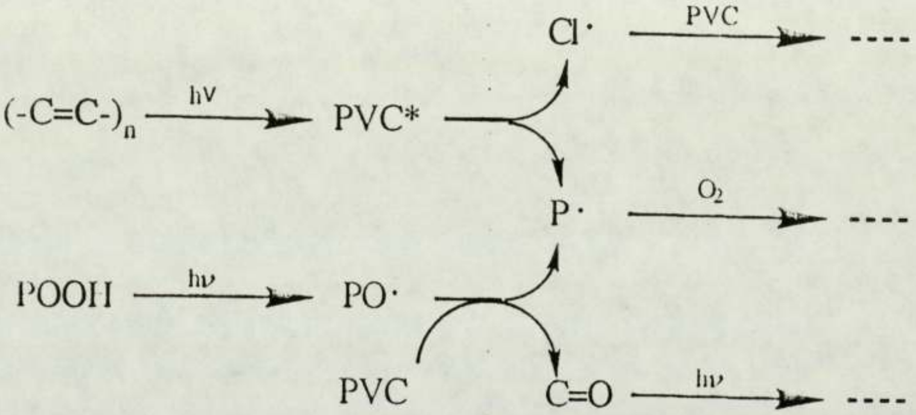


Screen type



Hinge type

Scheme 3.6 Plasticisation mechanisms.

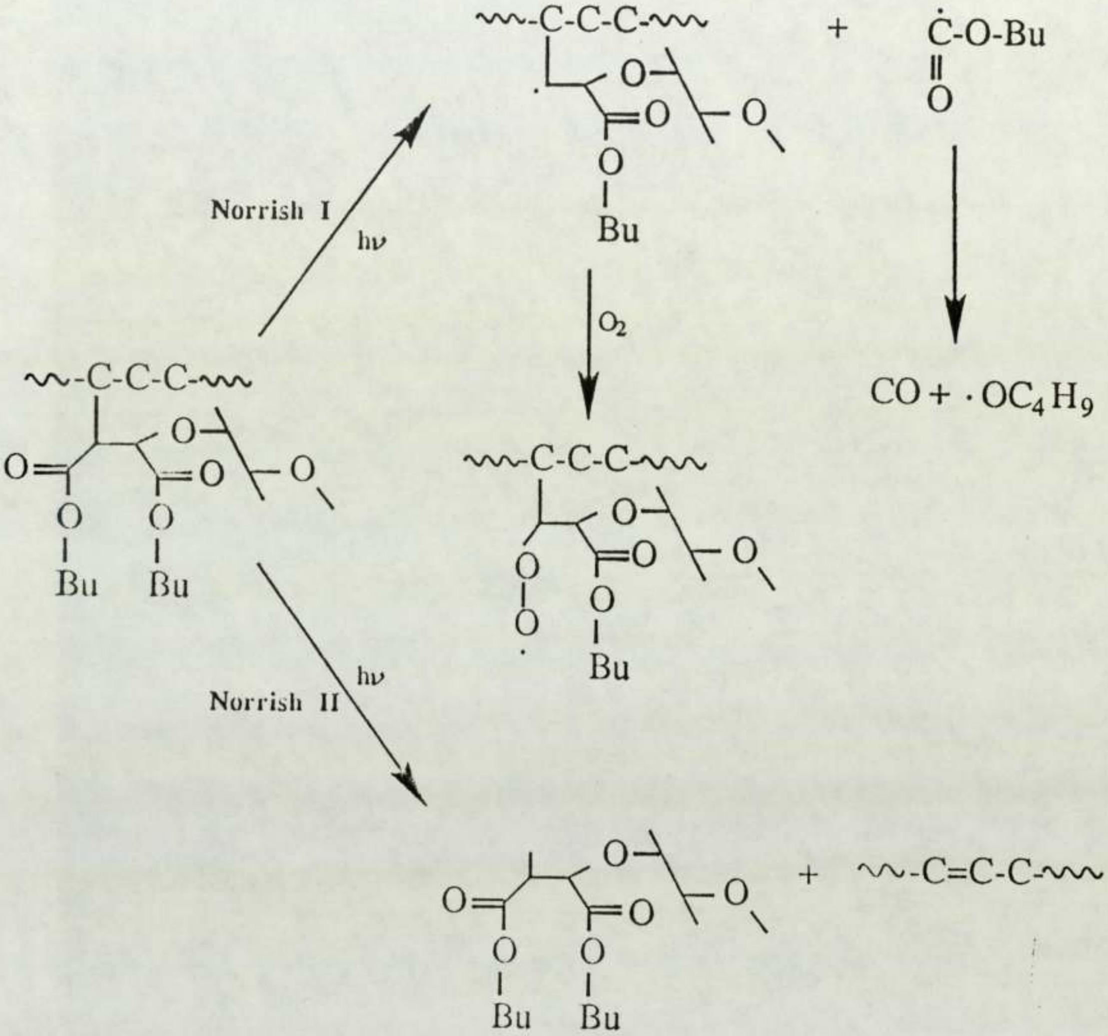


Scheme 3.7 Initiation of photooxidation of PVC during UV irradiation.

(Figs.3.41, 44 and 37), hydrogen chloride and oxygen-containing products (Figs.3.46-47).

For the modified PVC with structure I, no peroxides could be detected (Fig.3.26) and the level of unsaturation was much lower than that in the processed PVC (Figs.3.22 and 24). However, it was observed that (a) the embrittlement time of the samples containing structure I was about the same as that of the processed PVC (Table3.4) and (b) there was a difference in the discolouration between the samples containing structure I and the processed PVC, the former being almost transparent with a few brown spots whereas the latter changed from colourless and transparent to black. Since carbonyl groups would be introduced into the PVC chains through the binding of DBM with PVC, and since the absorption of these carbonyl groups is in the range 230 - 290 nm (Fig.3.23), which is near the maximum wavelength of the fluorescent lamps in the sunlight cabinet (317 nm), it is suggested that the carbonyl groups in the polymer chains are of importance in initiating the photooxidation of the modified PVC with structure I. The mechanism involves Norrish type I and Norrish type II reactions of the carbonyl groups under the action of the UV irridiation[207,208] (Scheme 3.8).

Chain scission and the loss of plasticisable groups by both Norrish I and Norrish II reactions results in a decrease in molecular weight (T3 in Fig.3.39), elongation (Curve T3 in Fig.3.36) and embrittlement time (T3



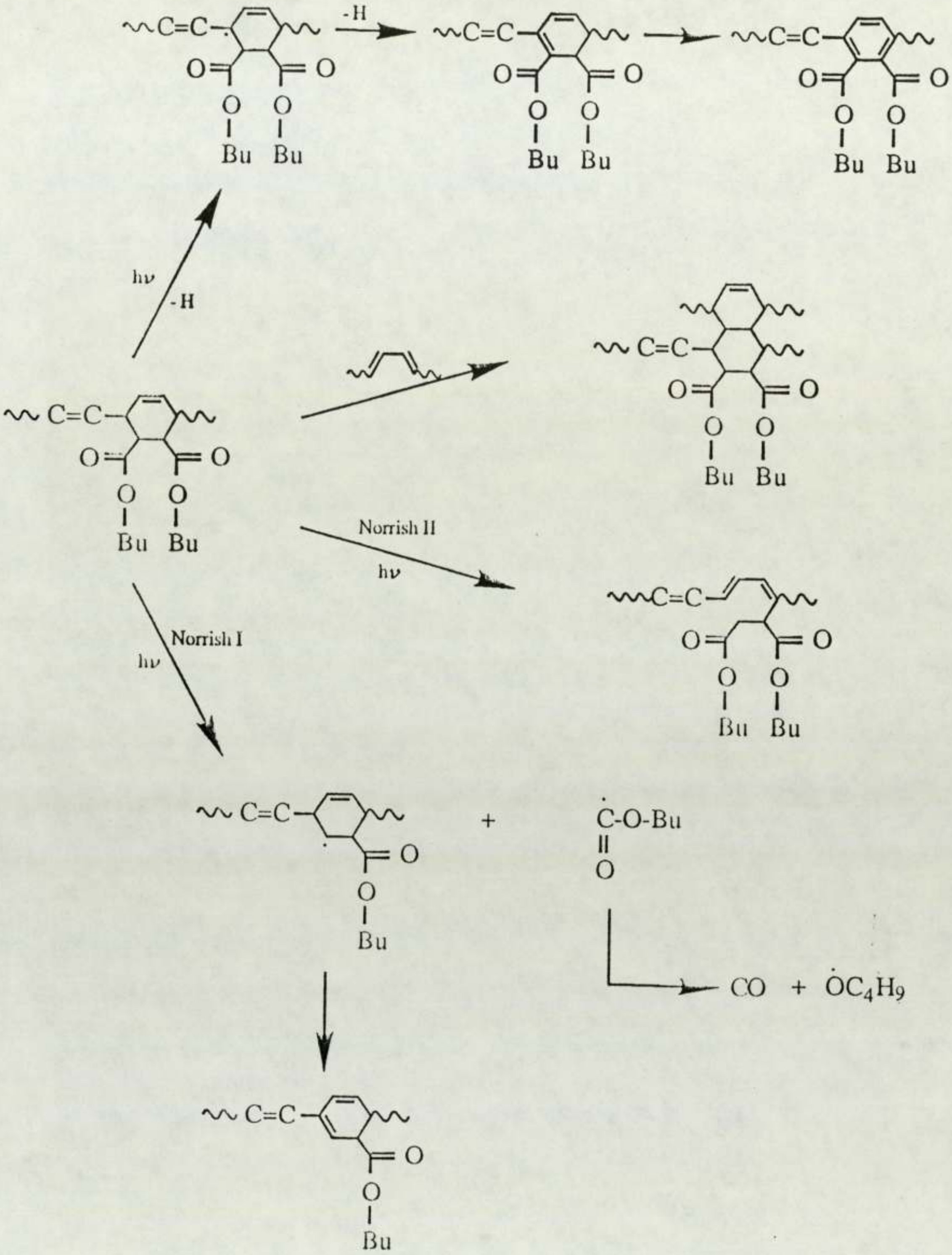
Scheme 3.8 Possible reactions in photooxidation of the modified polymer with structure I.

in Fig.3.35). On the other hand, a high content of plasticisable groups in the PVC chain could retard the formation of long sequences of conjugated double bonds (Fig.3.42). This could explain why discolouration of the photoaged samples was much less marked than was the case with the processed PVC.

For the modified PVC with structure II, peroxides could also not be detected (Fig.3.26). Although the level of unsaturation was about the same as that in processed PVC (Figs.3.22 and 24), it should be noted that the embrittlement times of the modified samples were much longer than that of the processed PVC (P50, A1, A2, A3 and T1 in Fig.3.35) and that the samples remained colourless and transparent after up to 2000 hours UV irradiation. It is suggested that the good photostability of the modified PVC arises from the inhibition of peroxide formation during processing and from the cyclic structure in the modified PVC chains, formed by the Diels-Alder reaction between conjugated double bonds in PVC and the C=C double bond in DBM. The suggested mechanism is shown in Scheme 3.9. This mechanism can be used to explain the following experimental results:

(1) the slight increase in molecular weight (P50 in Fig.3.39) as a result of crosslinking via a Diels-Alder reaction;

(2) the gradual reduction in the plasticibility (Fig.3.36) due to



Scheme 3.9 Possible reactions in photooxdation of the modified PVC polymer with structure II.

crosslinking and the relatively low degree of loss of the plasticisable groups;

(3) reduction in the extent of discolouration (Figs.3.37-38) due to the Diels-Alder reaction which results in shorter sequences of conjugated double bonds (Fig.3.43); and

(4) the longer embrittlement times (Fig.3.25) as a consequence of a Diels-Alder reaction and relatively low level of formation of radicals.

In reality, a modified PVC system may contain all three types of structure discussed above, that is to say the normal PVC structure, the structure I and the structure II. The photoageing performance of a modified PVC system would therefore depend on the proportion of these structures and, by careful design of the chain structure, it should be possible to control the photoageing performance. For example, a photodegradable PVC-based material could be obtained by binding a certain amount of carbonyl-containing compound (e.g. DBM) as a means of forming structure I (see T3). On the other hand, a photostable PVC material could be produced by binding DBM into PVC via the Diels-Alder reaction (see P50, T1 and A1). Modified PVC systems with a balance of properties would require the formation of both the structure I and II in suitable proportions.

CHAPTER 4

ACRYLATE MODIFIED PVC SYSTEMS

4.1 RESULTS

4.1.1 Formation of OA Modified PVC during Processing

A series of OA-PVC reaction systems (for details see 4.1.2) were processed in the closed mixer of a torque rheometer under various operating conditions. The extent of the reactions of OA was assessed qualitatively from IR measurements on the samples before and after 24 hours extraction in refluxing methanol, which is an excellent solvent for OA. The IR measurement results shown in Fig.4.1 indicate that most of the OA has been reacted and the results in Fig.4.2 indicate that unreacted OA can be completely removed from the OA modified system in 24 hours by means of extraction in refluxing methanol.

Because of the possibility that homopolymerisation of OA can occur as a side-reaction, a separation procedure was developed to identify the amounts of OA homopolymer and OA bound PVC. Benzene was selected as a solvent in the separation because experimental data (see Table 4.1) had shown that benzene is an excellent solvent of the homopolymer of OA but does not dissolve PVC

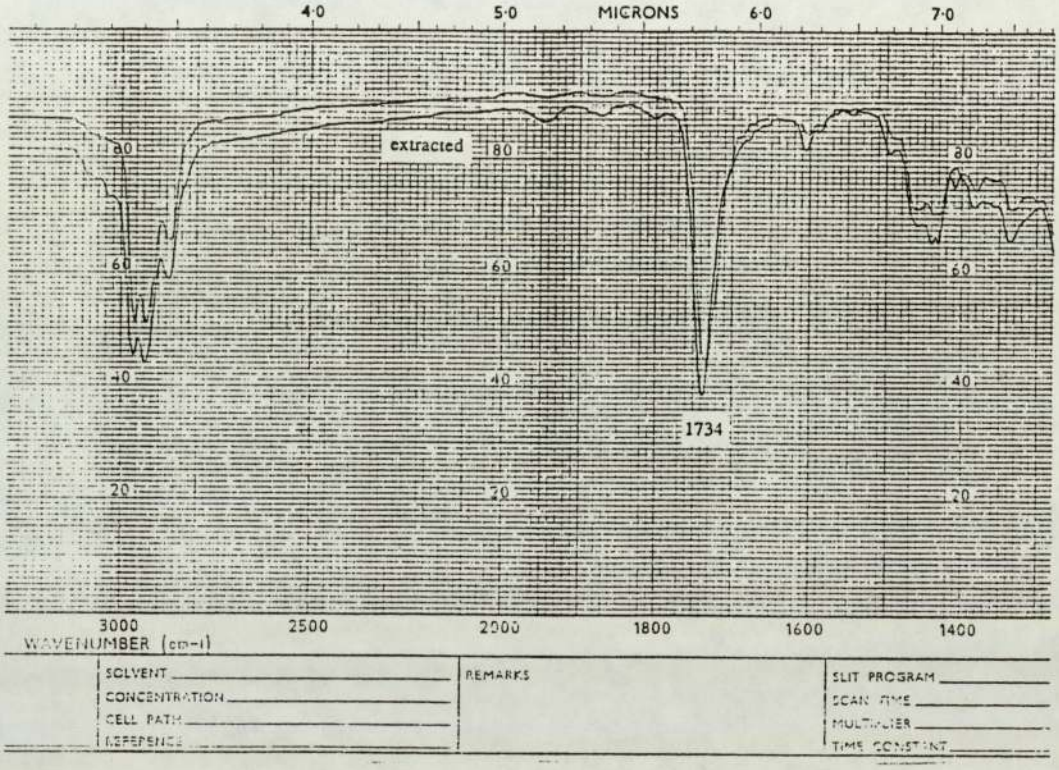


Fig.4.1 IR spectra of an OA modified PVC system. For detail of the sample, see AA1 in Table 4.1.

Above	unextracted
Below	extracted

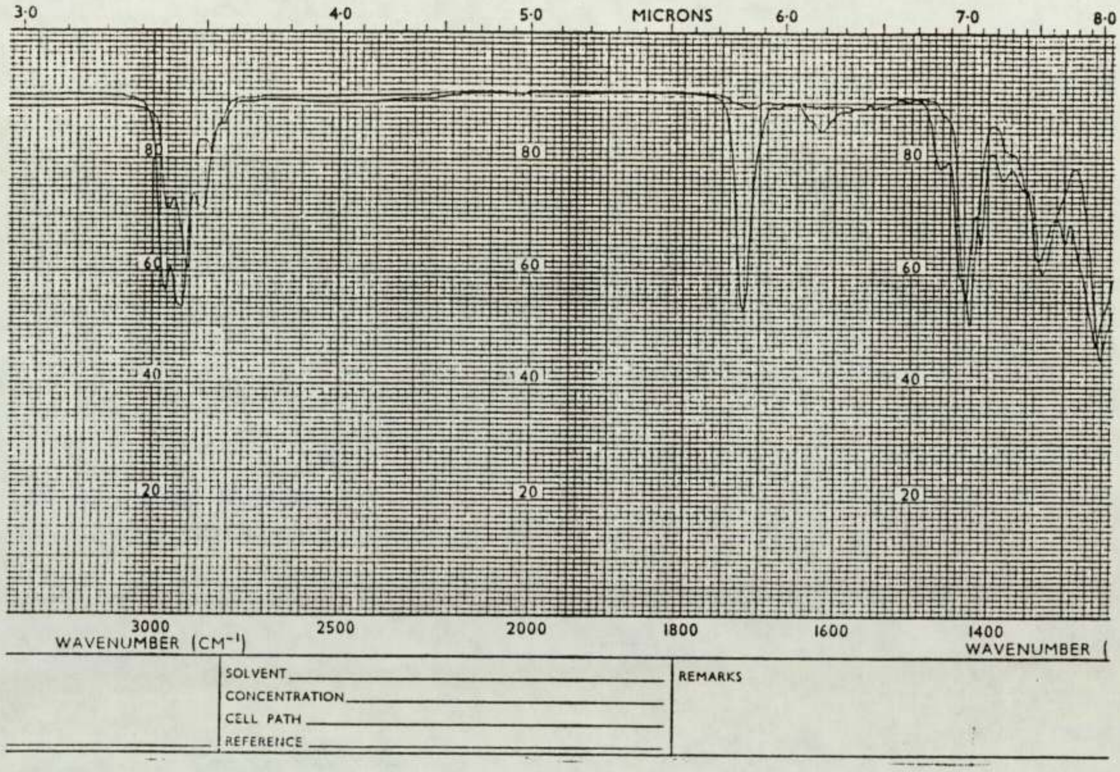


Fig.4.2 IR spectra of an OA-PVC reacted product. For detail of the sample, see AA0 in Table 4.1.

Below	unextracted
Above	extracted

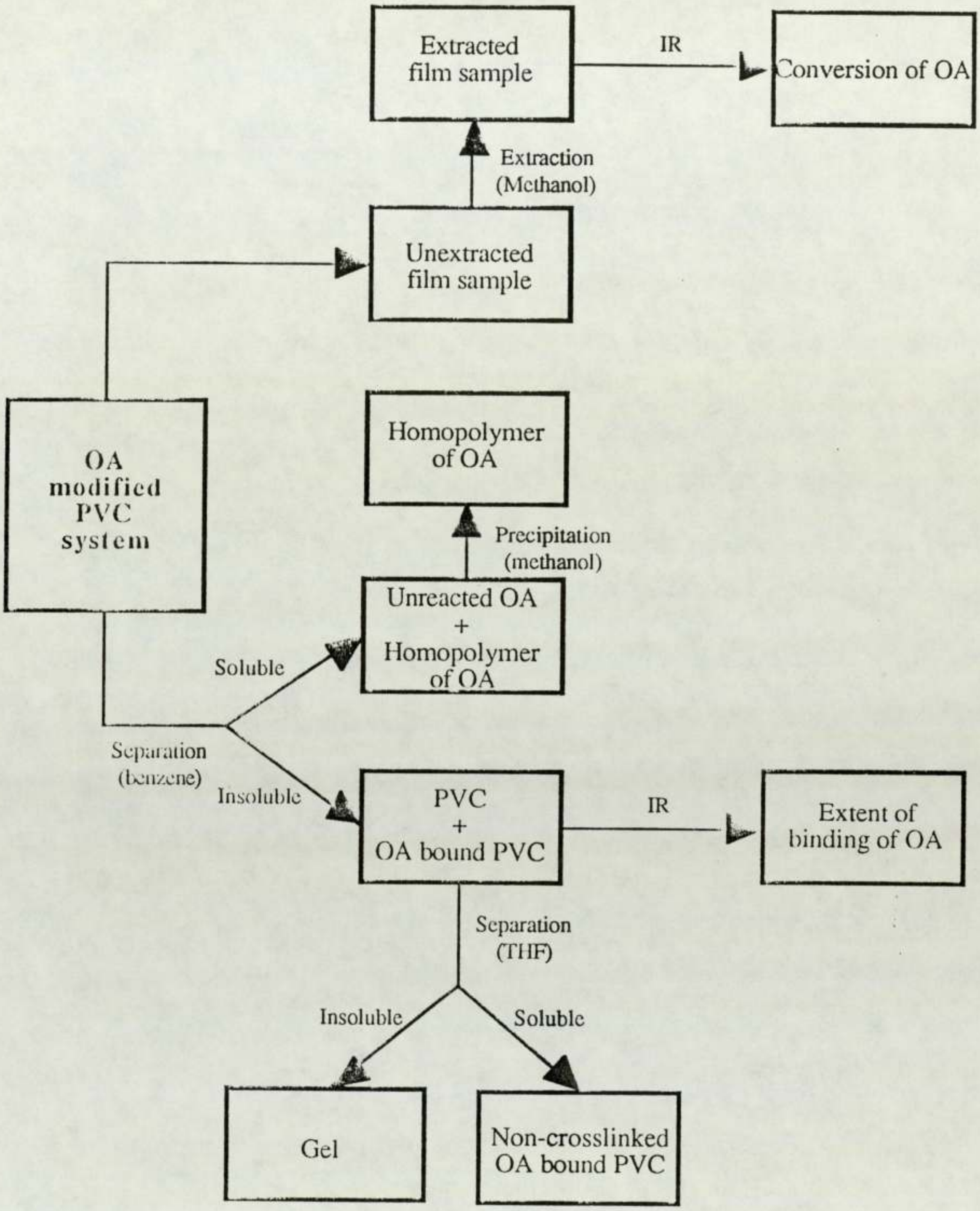
polymer and OA bound PVC. For further assessment of the gel content in an OA bound PVC, THF was selected as a solvent for the separation. The overall procedure for the separation of OA modified PVC systems is shown in scheme 4.1.

Results for three typical OA modified PVC systems using this procedure are shown in Table 4.1. It is clear that OA in sample AA0 underwent little reaction and was completely removed from the sample by means of either methanol extraction or benzene refluxing. Sample AA1 is seen to be an OA bound PVC with a low degree of crosslinking, in which a small amount of unreacted OA could be removed either by methanol extraction or by benzene refluxing. In the case of sample AT1, the conversion of OA was very high but the reacted OA was removed by benzene refluxing suggesting that the extent of binding of OA was low: because the homopolymer of OA was preferentially formed in this reaction system, AT1 is really a PVC/POA blending polymer.

4.1.2 Effect of Reaction Conditions on the Extent of Binding of OA

The reactive processing of OA-PVC reaction systems has been investigated under two conditions, i.e. in either the presence or absence of a radical generator.

In the presence of peroxide (Triganox101), OA reacts rapidly in the first few



Scheme 4.1 Separation of OA modified PVC system and determination of the conversion and the extent of binding of OA.

Table 4.1

Conversion and Extent of Binding of OA in Typical OA Modified PVC Systems

Sample	*Reaction System*				*Methanol*[a]		*Benzene*[b]		*THF*[c]		*Conversion*[d]	*Extent of Binding*[e]
	PVC	OA	ATM[g]	101[h]	Sol.	Insol.[f]	Sol.	Insol.[f]	Sol.	Insol.[f]		
	(g)	(g)		(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	
AA0	100	100	-	-	49.4	50.6	49.5	50.5	100.0	0.0	1.3	1.3
AA1	100	100	2.5	-	3.5	96.5	4.8	95.2	85.2	14.8	92.6	90.5
AT1	100	100	-	0.10	3.2	96.8	32.8	67.2	100.0	0.0	91.2	2.1

a. Refluxing extraction, 24 hours.

b. Refluxing, 3 hours.

c. Refluxing, 1 hour, for the benzene insoluble part of the sample.

d. By IR measurement, for the extracted sample.

e. By IR measuement, for the benzene insoluble part of the sample.

f. By weighing.

g. Trimethylolpropantriacrylate (mol·mol^{-1} OA, X 10^2)

h. Triganox101 (molar radical ratio to OA).

minutes of processing. In Fig.4.3 shows the conversion of OA in the OA-PVC reaction system containing 101. It can be seen that the conversion of OA increased rapidly in the first two minutes to reach a constant level dependent on the concentration of 101. Although very high levels of conversion of OA (> 90%) at a loading of OA (2.72 X 10^{-1} mol·100 g^{-1} PVC) were achieved, the extent of binding of OA is very low (see AT1 in Table 4.1). This indicates that the homopolymerisation of OA was predominant under the reaction conditions used. The rheological curves for this type of reaction system are shown in Fig.4.4. It is seen that the torque goes through a peak during the initial stage of processing and then drops sharply to a low level steady state. The torque peak here could be related to the homopolymerisation of OA.

In the absence of peroxide, the reactivity of OA is lower. Fig.4.5 shows the conversion of this type of reaction system during processing. It can be seen that OA hardly reacted in 10 minutes of processing at 180 C. However, OA is activated in the presence of ATM, a coagent, and high conversions of OA at a very high loading of OA (5.43 X 10^{-1} mol·100 g^{-1} PVC) were achieved in 10 minutes of processing following an induction period of around 5 minutes. The rheological curves for these reaction systems are shown in Fig.4.6. It will be seen that the torque dropped to a relatively low level when ATM was used and then increases very rapidly; this increase could be linked to the chain propagation process of OA. The analytical results following the separation procedure described in Scheme 4.1 show that the extent of binding of OA in this

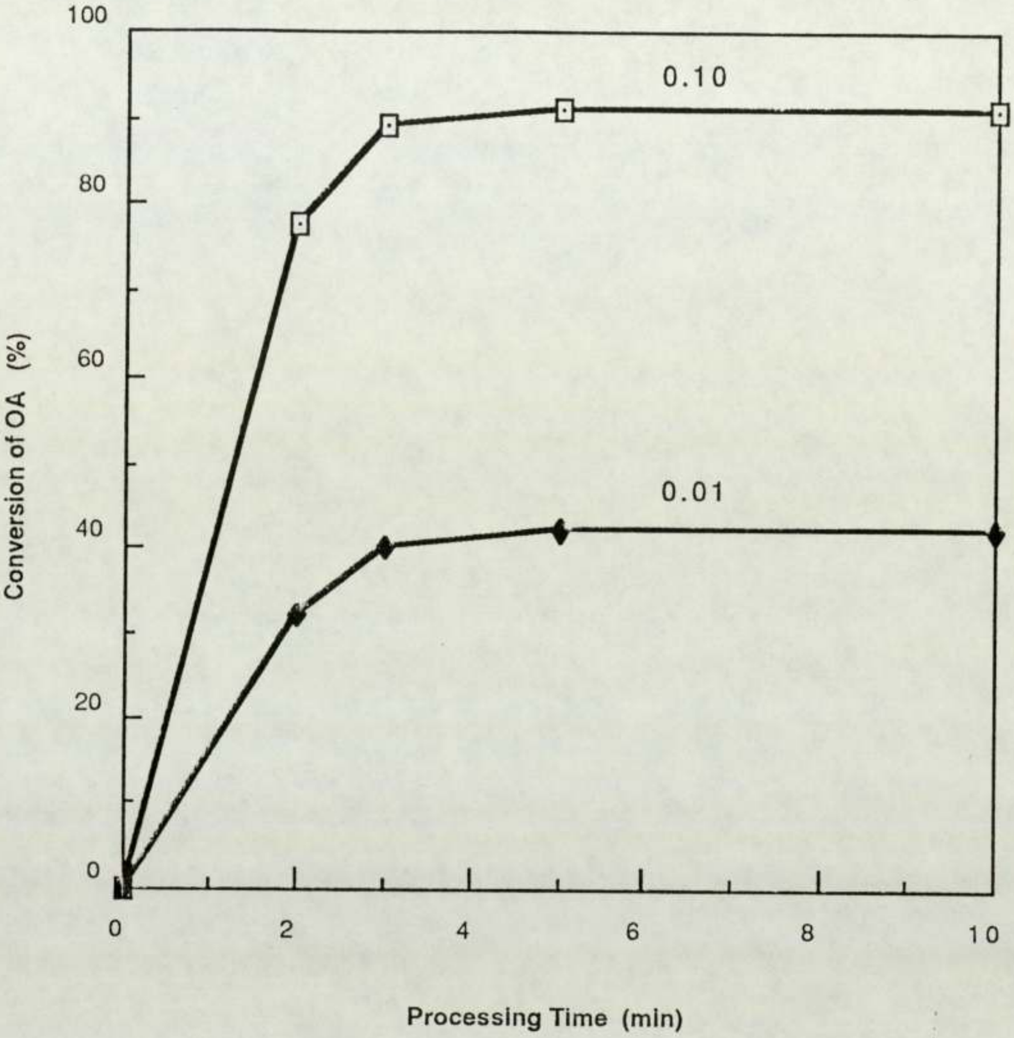


Fig.4.3 Conversion of OA in OA-PVC reaction systems containing Triganox101 during processing. Loading of OA was 2.72 X 10^{-1} mol·100 g^{-1} PVC (50 g/100 g PVC) in each case. Numbers on curves indicate the concentration of Triganox101 (molar radical ratio to OA). The processing temperature was 180 C.

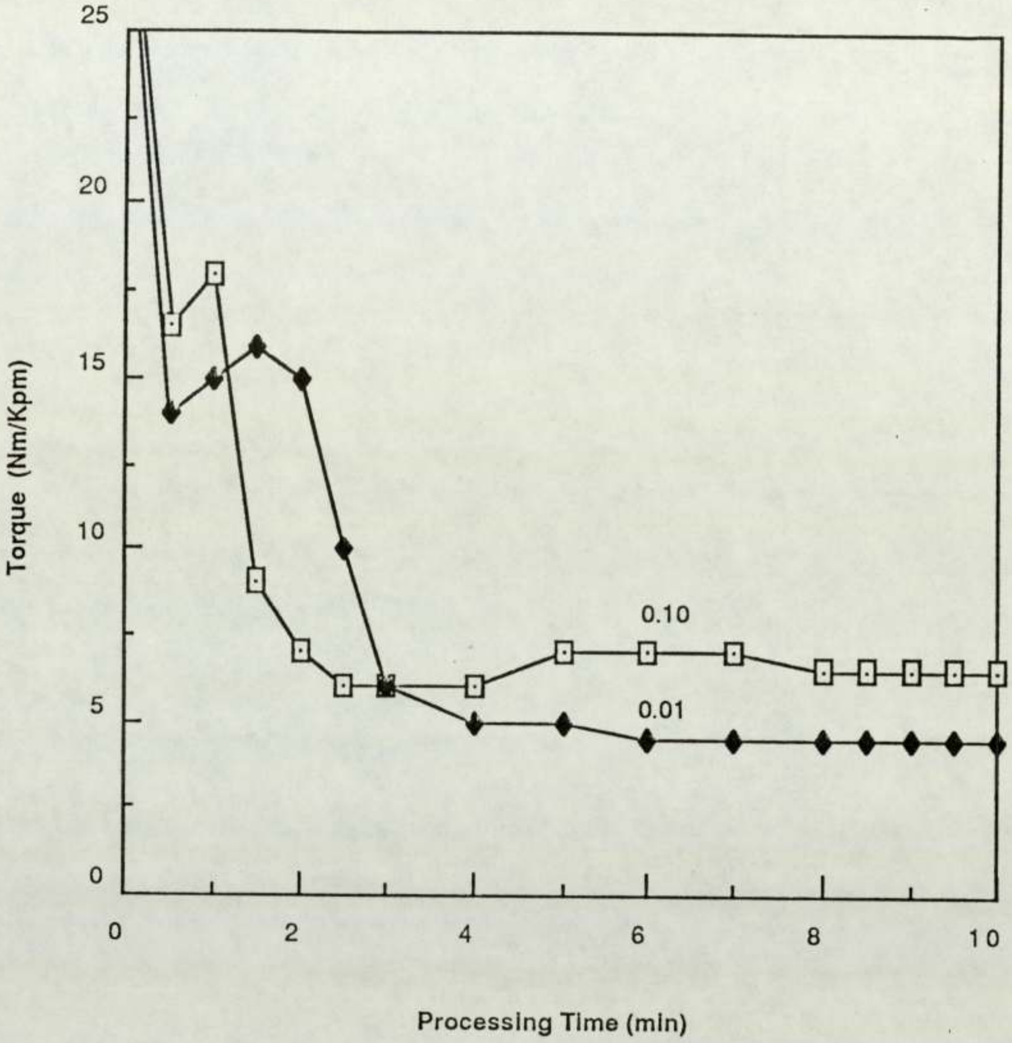


Fig4.4 Rheological curves for OA-PVC reaction systems containing Triganox101. Numbers on curves indicate concentration of 101 (molar radical ratio to OA). The reaction conditions are given in Fig.4.3.

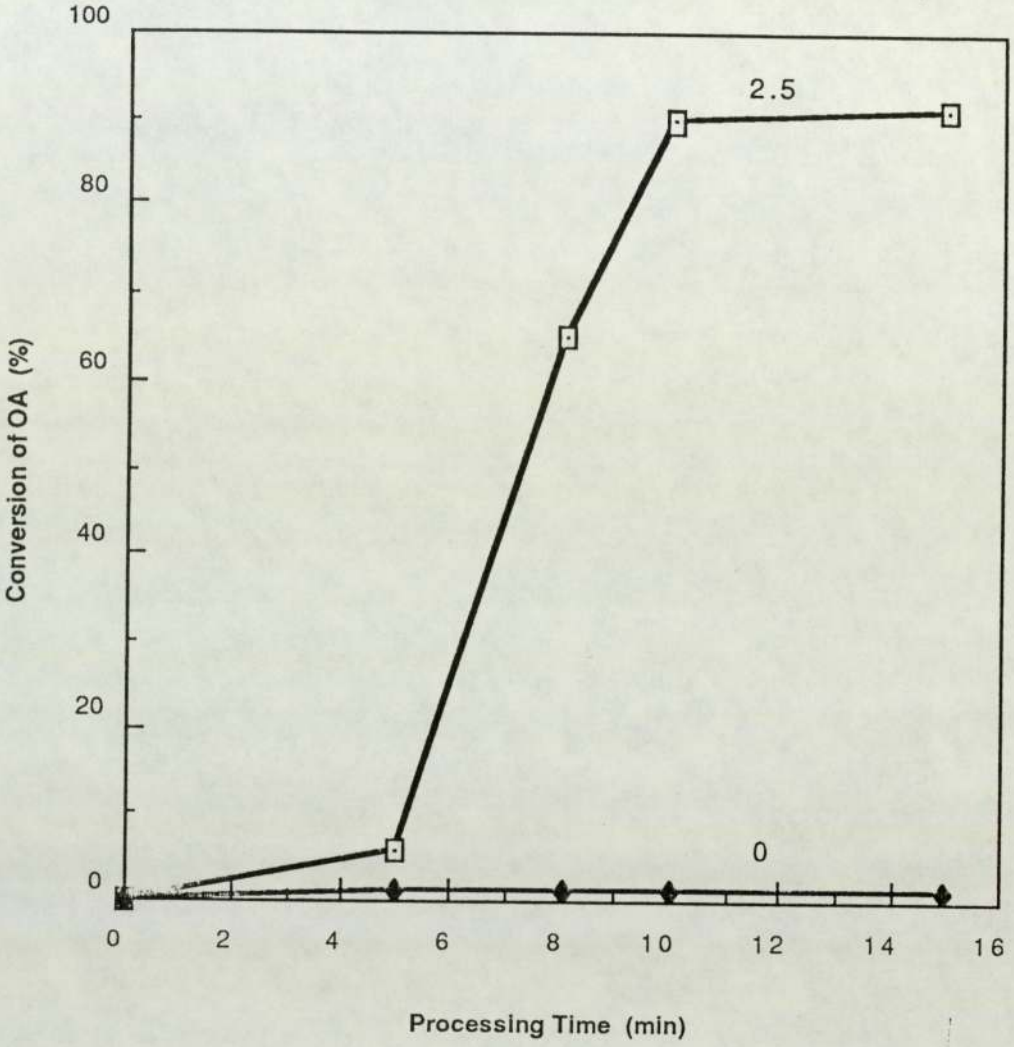


Fig.4.5 Conversion of OA in OA-PVC reaction systems during processing. Loading of OA was 5.43 X 10^{-1} mol·100 g^{-1} PVC (100 g/100 g PVC) in each case. Numbers on the curves indicate concentration of ATM (mol·mol^{-1} OA, X 10^{2}). The processing temperature was 180 C.

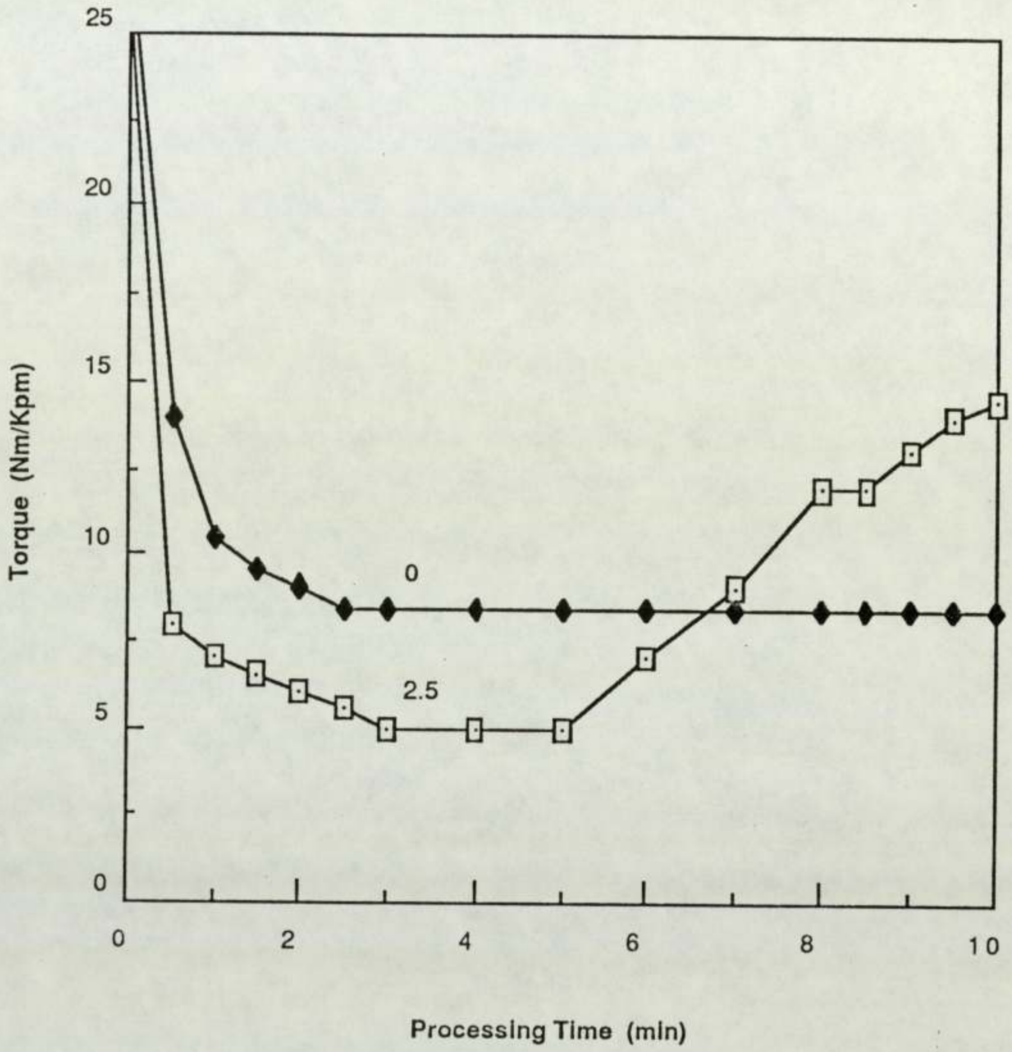


Fig4.6 Rheological curves for OA-PVC reaction systems. Numbers on curves indicate the concentration of ATM (mol·mol^{-1}OA, X10^{2}). The reaction conditions are given in Fig.4.5.

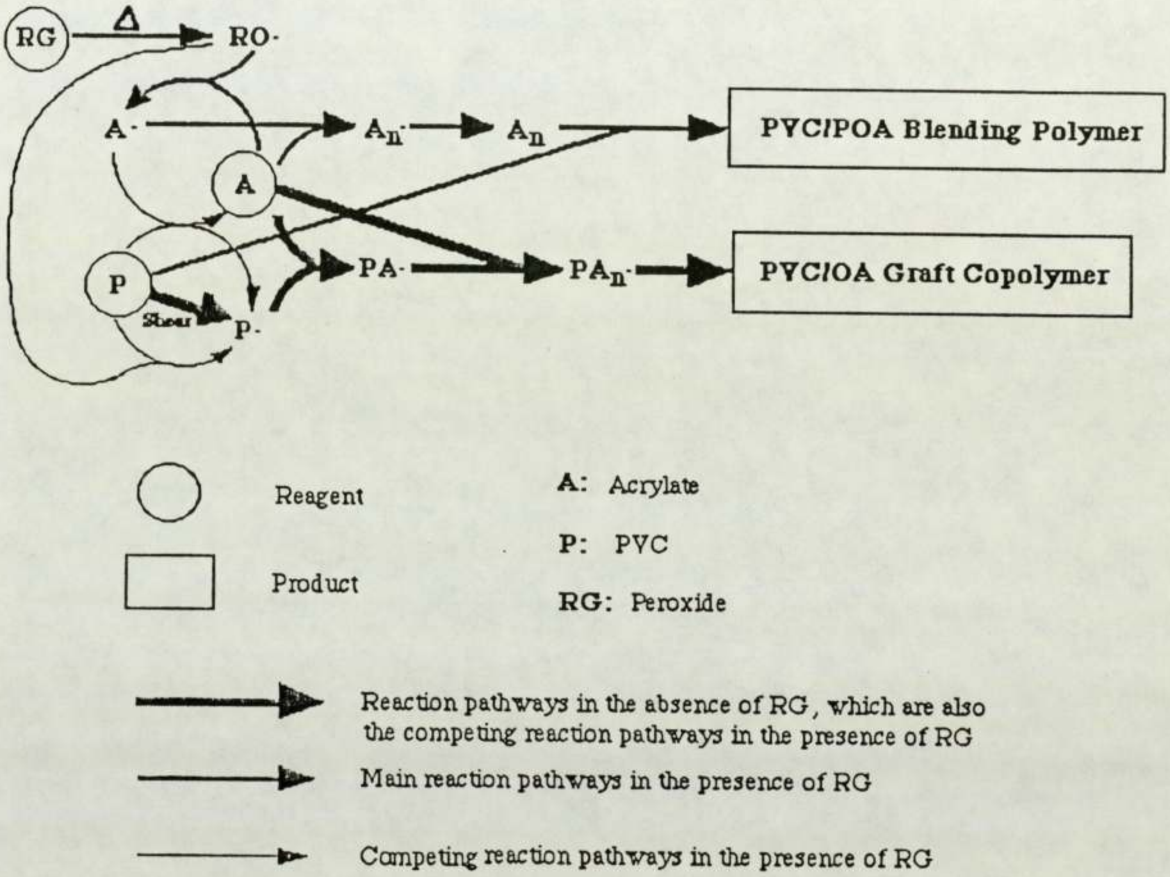
type of reaction system is Similar to the conversion of OA (see AA1 in Table 4.1). This indicates that OA had been bound into PVC backbones. The chain propagation process of OA is therefore a grafting process of OA in PVC. A certain amount of crosslinking may also arise in this type of OA / PVC graft copolymer.

4.2 DISCUSSION

4.2.1 Mechanisms of the Binding of OA with PVC during Processing

It is clear from the above results that there are at least two reaction pathways for OA in OA-PVC reaction systems. One is grafting copolymerisation of OA along PVC chains, the other is homopolymerisation of OA. Which one is predominant depends on the initiation conditions.

In the presence of a radical generator, OA takes part in radical homopolymerisation at an early stage of processing when PVC does not fuse well. As a result, the PVC/POA blending polymer is formed. In the absence of a radical generator, OA acts as a plasticiser for PVC during the early stages of processing, thus assisting the fusion of PVC and then copolymerises along PVC backbones due to the formation of PVC macro-alkyl radicals probably brought about by a mechanochemical chain scission of the PVC melt. This mechanism is



Scheme 4.2 Mechanism of reactions in OA-PVC reaction systems.

shown in Scheme 4.2.

Obviously, in the presence of 101, the reactivity of OA with the initiating radicals is higher than that of PVC so that reaction leads to blending polymer, even at the low concentration level of 101 (e.g. 0.01 molar radical ratio to OA) used in this work.

4.2.2 Melt Stabilisation of PVC through the Grafting Reaction of OA

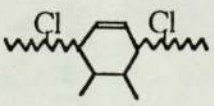
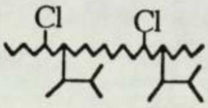
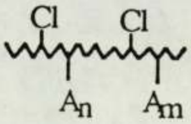
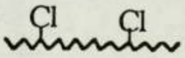
In the presence of OA but absence of radical generator, PVC can undergo severe processing conditions, i.e. higher temperatures (up to 180 C) and high shear action, to give stable PVC/OA graft copolymer without dehydrochlorination and discolouration. This indicates that OA can act as an effective heat stabiliser of the PVC melt. The reaction mechanisms could involve formation of PVC macro-alkyl radicals to initiate a grafting copolymerisation of OA and then termination of the radical reaction in a harmless way.

4.2.3 Comparison of DBM-PVC and OA-PVC Reaction Systems

DBM-PVC and OA-PVC reaction systems are different in many respects including the reaction mechanisms, extent of binding and chain structure of the modified polymers. These are summarised in Table 4.2.

Table 4.2

DBM-PVC and OA-PVC Reaction Systems

	DBM-PVC Reaction System		**OA-PVC reaction System**	
	Low [RG]	High [RG]	Without RG	With RG
Mechanism	Alder-Diels Reaction	Radical coupling between PVC radicals and DBM radicals	Grafting reaction of OA by initiation of PVC radicals	Homo-polymerisation of OA
Extent of Binding	Nearly 100% (Very low loading of DBM) ~ 15% (High loading of DBM)	~ 50% (High loading of DBM)	> 90% (Very high loading of OA)	Nearly 0% (High loading of OA)
Structure of Modified Polymer	Cyclic 	Pendant 	Grafting 	Blending  + ----A---A-----
Modified Product	DBM additional modified PVC	DBM substitutional modified PVC	PVC/OA graft copolymer	PVC/POA blending polymer

The differences can be attributed to the nature of the reactive additive: DBM is an unhomopolymerisable compound whereas OA is an active monomer. OA is easy to homopolymerise to high levels of conversion during processing as soon as it is initiated by radicals. If the reaction is of a grafting type, the extent of binding of OA is very high. By contrast, the bonding reaction of DBM can only be carried out between the reactive sites along PVC backbones and the DBM molecules. This makes it difficult to achieve very high levels of binding in the case of high loadings of DBM because of complex side-reactions.

4.2.4 Comments on the Reactive Processing of PVC

There are three marked and interesting characterstics in the reactive processing of PVC reaction systems which are as follows:

1. Variety. It is possible to make various modified products by adjusting the additives, operating sequences and processing conditions. This is very useful in the synthesis of desired specific materials.
2. High level of binding. High levels of binding of additives in PVC can be achieved at high loadings under the reaction conditions used in this work. This makes it possible to synthesise new materials by reactive processing of PVC.
3. High reaction rate. The binding reaction may be performed in less than

10 minutes under the reaction conditions used by the author. This suggests that it should be possible to synthesise modified PVC polymers using commercial extruders in an economical manner.

It should be noted that the binding reaction is carried out by exploiting the degradation of PVC. It is therefore necessary to understand the relationship between the binding reaction and melt stabilisation of PVC. Another special factor in the reactive processing of PVC is the degree of fusion of PVC: careful attention has to paid to this factor in order to achieve a high level of binding.

Two objectives in any further work are of special importance in the application of the reactive processing of PVC; these are:

1. to reach 100% binding at high levels of loading of the additive;
2. to select additives which meet the requirements of
    a. high reactivity leading to high levels of binding;
    b. providing specific properties after binding;
    c. nontoxicity;
    d. low cost.

If these objectives can be achieved, then reactive processing of PVC would become a very useful commercial method in the modification of PVC and synthesis of PVC-based materials.

CHAPER 5

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

5.1 CONCLUSION

1. It is possible to chemically modify PVC by binding vinyl compounds, such as maleate and acrylate, to PVC during reactive processing.

2. The chain structure of such modified PVC materials can be controlled by adjusting the reaction conditions, i.e. reaction system, operating sequence and processing conditions.

3. The extent of binding of a maleate (DBM) as a function of the loading shows two peaks: one in the case of relatively low loadings ($< 1.2 \times 10^{-2}$ mol·100 g^{-1} PVC) tends to 100 %, the other in the high loading region ($> 1.5 \times 10^{-1}$ mol·100 g^{-1} PVC), approaches 30 - 50 %.

4. The extent of binding of DBM depends on the concentration of DBM radicals, the concentration of PVC macro-alkyl radicals, the degree of

fusion of PVC and the operating sequence.

5. High levels of binding of DBM to PVC may be reached in less than 10 minutes under the reaction conditions used in the author's work.

6. A high extent of binding (> 90 %) with an acrylate (OA) in PVC at high loadings (> 5.0×10^{-1} mol·100 g^{-1} PVC) can be reached in less than 10 minutes of reactive processing in the presence of ATM.

7. The extent of binding of OA depends on the formation of PVC macro-alkyl radicals before homopolymerisation of OA. Homopolymerisation of OA will occur preferentially during the first few minutes of processing in the presence of peroxide (e.g. Triganox101) to reach very high conversion levels(> 90 %).

8. The binding reactions of vinyl compounds in PVC depend on the dehydrochlorination process of PVC. Mechanisms of binding are therefore related to the mechanisms of the melt stabilisation of PVC.

9. There are two mechanisms for the binding of DBM with PVC related to the two stages in the dehydrochlorination process of PVC. One is the radical coupling reaction between PVC macro-alkyl radicals and DBM radicals

formed by radical initiation via peroxide. The other is a Diels-Alder reaction between the conjugated double bonds in PVC and the carbon-carbon double bond in DBM. Which one predominant depends on the relative concentration of DBM radicals.

10. A DBM-peroxide stabiliser system has been shown to be effective in the melt stabilisation of PVC during closed processing at high shear, probably by destroying the PVC macro-alkyl radicals and inhibiting the formation of unsaturation in PVC.

11. It has been found that PVC macro-alkyl radicals, which are probably formed by mechanochemical chain scission, can be used to initiate the grafting polymerisation of acrylates e.g. ATM and OA during processing.

12. OA was found to be effective in the melt stabilisation of PVC during closed processing at high shear by using the PVC macro-alkyl radicals to carry out grafting polymerisation.

13. The effectiveness of initiation of three types of radical generator in the PVC-DBM reaction systems follows the order:

    Triganox101 > DCP > AIBN.

14. Some of the original functions of vinyl-based reactive additives in PVC systems are retained in the additive modified PVC polymer. Thus, DBM modified PVC polymer exhibits the behaviour of a plasticised PVC but the plasticising functional groups is not lost by extraction.

15. The properties of PVC modified by vinyl compounds depend on the chain structure and this may be controlled by the choice of additives and the reaction conditions. Thus, a photodegradable DBM modified PVC polymer may be made by increasing the content DBM bound in the PVC chains in the pendant form. By contrast, a DBM modified PVC polymer with improved photostability can be made by controlling the reaction conditions to form cycloaddition structures.

16. A benzene reflux separation procedure has been developed and is shown to be effective in separating the homopolymer of OA and OA bound PVC polymer. This makes it possible to identify the extent of binding of OA and the conversion of OA.

5.2 SUGGESTIONS FOR FURTHER WORK

Suggestions for further work are as follows:

1. to compare the processing properties of various types of PVC polymer to select an available PVC;

2. to select additives which are

   a. sufficiently reactive to enable high level of binding to be reached;
   b. capabable of retaining their functionality after binding with PVC;
   c. non-toxic;
   d. not expensive.

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