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Peroxide crosslinking of plasticized poly(vinyl chloride)

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The peroxide crosslinking of plasticized poly(vinyl chloride), PVC, blended with trimethylolpropane trimethacrylate, TMPTMA, has been studied by following gel formation and changes in mechanical properties. By applying the right preparation conditions and peroxide type, it was possible to avoid crosslinking while dry-blending the materials. During compression moulding, gel yield was found to increase with increased peroxide and TMPTMA concentrations and with curing time and temperature. The crosslinking process was found to be comprised of two primary reactions, a rapid polymerization of TMPTMA followed by grafting of the TMPTMA onto the PVC backbone. In the absence of either peroxide or methacrylate monomer no crosslinking was observed. Crosslinking was found to be independent of the tribasic lead sulfate stabilizer level and contrary to what is expected the crosslinked sheets showed excellent thermal stability. The softening temperature of the cured sheets increased with crosslinking. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Desirable properties of poly(vinyl chloride) (PVC), such as better heat and solvent resistance and improved mechanical properties, can be obtained by the formation of a chemical network structure. Numerous methods have been described to achieve crosslinking of PVC, however, most commonly these methods involve a costly process or relatively elaborate chemistry. The aim of the present work has therefore been to investigate the use of a simple peroxide crosslinking system.

Earlier studies have proved crosslinking involving organic peroxide to be unsatisfactory, since degradation predominates over crosslinking[1]. However, recently a study concerned with peroxide crosslinking of vinyl foam has been described[2]. If a suitable peroxide was well dispersed in the plastisol, and in the presence of a crosslinking monomer, uniform crosslinked foams could be produced. The crosslinking reaction in this study appeared to be similar to that occurring in irradiation crosslinking of PVC.

Irradiation crosslinking of PVC has been comprehensively studied, and is one of the few methods that has found commercial application. Irradiation of PVC by itself does not form any appreciable amount of crosslinking. In fact the main effect is to form a less stable polymer[3,4]. Miller[1] was the first to introduce the idea of crosslinking PVC with low irradiation doses in the presence of polyfunctional unsaturated monomers. The low irradiation dose minimized degradation of

the PVC, while the monomer enhanced the crosslinking efficiency. In the presence of a crosslinking monomer, irradiation produces homopolymerization of the monomer, graft copolymerization of the monomer onto PVC and graft crosslinking between PVC chains[1,5–14]. In principle, any polyfunctional unsaturated monomer is capable of promoting crosslinking. Various classes have been investigated, including divinylbenzene[1], allyl esters[5], triacrylates[7], dimethacrylates[1,7] and trimethacrylates[7,10–14]. Due to their good compatibility with PVC, the most effective monomers have shown to be polyfunctional acrylates and methacrylates, especially trifunctional monomers such as trimethylolpropane trimethacrylate (TMPTMA) and trimethylpropane triacrylate. Bowmer and coworkers[10–12] have shown that to effect good crosslinking in unplasticized PVC, TMPTMA loadings of about 20–40% are required. Phthalate plasticizers considerably enhance the crosslinking action[12] and sufficient crosslinking is achieved for plasticized compounds at lower TMPTMA levels[13]. Even though de Hollain[15] found that plasticizer type affects both the crosslinking efficiency and the network stability of TMPTMA crosslinked PVC, a phthalate plasticizer does not take part in the actual gel formation[13].

EXPERIMENTAL

Materials and sample preparation

All materials were used as received. The PVC compounds were prepared according to the formulations given in *Table 1*. The concentrations are given as parts per hundred of PVC resin (phr). Since TMPTMA, i.e.

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Table 1 Formulations

Chemicals/ materials	Formulations (phr)				
	A	B	C	D	E
PVC	100	100	100	100	100
DIDP	50-[TMPTMA]	40	40	50-[TMPTMA]	40
TBLS		7	7	7	3-7
TMPTMA	0. 10	10	10	0 15	10
Trigonox 101	0. 2	0 2		2	2
Trigonox 29-B90	0. 2		0 2		
Description	Blank	Effect of peroxide	Effect of peroxide	Effect of [TMPTMA]	Effect of [TBLS]

Table 2 Characteristics of peroxides, Akzo Chemie[21]

Trade name	Chemical name	Half-life time temperature[a] ($^\circ$C)	Activation energy (kJ mol^{-1})
Trigonox 101	2,5-Dimethyl-2,5-bis (*t*-butylperoxy)hexane	155	155.5
Trigonox 29-B90	1,1-Di-*t*-butylperoxy-3,3,5-trime thylcyclohexane	135	127.5

[a] After 5 min

$CH_3CH_2C(CH_2-O-CO-CCH_3 = CH_2)_3$, is itself an effective plasticizer, the concentration of plasticizer, di-isodecyl phthalate (DIDP), was reduced when TMPTMA was included in the formulations as indicated in the table. Characteristics of the two peroxides applied are given in *Table 2*.

Two formulations were dry-blended using a laboratory scale Fielder mixer at a mixing speed of 3000 rpm. At 50°C, suspension PVC (Evipol SH-7020) with a *K*-value of 71 and tribasic lead sulfate (TBLS, Associated Lead Chemicals Division), were added. At 70°C, DIDP (Exxon Chemicals), usually blended with TMPTMA (Perkalink 400, Akzo Nobel), and peroxide (Akzo Nobel) were added. The blending was continued until the temperature of the blend reached 110°C. The mixture was then dumped to a water-cooled chamber where it was agitated at 1000 rpm for 5 min. The powder was further homogenized and made into sheets approximately 0.6 mm thick by milling at different set temperatures (120–150°C) for 2, 5 and 7 min on a two-roll laboratory mill. The friction ratio of the rolls was 1:1.5. Two milled sheets were then compression-moulded to a thickness of 1.0 mm by pressing at a set temperature (170–200°C) for 2, 5 or 10 min (after 4 min preheat), at a pressure of 20 tons. The mould was then immediately transferred to a water-cooled press and cooled under a pressure of 10 tons.

Characterization

The gel content was determined by Soxhlet extraction (20 h) with tetrahydrofuran (THF). The final residue was dried and weighed. The gel yield was expressed as a percentage of the total amount of material which could form a gel.

Calorimetric measurements on the sheets were carried out using a DuPont thermal analyser fitted with a differential scanning calorimeter (d.s.c.) cell. The heating rate was 20°C min^{-1} and nitrogen was used as atmosphere.

A Mettler TA4000 fitted with thermomechanical TMA cell was used to measure the penetration of a loaded hemispherical probe (load: 0.10 N, diameter: 3 mm) as a function of temperature. The temperature was scanned from room temperature to 220°C at 10°C min^{-1}.

Residual unsaturation was assessed by Fourier transform infra-red (*FT* i.r.) spectrophotometry, Mattson 3000 *FT* i.r., directly onto the PVC sheets and using the ratio of absorbance at 1640 cm^{-1} to that of 690 cm^{-1}. The 1640 cm^{-1} resonance arises from the C=C stretching mode, while the 690 cm^{-1} resonance is from the C−Cl stretching[15-17]. A sheet of formulation A (10 phr TMPTMA) milled at 140°C for 5 min was assumed to contain 100% unsaturation.

Gel permeation chromatograms (g.p.c.s) of the solute portion of the sheets was obtained on a GPC-system from Polymer laboratories using a 10 m PLgel column. THF was used as solvent (5 mg sheet per 10 ml THF) and the flow rate was 1 ml min^{-1}.

Thermal stability was determined by degree of discolouration when exposed to heat (190°C) at controlled oven conditions. A sample (1.0 mm thick) was withdrawn from the oven every 10 min over a period of 2 h. Degree of discolouration given by Yellowness index (YI) was determined by the dr. Lange Micro Color instrument. Increasing YI corresponds to increasing colour of the sample (white paper is zero).

RESULTS AND DISCUSSION

D.s.c. data for liquid mixtures of DIDP and TMPTMA and peroxide when indicated are given in *Table 3*. Peak 1 corresponds to polymerization of TMPTMA monomer and peak 2 to peroxide decomposition. It is seen that the

Table 3 D.s.c. exotherms for mixtures of DIDP (40 parts) and TMPTMA (10 parts) with peroxide (2 parts) included when indicated

Formulation description	Peak 1		Peak 2	
	(°C)	(J g⁻¹)	(°C)	(J g⁻¹)
TMPTMA	198	10.0	–	–
Trigonox 101	142	55.3	198	19.7
Trigonox 29-B90	123	60.1	167	34.7
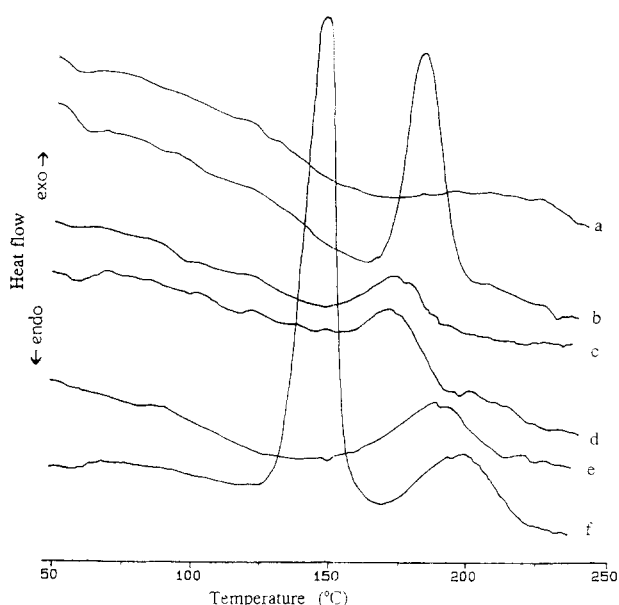
Figure 1 Thermograms of different formulations, milled at 140°C for 5 min. (a) Formulation A; (b) formulation A (10 phr TMPTMA); (c) formulation A (2 phr Trigonox 29-B90); (d) formulation C (2 phr Trigonox 29-B90); (e) formulation A (2 phr Trigonox 101); (f) formulation B (2 phr Trigonox 101)

presence of peroxide increases the conversion of the methacrylic monomer and catalyses the polymerization so that it starts at a lower temperature.

Milled sheets

Figure 1 shows d.s.c. profiles for milled sheets of different formulations. The A formulations represent a series of blanks based on PVC, DIDP and TBLS with various components included as indicated. The exothermic peak appearing at about 180°C in profile b is due to polymerization of the TMPTMA monomer. In profile e the peak is about 200°C, and in profile c that at about 170°C, are due to decomposition of Trigonox 101 and Trigonox 29-B90 respectively. *Table 4* gives the values of the exothermic enthalpies and peak temperatures

together with measured gel yields for different blank formulations. Measured gel yields suggested that no crosslinking had occurred in the blank formulations during milling (2% may indicate an experimental error). By comparing the results in *Tables 3* and *4*, it is seen that presence of PVC leads to a lower TMPTMA monomer homopolymerization temperature and increased monomer conversion (the enthalpies are measured per gram of sample). This may be explained by that free-radicals, which may catalyse the polymerization, are formed in PVC at elevated temperatures.

Profile f in *Figure 1* shows that the peroxide catalyses the initiation of TMPTMA so that the monomer homopolymerization begins at a lower temperature. This is in accordance with data in *Table 3*. It is also seen that the exothermic enthalpy increases when peroxide is present. This may again be explained by the fact that a low degree of the double-bonds in the trifunctional methacrylic monomer are reacted in absence of a free-radical source. Due to the bulky structure of the TMPTMA molecule, it is likely that these soon become sterically hindered due to restriction in mobility in a three-dimensional TMPTMA network and in a PVC-matrix. As discussed later for moulded sheets, it is also shown by i.r. spectrophotometry that the presence of peroxides improves the conversion of unsaturated bonds. The reason for the TMPTMA peak disappearance in profile d in *Figure 1* is discussed later (*Table 6*).

Exothermic enthalpies, peak temperatures and gel yields for samples containing both Trigonox 101 and TMPTMA are given in *Table 5*. It is seen that the sheets may be milled at temperatures up to 140°C without increasing homopolymerization of TMPTMA. At 150°C considerable polymerization has occurred with a resultant decrease in measured exothermic enthalpy, although no increase in gel yield is observed. G.p.c. profiles in *Figure 2a* also suggest that oligomeric molecules have been formed and that the PVC molecules are not involved in the reaction, i.e. the polymerization of TMPTMA has not produced a continuous network and there has not been sufficient initiation of reactive sites on the PVC backbone for grafting on to the PVC to occur.

Table 6 gives the exothermic enthalpies, peak temperatures and gel yields for samples containing both Trigonox 29-B90 and TMPTMA. With increased milling time and temperature, increased gel yields and decreasing exothermic enthalpies are observed, indicating monomer polymerization and peroxide decomposition. G.p.c. profiles in *Figure 2b* suggest that oligomeric molecules are formed and the shift in the PVC peak at

Table 4 D.s.c. exotherms and gel yields for blank formulations milled at 140°C for 5 min. Formulation A

Formulation description	(phr)	Peak 1		Peak 2		Gel yield (%)
		(°C)	(J g⁻¹)	(°C)	(J g⁻¹)	
Blank	–	–	–	–	–	0
TMPTMA	10	180	10.0		–	0
Trigonox 101	2	–	–	201	4.3	0
Trigonox 29-B90	2	–	–	172	2.1	2

Table 5 D.s.c. exotherms and gel yields for formulations milled at different temperatures and times. Formulation B (2 phr Trigonox 101)

Milling condition		Peak 1		Peak 2		Gel yield
(°C)	(min)	(°C)	(J g⁻¹)	(°C)	(J g⁻¹)	(%)
120	5	141	21.9	199	9.8	0
130	5	142	23.6	198	8.1	0
140	2	139	22.6	200	10.3	1
140	5	144	21.3	199	5.2	1
140	7	144	21.6	202	3.3	0
150	5	141	5.4	199	6.9	1

Table 6 D.s.c. exotherms and gel yields for Trigonox 29-B90 formulations milled at different temperatures and times. Formulation C (2 phr Trigonox 29-B90)

Milling condition		Peak 1		Peak 2		Gel yield
(°C)	(min)	(°C)	(J g⁻¹)	(°C)	(J g⁻¹)	(%)
120	2	121	9.7	170	7.0	1
120	5	122	8.4	172	4.8	4
120	7	121	1.9	169	3.6	17
130	5		–	170	3.5	27
140	5			172	2.7	23

Figure 3 Thermograms of different formulations, milled at 140°C for 5 min before being moulded at 180°C for 5 min. (a) Formulation A; (b) formulation A (10 phr TMPTMA); (c) formulation A (2 phr Trigonox 101); (d) formulation A (Trigonox 29-B90); (e) formulation B (2 phr Trigonox 101); (f) formulation C (2 phr Trigonox 29-B90)

Table 7 D.s.c. exotherms and gel yields for different formulations milled at 140°C for 5 min before moulding at 180°C for 5 min

Formulation description	(phr)	Peak 1		Peak 2		Gel yield
		(°C)	(J g⁻¹)	(°C)	(J g⁻¹)	(%)
Blankᵃ		--				1
TMPTMAᵃ	10					0
Trigonox 101ᵃ	2			202	5.70	1
Trigonox 29-B90ᵃ	2	–				0
TMPTMA and Trigonox 101ᵇ	10 2			201	5.90	40
TMPTMA and Trigonox 29-B90ᶜ	10 2	--				43

ᵃ Formulation A, ᵇ formulation B and ᶜ formulation C

the present work, so if it is crucial to avoid crosslinking during preparation, Tigonox 29-B90 may be difficult to use.

Moulded sheets

Figure 3 shows d.s.c. profiles for moulded sheets of different formulations. The area underneath the dotted line corresponds to the heat of fusion[18,19]. In *Table 7* the values of the exothermic peak areas and temperatures for corresponding samples are given together with gel yields. In all formulations the exothermic peak for the TMPTMA homopolymerization has disappeared, indicating that this reaction was completed during processing. In the absence of peroxide no gel formation was observed, further suggesting that the grafting of TMPTMA is peroxide-initiated, probably by H-abstraction from the PVC backbone. G.p.c. profiles in *Figure 4* also indicate that the monomeric homopolymerization which occurs during processing forms oligomeric molecules. Because it has a longer half-life than Trigonox 29-B90, Trigonox 101 leaves traces of undecomposed peroxide in the sample after processing. For some applications this contamination may cause problems.

The penetration resistance, measured by t.m.a. (thermal mechanical analysis), of the samples in *Figure 3* is shown

Figure 2 G.p.c. profiles for soluble fraction of sheets milled for 5 min. Blank is formulation A milled at 140°C. (a) Formulation B (2 phr Trigonox 101); (b) formulation C (2 phr Trigonox 29-B90)

the higher molecular mass end may indicate that the largest PVC molecules have been included in the gel. To mix and fuse the sheets properly the formulations need to be processed, at least at the lowest temperatures used in
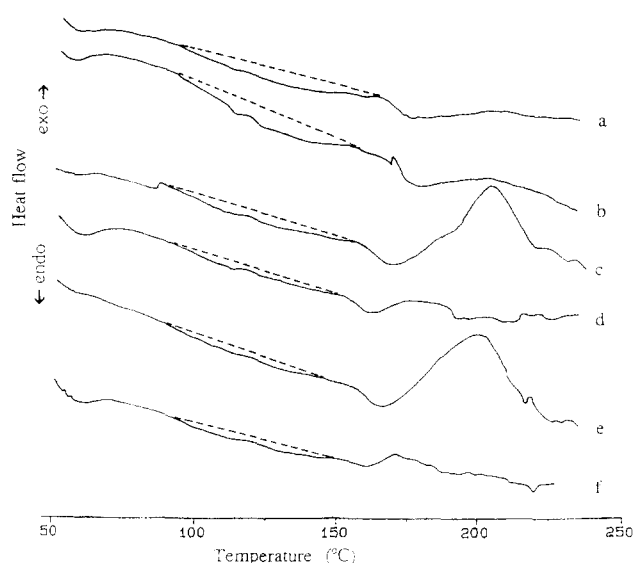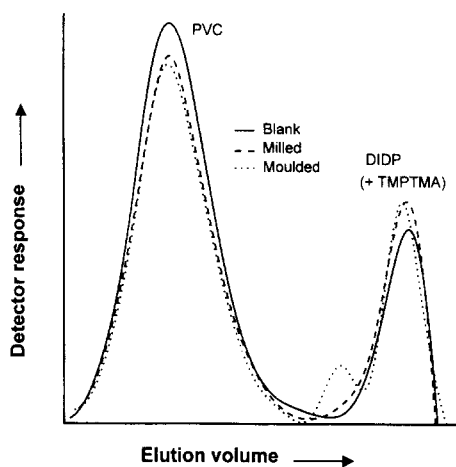
Figure 4 G.p.c. profiles of soluble fraction for milled (140°C, 5 min) and moulded (180°C, 5 min) sheets. Milled/moulded, formulation A (10 phr TMPTMA); and blank, moulded formulation A
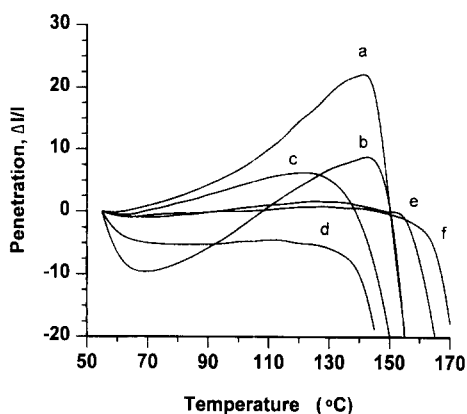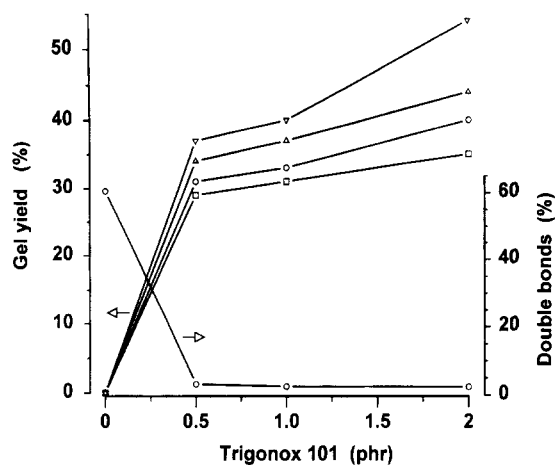

Figure 6 Influence of Trigonox 101 level and processing temperature on gel yield and residual unsaturation. Sheets milled at 140°C for 5 min before being moulded for 5 min. Formulation B. Mould temperatures: □, 170°C; O, 180°C; △,190°C and ▽, 200°C

Figure 5 T.m.a. traces of moulded sheets of different formulations. (a) Formulation A; (b) formulation A (10 phr TMPTMA); (c) formulation A (2 phr Trigonox 101); (d) formulation A (Trigonox 29-B90); (e) formulation B (2 phr Trigonox 101); (f) formulation C (2 phr Trigonox 29-B90)
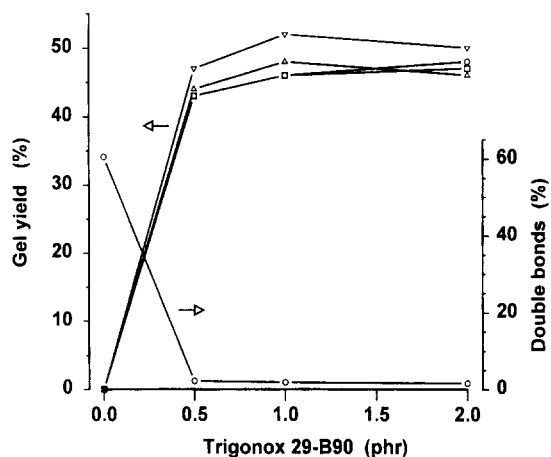

Figure 7 Influence of Trigonox 29-B90 level and processing temperature on gel yield and residual unsaturation. Sheets milled at 120°C for 5 min before being moulded for 5 min. Formulation C. Mould temperatures: □, 170°C; O, 180°C; △, 190°C and ▽, 200°C

in *Figure 5*. The resistance to penetration increases at elevated temperatures with crosslinking. Compared to the uncrosslinked samples, crosslinking reduces expansion during heating. The samples containing only peroxide were shown to have a softening point lower than the blank, indicating that PVC degradation may have occurred and/or crystallinity in these samples had decreased. D.s.c. profiles in *Figure 3* show lower heat of fusion for samples c and d than for sample a, indicating that samples containing the peroxides have a lower degree of crystallinity than the blank formulation. *Figure 3* also shows a lower heat of fusion for crosslinked samples, thereby suggesting a low degree of crystallinity. A decreasing level of crystallinity with increasing crosslinking is in accordance with the work of Tabtiang[20].

Figures 6 and *7* show the effect of peroxide level and curing temperature on gel yield at constant TMPTMA level for Trigonox 101 and Trigonox 29-B90 respectively. Trigonox 101 showed an increase in gel yield with increasing peroxide level and processing temperature. This tendency was less pronounced for Trigonox 29-B90. This can be explained by shorter half-life and weaker H-abstraction ability of Trigonox 29-B90[21]. *Figures 6*

and *7* also show the residual unsaturation of the sheets. A sample not containing TMPTMA (see *Figure 11*) was found to have only 0.5 percent unsaturation. Therefore, the major part of the unsaturation shown in *Figures 6* and *7* can most probably be ascribed to unreacted double bonds from the trifunctional methacrylic monomer. The much higher unsaturation in the absence of peroxide confirm the results from the d.s.c. measurements discussed above. Compared with a quite similar irradiation crosslinking system[13], the residual unsaturation in the crosslinked samples seem to become lower when using peroxides. When exposed irradiation dose of 4 Mrad, the residual unsaturation of a sample with 10 phr TMPTMA was approximately 20%.

The soluble fractions of crosslinked samples corresponding to those in *Figure 6* were examined with g.p.c. resulting in the profiles shown in *Figure 8*. As the curing proceeds, the amount of soluble PVC was depleted due to its incorporation into the gel and g.p.c. detector responses were reduced in size. These reductions in response are in accordance with the actual measured gel yields. A decrease in the average molecular weight of the
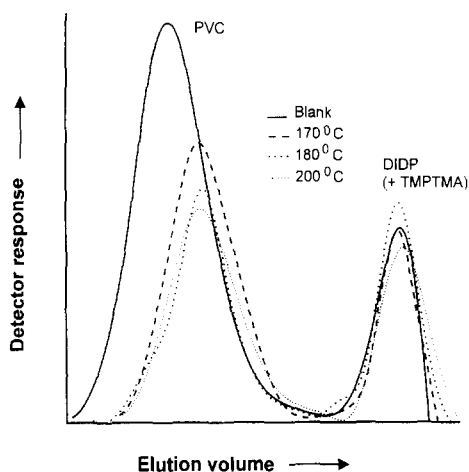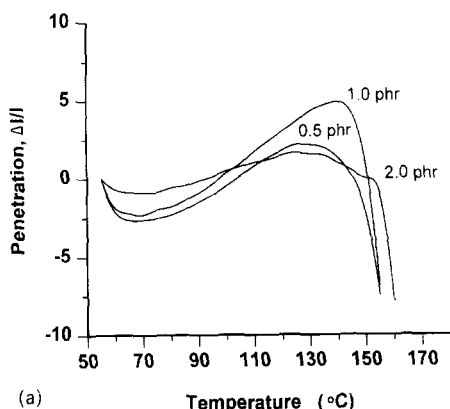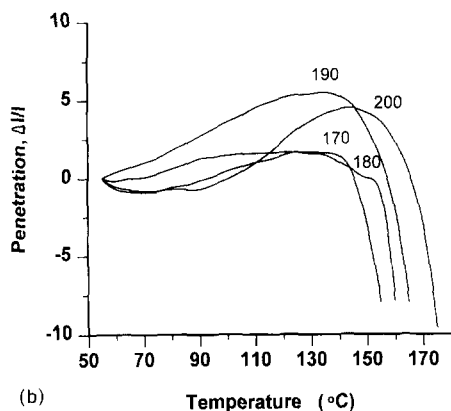
Figure 8 G.p.c. profiles of soluble fraction of samples processed at variable temperatures. Milled at 140°C for 5 min before moulding at 5 min, formulation B (2 phr Trigonox 101). Blank is formulation A moulded at 180°C

Figure 10 Influence of processing time and type of peroxide on gel yield. Trigonox 101 sheets milled at 140°C (formulation B) and Trigonox 29-B90 at 120°C (formulation C) for 5 min. Crosslinking temperature: 180°C. 2 phr peroxide. O, Trigonox 101; □, Trigonox 29-B90

Figure 11 Influence of TMPTMA level on gel yield and residual unsaturation. Samples milled at 140°C for 5 min before being moulded at 180°C for 5 min. Formulation D

area of this peak also indicates that the DIDP plasticizer is not involved to a large extent in the crosslinking reaction.

Figure 9 shows the penetration resistance of different Trigonox 101/TMPTMA crosslinked samples. It can be seen that when peroxide level and curing temperature increases, i.e. on increasing gel yield, the resistance to penetration rises.

The effect of curing time on gel yield for Trigonox 101 and Trigonox 29-B90 is shown in *Figure 10*. Trigonox 29-B90 shows less dependence on gel yield with respect to time than Trigonox 101. Again this is explained by the shorter half-life of Trigonox 29-B90

Figure 11 shows that gel yield increased with increasing TMPTMA concentration at a constant peroxide level. At the same time there is an increase in residual unsaturation. This may be explained by an increasing rate of formation of the three-dimensional network, causing restricted mobility at an early stage. For an irradiation crosslinking system, Bowmer *et al.*[10] have shown that the crosslinking rate, especially during the early stages of irradiation is proportional to the TMPTMA concentration. As was the case for residual unsaturation at variable peroxide concentrations (*Figures 6* and *7*), the level in the present peroxide system is

Figure 9 T.m.a. traces for samples prepared (a) with different Trigonox 101 concentrations (mould temperature: 180°C) and (b) at different moulding temperatures (2 phr Trigonox 101). Sheets milled at 140°C for 5 min before being moulded for 5 min. Formulation B

extractable PVC with crosslinking is also seen, indicating that the larger molecules are preferentially incorporated into the matrix. This is in accordance with what has also been observed by Bowmer *et al.*[10] and is as predicted by the statistical theory of crosslinking[22]. A decrease in TMPTMA monomer level should have occurred after processing. The fact that this was not observed in *Figure 8* may be explained by uncertainties occurring because the monomer and plasticizer peak are superimposed on each other in the measurements. The almost constant
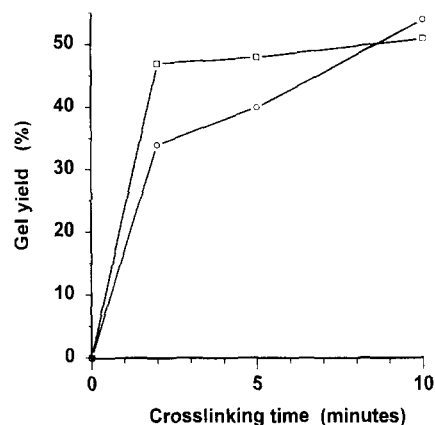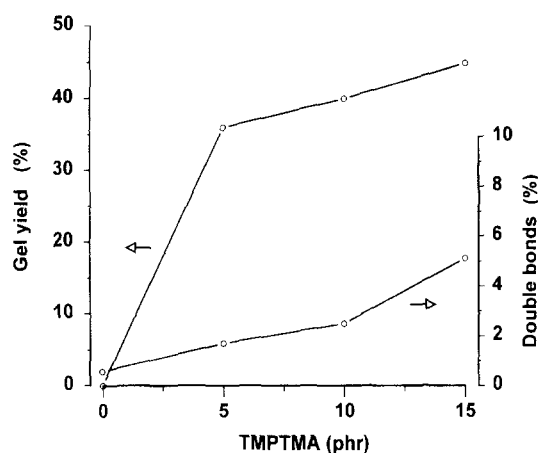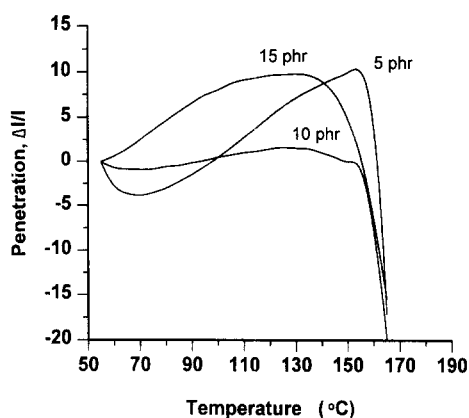
Figure 12 T.m.a. traces for samples prepared with different TMPTMA-levels. Milled at 140°C for 5 min before being moulded at 180°C for 5 min. Formulation D

Table 8 Effect of TBLS concentration and crosslinking temperature on gel yield. Samples milling at 140°C for 5 min before moulding for 5 min. Formulation E

Crosslinking temperature (°C)	Gel yield (%)		
	3 phr TBLS	5 phr TBLS	7 phr TBLS
170	35	37	35
180	39	39	40
190	49	46	44
200	51	55	54

not high compared to an irradiation system[13]. Surprisingly, the increase in gel yield with increasing TMPTMA level indicates no improvement of resistance to penetration, see *Figure 12*. This has to be explained by the type of network structure formed and/or decreasing degree of crystallinity. In a TMPTMA irradiation crosslinking system, Nethsinghe and Gilbert[13] indicated 10 phr TMPTMA to be an optimum level with respect to tensile properties. In the present system optimum thermomechanical properties seem to be obtained at the same or even lower concentrations.

Table 8 gives the effect of stabilizer (TBLS) concentration on gel yield at different curing temperatures. No gel formation was found in any of the milled sheets used. Reduced stabilizer concentration does not give any indication of increasing gel content. This can be explained by the mechanism of stabilization. TBLS stabilizes PVC by reacting with the HCl formed, not by hindering the formation of free radicals[23].

Thermal stability

Changes in sample colour with temperature are often used to characterize degree of chain degradation. For PVC discolouration occurs due to a degradation mechanism which produces polyene sequences in the backbone in addition to HCl formation. Discolouration is not necessarily a good estimate of PVC-backbone degradation and a more comprehensive study of this phenomenon would require Raman spectroscopy[24-26].

The thermal stability of different samples, analysed by YI, is given in *Figure 13*. It is seen that none of the samples increase their YI values much with time, i.e. a good thermal stability seems to have been achieved for all formulations. The low degree of discolouration
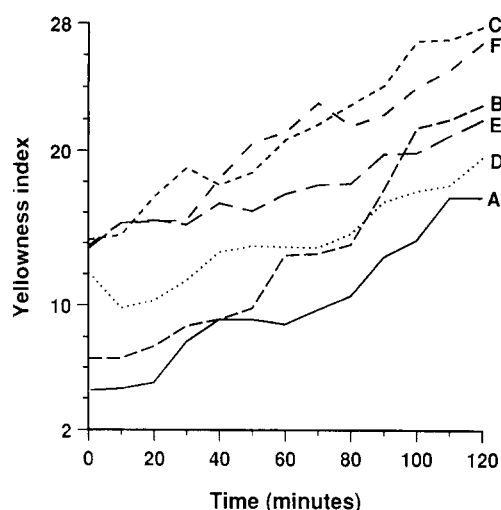

Figure 13 Thermal stability of different samples, measured by degree of discolouration (Yellownes Index). (A) formulation A; (B) formulation A (2 phr Trigonox 29-B90); (C) formulation C (2 phr Trigonox 29-B90); (D) formulation A (2 phr Trigonox 101); (E) formulation E (7 phr TBLS); (F) formulation E (3 phr TBLS)

measured by YI is in accordance with what was observed by human eye. Reducing the TBLS-stabilizer level from 7 phr to 3 phr (compare graphs E and F) gives only a small increase in YI difference with time for the two samples. Besides the stabilizing action of TBLS, polyfunctional materials are known to compete effectively with the degradation mechanism by reducing the length of conjugated sequences present[1,5,7]. In the present system even sheets containing peroxide and no TMPTMA (graphs B and D) showed little discolouration, indicating that the peroxides have little influence on the degradation mechanism. Bowmer et al.[10] found for irradiation crosslinking of a PVC–TMPTMA blend that the degradation mechanism became more pronounced with increasing curing temperature. However, this is not studied in the present peroxide crosslinking system.

CONCLUSIONS

By careful choice of peroxide type and preparation conditions it was possible to prepare plasticized PVC sheets which could be crosslinked by thermal curing.

The crosslinking process was found to be comprised of two primary reactions; a rapid polymerization of TMPTMA followed by grafting onto the PVC backbone. In absence of either peroxide or trimethylolpropane trimethyacrylate, TMPTMA, no crosslinking was found.

Gel yield increased with Trigonox 101 and TMPTMA concentration, and with curing temperature and time. Compared to Trigonox 101, Trigonox 29-B90 gave a higher gel formulation at the mildest thermal conditions and at the lowest peroxide levels. However, due to its lower half-life and less H-abstraction ability, Trigonox 29-B90 showed less dependence on crosslinking than Trigonox 101, with increasing peroxide level and curing time/temperature.

The resistance to penetration of the cured sheets increased at elevated temperatures with crosslinking. However, as opposed to the increased crosslinking achieved from increased peroxide level, increased gel yield obtained from increased TMPTMA level gave no

improvements in thermomechanical properties and an optimum TMPTMA level was found to be about 10 phr.

The crosslinking level was found to be independent of the amount of TBLS stabilizer and contrary to what is expected the crosslinked sheets showed excellent thermal stability.

ACKNOWLEDGEMENTS

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