

Peroxide Crosslinking of Unplasticized Poly(vinyl chloride)

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Received 21 October 1999; accepted 18 January 2000

ABSTRACT: A crosslinking system consisting of 1,1-di-*t*-butylperoxy-3,3,5-trimethyl cyclohexane peroxide and trimethylolpropane trimethacrylate (TMPTMA) has been used to introduce crosslinks into unplasticized poly(vinyl chloride) (PVC). The influence of the concentration of both reagents has been investigated, and crosslinking monitored by determination of the remaining sample weight after Soxhlet extraction with tetrahydrofuran. The system used (i.e., 0.5–2.0 phr peroxide with 5 to 15 phr TMPTMA) has been shown to be effective for crosslinking PVC. Gel contents of 30–40% have been obtained, premature crosslinking during processing is largely avoided, but thermal stability still needs to be improved. Considerable improvements in elevated temperature mechanical properties can be attained using an appropriate TMPTMA/peroxide concentration. The best tensile properties were obtained with 0.5 phr peroxide and 15 phr TMPTMA. Observed increases in T_g , also achievable with only 0.5 phr peroxide, but only slightly dependent on TMPTMA concentration, represent a useful increase in service temperature for the resulting compound. Lower peroxide levels may be adequate to achieve property improvements. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2657–2666, 2000

Key words: unplasticized poly(vinyl chloride); peroxide; crosslinking

INTRODUCTION

The utilization of rigid PVC for certain purposes is limited because its mechanical properties decrease considerably above its glass transition temperature. Crosslinking of PVC can improve elevated temperature properties by the formation of a permanent network structure.

In recent years a number of different methods for the chemical crosslinking of poly(vinyl chloride) (PVC) has been studied: these include the use of silanes^{1–12} and peroxides.^{13,14} Results have shown that it is possible to obtain crosslinkable formulations with both systems. It is necessary to

produce compounds that have an adequate gel content (i.e., % crosslinked polymer), and adequate thermal stability while avoiding premature crosslinking during processing.

Most published work is concerned with plasticized PVC. For rigid PVC, achieving the above requirements is considerably more difficult. Kelnar and Schatz^{3,4} reported that crosslinking of rigid PVC with mercaptosilanes was possible in presence of basic lead salts; however it is slower than in plasticized PVC, because crosslinks are produced by hydrolysis after processing. This involves the diffusion of water through the PVC, which is significantly slower in a rigid system. Reduced thermal stability in rigid crosslinked systems is also implied.

Polyfunctional acrylates and methacrylates have been widely used to initiate free radical po-

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Journal of Applied Polymer Science, Vol. 77, 2657–2666 (2000)
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Table I Formulations Used

Component	Concentration (phr)
PVC	100
TBLS	7
LoxioI G 53	1.2
LoxioI G 52	0.4
Hoechst PE 190	0.2
Paraloid K120N	1.5
TMPTMA	30, 20, 10
Trigonox 29-40B-pd	0, 0.5, 1, 2

lymerization processes, induced by both irradiation¹⁵⁻¹⁸ and the use of peroxides.^{14,19} Trimethylolpropane trimethacrylate (TMPTMA) appears to be the most widely used monomer for this purpose. It is a trifunctional monomer with the formula $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2-\text{O}-\text{CO}-\text{CCH}_3=\text{CH}_2)_3$. Bowmer et al.^{15,16} carried out radiation crosslinking of unplasticized PVC in the presence of the crosslinkable monomers TMPTMA and tetraethylene glycol dimethacrylate. Recently reported work from our laboratory¹⁹ has shown that rigid crosslinked PVC can be produced using both aminosilanes and peroxide, although optimization of formulations to improve thermal stability is still necessary. Peroxide crosslinking is discussed in more detail in this paper. It has already been shown to be very effective for plasticized PVC,¹⁴ and has the advantage that water diffusion is not involved. Crosslinking is activated by temperature in the presence of a polyfunctional monomer. This undergoes rapid homopolymerization, followed by grafting on to the PVC chains and subsequent crosslinking.¹⁵⁻¹⁷ Different kinds of monomer can be used, but good compatibility with PVC is required.

The aim of the present work is to study the peroxide crosslinking of rigid PVC in the presence of TMPTMA and investigate the influence of crosslinking on elevated temperature tensile properties, softening temperature, and thermal stability.

EXPERIMENTAL

Sample Preparation

Formulations used are shown in Table I. Proportions of materials used are expressed in parts per hundred of resin (phr). The quantities of peroxide and TMPTMA quoted in this table refer to the

actual amount of material used; the concentration of active component is lower (see below). The PVC used was the K60 PVC suspension resin EVIPOL SH6020, from EVC. The processing aid Paraloid K120N was supplied by Rohm and Hass, the waxes LoxioI G 52 and LoxioI G53 by Henkel, the wax PE 190 by Hoescht, and the tribasic lead sulphate (TBLS) by Addis. Crosslinking additives were TMPTMA 50 S (a 50% by weight blend of trimethylolpropane trimethacrylate and amorphous silica), AKM Products, Ltd., and Trigonox 29-40B-pd (1,1-di-*t*-butylperoxy-3,3,5-trimethylcyclohexane), incorporating 40% peroxide, from Akzo Nobel. This peroxide has a decomposition half-time of 6 min at 128°C¹⁸ and was previously shown to be effective for crosslinking plasticized PVC.¹⁴

Dry blends were prepared in a laboratory scale Fielder mixer. All components (except peroxide and TMPTMA) were placed in the mixer when a temperature of 50°C was reached. They were mixed at 2000 rpm until the temperature was 100°C, when crosslinking additives were added, and blending continued until 120°C was reached. Then the mixture was dumped to a cooled chamber.

Dry blends were milled for 3–4 min at temperatures from 120 to 140°C, depending on the formulation, then pressed for 5 min at 180°C, unless stated otherwise.

Testing and Characterization

Gel Content

The amount of insoluble (i.e., crosslinked) PVC was determined by Soxhlet extraction for 24 h using tetrahydrofuran (THF) as solvent. THF was removed by drying the extraction thimbles for 8 h at 100°C. Since the measured gel also included TBLS and silica, the term “THF-insoluble material” has been used instead of “gel content.”

Infrared Spectroscopy

The infrared spectra were obtained using a Mattson 3000 FTIR spectrometer. Samples were prepared by compression of the milled samples for 5 min using a pressure of 20 tons to produce sufficiently thin films.

Tensile Properties

The ultimate tensile strength (UTS) and the elongation at break were determined at 130°C using a

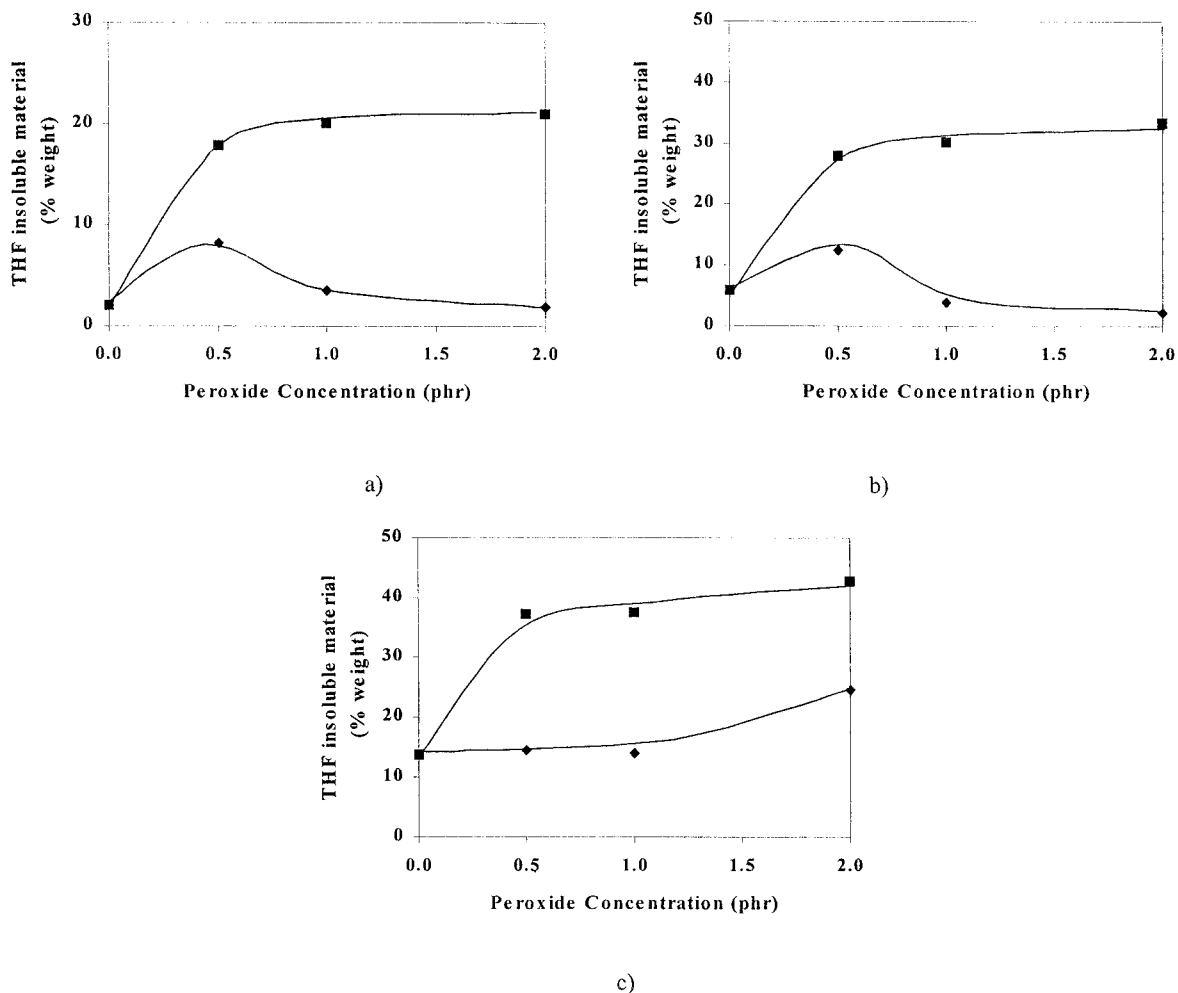


Figure 1 THF insoluble material for (◆) milled and (■) pressed samples with different peroxide concentration, and (a) 5 phr of TMPTMA, (b) 10 phr of TMPTMA, and (c) 15 phr of TMPTMA.

Hounsfield tester with a grip separation speed of 50 mm/min. Eight test pieces were used for each measurement. Testing was carried out at 130°C, since previous work has shown this to be a suitable temperature for assessing improvements in elevated temperature properties. Samples were preconditioned at this temperature for 20 min before testing.

Thermomechanical Analysis

A Setaram 92-16.18 Thermomechanical Analyser was used for determination of the softening point of the different samples under a 51 gram load. Samples were heated at 10°C/min with a 60 ml/min flow of helium.

Thermal Stability

The thermal stability of several formulations at 190°C was determined using an oven fitted with a

fan according to ASTM Method No. 115-67. Small strips of samples were cut and placed in an aluminium foil holder, which was put on an oven tray. Strips were removed from the oven every 10 min, and any change in color was observed.

RESULTS AND DISCUSSION

Gel Content

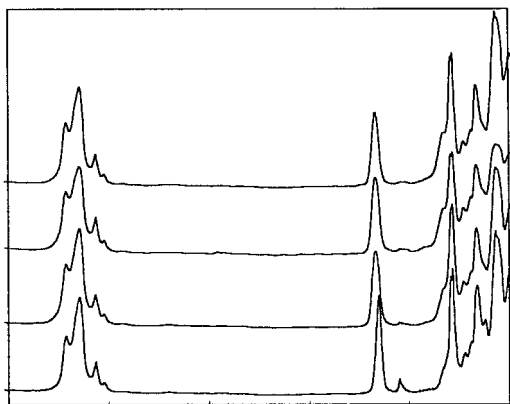
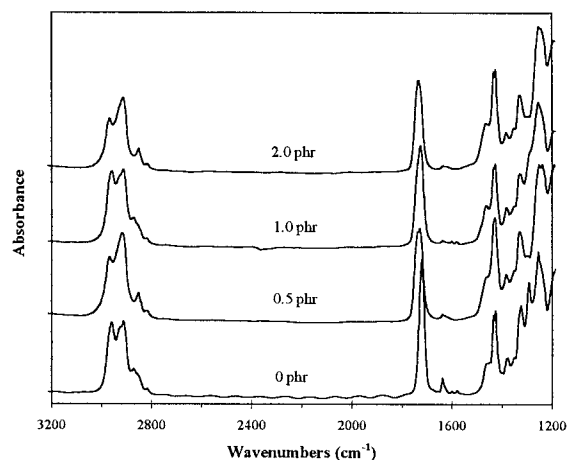
Figure 1 shows the effect of peroxide concentration, TMPTMA content, and processing on the amount of insoluble material. [Actual TMPTMA contents (i.e., 50% commercial material) are used throughout this discussion.] It is known that TBLS, the silica, and whiting carrier in the peroxide, and the silica present in TMPTMA will not dissolve in THF. The theoretical insoluble con-

Table II Theoretical and Actual % Insoluble Material in Milled Samples

phr Peroxide		phr TMPTMA		
		5	10	15
0	Theoretical % insoluble	10.0	13.0	15.7
	Actual % insoluble	2.0	6.0	13.8
0.5	Theoretical % insoluble	10.2	13.2	15.8
	Actual % insoluble	8.3	12.5	14.6
1.0	Theoretical % insoluble	10.4	13.4	16.0
	Actual % insoluble	3.5	4.0	14.0
2.0	Theoretical % insoluble	10.8	13.8	16.3
	Actual % insoluble	1.9	2.1	24.0

tents based on these components, and actual measured values, are shown in Table II for the milled samples. In the presence of 0.5 phr peroxide, and 5 or 10 phr TMPTMA, actual values reach a maximum, and the actual and theoretical values are very close together. Comparison with other "actual" data for samples with 5 and 10 phr TMPTMA suggests that the amount of crosslinking is relatively low, lying between 0 and 6%, which is desirable since it is not intended that premature crosslinking should occur during processing. For these compounds the amount of insoluble material in the absence of peroxide, or with higher levels, is lower than the theoretical values. Clearly there must be more than one effect to produce this result. In the absence of peroxide it appears that much of the "insoluble" material actually penetrates the extraction thimble. With 0.5 phr peroxide, the increased insoluble content could be due crosslinked TMPTMA, or because polymerized TMPTMA traps further TBLS, or

both. (Previous thermal analysis showed that the maximum in the exotherm for TMPTMA homopolymerization occurred at 198°C in the plasticizer alone, but at 180°C in the presence of PVC, and at 123°C when 2 phr Trigonox 29-B290 were added (This grade of Trigonox contains 90% peroxide, rather than the 40% in the grade used in the present work.) Thermal analysis also showed that the maximum for the peroxide decomposition did not occur until a temperature of about 170°C was reached.¹⁴) Reduction in insoluble content at higher levels of peroxide could be due to the nature of the network, as discussed later. When the TMPTMA concentration was increased to 15 phr, increased insoluble material was obtained at all peroxide levels, suggesting that more crosslinking occurred as the amount of unsaturation in the system increased. Pressing at 180°C enabled crosslinking, reflected by a significant increase in insoluble content, to occur, as this temperature

**Figure 2** Infrared spectra for samples with 5 phr of TMPTMA and different peroxide concentrations.**Figure 3** Infrared spectra of samples with 10 phr of TMPTMA and different peroxide concentrations.

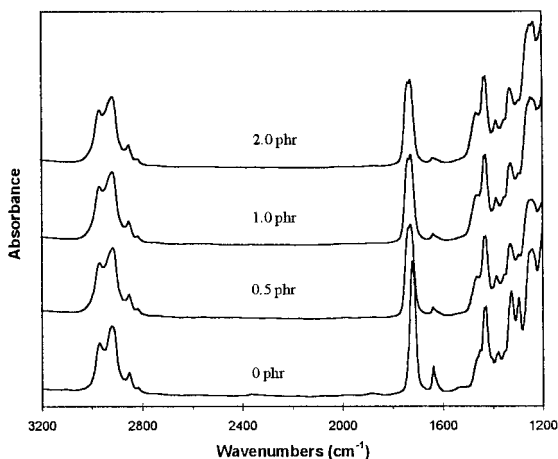


Figure 4 Infrared spectra of samples with 15 phr of TMPTMA and different peroxide concentrations.

was high enough for peroxide decomposition and subsequent reaction. Crosslinking was achieved with 0.5 phr peroxide; further increases in peroxide concentration had little effect. Similar results have been obtained for plasticized PVC.¹⁴ The level of crosslinking increased with TMPTMA concentration, as observed previously both for peroxide crosslinking¹⁴ and irradiation crosslinking¹⁷ of plasticized PVC, and for irradiation crosslinking of rigid PVC.¹⁵ The maximum gel content of 40% obtained in this work closely corresponded to the maximum obtained by irradiation crosslinking for a sample containing a similar TMPTMA level.¹⁵

Infrared Spectroscopy

Infrared spectroscopy was used to detect the presence of unreacted TMPTMA, using the absor-

bance band due to residual unsaturation observed at 1640 cm^{-1} . Excess TMPTMA is undesirable in the pressed samples both on grounds of cost and the stability of the material produced.

The 1640 cm^{-1} absorbance band is readily observed in samples with 0 phr of peroxide and 5 phr of TMPTMA (Fig. 2), but once the peroxide is present the 1640 cm^{-1} band disappears, because the peroxide catalyses its homopolymerization, improving the conversion of double bonds.¹⁴ With 10 phr of TMPTMA (Fig. 3), unsaturation cannot be observed above 1 phr of peroxide, but with 15 phr of TMPTMA (Fig. 4) the monomer is still detectable in the presence of 2 phr of peroxide. Although samples containing peroxide show discoloration (see below), observed intensities for the 1640 cm^{-1} absorbance band clearly correlate with TMPTMA content, and do not reflect PVC degradation. This was observed previously for irradiated plasticized PVC containing TMPTMA.¹⁷

Tensile Properties

Data obtained for elevated temperature properties of rigid PVC samples are shown in Figure 5. Standard deviations were between 0.03 and 0.05 MPa for UTS, and between 2 and 9% for elongation at break. In the absence of peroxide, an increase of TMPTMA concentration yields a polymer with lower UTS and elongation at break, since TMPTMA contains 50% weight of silica.

When peroxide is present, crosslinking occurs and the network formed restricts the deformation of the material yielding a higher UTS and lower elongation at break. The highest TMPTMA concentration produces the most marked changes in

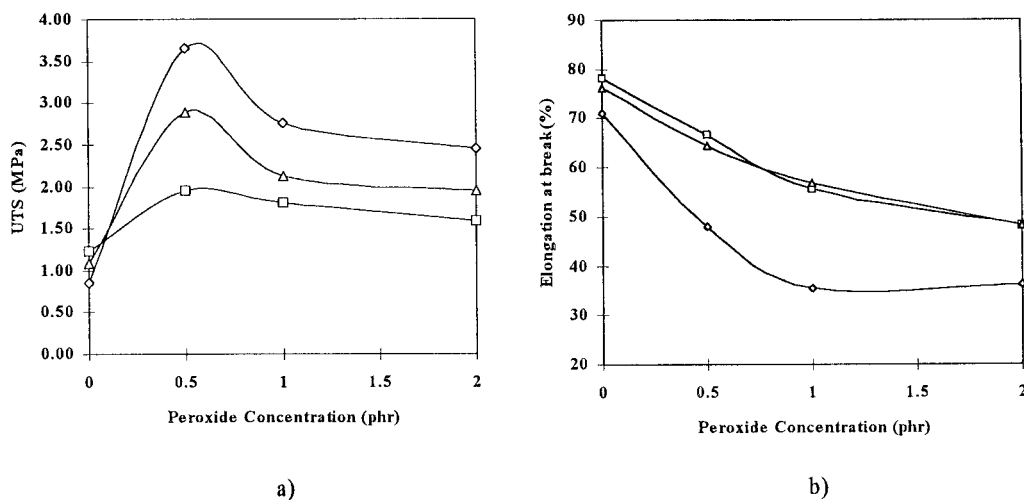


Figure 5 Tensile properties at 130°C for samples with different peroxide concentrations and (\square) 5phr of TMPTMA, (\triangle) 10 phr of TMPTMA, and (\diamond) 15 phr of TMPTMA.

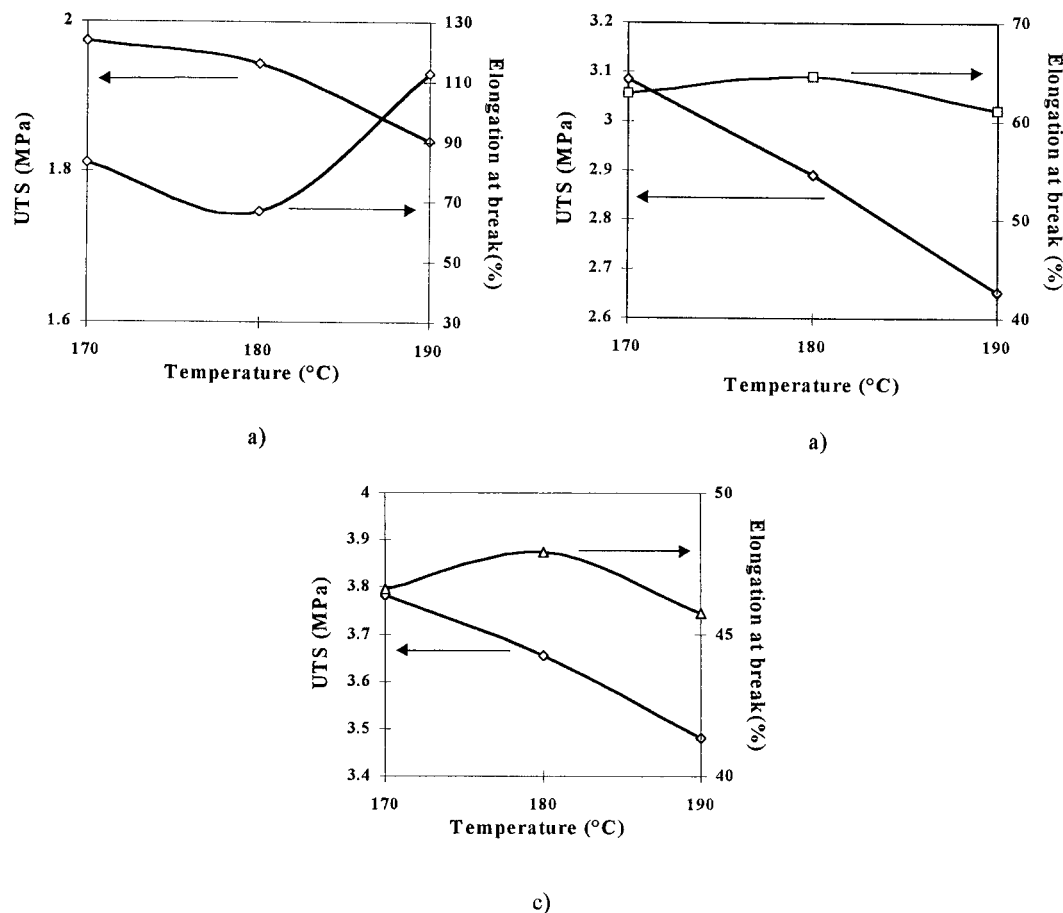


Figure 6 Tensile properties at 130°C for samples with 10 phr of TMPTMA and 0.5 phr of peroxide pressed at different temperatures.

these properties, since a high gel content has been attained. Optimum properties are achieved with 0.5 phr of peroxide. At higher peroxide concentrations UTS decreases, but then reaches a plateau. Possible reasons for this are discussed later.

Tensile properties also depend on the processing conditions. In general, it is expected that they will be improved by an increase in pressing temperature, since PVC fusion and crosslinking will occur to a greater extent. However, the actual behavior is more complex (Fig. 6). With all TMPTMA concentrations, UTS decreases as pressing temperature increases. Samples become more discolored with pressing temperature, so this could be due to degradation. However, other results imply the formation of different types of network under different conditions, and network type may also be important here. Elongation at break has been shown to be dependent on crosslink density as well as gel content.¹⁷ Formation of a "tight" network tends to reduce elonga-

tion at break, while a looser network has higher elongation. For samples with 10 and 15 phr of TMPTMA and 0.5 phr peroxide, a maximum elongation at break is observed at a pressing temperature of 180°C. When temperature is increased to 190°C, the combination of degradation and relatively high gel content have caused a decrease in elongation at break. With 5 phr of TMPTMA, the elongation at break decreases, then increases at a pressing temperature of 190°C.

Thermomechanical Analysis

Thermomechanical analysis (TMA) curves (Fig. 7) show the effect of peroxide crosslinking on the softening of the PVC compounds produced. Glass transition temperatures (T_g), obtained from the maximum of the derivative of the TMA curves, are shown in Figure 8. In the absence of peroxide, T_g decreases with increase in TMPTMA content, indicating that it is functioning as a plasticizer.

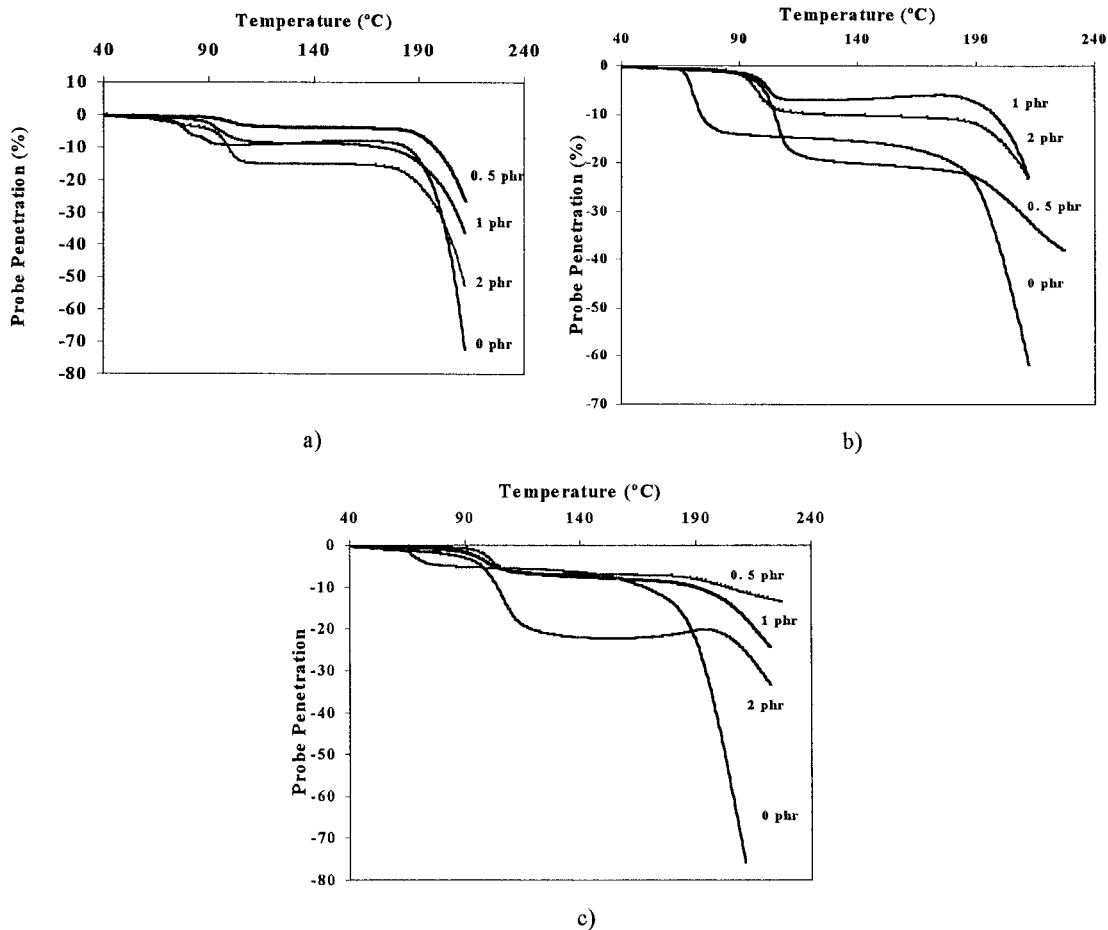


Figure 7 Probe penetration for samples with different peroxide concentrations and (a) 5 phr of TMPTMA, (b) 10 phr of TMPTMA, and (c) 15 phr of TMPTMA.

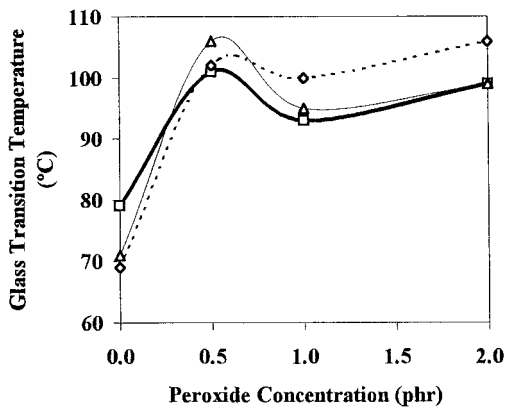


Figure 8 Glass transition temperatures for samples with different peroxide concentrations and (□) 5 phr of TMPTMA, (△) 10 phr of TMPTMA, and (◇) 15 phr of TMPTMA.

For all samples containing peroxide, T_g is increased, reflecting a useful increase in service temperature. The deflection at T_g is also reduced. Irrespective of TMPTMA content, a maximum in T_g for peroxide containing samples occurs with a peroxide content of 0.5 phr. Unlike UTS, the highest T_g at this peroxide concentration is observed in the presence of 10 phr TMPTMA. There is possibly still a plasticization effect operating, reducing the T_g of the sample containing 15 phr plasticizer, despite the homopolymerisation of TMPTMA. With 1.0 phr peroxide, there is a decrease in T_g , as observed for UTS; the ordering of T_g with TMPTMA concentration is also consistent with UTS and gel content results. All samples then show an increase in T_g with 2 phr peroxide, but no increase in gel content was observed for these compounds. Other results presented here also suggest the formation of a looser network at

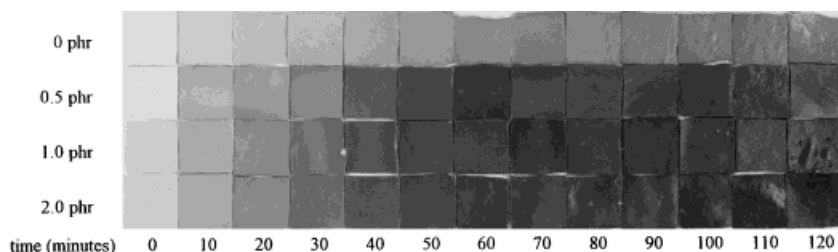


Figure 9 Color evolution with time (min) for samples with 5 phr of TMPTMA.

higher peroxide concentrations, which would not result in a higher T_g (see below). It can tentatively be suggested that observed increases in T_g relate to the formation of graft copolymer, with relatively short bulky chains of poly-TMPTMA linking the PVC molecules, as discussed by Dobó²¹ for the radiation crosslinking of PVC with ethylene glycol dimethylmethacrylate.

PVC also contains a network of crystallites, which act as physical crosslinks, and melt over a wide temperature range starting at about 110°C. Above T_g , softening depends on the melting of these crystallites, but can be modified by a chemical crosslinked network.²² The temperature at which high temperature softening was detectable was increased for all samples containing peroxide to approximately 190°C. The optimum peroxide concentration for minimum softening was 0.5–1.0 phr, and appeared to decrease within this range as TMPTMA concentration increased. The best performance was obtained for the sample containing 0.5 phr peroxide, and 15 phr TMPTMA, which had a gel content of about 35%. Increasing the peroxide to 2.0 phr resulted in poorer performance for compounds containing 10 or 15 phr TMPTMA, which could be attributed to the looser network discussed later.

Thermal Stability

Thermal stability tests can provide a general indication of relative thermal stability, by observing

color changes in heat aged samples. Figures 9–11 show that increasing TMPTMA concentration seems to improve the thermal stability slightly, whereas peroxide clearly promotes, as expected, the degradation of PVC. However, once the peroxide is present there is little further change in thermal stability when its concentration is increased at a given TMPTMA concentration.

Structure/Property Relationships

Changes in UTS and T_g with peroxide and TMPTMA concentration (Figs. 5 and 8) are generally very similar. Apart from the T_g with 0.5 phr peroxide and 15 phr TMPTMA discussed above, the highest values, as well as maximum gel content, are observed with the highest concentration of TMPTMA used, since more molecules are available for grafting onto PVC, hence crosslinking. A notable feature is the very distinct maxima observed with 0.5 phr peroxide. The subsequent decrease in properties with higher peroxide concentration is not attributable to gel content (Fig. 1). It is known that the first double bond to react in a molecule such as TMPTMA is significantly more reactive than the other double bonds, due to steric hindrance.^{15–17,21} It seems reasonable to postulate that with a low level of peroxide, most reactions involve only the first double bond in TMPTMA. Infrared spectroscopy indicates that there is residual unsaturation in all samples with 0.5 phr peroxide. When peroxide content in-

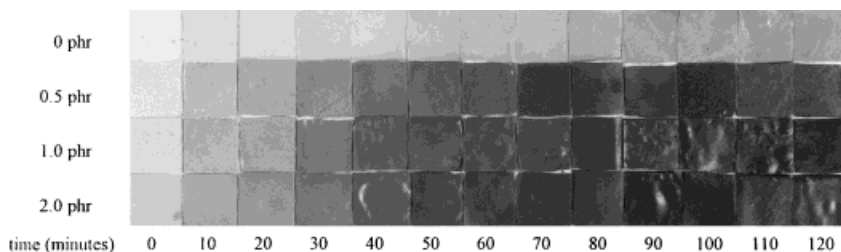


Figure 10 Color evolution with time (min) for samples with 10 phr of TMPTMA.

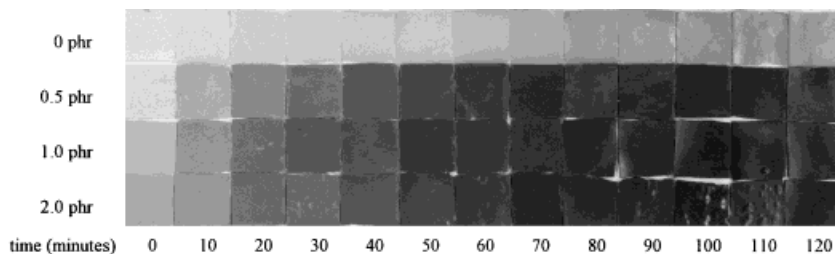


Figure 11 Color evolution with time (min) for samples with 15 phr of TMPTMA.

creases, it is likely that further double bonds will react per TMPTMA molecule, tending to produce longer poly-TMPTMA chains to graft on to the PVC molecules, resulting in a “looser” network, with lower UTS. This would also be consistent with observed changes in elongation at break, which is decreased by crosslinking, but does not continue to decrease when peroxide concentration is increased. T_g decreases when peroxide concentration is increased to 1 phr, again consistent with a looser network. However, it increases again with 2 phr peroxide, possibly because reaction of the third double bond of TMPTMA could result in branching in poly-TMPTMA, and a T_g increase for the PVC/poly-TMPTMA copolymer. Effects of temperature on UTS (Fig. 6) may be explained in a similar way. Increased temperature will increase the reaction rate of the double bonds in TMPTMA, so additional bonds could react, forming a looser network. This would lead to lower UTS as observed. A looser network can have a higher elongation at break, as observed when the pressing temperature for samples containing 10 or 15 phr TMPTMA is increased from 170 to 180°C. Small decreases observed when the temperature is increased to 190°C may be due to degradation and high gel content. The sample containing 5 phr TMPTMA behaves differently; the decrease in UTS is small, while elongation at break increases dramatically at 190°C. These samples have a lower gel content, and uncrosslinked material will also affect properties.

In the absence of peroxide, TMPTMA slightly improves the aging performance of the PVC compounds, presumably because the double bonds in TMPTMA are able to react with radicals produced during PVC degradation. For unaged samples, degradation increases with increased peroxide concentration, because the radical concentration in the system is increased. The presence of any peroxide significantly impairs accelerated ageing, almost irrespective of peroxide concentration, so

that the introduction of even the lowest concentration of free radicals is sufficient to cause reduced thermal stability. (It is interesting to note that discolouration did not occur when a similar system was used to crosslink plasticized PVC,¹⁴ which could be due to the lower shear experienced during processing, or the different form of peroxide used).

CONCLUSIONS

The system used (i.e., 0.5–2.0 phr peroxide with 5–15 phr TMPTMA) has been shown to be effective for crosslinking PVC. Gel contents of 30–40% have been obtained, premature crosslinking during processing is largely avoided, but thermal stability still needs to be improved.

Considerable improvements in elevated temperature mechanical properties can be attained using an appropriate TMPTMA/peroxide concentration. The best tensile properties were obtained with 0.5 phr peroxide and 15 phr TMPTMA. Observed increases in T_g , also achievable with only 0.5 phr peroxide, but only slightly dependent on TMPTMA concentration, represent a useful increase in service temperature for the resulting compound. Lower peroxide levels may be adequate to achieve property improvements.

The authors of the paper wish to thank Rohm and Hass, Henkel, Hoescht, AKM Products Ltd. and Akzo Nobel, who provided materials used in the present work.

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