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Crosslinking of rigid poly(vinyl chloride)

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Various formulations for the crosslinking of rigid poly(vinyl chloride) have been investigated including three different thermal stabilisers: a tin maleate; an octyl thio tin stabiliser; and a tribasic lead sulphate. The possibility of using aminosilanes and peroxides as crosslinking agents was considered and the additives used in the formulations were bis(γ -trimethoxysilylpropyl)amine, a blend of trimethylol propane trimethacrylate and amorphous silica, and 1,1-di-*t*-butylperoxy-3,3,5-trimethyl cyclohexane incorporating 40% peroxide. It was shown that rigid poly(vinyl chloride) can be crosslinked using both aminosilane and peroxide systems and the optimum level of the aminosilane was found to be ~ 2 phr while significant property improvements were achieved with only 0.5 phr peroxide. The effects of the various thermal stabilisers and crosslinking additives are presented and discussed. PRC/1554

© 1999 IoM Communications Ltd. Dr Gilbert is at the Institute of Polymer Technology and Materials Engineering, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK and Dr García-Quesada is in the Department of Chemical Engineering, University of Alicante, E-03080 Alicante, Spain. This paper was presented at PVC 99 – From strength to strength, held in Brighton, UK on 20–22 April 1999.

INTRODUCTION

Crosslinking of poly(vinyl chloride) (PVC) can result in the improvement of a number of properties, particularly at elevated temperatures. In the 1990s there has been renewed interest in the chemical crosslinking of PVC, with most work focussing on plasticised compounds. Two methods, which have been studied in some detail, are the use of silanes,^{1–12} and to a lesser extent, peroxides.^{13,14} Work has shown that both systems can produce successful crosslinkable formulations. The requirements of these, which are to some extent conflicting, are adequate gel content (i.e. percentage crosslinked polymer), adequate thermal stability, and the avoidance of premature crosslinking during processing. Less attention has been devoted to the chemical crosslinking of rigid PVC, for which achieving the above requirements is considerably more difficult. The most significant work is that of Kelnar and Schatz^{3,4} who reported the crosslinking of rigid PVC using mercaptosilanes. They showed that high levels of crosslinking could be achieved in the presence of basic lead salts, but did not comment on the thermal stability of the compounds produced, although reduced thermal stability was implied. Crosslinking of rigid PVC was shown to be slower than for plasticised PVC, an effect attributed to the reduced diffusion of water, required to hydrolyse the silane, in the rigid material.

In this work, the possibility of using aminosilanes and peroxides to crosslink rigid PVC was investigated. The effects of different thermal stabilisers were also studied.

EXPERIMENTAL

Sample preparation

The formulations investigated in the present work are given in Tables 1 and 2. The PVC used was the K60 PVC resin EVIPOL SH6020, from EVC. The processing aid Paraloid K120N was supplied by Rohm

and Hass, the waxes Loxiol G 52 and Loxiol G 53 by Henkel, and the wax PE190 by Hoescht. Three different thermal stabilisers were used: the tin maleate, Tinstab BM 400; the octyl thio tin stabiliser, Tinstab OTS 17-D from Akcros; and tribasic lead sulphate (TBLS), Addis. Crosslinking additives were the silane Silquest A1170 (bis(γ -trimethoxysilylpropyl)amine) by OSi Specialities and for peroxide crosslinking, a TMPTMA 50 S (a 50 wt-% blend of trimethylolpropane trimethacrylate and amorphous silica), AKM Products Ltd and Trigonox 29-40B-pd (1,1-di-*t*-butylperoxy-3,3,5-trimethyl cyclohexane), incorporating 40% peroxide, from Akzo Nobel.

Dry blends were prepared in a laboratory scale Fielder mixer. All the powder components were placed in the mixer when a temperature of 50°C was reached. They were mixed at 2000 rev min⁻¹ until the temperature was 80°C, when any liquid additives (e.g. thermal stabiliser) were added. For the peroxide based systems, crosslinking additives were added at 100°C, then blending continued until 120°C was reached when the mixture was dumped to a cooled chamber.

Dry blends were milled for 3–4 min at temperatures in the range 120–140°C, depending on the formulation, then pressed for 1–8 min at 180°C.

Silane compounds were crosslinked by immersion in water. Two different time–temperature conditions were used: immersion in water at 80°C for 4 h and immersion in water at 90°C for 24 h. In the case of the lead stabilised compounds, 1% dibutyltin dilaurate was added to the immersion water. No tin catalyst was added when tin was included in the thermal stabiliser composition.

Testing and characterisation

Gel content

The amount of insoluble (i.e. crosslinked) PVC was determined by Soxhlet extraction for 24 h using tetrahydrofuran (THF) as solvent. The THF was removed

by drying the extraction thimbles for 4 h at 80°C under vacuum.

Tensile properties

The ultimate tensile strength (UTS) and the elongation at break were determined at 130°C using a Hounsfield tester with a grip separation speed of 50 mm min⁻¹. Samples were preconditioned at this temperature for 20 min before testing.

Thermomechanical analysis

A Du Pont 990 thermal analyser fitted with a thermal mechanical analysis (TMA) attachment was used for the determination of the softening point of the different samples. Samples were 1 mm thick and 2–3 mm square. A load of 5 g was applied and samples were heated at 10 K min⁻¹.

Infrared spectroscopy

The infrared spectra of the different samples were obtained using a Mattson 3000 FTIR spectrometer. Measurements were carried out at room temperature and the sample area was in excess of the dimensions of the beam of IR radiation. Samples were prepared by compression of the milled samples for 5 min using a pressure of 20 t to produce sufficiently thin films.

Thermal stability

The thermal stability of several formulations was determined in an oven fitted with a fan at 190°C according to ASTM 115-67. Small strips of samples were cut and placed in an aluminium foil holder, which was put on one of the oven trays. Strips were removed from the oven every 10 min, and any change in colour observed.

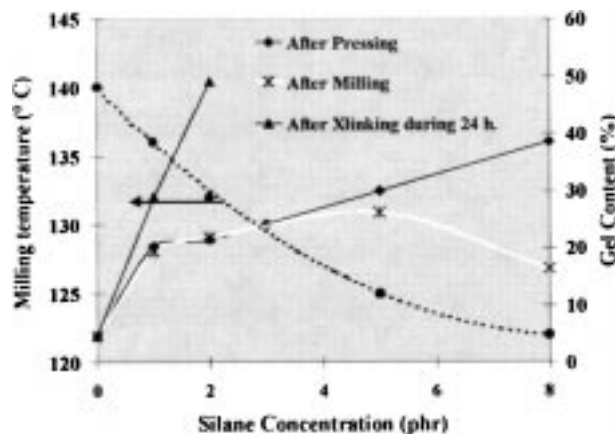
RESULTS AND DISCUSSION

Silane systems

The objective is to graft silane on to the PVC chains during milling by reaction of the amine group on the silane with chlorine on the PVC. Crosslinking should then occur when samples are immersed in water, causing hydrolysis of methoxy groups and subsequent condensation to produce crosslinks. Ideally therefore, gel content should be minimal after milling and pressing, but increase significantly on water immersion.

Gel contents for compounds containing different levels of silane are shown in Fig. 1. On addition of silane, compounds became sticky, and it was found necessary to reduce the milling temperature. Actual milling temperatures are also shown in Fig. 1.

Gel content is drastically affected by the processing temperature and silane concentration. The shape of



1 Gel content and milling temperature v. silane concentration

the curve for the milled samples is the result of the superposition of two effects: gel content increases with silane concentration, since there is more reagent available to achieve the grafting and crosslinking processes but decreases with the decrease in temperature owing to a decrease in the grafting and crosslinking rates. As a result of these two processes, as the silane concentration is increased from 1 to 5 phr, the gel content is also increased, but beyond this concentration the influence of the decrease in the milling temperature is more important than the increase in the silane concentration. After the compression moulding of the samples, the gel content increased significantly for the samples containing 5 and 8 phr silane, indicating that the crosslinking process was continuing. After immersion in hot water, the samples with 1 and 2 phr silane show an increase in the amount of gel, indicating that the crosslinking process has continued further. The sample containing 2 phr silane shows the best performance with respect to that required.

The tensile properties of samples with tin and lead stabilisers are shown in Figs. 2 and 3, respectively. For samples that include the tin maleate thermal stabiliser Tinstab BM 400 it is noticed, as expected, that the UTS increases as the silane concentration increases, but reaches a plateau (Fig. 2) at 5 phr silane, probably because of severe thermal degradation beyond this concentration. Changes in the elongation at break are less clear, owing to greater scatter in the experimental results. When comparing samples before and after immersion in hot water, neither UTS nor the elongation at break are improved (even for 24 h crosslinking time), although the gel

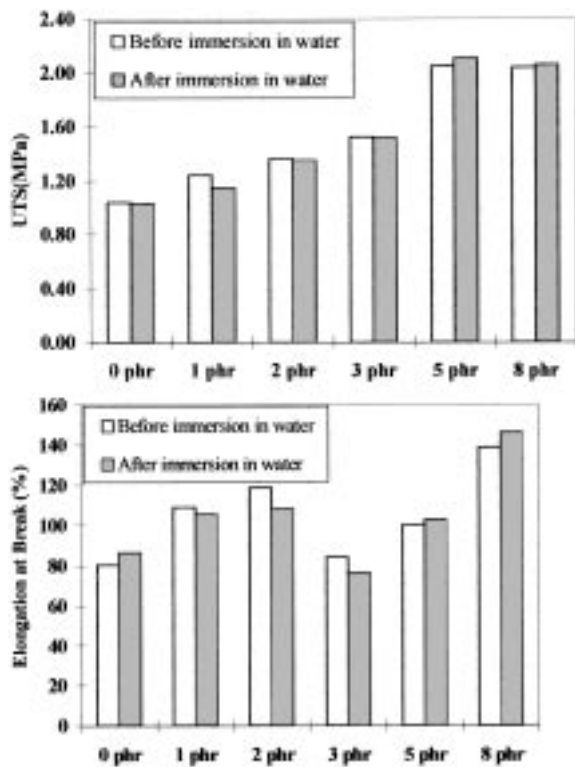
Table 1 Formulations of silane based compounds

Component	Concentration, phr
PVC	100
Paraloid K 120 N	1.5
Thermal stabiliser	*1.5, 3.0, 7.0
Loxiol G 53	1.2
Loxiol G 52	0.4
Hoechst PE190	0.2
Silquest A 1170	0–8

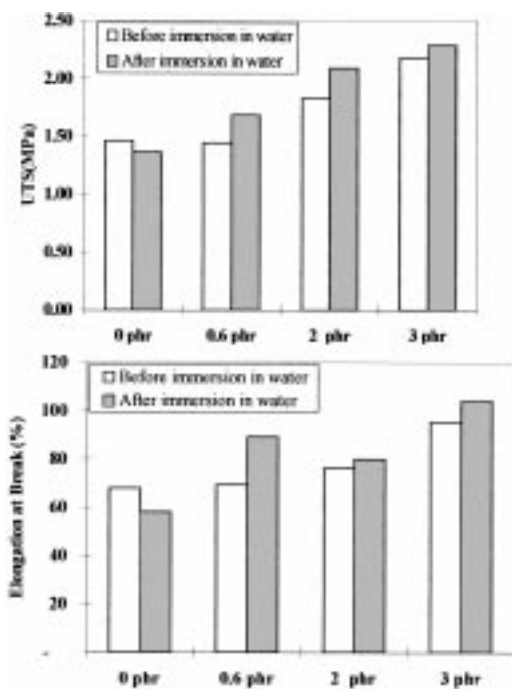
* Depending on stabiliser type: 1.5 phr Tinstab OTS; 3.0 phr Tinstab BM 400; and 7.0 phr TBLS.

Table 2 Formulations of peroxide based compounds

Component	Concentration, phr
PVC	100
TBLS	7
Loxiol G 53	1.2
Loxiol G 52	0.4
Hoechst PE190	0.2
Paraloid K 120 N	1.5
TMPTMA	5, 10, 15
Trigonox 29-40B-pd	0, 0.5, 1, 2



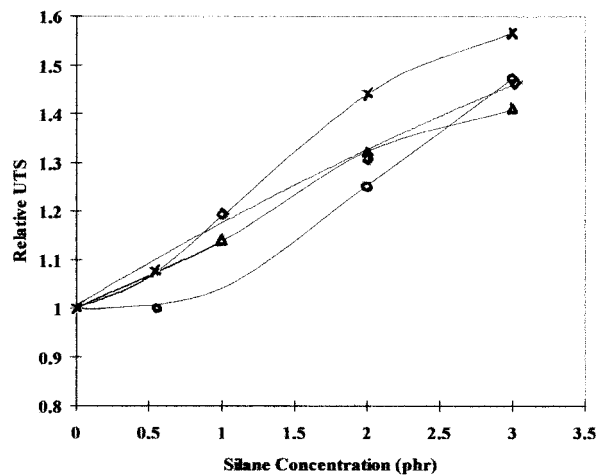
2 Tensile properties at 130°C for samples with BM for various silane contents



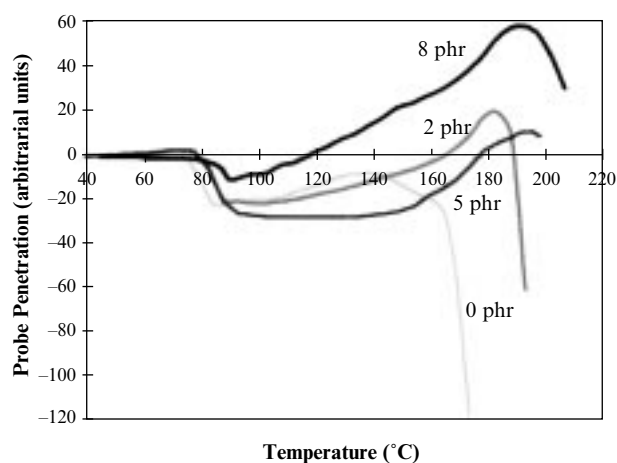
3 Tensile properties at 130°C for samples with TBLs for various silane contents

content has increased. Very similar results were obtained when the octyl thio tin stabiliser OTS was used. In these compounds the tin stabiliser also acts as a catalyst and the atmospheric moisture is clearly sufficient to cause crosslinking.

When the lead stabiliser was used, grafting and crosslinking also took place during the milling and pressing of the samples, although there was no tin



4 Relative increase in UTS using different thermal stabilisers: (◇) BM; (△) OTS; (○) TBLs; and (×) TBLs after immersion in water

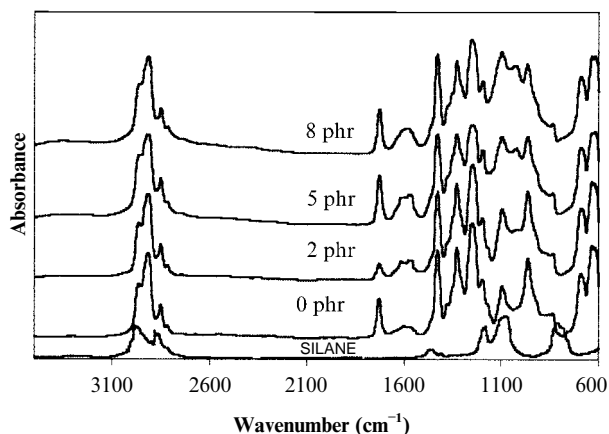


5 TMA curves for BM stabilised samples with 0, 2, 5, and 8 phr silane

catalyst present. Both UTS and the elongation at break increase with silane concentration, as expected (Fig. 3), but after immersion in hot water plus catalyst both properties increase further, in contrast to the previous formulations containing tin stabilisers.

The UTS shown by samples containing different thermal stabilisers is quite different, even in the absence of crosslinking. In order to compare all the formulations, a relative UTS was calculated as the actual UTS divided by the UTS obtained in absence of silane; this relative UTS *v.* silane concentration for formulations with different thermal stabilisers is shown in Fig. 4. This figure shows that the effect of the silane with either tin stabiliser is very similar. In the formulation with the lead stabiliser, the increase observed in the UTS is not as high as in the tin formulation, indicating that less premature crosslinking has occurred. However after immersion in hot water plus catalyst, crosslinking continues, and a further increase in UTS can be observed, so that after immersion the relative UTS is highest for the lead stabilised systems.

The TMA curves showing the probe penetration as a function of the temperature are shown in Fig. 5. The following trends can be observed: above the glass

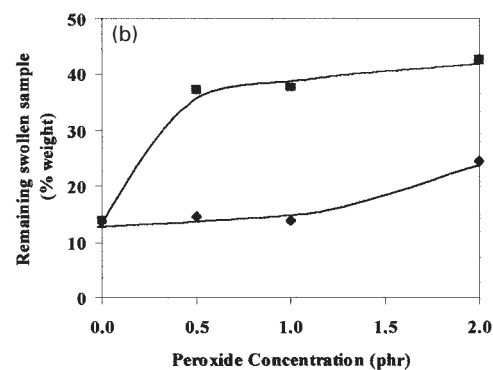
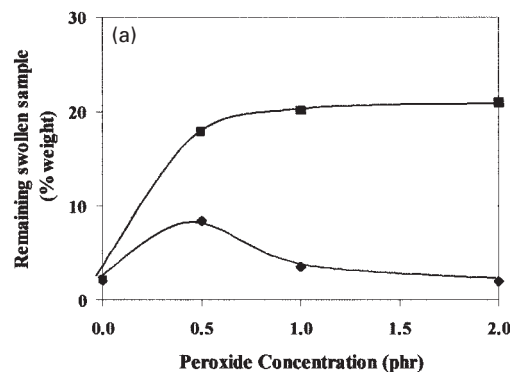


6 Infrared spectra for samples with BM and 0, 2, 5, and 8 phr silane

transition temperature (i.e. around 80°C) some thermal expansion is observed. For the sample without silane, this was followed by significant probe penetration at $\sim 160^\circ\text{C}$. However samples with silane show marked thermal expansion after the glass transition, while the softening of the PVC occurs at higher temperatures. Therefore, crosslinking of unplasticised PVC with the silane used notably improved its properties above the glass transition, even at low concentration (2 phr).

As expected the silane significantly affects the thermal stability of the PVC preventing its utilisation above a certain concentration, the actual concentration depending on the thermal stabiliser used. Thermal stability tests for samples containing 2 phr silane show that compounds with the tin stabiliser BM have the best thermal stability, followed by lead stabilised compounds, while those containing OTS are least stable. Further work is needed to find whether optimum stabiliser levels have been used.

Evidence of crosslinking can be demonstrated by infrared spectroscopy as illustrated in Fig. 6, which shows spectra obtained for the silane itself and the compounds containing the thermal stabiliser BM with various silane concentrations. These show marked differences, mainly in two regions. The silane itself has a major peak due to Si–O at $\sim 1080\text{ cm}^{-1}$. In the crosslinked PVC compounds, this is replaced by an absorbance at 1025 cm^{-1} which increases with silane concentration, but was unaffected when the processing temperature was increased. This can be attributed to the formation of Si–O–Si crosslinks. Changes were also observed in the $1550\text{--}1640\text{ cm}^{-1}$ region. Absorbance in this region could be due to the presence of double bonds formed after the partial degradation of PVC, but it did not appear in the infrared spectra of samples with lower thermal stability (i.e. with the stabilisers OTS and TBLS). In addition, the intensity of the absorbance did not change with processing temperature, although after immersion in hot water a sharper peak appeared close to 1500 cm^{-1} . For these reasons, it is possible that the absorbance could be associated with a product of the reaction of the crosslinking agent with the thermal stabiliser.



7 Gel content of samples containing a 5 phr and b 15 phr of TMPTMA: (■) pressed; (◆) milled

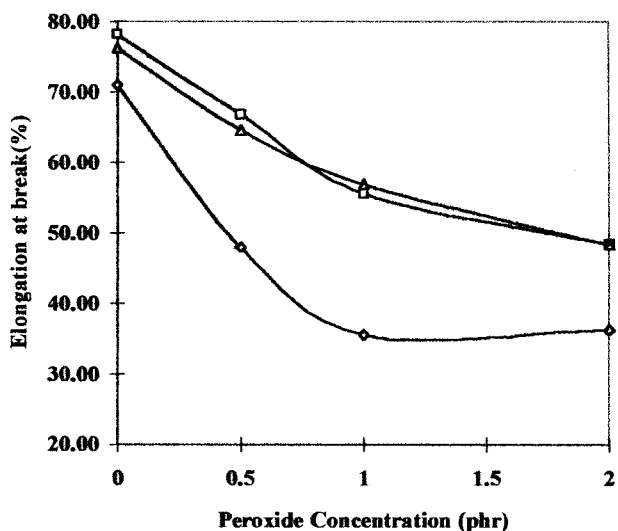
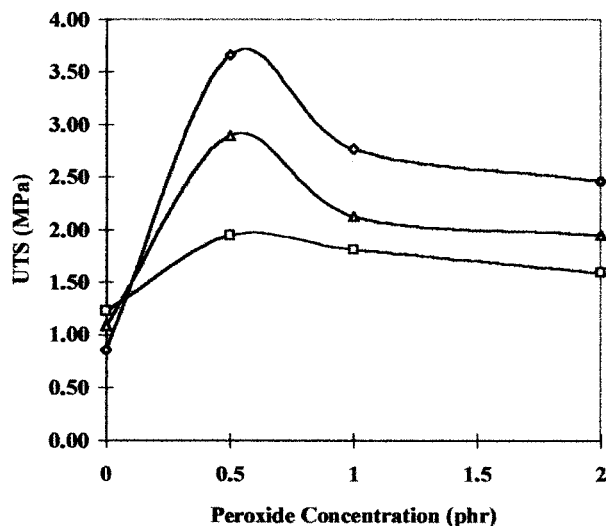
Peroxide systems

It is known that plasticised PVC can be crosslinked by peroxides in the presence of TMPTMA.¹⁴ Rapid polymerisation of TMPTMA is followed by grafting on to the PVC backbone, and subsequent crosslinking. Gel content measurements for rigid PVC samples containing 5 and 15 phr TMPTMA are shown in Fig. 7. Intermediate values are obtained when 10 phr TMPTMA is used. The actual values include TBLS and silica, so are plotted as 'remaining swollen sample'.

Ideally, gel contents should be reasonably low after milling and to a large extent this has been achieved. Gel contents increase on pressing, and with TMPTMA content, as would be anticipated; 0.5% peroxide proves to be sufficient to obtain maximum gel content for a given system.

Data obtained for elevated temperature properties of rigid PVC samples are shown in Fig. 8. In the absence of peroxide, an increased TMPTMA concentration yields a polymer with lower UTS and elongation at break (note that the TMPTMA includes 50 wt-% of silica).

When peroxide is present, crosslinking occurs and the network formed restricts the deformation of the material resulting in a higher UTS and lower elongation at break. The highest TMPTMA concentration produces the most marked changes in these properties, since a more compact structure has been obtained. Optimum properties are achieved with 0.5 phr peroxide. At higher peroxide levels UTS decreases, an effect probably attributable to degradation of the PVC. Properties also depended on pressing time and temperature. Data for samples containing 0.5 phr of peroxide, and 5 and 10 phr TMPTMA are shown in Fig. 9. As the processing

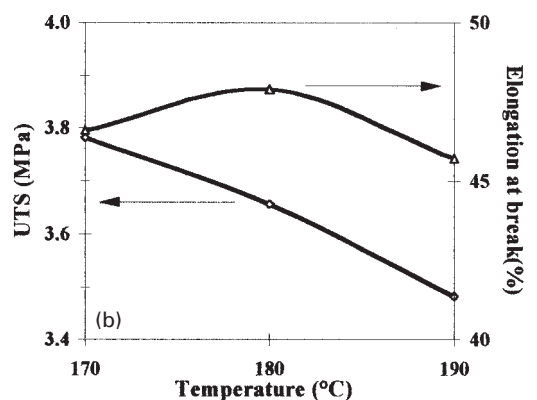
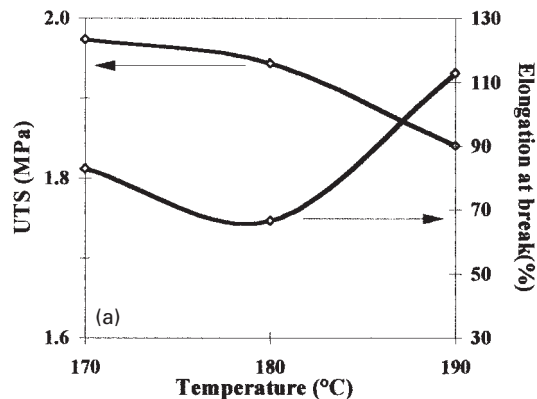


8 Tensile properties at 130°C of samples containing (□) 5, (△) 10, and (◇) 15 phr

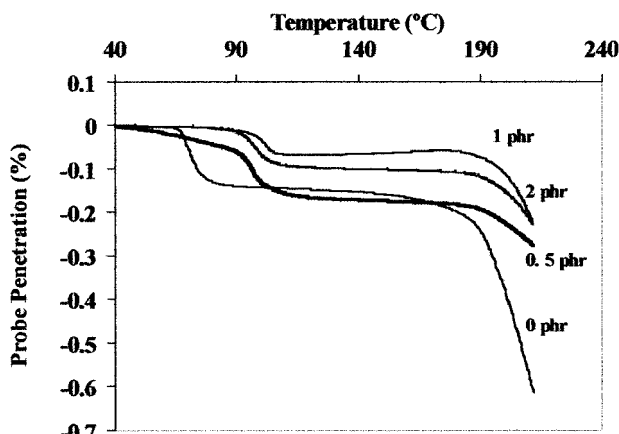
temperature increases, the tensile properties are improved because further fusion of PVC can be achieved, but at the same time the peroxide tends to degrade the PVC. Figure 9 suggests that 180°C is the optimum processing temperature; above this temperature degradation of PVC occurs.

The TMA traces for compounds containing peroxide are shown in Fig. 10. In contrast with Fig. 5, these traces show clearly that peroxide crosslinking actually increases the glass transition temperature of the PVC. Again the effect of increasing peroxide concentration is not important. Thermal stability tests on the peroxide crosslinked samples showed that TMPTMA seems to improve thermal stability slightly, whereas peroxide, as expected, clearly accelerates the degradation of PVC. The crosslinked compounds generally have poor thermal stability. However, once peroxide is present, there is not a marked difference in the thermal stability of blends with the different peroxide concentrations used.

Infrared spectroscopy was used to monitor the presence of unreacted TMPTMA, via the residual unsaturation observed as an absorbance at 1640 cm^{-1} . In samples without peroxide, unreacted TMPTMA is readily detectable as expected. When



9 Tensile properties at 130°C for a 5 and b 10 phr TMPTMA samples pressed at various temperatures

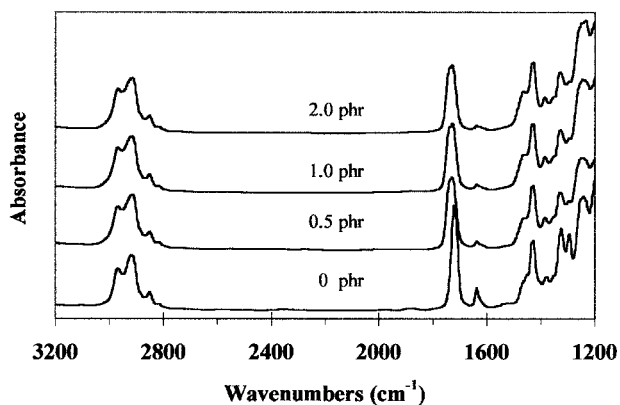


10 TMA curves of samples containing various peroxide concentrations and 5 phr TMPTMA

peroxide concentration increases to 0.5 phr, the area of the band at 1640 cm^{-1} decreases rapidly, indicating that TMPTMA monomer is disappearing. With 5 phr of TMPTMA no unsaturation can be observed in samples with peroxide present. When 10 phr of TMPTMA was used, the peroxide concentration had to be increased to 1 phr in order to consume all the monomer. Finally, with 15 phr of TMPTMA, the monomer is still present in the presence of 2 phr of peroxide (Fig. 11).

CONCLUSIONS

It has been shown that rigid poly(vinyl chloride) can be crosslinked using both aminosilane and peroxide



11 Infrared spectra of samples with 15 phr TMPTMA and various peroxide concentrations

crosslinking systems. The optimum level of bis(γ -trimethoxysilylpropyl)amine is approximately 2 phr. With the silane, premature crosslinking during processing is reduced by the use of tribasic lead sulphate as stabiliser. However, the thermal stability of the tin maleate stabilised compounds is generally better. Better elevated temperature properties are obtained with the peroxide system, and in this case the glass transition temperature of the poly(vinyl chloride) is also increased. Significant property improvement is achieved with only 0.5 phr peroxide, and it is possible that this amount could be reduced further. The thermal stability of these compounds still needs to be improved. In order to do this, the trimethylolpropane trimethacrylate-amorphous silica blend content

should be as low as possible. Lead stabilised compounds were used in the present work; stability may be improved by alternative stabilisers, such as tin maleate.

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