

Interpenetrating Polymer Network of Poly(vinyl Chloride) and Polymethacrylates*

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SYNOPSIS

A curable polymeric composite was prepared using equal weights of poly(vinyl chloride) (PVC), reactive polyfunctional methacrylate monomers, and inorganic fillers. Peroxide initiated in situ polymerization of the polyfunctional methacrylate monomers in the PVC matrix produced an interpenetrating polymer network (IPN) structure. The polymerization kinetics and the degree of polymerization were investigated using differential scanning calorimetry (DSC), carbon-13 nuclear magnetic resonance (^{13}C NMR), and solvent extraction. All measurements indicated that during polymerization, the PVC is either cross-linked by or grafted onto the methacrylate three-dimensional network structure. The rheological properties of the composite were measured before curing using a Rheometrics mechanical spectrometer and found to exhibit mainly viscous behavior and diminished elasticity. The PVC and the methacrylate monomers form a two-phase system when mixed at room temperature. However, when heated to 100°C the PVC dissolves in the monomers and forms a one-phase optically clear blend with a single glass transition temperature. In the presence of peroxide, the one-phase blend is stable and does not separate out upon cooling and storing at room temperature.

INTRODUCTION

A polymeric composite that can be cured to form strong, hard, sandable, and paintable materials has many uses, such as for repairing discontinuities in surfaces or for making models. This article describes one approach for making such a composite using a blend of a polymer, a compatible reactive monomer, and fillers. Before curing, the liquid reactive monomer functions as a plasticizer for the polymer and enhances the flow characteristics of the blend. After curing the polymer acts as an impact modifier and decreases the brittleness of the three-dimensional network formed by the reactive monomer.

EXPERIMENTAL

Materials

For developing the polymeric composite we used a polymer, several reactive monomers, heat stabilizers, inorganic fillers, peroxide crosslinking agents, waxes, and oils. A major consideration for choosing the ingredients is that they should be nontoxic and safe to handle. The polymer used is poly(vinyl chloride) (PVC) obtained from the B. F. Goodrich Chemical Group. Three powder grades of the polymers were tried, all having small average particle sizes ($0.56\text{--}1.6\ \mu\text{m}$) and low gel temperatures ($66\text{--}96^\circ\text{C}$).

The reactive monomers used are trimethylolpropane trimethacrylate (TMPT), glycidyl methacrylate (GMA), tetraethylene-glycol dimethacrylate (TEGDMA), and 1,3-butylene glycol dimethacrylate (BEGDMA), obtained from the Sartomer Company. The reactive monomers are all liquids and act as plasticizers for PVC. Other plasticizers tried in-

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cluded ethylene glycol (Eastman Chemical Product), diundecyl phthalate (Monsanto), dioctyl sebacate (DOS, Harwick Chemical), and dioctyl phthalate (B. F. Goodrich Chemical Group).

Two PVC heat stabilizers were used, namely barium stearate and a blend of organic compounds of barium, cadmium, and phosphate (Synthetic Products Company). Barium stearate also acts as a lubricant and a filler. Other fillers incorporated into the formulation are Hydrate clay (Georgia Kaolin) and Mistron Vapor talc (Cyprus Mines). The agents used for crosslinking the polymer and polymerizing the reactive monomers included dicumyl peroxide (DiCup 40 KE, Hercules) and *t*-butyl peroctoate (Pennwalt).

Mixing Procedures

The formulations were mixed using either a two-roll mill or a Banbury internal mixer. In both cases, a uniform material was obtained.

Procedures for Characterizing the Polymeric Composite

The main requirements for the polymeric composite is that it should flow under hand-applied pressure to form a continuous film without providing any resistance to the flow. In other words, it should be void of elasticity. Subsequent layers should adhere well to the original layer. Upon curing, it should not shrink and should have a hard, sandable, repairable, and paintable surface. We used these guidelines for the development of the optimized composite formulations.

To characterize the developed formulations, we used quantitative techniques. These included a Rheometrics mechanical spectrometer to characterize the flow properties of the uncured clay at two temperatures, room temperature (25°C) and 50°C; three strain amplitudes of 1, 10, and 100%, and a strain rate or frequency range of 0.1–100 rad/s. The sample cavity consisted of two parallel disks.

The morphology of the material was also investigated using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and cloud point measurements. DSC measurements using the DuPont 990 thermal analysis system were conducted to investigate the behavior of the glass transition of the polymer–reactive monomer blends before and after curing.

DMA measurements were conducted using the

DuPont 1090 thermal analysis system with the 982 dynamic mechanical analyzer. The DMA spectra were measured at temperatures of –100 to +200°C and at a heating rate of 5°C/min. The cloud point measurements were conducted using a home-made apparatus (Fig. 1) consisting of a melting point apparatus (The Nalge Co.) equipped with a heating plate and a light source and an Optical Associates model 202-LED photometer. The cloud point was determined by measuring the light transmittance through the sample placed between two circular microscope cover glass (22 mm diameter by 2 mm thick) and heated at a controlled rate from room temperature to 100°C. The sample is then cooled to room temperature. A recorder was used to monitor the temperature and the light transmittance during the heating and cooling cycles.

The kinetics of the cure was investigated using a DuPont 990 thermal analyzer to conduct DSC measurements and a Monsanto rotating disk rheometer to measure torque versus time of curing at temperatures ranging between 93 and 121°C.

The chemistry of the cure was investigated by extraction measurements using tetrahydrofuran (THF) as a solvent. Both cured TMPT and cured PVC/TMPT blends were extracted to determine the amount of unreacted TMPT monomer and to find out if PVC is grafted to the TMPT during curing. Two extraction procedures were carried out for each of the samples of the cured PVC–reactive monomer blends. Prior to extraction the samples were pulverized in a mortar using dry ice when necessary. In the first procedure a Soxhlet apparatus was used for the extraction. The extracted samples were placed in small platinum mesh thimbles. The extraction was carried out for 72 h using THF as the solvent. The second procedure was a room temperature soaking of the pulverized samples for a period of 28 days in THF.

The chemistry of the cure was also investigated using carbon-13 nuclear magnetic resonance (¹³C NMR) spectroscopy. The uncured resins were dissolved in deuteriochloroform and the NMR spectra were obtained at 67.9 MHz using an IBM, WP200SY instrument. Solid-state NMR spectra of the cured samples were also obtained. Two types of experiments were conducted: a Bloch decay experiment (also called direct polarization experiment) with low-power decoupling and magic angle spinning was used to determine the “mobile” carbons, while a cross-polarization experiment with high-power decoupling and magic angle spinning was used to examine the rigid carbon structure.

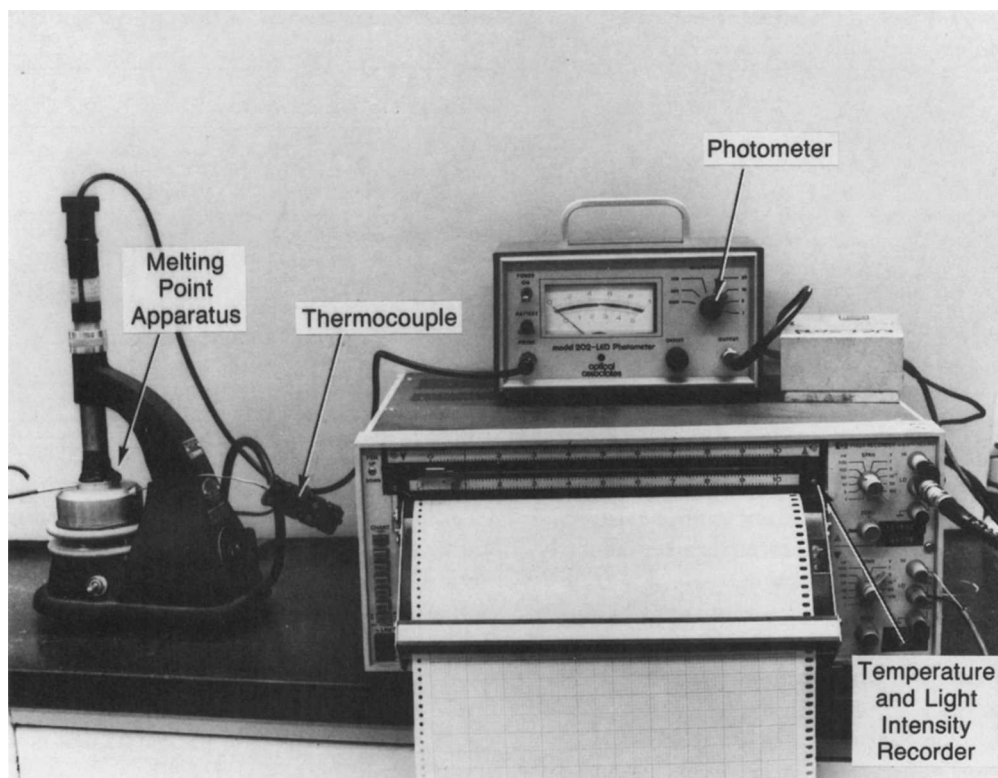


Figure 1 Cloud point apparatus.

RESULTS AND DISCUSSION

Rheological Properties

Since the intended applications of the polymeric material are for making models and repairing surface discontinuities, the essential properties of the material are the right rheology and viscoelasticity. The material is expected to flow in a continuous manner under hand pressure to form a thin film. It should provide minimum resistance to the applied force and should not spring back or shrink after spreading. In other words, it should have pronounced viscous character and minimum elasticity. The Rheometrics mechanical spectrometer was used to evaluate the rheological properties of the polymeric material. Measurements of the complex viscosity, the storage modulus, the loss modulus, and $\tan \delta$ (loss modulus/storage modulus) of the formulations were conducted at shear rates or frequencies of 0.1–100 rad/s, strain amplitudes of 1, 10, and 100%, and temperatures of 50 and 25°C (room temperature).

The complex viscosity data for the material is summarized in Table I. The material exhibits marked non-Newtonian behavior, i.e., appreciable shear thinning as evidenced by the drop in viscosity with increased shear rate. Shear thinning has been

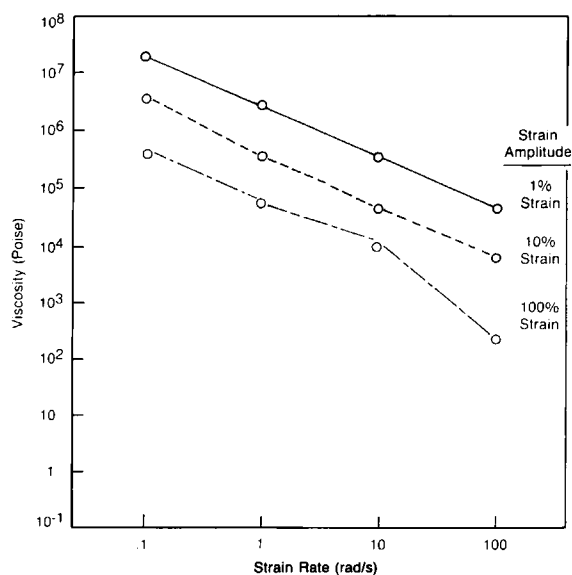
observed for other unfilled and filled polymeric systems such as polymeric coatings,¹ polymer composites,² and elastomers.³ At low filler loadings the melt viscosity of filled polymers is similar to unfilled polymers. However, at moderate and high filler loadings yield behavior is observed.³ For these systems the viscosity is very high at low shear rates and decreases rapidly with increasing shear rate.⁴⁻⁷ Examination of the viscosity data in Figures 2 and 3 show that yield is noticeable for this material at high strain amplitudes (10 and 100%) as evidenced by the concave shape of the curve at strain rates of 0.1–10 rad/s. The yield had been attributed to the breakdown of particle–particle interactions in agglomerates of highly filled low-viscosity polymer matrices.^{5,8-10} The viscosity of the material exhibits a large drop at strain rate of 100 rad/s and strain amplitude of 100%. This is probably due to discontinuities (tears) in the samples at the high strain amplitudes.

The effect of increasing the temperature from 25 to 50°C is shown in Table I and Figure 3. As expected, a sharp drop in viscosity is observed at the high temperature. Otherwise, the shapes of the viscosity–strain rate curves are similar for both temperatures.

Table I Complex Viscosity Values for the Polymeric Material Measured at Different Strain Rates, Strain Amplitudes, and Temperatures

Temperature (°C)	Strain Amplitude (%)	Viscosity at Various Strain Rates, $\times 10^{-4}$ (P)			
		0.1 rad/s	1.0 rad/s	10 rad/s	100 rad/s
25	1	2074	282.5	32.02	4.031
25	10	397.8	35.60	4.098	0.6297
25	100	58.26	6.090	1.215	0.02253
50	1	701.5	75.42	8.098	1.023
50	10	109.4	10.28	1.299	0.2330
50	100	22.07	1.842	0.4174	0.06909

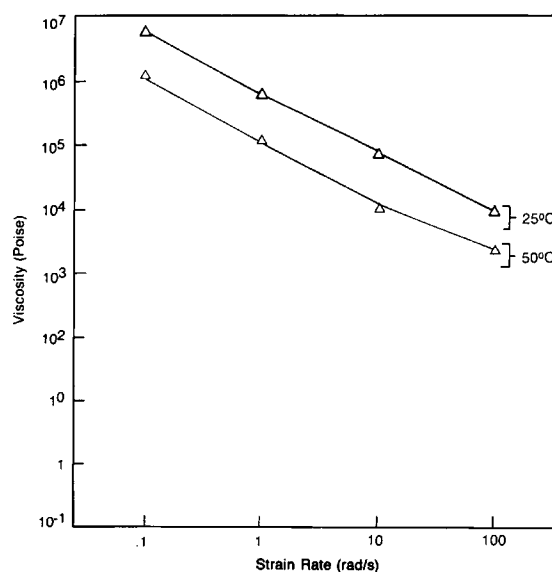
The storage modulus, loss modulus, and $\tan \delta$ values of the material at different temperatures, strain amplitudes, and strain rates are shown in Figures 4 and 5 and Table II, respectively. Figure 4 shows that the storage or elastic modulus of the material is only slightly increased by an increase in strain rate especially at low strain amplitude (1%). The increase in the elastic modulus with strain rate is more noticeable at higher strain amplitudes of 10 and 100%. A very sharp drop in elastic modulus is observed by increased temperature and more so by increased strain amplitude. The variations in the loss modulus with strain rate, strain amplitude, and temperature (Fig. 5) are similar to those observed in the case of the storage modulus except that the effects are smaller in magnitude. For this reason higher values of $\tan \delta$ are generally observed at

**Figure 2** Complex viscosity versus strain rate of the polymeric material measured at room temperature and three strain amplitudes.

higher temperatures and higher strain amplitudes (Table II). Small decreases in $\tan \delta$ values are generally observed with the increase in strain rates. Strain amplitudes seem to have a greater influence on the values of $\tan \delta$ than the other two variables. The material exhibits high viscous flow and low elasticity especially under the conditions of low strain rates, high strain levels, and high temperature (50°C). These are the expected use conditions of the material.

Kinetics of Curing of the Polymeric Modeling Material

The kinetics of the cure, or polymerization, of the material was investigated by DSC measurements and rheometer torque measurements. The chemistry

**Figure 3** Complex viscosity versus strain rate of the polymeric material at a strain amplitude of 10% and temperatures of 25 and 50°C.

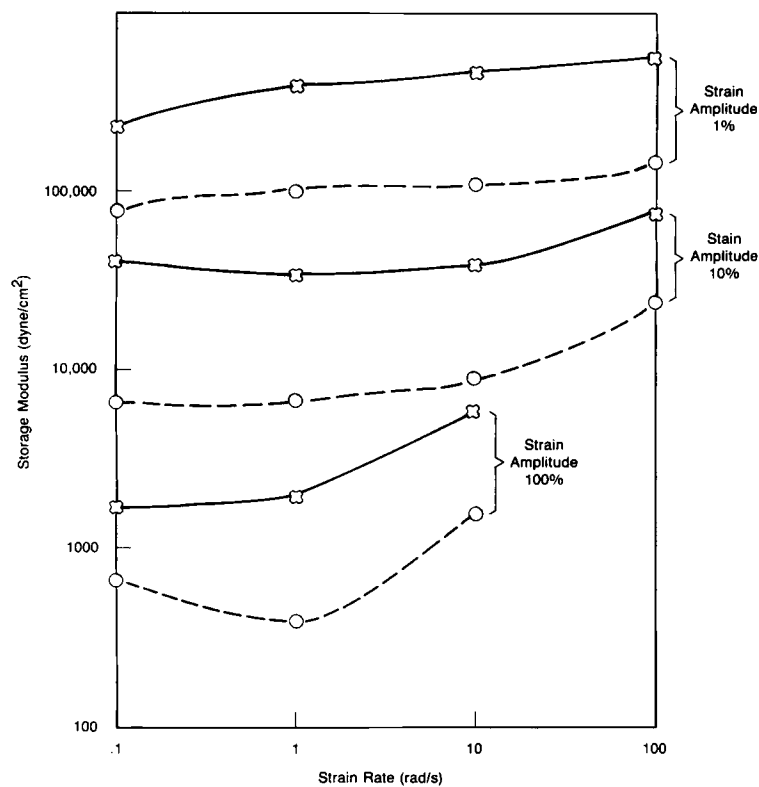


Figure 4 Storage modulus of the polymeric material versus strain rate. Measurements conducted at 25°C (—) and 50°C (---) and three strain amplitudes of 1, 10, and 100%.

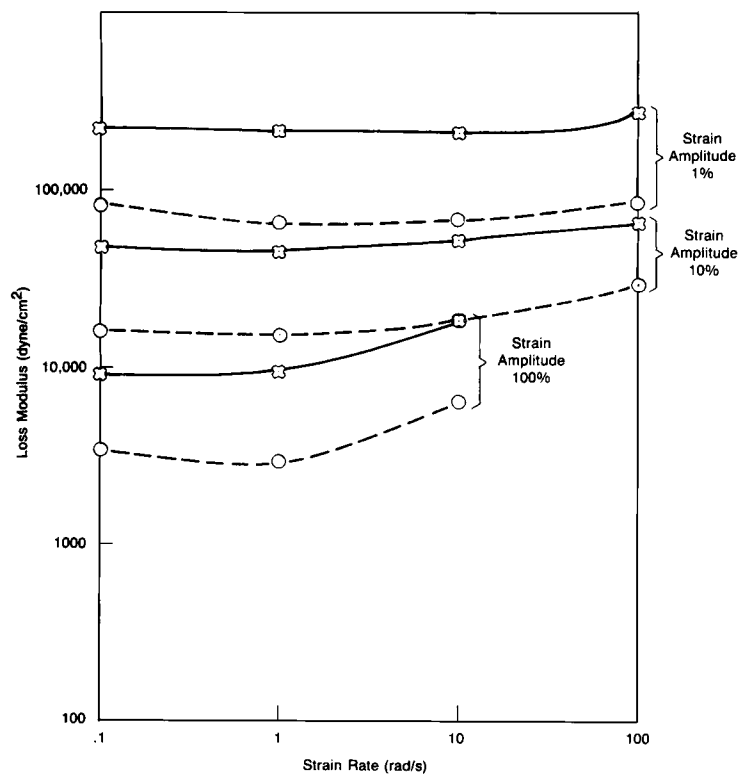


Figure 5 Loss modulus of the polymeric material versus strain rate. Measurements conducted at 25°C (—) and 50°C (---) and three strain amplitudes of 1, 10, and 100%.

Table II Tan δ Values for the Polymeric Material Measured at Different Strain Rates, Strain Amplitudes, and Temperatures

Temperature (°C)	Strain Amplitude (%)	Tan δ at Various Strain Rates			
		0.1 rad/s	1.0 rad/s	10 rad/s	100 rad/s
25	1	0.9435	0.5249	0.4465	0.4578
25	10	1.184	1.350	1.320	0.8990
25	100	6.501	4.801	2.884	1.634
50	1	1.042	0.6633	0.6259	0.5880
50	10	2.601	2.409	2.072	1.196
50	100	5.292	7.615	4.082	2.144

of the cure was investigated by ^{13}C NMR and by extraction experiments. Most of the measurements were conducted using simplified material formulations shown in Table III. However, in some cases fully formulated materials containing fillers were investigated.

The DSC curves of a blend containing TMPT and TEGDMA reactive monomers (system 2, Table III) are shown in Figure 6. The DSC of the blend prior to any oven curing is shown in Figure 6, curve *a*. Two exothermic peaks are observed in this figure at 118 and 169°C attributable to curing or polymerization of the two monomers. The total energy under the peaks is 117.81 cal/g of methacrylate monomer.

The DSC of the same formulation, but after it had been cured in an oven for 30 min at 100°C is shown in Figure 6, curve *b*. Only one exothermic peak is observed at 173°C, attributed to further curing of the sample. The total energy underneath the exothermic peak is 50 cal/g of methacrylate. A parallel DSC investigation was also conducted for the samples containing PVC in addition to the methacrylate monomers (system 1, Table III). Significant changes are observed in the DSC curves due to the presence of PVC (Fig. 7). The exothermic peaks for

the polymerization of TMPT and TEGDMA shifted to lower temperatures of 105 and 130°C (Fig. 7, curve *a*), indicating that the presence of PVC encourages the cure or polymerization of methacrylate monomers. The total energy under the exothermic peaks is 100 cal/g of methacrylate. The results of parallel experiments conducted on the preceding material after it has been oven cured at 100°C for 30 min is shown in Figure 7, curve *b*. Two exothermic peaks are observed: a small peak at 135°C and a larger peak at 204°C, perhaps indicating additional curing of the methacrylates and/or a reaction of the PVC with the methacrylate. The total energy under the exothermic peaks is 33 cal/g of methacrylate.

The curing of three fully formulated polymeric materials was also investigated. One of the formulations contained only one methacrylate, TMPT, while the other two contained both TMPT and TEGDMA. Also, one of the formulations contained talc as a filler while the other two contained both talc and clay. The DSC curves of all three formulations were very similar. All exhibited one polymerization peak at 112°C (see, e.g., Fig. 8). The calculated heat of polymerization per gram of methacrylate for all systems was around 98 cal/g, which

Table III Simplified Formulations of the Polymeric Material

Ingredients	System 1	System 2
Polyvinylchloride	49.3	—
Trimethylolpropane trimethacrylate	39.1	81.0
Tetraethyleneglycol dimethacrylate	5.7	11.9
Stabilizer	1.1	2.3
<i>t</i> -Butyl peroxoate	4.8	4.8

Table IV Flexural Properties of a Fully Formulated Polymeric Material after Curing at Different Temperatures and Time Intervals

Cure Temperature (°C)	Cure Time (min)	Flexural Modulus (MPa)	Flexural Strength (MPa)
93	5	1589	9.67
100	5	1874	11.0
100	30	2261	13.8
110	5	2021	11.9
120	5	2223	12.4

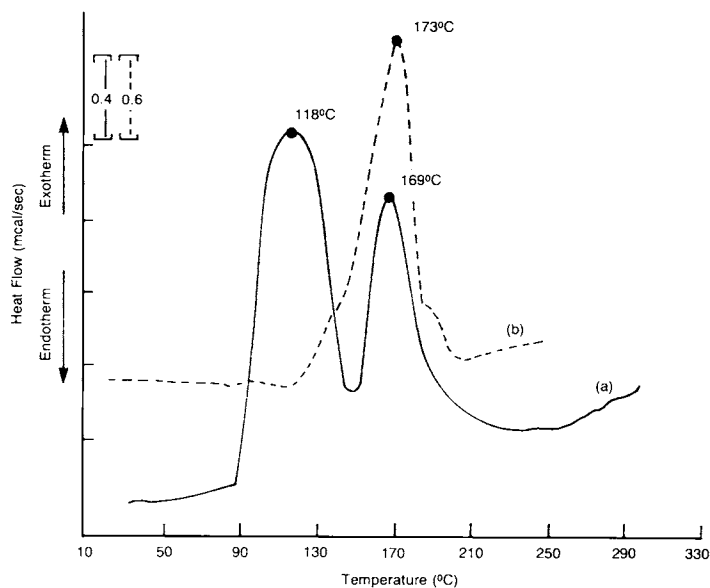


Figure 6 DSC curves of methacrylate monomers and peroxide (system 2, Table III) showing polymerization (curing) peaks: (a) sample (5.4 mg) before curing; (b) sample (11.1 mg) after curing in an oven for 30 min at 100°C.

is similar to heat of polymerization values measured for the simple blends (Figs. 6 and 7). For all formulations an endothermic peak was measured at about 140°C (Fig. 8). This was identified as the melting peak of barium stearate that is present in all the formulations. For the cured samples, only the barium stearate melting peak is observed (Fig. 8, curve *b*).

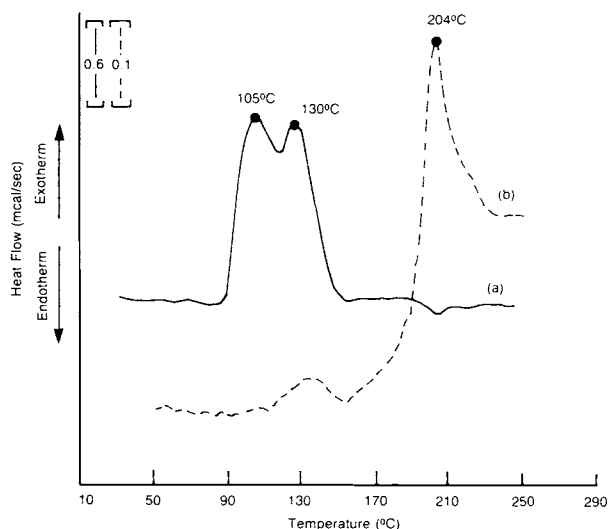


Figure 7 DSC curves of PVC-methacrylate monomer blends and peroxide (system 1, Table III) showing polymerization (curing) peaks: (a) sample (6.9 mg) before curing; (b) sample (3.8 mg) after curing in an oven for 30 min at 100°C.

The curing of the polymeric material was also investigated using a Monsanto rheometer. Figure 9 shows the cure curves at 93 and 121°C of a typical fully formulated material. At 93°C a broad curing peak with two maxima is observed after 6–11 min of heating, while at 121°C only one peak is observed after 4.5 min. The torque due to curing is considerably higher in the case of the 121°C curing as compared to the lower temperature curing.

Chemistry of Curing

The chemistry of the curing of the PVC-TMPT system was investigated using NMR spectroscopy and extraction experiments. Carbon-13 NMR experiments were conducted for uncured and cured samples of the formulations shown in Table III. The uncured samples were dissolved in deuteriochloroform and, their ¹³C NMR spectra were obtained at 67.9 MHz. The spectral assignments were made for the functional groups of TMPT and TEGDMA, as shown in Figure 10. Since PVC is only slightly soluble in the deuteriochloroform at room temperature, very small peaks at 46 and 56 ppm are observed, which are indicative of this polymer.

After curing, system 1 and 2 materials yield insoluble solids. These samples were analyzed by ¹³C magic angle spinning solid-state NMR. The spectra were generated using cross-polarization and high-power decoupling (CPPA) to examine functional groups that are held rigidly in the matrix. Spectra

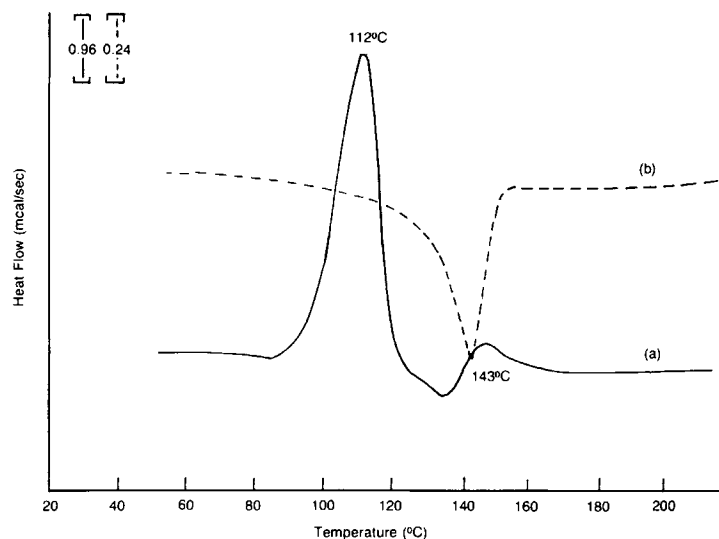


Figure 8 DSC of the polymeric material, containing filler, showing polymerization peaks: (a) sample (20.9 mg) before curing; (b) sample (10.8 mg) after curing in an oven for 30 min at 100°C.

were also generated by simple Bloch decays and low-power decoupling (also called direct polarization experiments) to determine the mobile functional groups. The cross-polarized spectra of system 1 and 2 samples are shown in Figures 11 and 12, respectively. Assignments of the peaks to reacted and unreacted functional groups are shown in Figure 12.

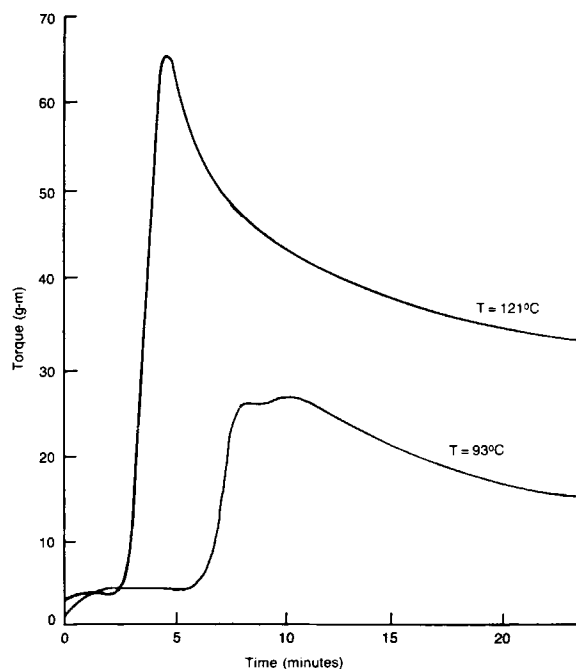


Figure 9 Torque versus time during curing of the polymeric material in a Monsanto rheometer.

From this data it was calculated that 83% of the methacrylate groups are reacted in system 1 and only 77% in system 2. Hence, the presence of PVC in system 1 drives the polymerization of the methacrylate more toward completion. The results are in agreement with the data from DSC discussed earlier. It is interesting to note that the unreacted methacrylate groups measured by this technique are actually held rigidly inside the matrix and not in the form of mobile monomer. The Bloch decay spectra that are sensitive to mobile groups are shown in Figures 13 and 14. The system 1 spectrum (Fig. 13) shows no mobile groups, whereas the system 2 spectrum (Fig. 14) shows some mobile acrylate groups at 136 and 146 ppm, attributable to the unreacted monomer. The bands at 20 ppm are attributed to the methyl group of the methacrylate portion of the molecules (see band assignments in Fig. 10).

The presence of unreacted monomer in system 2 was further evidenced by extraction experiments. Two types of procedures were used for the extraction of pulverized system 1 and 2 samples. The first was a Soxhlet extraction conducted for 72 h on samples placed in platinum baskets. The second was room temperature immersion of the samples for 28 days. In both cases THF was used as the solvent. System 1 samples, which contain PVC, lost 2.86% by weight in the Soxhlet extraction and 5.9% by the immersion experiment. The system 2 samples, which do not contain PVC, lost 10.5% by weight under Soxhlet extraction and 10.9% by the immersion experiment. The extractables were identified by NMR as meth-

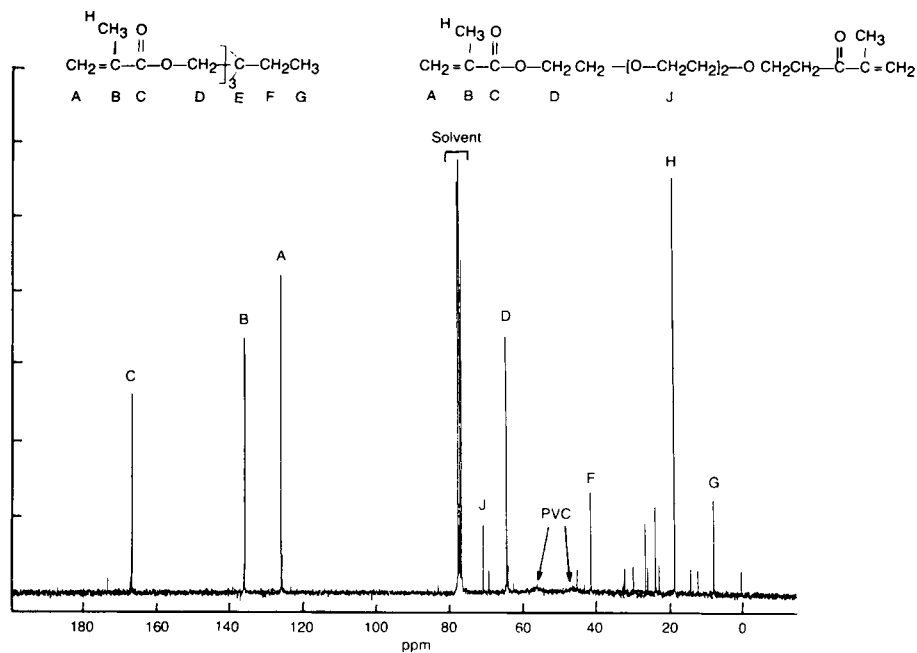


Figure 10 A carbon-13 inverse gated decoupled spectrum of system 1, before curing, dissolved in deuteriochloroform. (The PVC is not soluble in this solvent and thus only two small and broad resonances are observed.)

acrylate monomers. This experiment hence confirms that the methacrylates are polymerized to a higher degree in the presence of PVC and that the PVC polymer is rendered insoluble by the methacrylate monomers. It is either crosslinked by the TMPT and TEGDMA or it is grafted onto the three-dimensional network structure formed by the meth-

acrylates. In either case the polymerized system fits the description of a true interpenetrating network polymer defined as two polymers crosslinked or synthesized in the presence of each other, and both components are thermoset or crosslinked.¹¹ The crosslinking of PVC by TMPT during electron beam irradiation had been observed previously.¹²⁻¹⁵

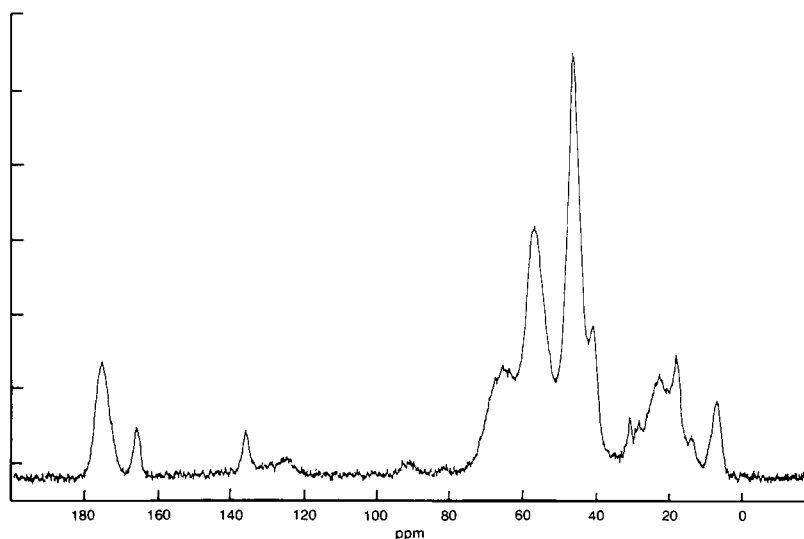


Figure 11 A cross-polarized spectrum for the solid system 1 sample after curing in an oven for 30 min at 100°C.

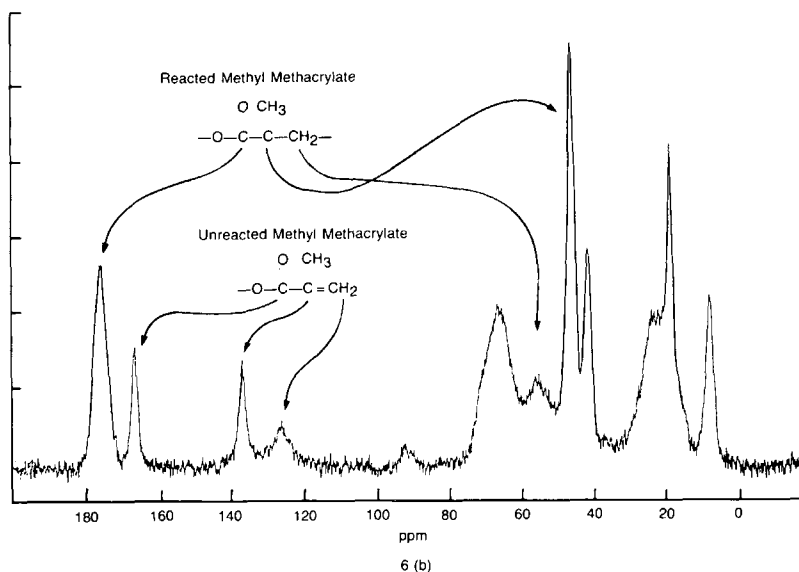


Figure 12 A cross-polarized spectrum for the solid system 2 sample after curing in an oven for 30 min at 100°C.

Morphology

In this study DSC, DMA, and light transmittance measurements were used to investigate the morphology of the PVC-reactive plasticizer blends before and after curing to determine whether the blends form a one-phase or a two-phase system. Glass transition temperatures of the blends were measured using DSC and compared to those of the pure components. The DSC curves in the temperature range of -80 to 120°C are shown in Figure 15. Curve A shows the DSC for PVC. The glass tran-

sition temperature for this polymer is 77°C . Curve B represents the DSC of the pure TMPT. The glass transition temperature of this reactive plasticizer is -59°C . When TMPT is mixed with 14.6% (w/w) TEGDMA, the glass transition shifts to -62°C (curve C). The large exotherm observed in this curve at temperatures above 60°C is due to polymerization of the monomers in the presence of peroxide, which had been added to the blend. When PVC is mixed with the reactive monomers (TMPT and TEGDMA) at room temperature, two T_g 's are observed, one at -60°C for the reactive monomers and

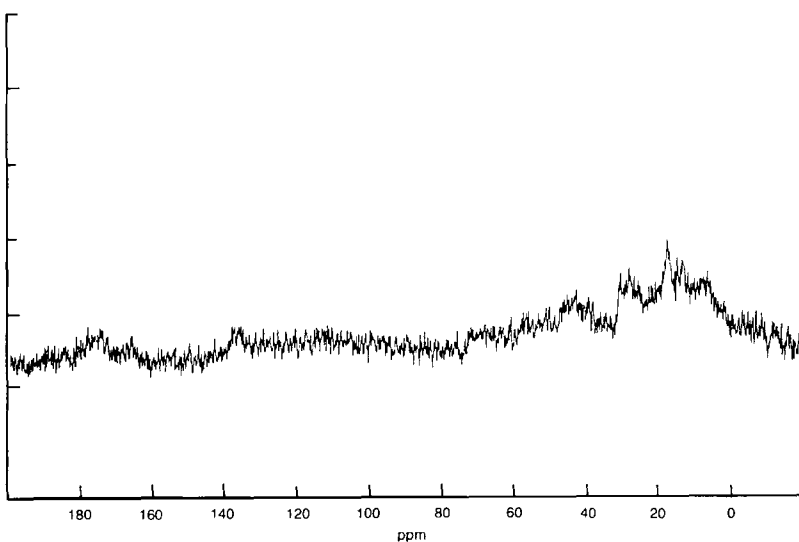


Figure 13 A Bloch decay spectrum for the solid system 1 sample after curing in an oven for 30 min.

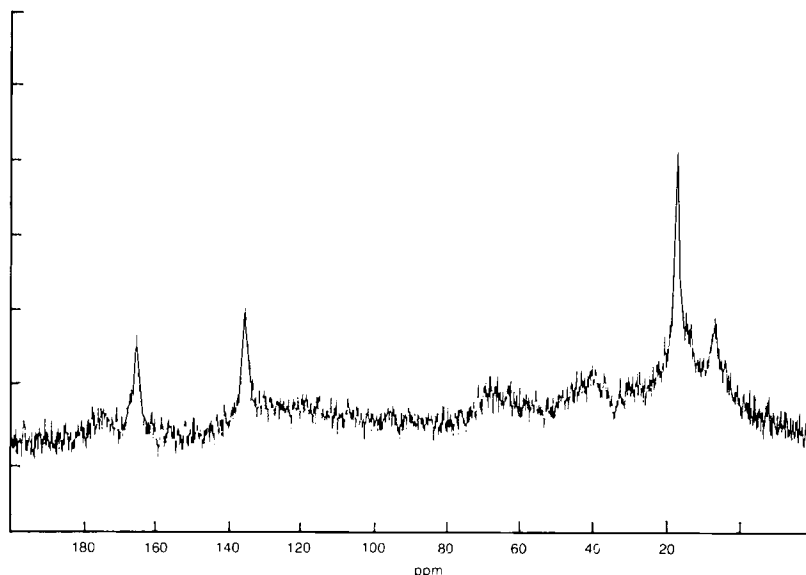


Figure 14 A Bloch decay spectrum for the solid system 2 sample after curing in an oven for 30 min at 100°C.

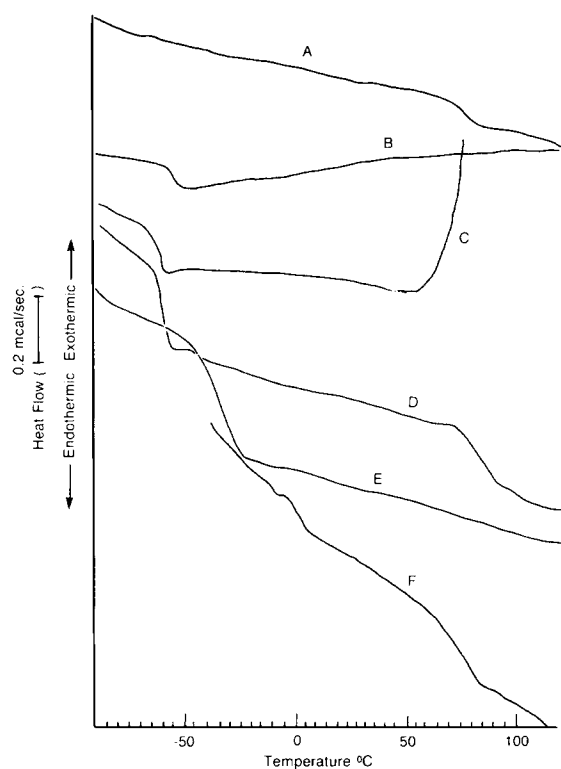


Figure 15 DSC curves showing the glass transition (T_g) temperatures of (A) polyvinyl chloride (PVC); (B) trimethylolpropane trimethacrylate (TMPT); (C) TMPT and tetraethylene-glycol dimethacrylate (TEGDMA); (D) PVC and TMPT and TEGDMA before heating; and (E) PVC and TMPT and TEGDMA after heating once to 120°C and then cooling in the DSC cell. (F) PVC and TMPT and TEGDMA after heating in an oven for 30 min at 100°C.

the other one at 77°C for the PVC (curve *D*). However, when this PVC-methacrylate blend is heated in the DSC cell to temperatures of 100°C or higher and then cooled, the material changes from cloudy to clear. The DSC curve of the clear material shows only one T_g at -35°C, as seen in curve *E*. Hence, the PVC-methacrylate reactive plasticizer system forms a two-phase blend at room temperature. However, after heating to 100°C the PVC polymer dissolves in the methacrylate monomers to form a one-phase system with a single T_g . The low T_g value (-35°C) of this blend indicates the presence of an appreciable concentration of the TMPT plasticizing monomer. When the blend is heated for 30 min at 100°C in an oven, the T_g shifts upscale to 79.5°C, as shown in curve *F* (Fig. 15). The anomalous behavior observed in curve *F* at 0°C is attributed to the melting of ice from atmospheric moisture. This is always observed if the DSC samples are not carefully dried.

The morphology of the PVC-methacrylate blend (system 1, Table III), after curing in a compression mold for 1 h at 100°C, was also investigated using DMA. The DMA data is shown in Figure 16. Tensile storage modulus, loss modulus, and $\tan \delta$ values of the material are plotted against temperature. The presence of one break in the storage modulus curve and one peak in the $\tan \delta$ and loss modulus curves confirms that the material forms a one-phase system after curing and hence has only one glass transition temperature.

The effect of curing on the morphology of the blend was investigated by measuring light trans-

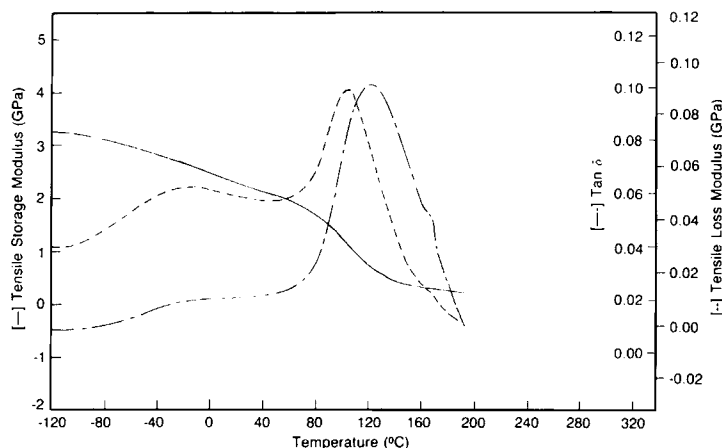


Figure 16 Dynamic mechanical spectra of the cured PVC-methacrylate blend (system 1) showing tensile storage modulus, tensile loss modulus, and $\tan \delta$ at temperatures of -120 to 200°C .

mittance through the material before, during, and after heating in the apparatus described earlier in the experimental section (Fig. 1). Two blend formulations were investigated, namely, the one shown under system 1 in Table III and a similar formulation but without the peroxide. The formulations are mixed and allowed to set overnight to equilibrate. They form cloudy viscous liquids. A sample of this liquid sandwiched between two microscope cover glasses and placed in the apparatus exhibits a very low light transmittance of 10%. As the sample is heated, it stays opaque until it reaches a temperature of about 70°C . The transmittance then increases with temperature in an S-shaped behavior, shown in Figures 17 and 18. For the peroxide-containing

formulation (Fig. 17), the light transmittance reaches 90% at 100°C and increases only slightly upon further heating. During cooling from about 100°C to room temperature the sample remains essentially clear, indicating that a one-phase interpenetrating network of PVC and methacrylate polymers has been formed. Heating at different rates showed that the transition from opaque to clear is temperature dependent rather than time dependent. The transition is always observed when the temperature reaches 70°C in spite of the fact that the time it took to reach this temperature varied between 3.5 and 22 min. For the formulation without the peroxide (Fig. 18), light transmittance reaches only about 30% at 100°C and increases to 40% upon

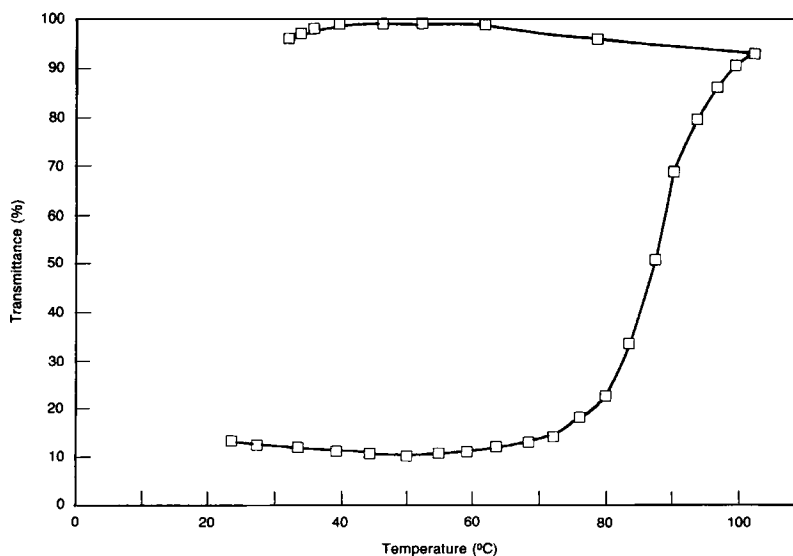


Figure 17 Light transmittance through PVC-methacrylate blend containing peroxide, heated from room temperature to 100°C and then cooled to room temperature.

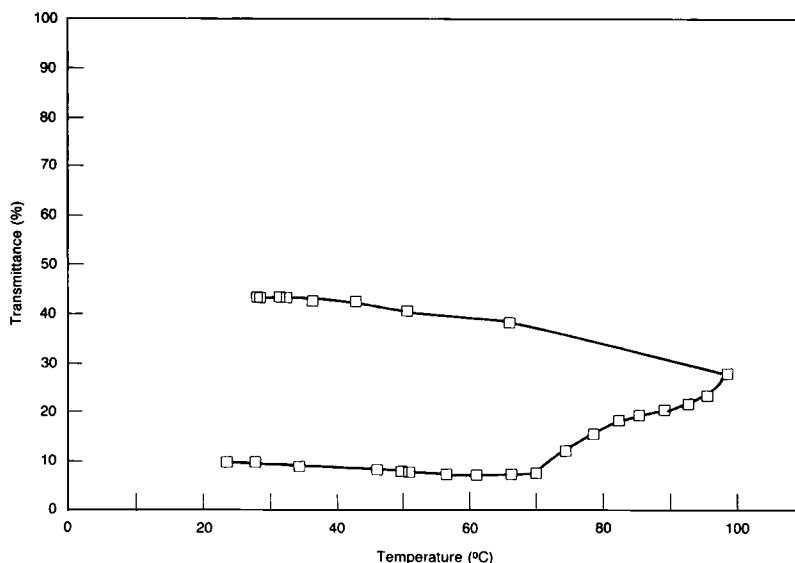


Figure 18 Light transmittance through a PVC-methacrylate blend, not containing peroxide, heated from room temperature to 100°C and then cooled to room temperature.

cooling to room temperature. It is apparent, then, that the polymerization of the monomer and/or interactions between the PVC and the polymethacrylate help compatibilize the blend to form a one-phase interpenetrating polymer network. Cross-linking and enhanced grafting had been found to hinder the phase separation and enhance miscibility of polymer interpenetrating networks of polyacrylate and polystyrene.^{16,17} The morphology of this composition is what makes the product behave successfully in application. Before curing, the methacrylate monomer plasticizes the PVC and imparts the right flow properties. After curing and the formation of the interpenetrating network, the PVC plasticized by residual unreacted monomer imparts strength and toughness to the blend (Table IV).

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REFERENCES

1. H. H. Kuo, *J. Coating Tech.*, **57**(727), 57 (1985).
2. D. R. Sain, A. V. Shenoy, and V. M. Nadkarn, *Polym. Composites*, **7**(4), 193 (1986).
3. J. L. White, in *Science and Technology of Rubber*, F. R. Eirich, Ed., Academic Press, New York, 1978, pp. 223-289.
4. B. L. Lee and J. L. White, *Trans. Soc. Rheol.*, **19**, 481 (1975).
5. N. Minigawa and J. L. White, *J. Appl. Polym. Sci.*, **20**, 501 (1976).
6. S. Onogi, T. Matsumoto, and Y. Warashina, *Trans. Soc. Rheol.*, **17**, 175 (1973).
7. N. V. Zakhaveno, F. S. Tolstukhina, and G. M. Bartener, *Rubb. Chem. Tech.*, **35**, 326 (1962).
8. F. M. Chapman and T. S. Lee, *SPE J.*, **26**, 37 (1970).
9. V. M. Lobe and J. L. White, *Polym. Eng. Sci.*, **19**, 617 (1979).
10. H. Tanaka and J. L. White, *Polym. Eng. Sci.*, **20**, 949 (1980).
11. T. J. Hsu and L. J. Lee, *J. Appl. Polym. Sci.*, **33**, 793 (1987).
12. T. N. Bowmer, D. D. Davis, T. K. Kwei, and W. I. Vroom, *J. Appl. Polym. Sci.*, **26**, 3669 (1981).
13. T. N. Bowmer, M. Y. Hellman, and W. I. Vroom, *J. Appl. Polym. Sci.*, **28**, 2083 (1983).
14. T. N. Bowmer, W. I. Vroom, and M. Y. Hellman, *J. Appl. Polym. Sci.*, **28**, 2553 (1983).
15. T. N. Bowmer and W. I. Vroom, *J. Appl. Polym. Sci.*, **28**, 3527 (1983).
16. M. S. Silverstein and M. Narkis, *Polym. Eng. Sci.*, **29**, 824 (1989).
17. L. H. Sperling and J. M. Widmaier, *Polym. Eng. Sci.*, **23**, 693 (1983).

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