

Vitrification and Curing Studies of a Photopolymerizable Semi-Interpenetrating Polymer Network. II

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Synopsis

The photopolymerizable semi-interpenetrating polymer network-II being studied consists of a linear copolyester, a crosslinked network of multifunctional acrylate monomers and a very efficient photoinitiator system. Using both Raman and dynamic mechanical spectroscopy (DMS), it has been determined that the polymerizing network vitrifies after a very low level of crosslinking is attained. This results in a sample that has a T_g which is substantially lower than would be expected from knowledge of the values of T_g for the individual components of the blend. The extent of reaction and, therefore, the glass transition temperature can be increased by heating the sample during photopolymerization. In addition, the glass transition temperature of the network can be increased by thermally curing the sample after photopolymerization. It has been found that once the network has been fully cured, the glass transition temperature is much higher than would be predicted. This has been interpreted in terms of synergistic effects; conceivably, the acrylates form a tight matrix around the linear copolyester and effectively reduce the molecular mobility of the components. The results also show that the acrylates and the copolyester are not inherently miscible. However, if a sufficient concentration of acrylates is present, it is possible to prevent the copolyester from phase separating. Dynamic mechanical spectroscopy data do indicate that these semi-interpenetrating polymer networks-II (semi-IPN-II) samples are somewhat heterogeneous; however, there does not seem to be any gross phase separation. Transmission electron microscopy (TEM) results show that the most fully cured sample has domains on the order of 50–250 Å associated with the copolyester phase.

INTRODUCTION

Polymer blending is often used to obtain properties which cannot be achieved from the use of homopolymers or copolymers alone. The properties of a blend are determined by the glass transition temperature (T_g), modulus, and other properties of the individual components of the blend, and by the miscibility of these components. A miscible polymer blend will exhibit a single glass transition temperature or loss peak between the T_g 's of the components with a sharpness of the transition which is similar to that of the individual components. The glass transition temperature of a miscible blend can be represented to a first approximation by the Fox equation, where w_1 and w_2 are the weight fractions and T_{g1} and T_{g2} are the glass transition temperatures of the individual components^{1,2}:

$$T_g = w_1 T_{g1} + w_2 T_{g2} \quad (1)$$

When no specific interactions between polymers are involved, in most cases, the formation of a miscible blend is rare because for two polymers to be miscible on a molecular level their free energy of mixing should be negative. Taking the simple Flory-Huggins approach, one can express the free energy in terms of a combinatorial entropy of mixing (which, unlike with small molecules, will be small) and a enthalpy of mixing which for weakly interacting systems (van der Waals or London dispersion forces) will be positive.³

A relatively new approach to improve the homogeneity of polymer blends through reducing the domain sizes of the phases is based on the formation of interpenetrating polymer networks (IPNs).⁴⁻¹¹ In general, an IPN is formed from a combination of two polymers in which at least one of the polymers has been synthesized and/or crosslinked in the presence of the other.⁴ Researchers have shown that by controlling the level of crosslinking in each of the polymers present, it is possible to exert control over the morphology of the blend.^{12,13}

A number of different types of IPNs have been distinguished by Sperling.⁵ As an example, a simultaneous IPN is one in which both monomers and their associated crosslinking agents are dissolved in a common solvent. The monomers are then polymerized simultaneously usually by two different mechanisms (i.e., free radical and condensation). A sequential semi-interpenetrating network (semi-IPN) is formed if only one of the two components is crosslinked. If the first polymer is crosslinked and the second polymer is linear and is polymerized in its presence, the blend formed is called a semi-interpenetrating network of the first kind (semi-IPN-I). Conversely, if the first polymer is linear and the second is crosslinked in its presence, the blend is designated as a semi-IPN of the second kind (semi-IPN-II).

Although IPNs have been extensively studied in the last decade, only a few papers have explored the use of semi-IPN-II.¹³⁻¹⁶ In this study a high T_g linear polymer which can provide flexibility and processability was blended with photopolymerizable crosslinkable acrylate monomers. In order to understand how to control the phase morphology and thus the physical properties of this multicomponent system, knowledge of the vitrification and thermal curing of this system is of great importance. With the use of both infrared and Raman spectroscopy, it has been demonstrated that the addition of the linear copolyester retards the initial photopolymerization process. However, it is possible to subsequently cure the network thermally at elevated temperatures in order to increase the extent of conversion of the reaction. Dynamic mechanical spectroscopy (DMS) has been used to investigate the viscoelastic properties of these crosslinked systems since the technique is sensitive enough to measure the changes occurring as the network goes from the glassy to the rubbery state. This technique also provides information about the miscibility of the components in the blend.²

After the sample is completely cured, the glass transition temperature of the network (measured by DMS) is higher than would be predicted by the Fox equation. Both infrared spectroscopy and extraction studies were used to determine whether the high glass transition temperature was the result of degradation or cross reactions between the acrylates and the copolyester. The results of both studies suggest that a minimum of degradation and cross reactions occur. In addition, these studies have shown that the copolyester and the acrylates are not inherently miscible and that it is necessary to have suf-

ficient amounts of the multifunctional acrylates present in order to prevent phase separation.

EXPERIMENTAL

Sample Preparation

The negative resist is a blend of a linear polymeric binder, poly(4,4'-(2-norbornylidene)bisphenylene acetate-co-terephthalate (60 : 40)), and a cross-linked network of monomer I [tris (2-acryloylethyl) 1,2,4-benzene tricarboxylate] and monomer II [1,4-bis(2-acryloyloxyethoxy) cyclohexane]. These acrylates are photopolymerized, using a very efficient initiator system which consists of an activator (ethyl *p*-dimethylamino benzoate) and a sensitizer [3-(4-cyanobenzoyl)-5-di-*n*-propoxycoumarin] in the presence of the copolyester.^{17,18} In principle, the binder is nonactive and should remain chemically unchanged during this process. The molecular structures and composition of the formulations are presented in Figure 1 and Table I, respectively.

The samples were coated from a 25 to 40 wt % solids solution in dichloromethane onto a copper support at a 12 mil wet thickness. The coatings were dried first for 5 min at 20°C, then for 10 min at 55°C, and finally for 10 min at 90°C in an air oven. Once the samples were dried, a thin Mylar cover sheet was laminated to the surface. The samples were irradiated with a Colight Model M218 U. V. source. The exposed strips were held at room temperature for 15 min, separated from the Mylar cover sheet, and subsequently developed for 2 min with clean 1,1,1-trichloroethane. Post-curing of the strips was accomplished by placing the sample in either an air or vacuum oven for various periods of time.

Dynamic Mechanical Spectroscopy (DMS)

Dynamic mechanical measurements were performed using either a Rheovibron DDV-II dynamic tensile tester (Toyo Measuring Instruments, Ltd., Japan) automated by IMASS, Inc. or a Polymer Laboratories dynamic mechanical analyzer (DMTA). The Rheovibron data were taken between -150 and 250°C at a driving frequency of 11 Hz. The heating rate during the experiments was approximately 1.5°C/minute. The DMTA data were normally obtained between 0 and 300°C at a frequency of 10 Hz. The experimental data are presented as the dynamic tensile storage modulus (E') and loss modulus (E'') plotted as a function of temperature. The temperature which corresponds to the maximum in the α peak, given by the log E'' curve, $T(E''\text{max})$, is defined as the glass transition temperature.

Extraction and Size Exclusion Chromatography (SEC)

Extractions were performed on several samples using dichloromethane as the extracting solvent. Dichloromethane is a good solvent for all of the components in the sample. Three different extraction procedures were used and are described in Table II. After the extraction step, all solutions were filtered by gravity and both the gel fraction (insolubles) and the soluble fraction were collected and dried under vacuum for 2 h at ambient temperature and at 70°C

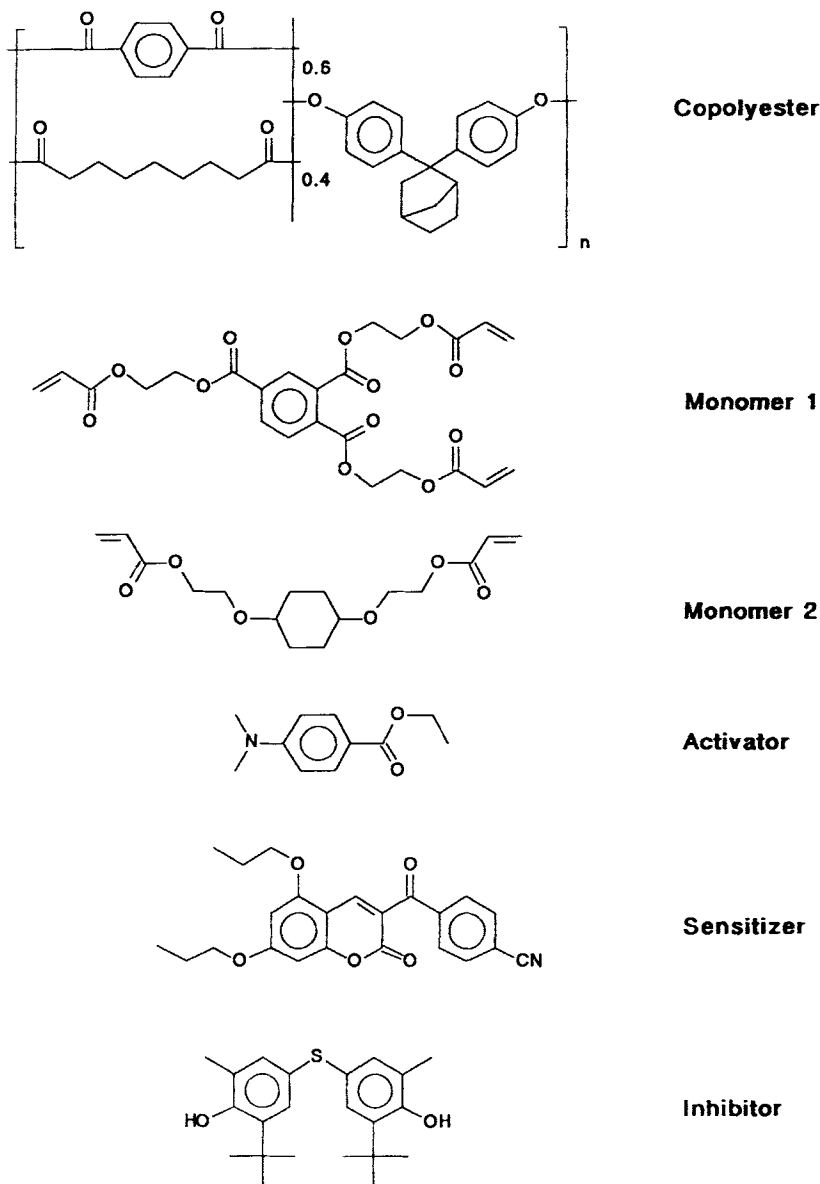


Fig. 1. Components in the formulation.

for more than 60 h. At this point constant weight was obtained and no extra weight loss was observed when a portion of the sample was dried under vacuum at 200°C for 1 h. At this elevated temperature, however, some of the soluble fraction became insoluble in dichloromethane, probably as a result of additional crosslinking of the residual acrylate monomers. Size exclusion chromatography was performed in THF on the soluble fractions using a high performance chromatograph with μ -styragel columns. The columns were calibrated with monodisperse polystyrene standards and the results are given as polystyrene equivalent molecular weights.

TABLE I
Compositions of the Formulations (wt %)

Component	Formula 1	Formula 2	Formula 3	Formula 4	Formula 5
Copolyester	53.0	50.0	64.0	64.0	34.0
Monomer 1	22.5	24.0	0.0	34.0	64.0
Monomer 2	22.5	24.0	34.0	0.0	0.0
Activator	1.5	1.5	1.5	1.5	1.5
Sensitizer	0.25	0.25	0.25	0.25	0.25
Inhibitor	0.25	0.25	0.25	0.25	0.25

Infrared and Raman Spectroscopy

Transmission infrared spectra were obtained from approximately 1.8-mil-thick films with either a Nicolet 5ZDX FTIR using 64 scans at 4 cm^{-1} resolution or with an IBM 44 FTIR with an attached microscope using 500 scans at 4 cm^{-1} resolution. Raman spectra were obtained from approximately 1.8-mil-thick films coated on copper using conventional 90° scattering with 50 mW, 647 nm^1 excitation from a SP165 Kr ion laser. Raman scattering was analyzed with a SPEX 1877 triple spectrograph and detected with an EG&G Par 11420 Reticon multichannel detector and OMA II. Resolution was 4 cm^{-1} .

RESULTS AND DISCUSSION

Vitrification Studies Using Raman Spectroscopy

In order to determine the effect of the copolyester on the vitrification of the photopolymerization reaction, the di- and trifunctional acrylates were photopolymerized with the use of a very efficient initiator system, and the extent of the reaction was determined with the use of Raman spectroscopy. Raman spectroscopy was used to monitor the conversion of the acrylate double bonds by measuring the peak height of the carbon-carbon double bond stretching vibration at ca. 1636 cm^{-1} . The spectral intensities are normalized by dividing the intensity of the 1636 cm^{-1} band of the irradiated sample by the intensity of a reference nonirradiated sample. As shown in Figure 2, as the irradiation time

TABLE II
Extraction Methods

Method #	Procedure
I	Extract the sample in dichloromethane at ambient temperature with gentle stirring for > 73 h (wt solids < 0.5%)
II	Extract the sample in dichloromethane using a Soxhlet extractor (the temperature inside the sample flask was 39°C) for > 50 h (wt solids < 0.2%)
III	Extract the sample in dichloromethane with constant stirring for 17 h at ambient temperature, followed by 7 h in boiling solvent (39°C), followed by 18 h at ambient temperature (wt solids < 0.2%)

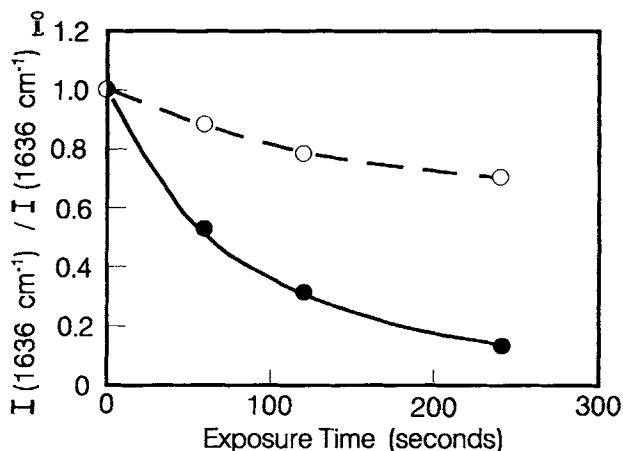


Fig. 2. Photopolymerization efficiency as monitored by Raman spectroscopy: (●) copolymerized di- and trifunctional acrylates; (○) formula 1 photopolymerized.

increases, the conversion of the acrylate double bonds also increases. After just a 60 second exposure greater than 50 percent of the acrylate double bonds react, and after 240 seconds the reaction conversion increases to over 80 percent. Upon further exposure there is no increase in the reaction conversion. This is expected based on the work of Kloosterboer et al.,¹⁹⁻²² where they have showed that when difunctional acrylates are photopolymerized, the photopolymerization reaction does not go to completion due to vitrification.

The copolyester was then mixed with the acrylates (formula 1) and coated onto a copper support. After similar exposure times, a substantial reduction in the conversion of the acrylate double bonds, compared to the formulation without the copolyester, is observed. In fact, after a 60-s irradiation just 10% of the acrylates react, and after 240 s only 25% of the acrylate double bonds are consumed.

The difference between the extent of reaction in the formulation containing the copolyester and the formulation with the acrylates alone can be explained in terms of the vitrification of the material. It is known that with free radical polymerizations the extent of reaction is strongly dependent on the mobility of the reactive functional groups. In fact, studies have shown that if methyl methacrylate is polymerized at a temperature above the T_g of the homopolymer, it is possible to nearly completely react all of the acrylate double bonds.^{23,24}

The T_g of the unpolymerized acrylates without the polyester is -50°C . Therefore, it is possible to achieve a very large degree of conversion of the acrylates before the glass transition temperature of the reaction mixture reaches 35°C (this is the temperature at which the samples are irradiated). Conversely, the T_g measured by dynamic mechanical analysis of the as-coated formulation containing the copolyester prior to polymerization of the acrylates was 5.5°C . The copolyester ($T_g = 203^\circ\text{C}$) increased the glass transition temperature of the overall formulation, and, in this case, the difference in temperature between the isothermal cure temperature and the T_g of the as-coated film is only 29.5°C . Under these conditions only a limited increase in acrylate molecular weight can occur before the sample vitrifies. The irradiated films all exhibit glass tran-

sition temperatures near 50°C in agreement with predictions that the T_g of the UV-cured reaction mixture should be within 20–40°C of the reaction temperature.²⁰

Heating during Exposure

Since it is known that the extent of reaction is strongly dependent on the mobility of the reactive species, it is possible to heat the sample during exposure in order to increase the extent of reaction. The samples were placed on a heated platen whose temperature was controlled to $\pm 1^\circ\text{C}$. Figure 3 illustrates that, as the temperature at which the sample is maintained during exposure increases, there is a corresponding increase in the glass transition temperature of the coating (as measured by DMTA). In addition, with the use of infrared spectroscopy it is possible to measure the consumption of double bonds. In order to account for thickness and composition variations from sample to sample, it is necessary to normalize the intensity of the 1636 cm^{-1} acrylate double bond absorbance band by dividing it by the intensity of the 1578 cm^{-1} absorbance band which is attributed to a copolyester ring mode. Therefore, as shown in Figure 3, the increase in the glass transition temperature with increased exposure temperature is directly correlated with the increased consumption of acrylate double bonds.

The glass transition temperature of each resulting coating is only slightly higher than the irradiation temperature because the propagation rate of the reacting species becomes diffusion-limited, and the free radicals become trapped in the glassy matrix upon vitrification. Several papers have reported that these trapped radicals have relatively long lifetimes at room temperature. In fact, when certain dimethacrylates (such as 1,6-hexanediol diacrylate and bis(2-hydroxyethyl acrylate bisphenol-A dimethacrylate) are photopolymerized, the lifetime of the free radicals exceeds 5 months.^{25,26} The incomplete conversion of the double bonds suggests that we have not yet attained the ultimate properties that the network could exhibit. The unreacted double bonds could be present as monomers which would act to plasticize the system or as pendant

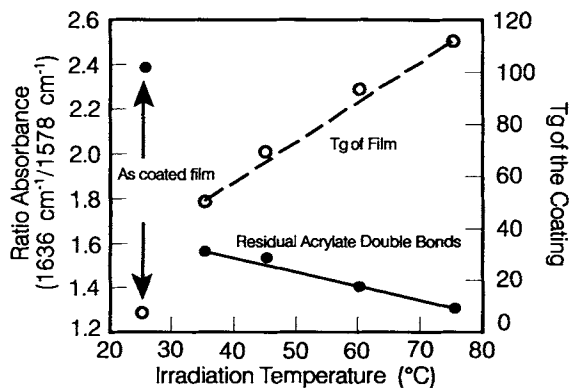


Fig. 3. The effect of photoirradiation at elevated temperature.

groups on the network which would influence the mechanical properties of the network in a different way.

In order to obtain a higher glass transition temperature and a correspondingly higher conversion of the acrylate double bonds, it is necessary to thermally cure the network at higher temperatures. The mechanism by which the thermal cure proceeds is not well understood. However, electron spin resonance (ESR) studies have shown that free radicals are trapped in the vitrified glass and are present in the sample after the photopolymerization. Although it was not possible to identify the nature of the free radicals, at least two different species were present. One of the free radicals decayed within the first 48 h after irradiation whereas the other decayed very slowly over a period of weeks. The fact that either of these radicals was able to initiate the secondary thermal reaction was not established but certainly exists as a possibility.

Dynamic Mechanical Properties and Curing

The dynamic mechanical properties of the linear copolyester, the copolymerized di- and trifunctional acrylates, the coating of the copolyester with the monomeric di- and trifunctional acrylates prior to irradiation, and the semi-IPN-II formed after photopolymerization at 35°C are presented in Figure 4. All of the loss modulus curves show the presence of a major damping peak, the α peak,²⁷ associated with the glass transition temperature T_g . This peak is also accompanied by a substantial drop in the storage component of the tensile modulus E' . As seen from the data in Figure 4, the T_g of the copolyester occurs at about 203°C. The transition from the glassy to the rubbery state for the crosslinked monomers occurs over a wide temperature region centered at 80°C. For the linear copolyester at temperatures above T_g , the linear copolyester chains are able to freely translate past each other, and the material enters into a viscous flow regime whereas the copolymerized acrylates exhibit only a drop in the storage modulus of a decade. The extended rubbery plateau of the co-

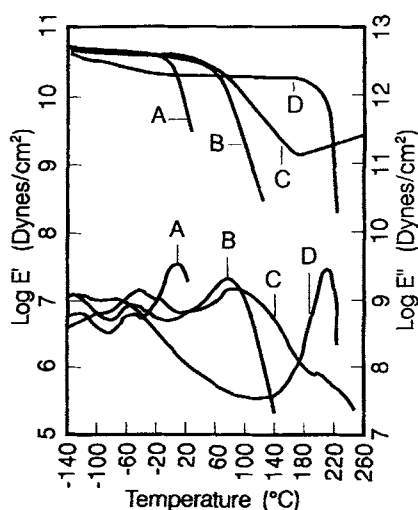


Fig. 4. Storage and loss modulus vs. temperature for: (A) unirradiated formula 1; (B) formula 1 irradiated for 2 min at 35°C; (C) the photopolymerized di- and trifunctional acrylates; (D) the copolyester.

polymerized acrylates is essentially constant out to the decomposition temperature of the acrylates ($> 300^{\circ}\text{C}$).

The glass transition temperature for the semi-IPN-II, which should ideally fall in the temperature region between the linear copolyester and the copolymerized acrylates,⁴ is seen to occur at a much lower temperature than expected. The transition is very broad and the maximum in the $\log E''$ peak occurs at 55°C . This lowering of the T_g is the result of a very low degree of crosslinking caused by a substantial decrease in the rate of reaction as the T_g of the system approaches the temperature at which the sample was prepared. It is expected that both the presence of the unreacted monomers and short chains of reacted monomers which are attached to the network at only one end (the other end being unreacted) would contribute to a lowering of the T_g . The T_g observed by DMS for the nonirradiated sample is about 5.5°C .

This low T_g , combined with the presence of potentially reactive free radical sites, will lead to a continuously changing sample. This idea was substantiated when a coating (formula 1) was aged for a short period of time. The DMS results indicated that the glass transition temperature obtained initially upon its receipt, after exposure, was centered around 40°C . After the sample had been stored in a drawer for 5 months, the T_g had increased to 60°C . An increase in the T_g of sample (as initially received) can also be obtained by annealing the sample at 80°C . After 10 min the T_g had increased to 55°C ; however, after prolonged annealing, the T_g increased only to 65°C .

Even though the T_g did not shift very much with prolonged heating at 80°C , the crosslinking reaction can be driven further by curing the samples at higher temperatures. After a number of experiments were done to ensure that none of the major components was degrading, it was decided to post-cure the samples at 200°C . Both the storage and loss moduli are shown in Figure 5 for a series of samples which were post-cured at 200°C for various periods of time. Clearly, as the post-curing time increased first from 0 to 5 min and then subsequently up to 120 min, there is a corresponding increase in the glass transition tem-

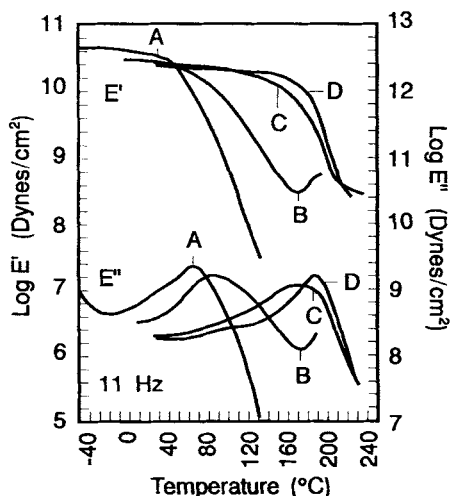


Fig. 5. Storage and loss modulus vs. temperature for formula 1. Samples were first irradiated for 120 s at 35°C and subsequently post-baked at 200°C for: (A) 0 min; (B) 5 min; (C) 30 min; (D) 120 min.

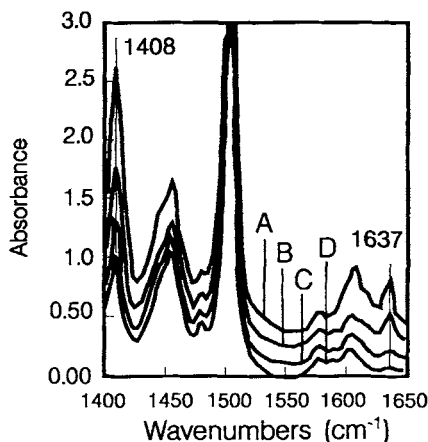


Fig. 6. FTIR spectra of formula 1 after UV cure and baking for (A) 0 min, (B) 5 min, (C) 20 min, and (D) 120 min at 200°C.

perature. After a 30-min bake the glass transition temperature is ca. 160°C, and after 120 min the glass transition temperature of the semi-IPN-II is 189°C.

The extent of reaction was followed using infrared spectroscopy. As shown in Figure 6, there is a corresponding decrease in both the intensity of the 1636–1637 cm^{-1} absorbance band and the 1408 cm^{-1} band, which are both due to the acrylate carbon-carbon double bonds, as the post-curing time increases. These results show that it is necessary to post-cure the network for 120 min at 200°C in order to reduce the residual double bond content to below 5%.

The values of $T(E''_{\text{max}})$ are summarized in Figure 7(a) for various annealing times at a few different temperatures (the lines connecting the points are only there to illustrate the trends and have no physical meaning). Several samples were annealed for 2 h or more at the specified temperatures; the values obtained for $T(E''_{\text{max}})$ as a function of anneal temperature are shown in Figure 7(b). These results show that the crosslinking reaction proceeds rapidly at first; then as the T_g of the system approaches the temperature of annealing, the mobility

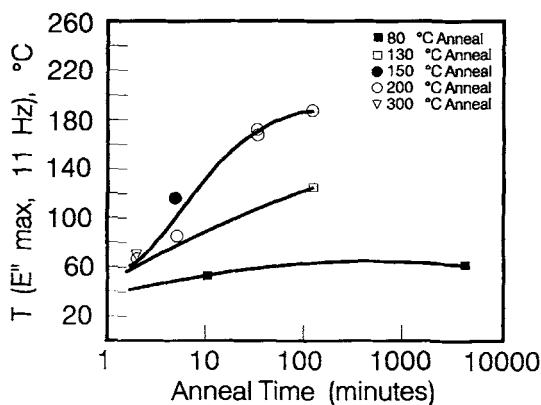


Fig. 7(a). Dependence of $T(E''_{\text{max}})$ on annealing time.

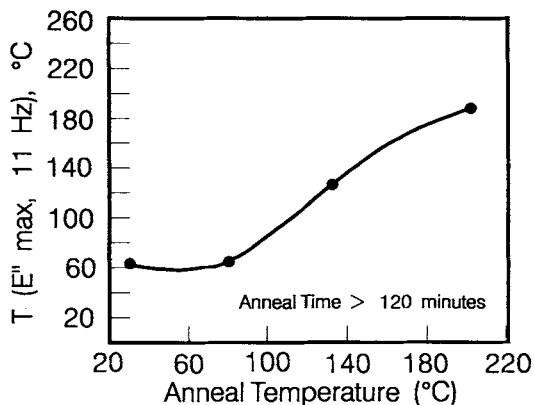


Fig. 7(b). Dependence of $T(E''\text{max})$ on annealing temperature.

in the system slows down and so does the reaction. Thus, the maximum value of T_g that can be obtained will be close to that of the annealing temperature.

The magnitude of the rubbery plateau modulus of a crosslinked system at temperatures higher than T_g is proportional to the crosslink density of the network. Values obtained for the plateau modulus are relatively constant for all of these semi-IPNs-II ($\log E' = 8.0\text{--}8.5 \text{ dyn/cm}^2$).

A broadening of the glass transition is often an indication of the presence of phase separation; a single broad transition is characteristic of extensive but incomplete mixing of the blend components on a molecular level.⁴ The loss peaks shown in Figure 5 are quite broad and indicate that most of the IPN samples are somewhat heterogeneous. The fact that two distinct peaks are not observed suggests that the extent of phase separation is not great and there do not exist large domains which consist predominantly of one component. Irradiation of the samples at different temperatures or annealing at elevated temperatures does not greatly affect the breadth of the loss peak with the exception of the samples which were annealed at 200°C for a prolonged period of time. In the latter case a narrowing of the loss peak is particularly apparent for the sample baked for 120 min at 200°C. This suggests that the sample is becoming more homogeneous. Also, the T_g obtained for this sample is much higher than expected (189°C) from a mixture of the copolyester and of the crosslinked monomers [see eq. (1)]. The size of the copolyester phase domains present in this sample was determined by TEM to be on the order of 50–250 Å.

Infrared and Extraction Studies

Since the glass transition temperature of the network is much higher than is expected, it is possible that cross reactions between the acrylates and the copolyester are occurring at the high cure temperatures. This possibility is not substantiated by either infrared spectroscopy or extraction studies. Figure 8 shows a plot of the normalized intensity of the acrylate carbon-carbon double bond, for both formulas (1) and (5), vs. the glass transition temperature as measured by DMTA (frequency at 10 Hz) for samples heated for various times

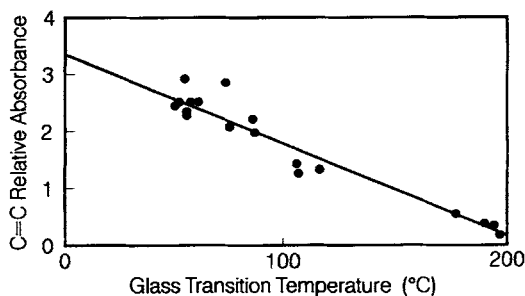


Fig. 8. The extent of cure of samples (formulas 1 and 5) which were irradiated for 120 s at 35°C and post-baked for various times at 200°C. The consumption of double bonds was measured by IR spectroscopy at 1636 cm^{-1} and the glass transition temperature was measured by DMTA.

at 200°C. The results clearly show that, as the acrylate double bonds are consumed, there is a corresponding linear increase in the glass transition temperature of the network. If all the acrylate double bonds are consumed after 30 min (which is not the case), and if a continual increase in the T_g is observed with further heating, this would argue for cross reactions or chemical changes of the components.

In addition, extraction studies were done on a number of the semi-IPN-II samples in order to determine whether the linear copolyester could still be extracted even after extended baking times. The extraction procedures are described in the experimental section and the results are given in Table III. Essentially the same amount of soluble material was extracted using methods I and II whereas method III succeeded in extracting about 10 wt % more soluble material from the films; this latter method involved vigorous boiling of the solvent during the extraction. When subjected to methods I or II, most of the samples completely lost their physical integrity. Samples which were irradiated and cured at 130°C for 2 h or at 200°C for 30 min broke up into smaller pieces, but retained some of their film form. Only the sample that was irradiated and subsequently baked for 120 min at 200°C remained intact. When subjected to

TABLE III
The Effect of Irradiation and Curing for Formula 1 Samples^a

Sample no.	Extraction method	Gel fraction (wt %)	Soluble fraction (wt %)	PS equivalent ^b		Thermal treatment
				$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	
A	I	58	42	46.4	23.9	None
B	I	77	23	39.1	21.1	30 min, 200°C
B	II	71	29	39.3	22.5	
C	I	78	22	28.4	14.6	120 min, 200°C
C	II	76	24	—	—	
C	III	63	37	26.8	14.2	

^a All samples were irradiated for 120 s (150 mJ/cm^2) at 35°C.

^b These are the average molecular weights for the higher molecular weight peak only. All $\overline{M}_w/\overline{M}_n$ values range between 1.75 and 2.38.

method III, all samples totally lost their physical integrity and broke up into very small pieces.

From the stoichiometry given in Table I for formula 1, and assuming that all soluble material is extracted and that no grafting is occurring between the crosslinked network and the linear polyester, the weight fraction of the gel is expected to be 47% and that of the soluble fraction to be 53%. However, the sample which was irradiated and not annealed showed significantly less soluble fraction (42%) than would be expected (53%). Assuming the irradiation has no effect on the copolyester, these results suggest that even after irradiation alone it is difficult to extract out all the linear copolyester because the polymer is highly entangled in the matrix. Perhaps longer extraction times than we utilized are necessary to completely extract the copolyester; however, it has been reported in the literature that the entire soluble fraction of an IPN can be successfully extracted by the methods described above for both densely²⁸ and lightly crosslinked samples.²⁹ FTIR results confirm the presence of copolyester in the gel fractions of these samples, but it is not possible to determine whether or not it is grafted to the acrylates.

The extracted solubles were analyzed by size exclusion chromatography (SEC). The results show two peaks, one at low molecular weights and the other at higher molecular weights. This latter peak elutes in the same region as does a pure sample of the copolyester taken from the same batch of polymer as that used to make the semi-IPNs-II. The low molecular weight peak is due to monomers or very low molecular weight oligomers of the di- and trifunctional acrylates.

The SEC results also reveal several other interesting features: (1) The averages obtained from the high molecular weight peaks remained constant independent of the extraction method, suggesting that method III does not degrade the polymer to a greater extent than the other methods. (2) Although more soluble material is extracted by using method III, it appears that the additional material does not consist of higher molecular weight chains. (3) There is a notable decrease in these molecular weight averages of the extractables as the

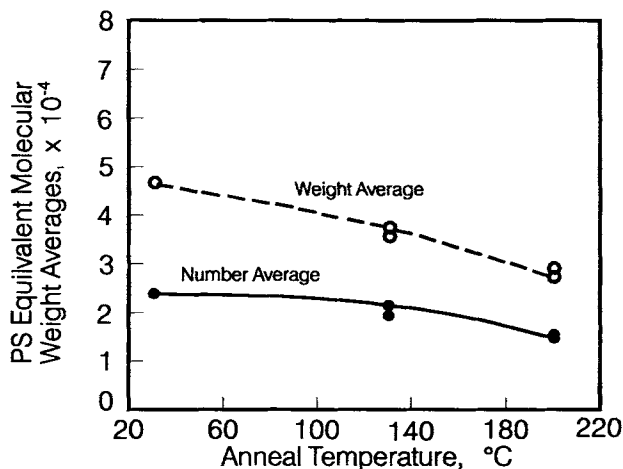


Fig. 9(a). Polystyrene equivalent molecular weights as a function of annealing time.

samples are annealed at elevated temperatures. This is shown in Figures 9(a) and 9(b). The weight average molecular weight decreases more rapidly than the corresponding number average values as a function of high temperature curing. Since the weight average molecular weight values are highly weighted by the longer chains, and the longer chains are harder to extract, this adds credence to the suggestion that the observed decrease in molecular weight average is simply a chain entrapment problem. Clearly in this case, the higher molecular weight fraction of the copolyester is not eluting. This evidence along with the infrared measurements suggests that the reaction proceeds relatively free of any cross reactions between the acrylates and the copolyester. Although we do not wish to preclude the occurrence of cross reactions or degradation, the data indicate that these mechanisms are not predominately responsible for the high glass transition temperature of the network.

Influence of Composition

A series of samples were prepared in which the ratio of the major components was varied in order to understand the influence of the multifunctional acrylates on the phase morphology and physical properties of the network. The various formulations prepared are shown in Table I and the dynamic mechanical spectra of these formulations after irradiation and a 5-min post-cure at 200°C are shown in Figures 10(a) and 10(b).

The formulations containing nearly 50% acrylates and 50% copolyester (formulas 1 and 2) show that only a single, although broad, loss peak is observed, suggesting that the blends are exhibiting microheterogeneous morphologies. For the samples containing 65% of the copolyester (formulas 3 and 4) two distinct loss peaks were observed. However, the depth of the valley between the transitions is not very deep, suggesting that there is some molecular mixing.³⁰ The sample containing 65% acrylates (formula 5) exhibits only a single loss peak after the 5-min bake, but does exhibit a significantly lower glass transition temperature than the samples containing 50% acrylates. Additional time of curing of formulas 1, 2, and 5 at 200°C results in higher glass transition tem-

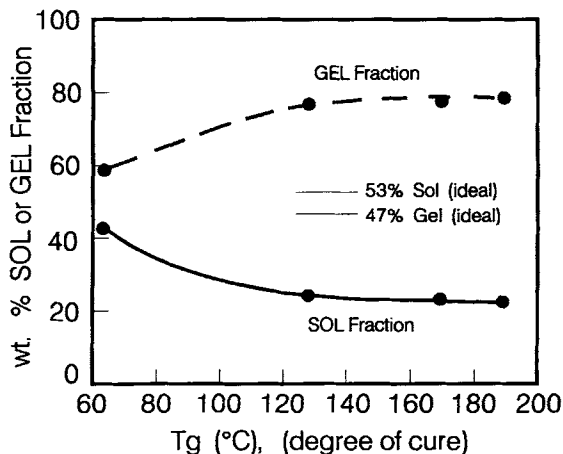


Fig. 9(b). Percentage of soluble fraction as a function of annealing temperature.

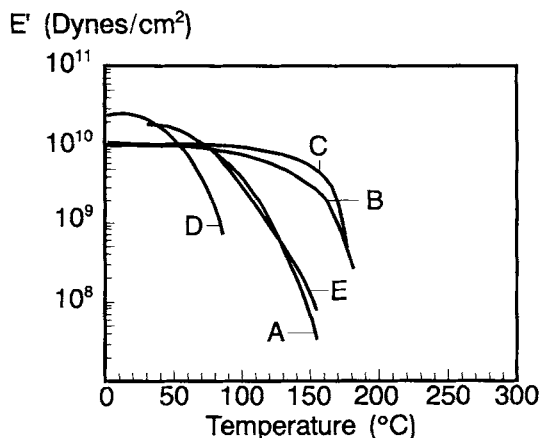


Fig. 10(a). Storage modulus vs. temperature for samples that were irradiated for 2 min at 35°C and subsequently post-baked at 200°C for 5 minutes: (A) formula 1; (B) formula 4; (C) formula 3; (D) formula 5; (E) formula 2.

peratures with a single loss peak, and formulas 3 and 4 continue to show two distinct loss peaks with a very shallow valley between the peaks.

In addition, the dynamic mechanical analysis results indicate that the same morphology developed in formulas 3 and 4 is present if the sample contained 65% copolyester, 17.5% difunctional acrylate, and 17.5% trifunctional acrylate. Differential scanning calorimetry has shown that when the linear analog of the trifunctional acrylate (the monofunctional acrylate) is polymerized and then blended with the copolyester, a phase-separated system results and two distinct glass transition temperatures are observed.

These results show that in order to form a miscible blend between the acrylates and the copolyester, multifunctional acrylates must be present. In addition, there needs to be a sufficient percentage of acrylates present in order to "lock-in" the morphology and prevent the copolyester from phase separating.

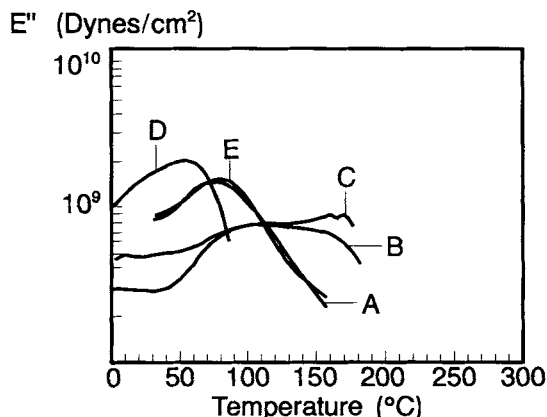


Fig. 10(b). Loss modulus vs. temperature for samples that were irradiated for 2 min at 35°C and subsequently post-baked at 200°C for 5 min: (A) formula 1; (B) formula 4; (C) formula 3; (D) formula 5; (E) formula 2.

CONCLUSIONS

This work has demonstrated that when certain multifunctional acrylates are photopolymerized, 80% of the acrylate double bonds are consumed during the initial photopolymerization. Further, the extent of the photopolymerization reaction is dramatically reduced by the addition of a high glass transition temperature copolyester. The reduction in the extent of reaction is due to vitrification of the sample since the glass transition temperature of the coating is within 20–40°C of the reaction temperature. An increase in the extent of the reaction is realized if the sample is heated during the photopolymerization reaction.

When the sample vitrifies, free radicals are believed to be trapped within the glassy matrix and it is possible to increase the extent of reaction by thermally curing the sample. An increase in the glass transition temperature of the coating is realized by increasing the extent of cure. After nearly 120 min at 200°C more than 95% of the acrylate double bonds are consumed, and this results in a coating with a glass transition temperature of 189°C. This glass transition temperature is much higher than would be expected based on either the Fox or Gordon–Taylor equations.^{1,2,31}

Infrared studies have shown that there is a linear relationship between the extent of cure of the reaction and the increase in the glass transition temperature of the coating. Extraction studies showed that it is not possible to extract all the linear copolyester from the matrix, suggesting the possibility of some cross-reactions between the acrylates and the copolyester. However, size exclusion chromatography results on the extracted fractions suggest that the lower molecular chains are being extracted more readily than the higher molecular weight chains, which may indicate that the chains are not chemically bound, but rather physically bound by entanglements in a very tightly formed network.

There appears to be synergistic effects between the acrylates and the copolyester which raise the glass transition temperature to values higher than would be predicted. This phenomenon may be due to the acrylates polymerizing so tightly around the polyester that segmental motion of both polymers is restricted.

As seen from the DMS data, there does not seem to be any gross phase separation in the crosslinked samples of formula 1; the most fully cured sample has phase domains on the order of 50–250 Å, which are associated with the copolyester phase. The copolyester is not inherently miscible with the multifunctional acrylates since it has been demonstrated that the copolyester is not miscible with the monofunctional analog of the trifunctional acrylate, and there is a critical concentration of multifunctional acrylates necessary in order to form a miscible blend.

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