Castor Oil Based UV-Curable Polyurethane-Acrylate Interpenetrating Networks

JAMES G. HOMAN, XUE-HAI YU,* TIMOTHY J. CONNOR, and STUART L. COOPER†

Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706

SYNOPSIS

Castor oil was reacted in varying ratios with β-isocyanatoethyl methacrylate to form a liquid urethane–methacrylate prepolymer. This prepolymer was then cured using ultraviolet radiation to form a series of base polymer networks or using various methacrylates to form conetworks. By swelling the base networks with the appropriate methacrylate monomers, semi- and full interpenetrating networks (IPNs) were prepared with similar compositions. All of the materials formed transparent films. Results of swelling experiments, dynamic mechanical analysis, differential scanning calorimetry, and small angle x-ray scattering are discussed.

INTRODUCTION

Interpenetrating polymer networks (IPNs) exhibit a variety of interesting properties and have been the subject of recent reviews.[1,2] An IPN may be defined as "a combination of two polymers in network form, at least one of which is synthesized and/or cross-linked in the presence of the other."[1] This method of forming the networks allows the morphology of the resultant material to be controlled. In particular, the extent to which the component networks phase-separate is limited.

One of the more useful properties of IPNs is their damping behavior.[3,4] Homopolymers exhibit high mechanical loss properties over a relatively narrow temperature range near their glass-transition temperature, T_g. Phase-separated multicomponent polymers exhibit good damping near the T_gs of the constituent polymers, but not at other temperatures.[5] The limited phase-separation caused by the unique microstructure of IPNs broadens the glass transition regions of the component networks and can merge them into a single transition covering a wide temperature range.[3,4] It is these broad transi-

tion ranges which make IPNs likely candidates for high-damping applications.

Several series of UV-curable polyurethane–acrylates with various soft segments, diisocyanates, and reactive diluents have been previously investigated in our laboratories.[6–9] In the present investigation, a new series of castor oil based polyurethane–acrylates was synthesized by reacting castor oil with varying amounts of β-isocyanatoethyl methacrylate and with other methacrylates as diluents. Although castor oil as a urethane component and in IPNs is not new,[10–13] it was chosen for this study for several reasons. The low molecular weight of the prepolymers results in low viscosity, making it possible to use these materials as solventless coatings. The final materials are transparent films which exhibit low toxicity, and castor oil exhibits good compatibility with both hydrophobic and hydrophilic components. One of the major interests, as indicated above, is the high-damping characteristics of these materials.

In this contribution, castor oil and β-isocyanatoethyl methacrylate were reacted in varying ratios to form a series of liquid urethane–methacrylate prepolymers. These prepolymers were then cured with a number of methacrylates using ultraviolet radiation to form conetworks. Base polymers were formed by curing the prepolymer without an additional methacrylate. Semi-IPNs and full IPNs were prepared by swelling the base networks with methyl methacrylate, and propylene glycol dimethacrylate

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for the full-IPNs, and then curing a second time with UV radiation. All of the materials were obtained as transparent films. The motivation for this study was to compare the properties of materials with similar overall composition but with varying microstructure due to the method of preparation. Results of swelling experiments, dynamic mechanical analysis, differential scanning calorimetry, and small-angle x-ray scattering are reported.

EXPERIMENTAL

Castor oil was obtained from Aldrich Chemical Co. and was dehydrated under vacuum at 70°C for 24 h before use. The β-isocyanatoethyl methacrylate (IEM) was obtained from Polysciences and was used as received. The reactive diluents were a series of methacrylates, obtained from Aldrich Chemical Co., containing inhibitor, and were used as received. Prepolymers were synthesized by slowly adding the IEM to the dried castor oil with stirring, maintaining the temperature below 50°C to avoid appreciable thermal polymerization of the acrylate (Fig. 1). The mixture was allowed to stand overnight, and complete reaction of the isocyanate was confirmed by infrared spectroscopy. Prepolymers of different compositions were formed by varying the ratio of IEM to castor oil.

Conetworks were formed by adding a reactive diluent and 0.6 wt % 2,2'-diethoxyacetophenone as a photoinitiator. The reactive diluents were: methyl methacrylate (MMA), ethyl methacrylate (EMA), hydroxyethyl methacrylate (HEMA), butyl methacrylate (BMA), lauryl methacrylate (LMA), and iso-bornyl methacrylate (iBMA). Base networks were also formed by curing the prepolymer with no reactive diluent. The mixture of prepolymer, photoinitiator, and reactive diluent was poured onto poly(ethylene terephthalate) (PET) film and covered with another piece of PET film to make a uniform thickness. The sample was exposed to UV light from one side using a bank of 20 W mercury lamps (λ = 365 nm) as the radiation source. An irradiation time of 30 min was found to completely cure the samples. After UV-curing, all samples were dried under vacuum at 60–70°C for at least 12 h to remove any unreacted diluent. All samples were transparent to visible light.

Semi-interpenetrating networks (semi-IPNs) were formed by swelling the base networks with a mixture of reactive diluent and 0.6 wt % photoinitiator and curing by UV radiation. In a similar manner, full IPNs were formed by swelling the base net-
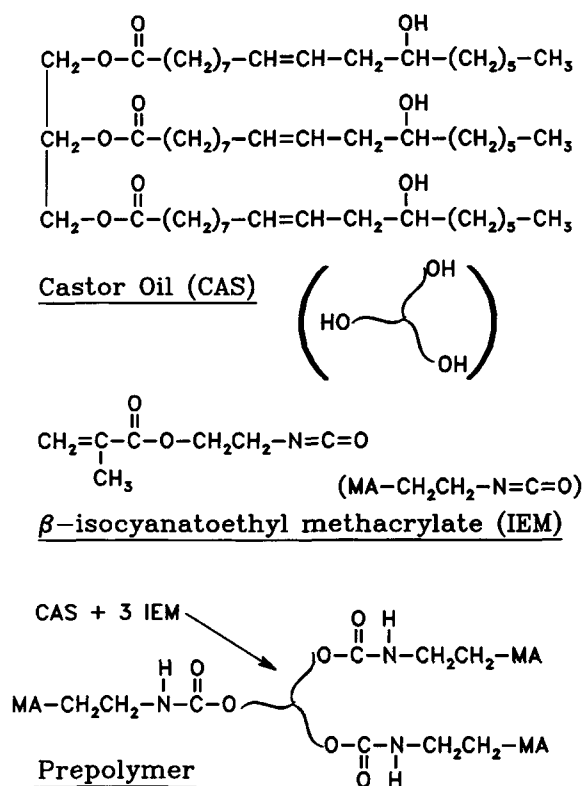

Figure 1   Reaction to form the prepolymer used in making all subsequent materials. The ratio of IEM to castor oil was varied from 1.5 to 3 (shown).

works with a mixture of reactive diluent, 2 wt % propylene glycol dimethacrylate as a crosslinker for the second network, and 0.6 wt % initiator. Equilibrium swelling was achieved in less than 4 h. Sample compositions were determined from the weight of the base network and swollen base networks. The swollen films were again sandwiched between two pieces of PET film and were exposed to UV radiation for 5 min. The samples were postcured at 70°C under vacuum overnight. A description of the materials which were synthesized for this investigation is given in Table I.

Dynamic mechanical data were obtained using a computer controlled Rheovibron DDV-II-C. Data were taken from −50°C to 200°C at a frequency of 110 Hz and at a heating rate of 2°C per min.

Swelling measurements were made by soaking the samples in solvent until an equilibrium weight was achieved (2 to 4 d). Weight measurements were made by blotting the samples dry and immediately placing them into a pre-tared capped vial. The swelling solvent was then removed by heating the samples to 60°C under vacuum until equilibrium weight was again achieved. The reported swelling

Table I   Description of Samples

Sample	IEM/CAS Mole Ratio	Wt % IEM and CAS	
CAS-IEM-3.0-0	3.0	100	Base networks
CAS-IEM-2.5-0	2.5	100	Base networks
CAS-IEM-2.0-0	2.0	100	Base networks
CAS-IEM-1.5-0	1.5	100	Base networks
CAS-IEM-2.5/MMA Conetwork	2.5	86	Conetworks
CAS-IEM-3.0/HEMA Conetwork	3.0	80	Conetworks
CAS-IEM-3.0/IsobornylMA Co	3.0	80	Conetworks
CAS-IEM-3.0/LMA Conetwork	3.0	80	Conetworks
CAS-IEM-3.0/EMA Conetworks	3.0	80	Conetworks
CAS-IEM-3.0/PMMA Semi-IPN	3.0	82	Semi-IPNs
CAS-IEM-2.5/PMMA Semi-IPN	2.5	86	Semi-IPNs
CAS-IEM-2.0/PMMA Semi-IPN	2.0	87	Semi-IPNs
CAS-IEM-1.5/PMMA Semi-IPN	1.5	88	Semi-IPNs
CAS-IEM-3.0/PMMA Full IPN	3.0	86	Full IPNs
CAS-IEM-2.5/PMMA Full IPN	2.5	86	Full IPNs
CAS-IEM-2.0/PMMA Full IPN	2.0	87	Full IPNs
CAS-IEM-1.5/PMMA Full IPN	1.5	96	Full IPNs

percentages were determined from the equilibrium swollen weight and the final equilibrium dried weight to account for solvent extraction of low molecular weight components.

Differential scanning calorimetry (DSC) thermograms were recorded from −130°C to 200°C using a Perkin-Elmer DSC 2 at a heating rate of 20°C per min. The data processing unit allowed automatic baseline subtraction and normalization of the thermograms by sample weight.

Small-angle x-ray scattering (SAXS) patterns were obtained using a modified compact Kratky camera. X-rays were generated by an Elliot GX-21 rotating anode operating at 30 kV accelerating potential and 40 mA emission current. The scattered x-rays were detected by a one-dimensional position sensitive detector and associated electronics. The x-rays were filtered by nickel foil and a pulse height discriminator was used in the detector electronics to limit the x-rays to a predominant wavelength of 0.1542 nm (CuKα). Corrections were made to the data to take into account detector sensitivity, detector linearity, detector dark current, parasitic scattering, and sample transmittance. Relative intensity data were converted to absolute intensity using a Lupolen polyethylene standard. An experimentally measured slit-length weighting function, convoluted with a function that accounted for a finite detector window, was used to desmear the data by the iterative method of Lake.[14]

RESULTS AND DISCUSSION

Figure 2 shows the dynamic mechanical data for two of the base networks. As the crosslink density is increased because of a higher IEM to castor oil ratio,
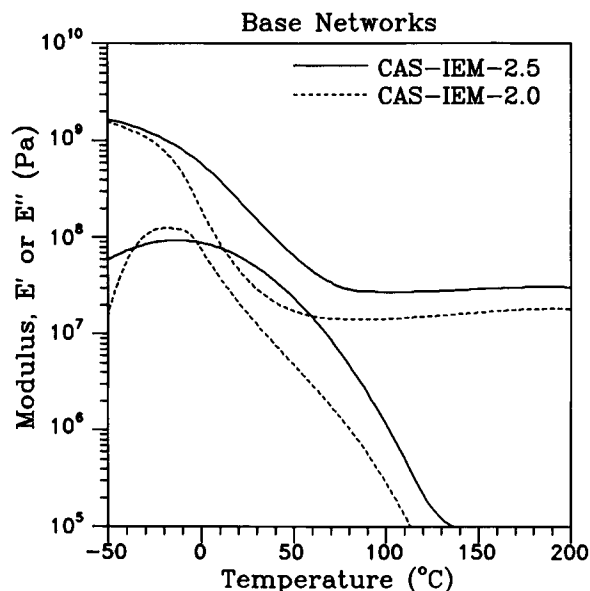

Figure 2   Dynamic mechanical data from two of the base networks. In all plots of dynamic mechanical data, the upper curves are the storage modulus (E′) while the lower curves are the loss modulus (E″) or tangent δ.

the high temperature storage modulus (E') plateau is increased, and the glass transition temperature (T_g—the peak in the loss modulus, E") moves to a higher temperature. The increase in T_g with the IEM to castor oil ratio reflects the increase in the methacrylate component, which has the higher inherent T_g.

Figures 3(a) and 3(b) show the dynamic mechanical data for four of the conetworks made with various methacrylates. These figures demonstrate that both the T_g and the storage modulus plateau
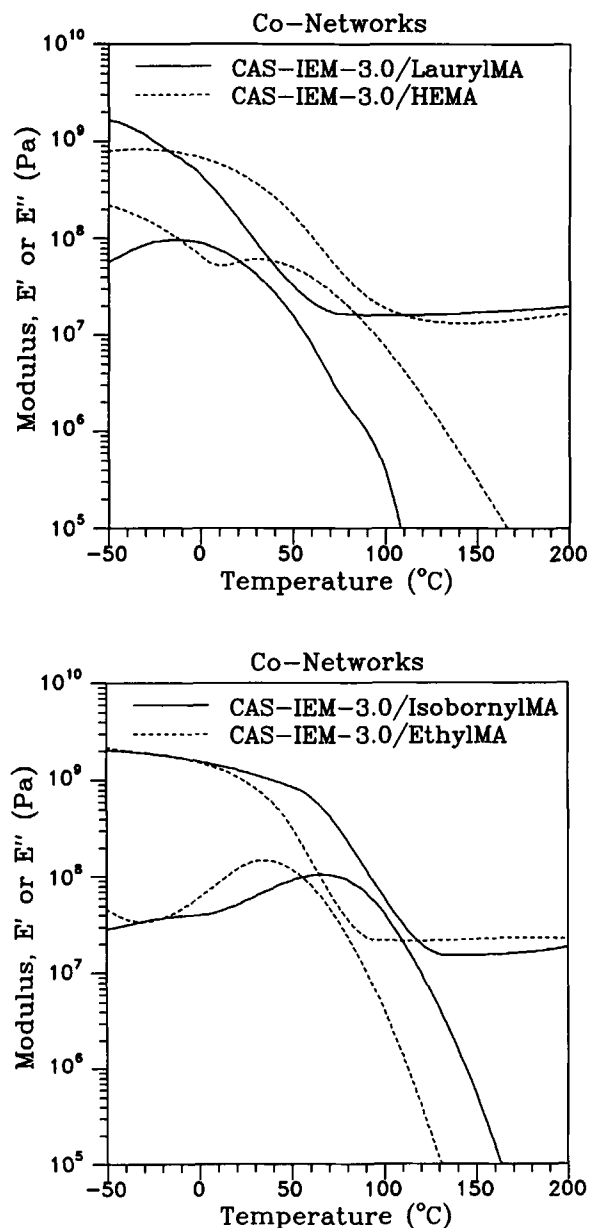

Figure 3 (a) and (b) Dynamic mechanical data from the methacrylate conetworks.

are affected by sample composition, but that the two do not necessarily follow the same trends. The position and breadth of the glass transition depends on the T_g of the component materials and the degree to which the components are phase separated. A two-phase material can exhibit two distinct T_gs, with each T_g resulting from one of the phases. A broader glass transition results when a phase is not completely homogeneous, but instead contains a composition distribution. In the conetworks, it is probable that the broad glass transitions are due to a single broad composition distribution ranging from methacrylate-rich to castor-oil-rich regions within what is essentially one phase.

The high-temperature storage modulus of these conetworks is more strongly affected by the crosslink density. The differences in the storage modulus plateau are probably due to differences in the average molecular weight between crosslinks. If the reactivity ratio of a growing chain favors reaction with methacrylate monomer over reaction with pendant methacrylate on the prepolymer, a higher molecular weight between crosslinks, and therefore a lower crosslink density, will result. The lower crosslink density is observed as a lower plateau modulus.

The effect of sample structure on the dynamic mechanical properties of the networks is shown in Figure 4. In going from the base network to the conetwork, to the semi-IPN, to the full IPN, T_g is seen to increase. The breadth of the glass transition, as indicated by the breadth of the peak in E", is also seen to increase for the two IPN samples. The high temperature storage modulus plateau is lower for the conetwork than it is for the base network. Though these property changes due to differences in structure are smaller than those due to differences in composition, some trends are observed. The increase in T_g is primarily due to the increased methacrylate content in the conetwork and in the IPNs. The narrower breadth of the glass transition peak for the conetwork is due to a narrower composition distribution of the phase which yields the peak.

The lower storage modulus of the conetwork, as compared to the base network, reflects the lower crosslink density or higher molecular weight between crosslinks, which exists in the conetwork. The higher molecular weight between crosslinks is due to the poly(methyl methacrylate) part of the conetwork. The fact that the storage modulus plateau of the semi-IPN is the same as that of the base network indicates that it is the base network component of the semi-IPN which is responsible for the structural integrity of the sample at higher temperatures. The higher storage modulus plateau of the full IPN is
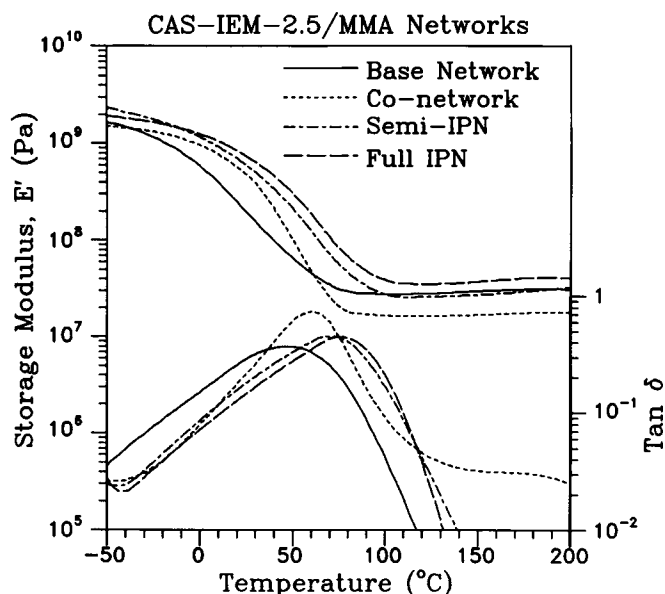
Figure 4 Dynamic mechanical data from the series of materials formed from the pre-polymer with a 2.5 : 1 ratio of IEM to castor oil.

due to the additional load bearing capacity of the second methacrylate network.

The dynamic mechanical data for the semi-IPNs are shown in Figure 5. These data basically show the same trends as the base networks. As the cross-link density of the base network component is increased, the storage modulus plateau and the T_g increase, and the glass transition peak narrows. The dynamic mechanical data from the full IPNs are

shown in Figure 6. Sample CAS-IEM-1.5/PMMA Full IPN failed at about 90°C during testing and was not retested. Again the same trends in T_g and the breadth of the transition are seen. The trend in the storage modulus plateau is not as evident in this series of materials. The reasons for this are not clear, but one should recall that the storage modulus plateau has contributions from both networks and one should also note that CAS-IEM-1.5/PMMA Full
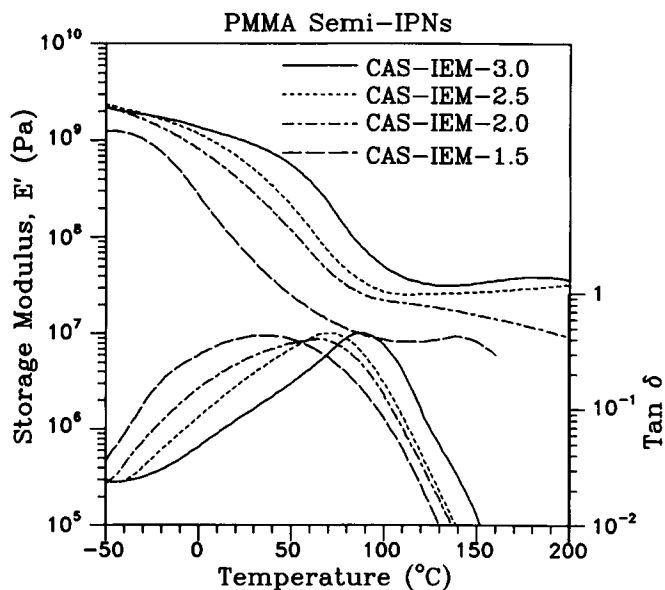

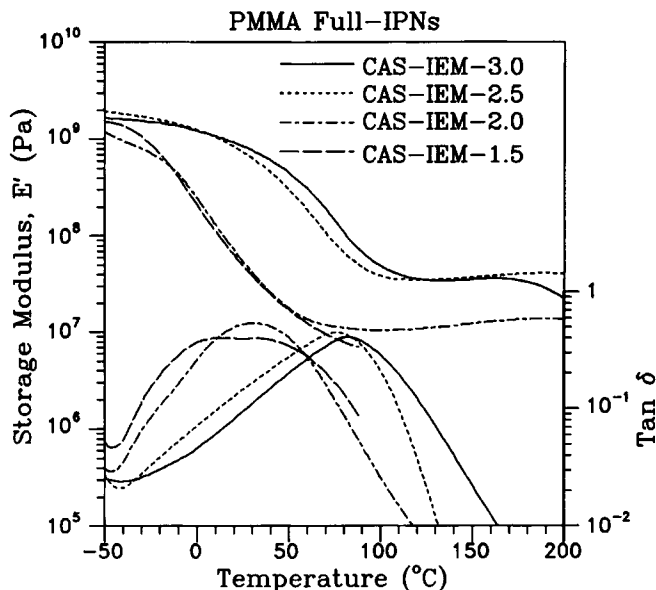**Figure 5** Dynamic mechanical data from the PMMA Semi-IPN materials.

Figure 6 Dynamic mechanical data from the PMMA Full IPN materials.

IPN has a significantly lower PMMA content. As with the base networks, the increases in T_g with IEM content are due to the higher overall methacrylate content of the samples.

The materials for this investigation were designed with the idea that the unreacted arms of the castor oil, in the materials where the IEM to castor oil ratio was less than three, would increase the damping characteristics of the materials. This expectation is supported by the dynamic mechanical data for

the IPNs. While the magnitude of the maximum in the damping peak is essentially the same for all of the materials, the peak narrows as the IEM to castor oil ratio is increased. This narrowing of the peak indicates that the unreacted arms of the castor oil are mixed into the methacrylate phase, but with a broader composition distribution as more arms are available.

An example of one of the DSC thermograms is shown in Figure 7. A glass transition is seen at
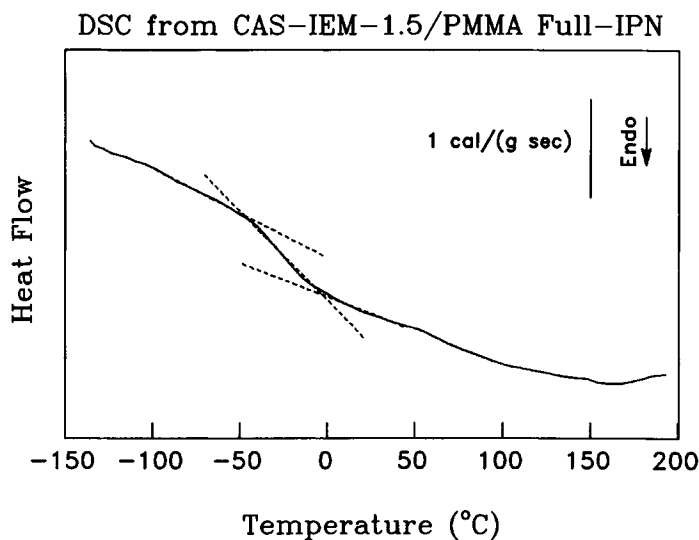

Figure 7 DSC thermogram from CAS-IEM-1.5/PMMA Full IPN. The T_g is −25°C for this material, but was difficult to observe in general.

−25°C. Only a few materials were tested using DSC. The glass transitions in these materials as measured by DSC, if present, were broad and difficult to find. When it was possible to determine a T_g from DSC thermograms, it occurred at a lower temperature than that determined from dynamic mechanical measurements.

Figure 8 shows the results of swelling experiments on CAS-IEM-3.0/PMMA Full IPN. The solvents used are all classified as moderately hydrogen-bonding.[15] From the plot it is evident that the solubility parameter of this sample is near 9 (cal cm^{-3})$^{1/2}$. The other samples undoubtedly have different solubility parameters due to their varying compositions. Dioxane was chosen as the solvent for the other swelling experiments because the tetrahydrofuran caused this sample to fracture. The dioxane also gave a reasonable balance between low solvent volatility at room temperature, which allowed for relatively easy sample weight determination, and ease of solvent removal under vacuum at 60°C.

Figure 9 shows the results of swelling experiments in dioxane for several of the materials. As expected, the swelling percentage decreases as the crosslink density increases (increasing IEM/castor oil ratio). The generally higher swelling percentage of the full IPNs is due to the fact that the solubility parameter of the methacrylate network is nearer to the solu-
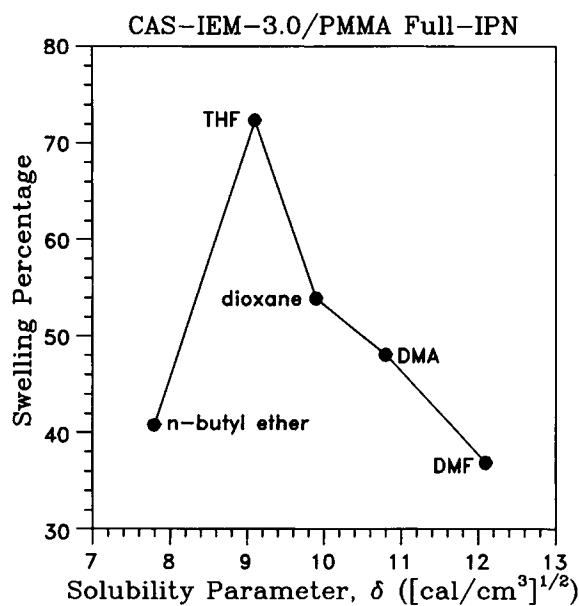

Figure 9 Swelling percentage of networks in 1,4-dioxane.

bility parameter of the solvent, 1,4-dioxane [10.0 (cal cm^{-3})$^{1/2}$], than that of the base network. [The solubility parameter of methyl methacrylate is reported[14] to be in the range of 9.0 to 9.5 (cal cm^{-3})$^{1/2}$.] The reason that CAS-IEM-1.5/PMMA Full IPN swells less than the base network is not clear, but as seen in Table I, this sample contains only 4 wt % methacrylate network.

Small-angle x-ray scattering from the materials based on CAS-IEM-3.0 is shown in Figure 10. In all of the materials, there is only a broad low intensity peak indicating that these materials are weakly phase separated with a low electron density contrast between the phases. The position of the peak would correspond to a Bragg spacing of 10 to 15 Å. Though it is not unexpected that the electron density of the castor oil phase is similar to that of the methacrylate phase, the lack of any sharp features in the SAXS pattern indicates that there is not a significant amount of order within these materials. Note that the addition of the second component does not significantly change the scattering pattern. This indicates that the poly(methyl methacrylate) component is in intimate contact with the base network. It is likely that the "structure" in these materials, as observed by the SAXS pattern, is due to the correlation-hole effect.[16,17] The phase structure of these materials is probably due more to chain architecture than to actual thermodynamic incompatibility between the component phases. That is, the three arms

Figure 8 Swelling percentage of CAS-IEM-3.0/PMMA Full IPN in a series of moderately hydrogen-bonding solvents of varying solubility parameter.
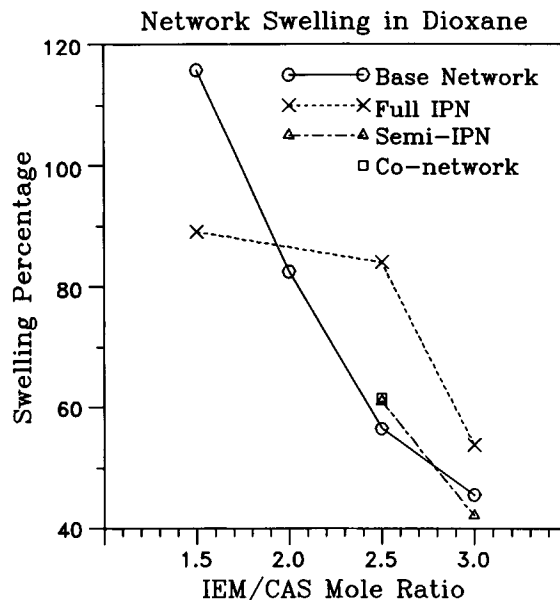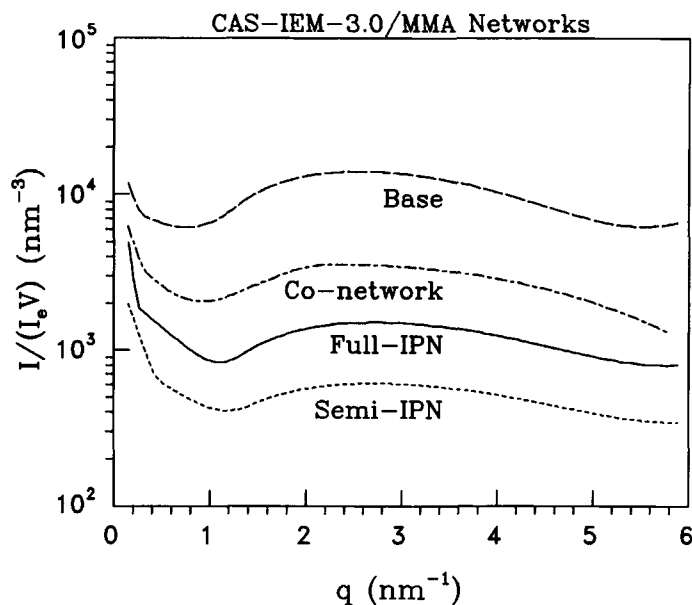
Figure 10 Small-angle x-ray scattering from the CAS-IEM-3.0 networks. The data for the full IPN are to scale, the other data have been shifted in half decade increments for clarity.

of the original castor oil are covalently linked and so there are regions in the final materials which are locally rich in castor oil due to steric considerations.

SUMMARY

A number of polyurethane–methacrylate base networks, conetworks, semi-IPNs and full IPNs have been synthesized. These materials were obtained as transparent films and were characterized by swelling experiments, dynamic mechanical analysis, differential scanning calorimetry, and small-angle x-ray scattering.

As the crosslink density was increased within each of the base network, semi-IPN, and full IPN series: a higher high temperature storage modulus plateau was observed; the T_g moved to higher temperature; the tan δ (or E'') peak narrowed; and the swelling percentage decreased. All of these results are due to the higher crosslink density and the fewer dangling chains within the networks that result from a higher IEM to castor oil ratio in the prepolymer.

Both of the IPN series of materials exhibit a higher T_g and a broader loss peak than the corresponding conetwork of similar composition. At the same time, however, small-angle x-ray scattering indicates that the basic morphology of the IPN materials is relatively unchanged from that of the base networks. Both of these results are due to the interpenetrating structure of the materials. The base

network cannot change its morphology when the second component is introduced to make the IPN materials. Since methyl methacrylate is a good solvent for the base network, it polymerizes in intimate contact with the network.

The high temperature storage modulus plateau of a full IPN is higher than those of the corresponding semi-IPN or base network, which are in turn higher than that of the corresponding conetwork. This is because the full IPN, semi-IPN, and base network all have the same base network component, and the full IPN has the additional methacrylate network to bear loads at higher temperatures. The conetwork has a higher average molecular weight between crosslinks and thus has a lower storage modulus plateau.

In general, these results indicate that the glass transition in these materials may be broadened by incorporating more dangling chains into the structure. In these materials, this corresponds to a lower IEM to castor oil ratio and, hence, a lower crosslink density in the base polymer network. The position of the T_g is primarily determined by the overall chemical composition of the system. Presumably, the magnitude of the damping peak (in E'') is determined primarily by the chemical composition as well. While the low temperature properties and damping properties do not seem to be affected by introducing crosslinks into the methacrylate, this is a good way to increase the high temperature strength of these materials.

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