Multiphase Materials with Lignin. VIII. Interpenetrating Polymer Networks from Polyurethanes and Polymethyl Methacrylate

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Synopsis

Several types of interpenetrating polymer networks (IPNs) from polyurethane/polymethyl methacrylate (LPU/PMMA) on the basis of lignin were prepared. All composites were judged to possess two phase morphology. The composition and the presence of crosslinking were found to influence the thermal and mechanical properties of the solvent-cast films. The mechanical properties were assessed by dynamic mechanical analysis and by tensile testing, and they were found to vary consistently with composition and the presence of crosslinks. The modulus behavior of the different IPNs could be explained by models which accounted for either dual phase continuity or phase inversion.

INTRODUCTION

Interpenetrating polymer networks (IPNs) constitute a group of polymer-polymer composite materials possessing unique properties which are related to their method of synthesis.[1-3] IPNs typically consist of a flexible elastomer and one or more rigid, high modulus component. IPNs prepared with a flexible and a rigid component often show a synergistic effect in some material properties.[1-3] In IPN terminology,[1] a "full IPN" is a system in which both polymer components, flexible and rigid, are crosslinked. This produces a "simultaneous IPN" if both networks are cured together, and a "sequential IPN" if one component is polymerized followed by swelling with the second monomer which is then reacted. A "semi-IPN" is a material which contains only one crosslinked component,[1] whereby the initially formed polymer may either be the crosslinked (i.e., "semi-1-IPN") or the linear (i.e., "semi-2-IPN"). Each of these variations can affect the IPN morphology and, thus, the thermal and mechanical properties.[1-3]

One of the most widely studied IPNs consists of a flexible polyurethane and a rigid polyacrylate in IPN or semi-1-IPN form.[4-8] The properties of these composites have been found to depend on molecular weight between crosslinks (M_c), and on acrylate type. Addition of a high T_g or high-modulus component generally raises the T_g and/or modulus of the composite.[9] The sensitivity to composition, phase separation and morphology increases with (chemical) differences between IPN components.

Another critical variable which controls IPN character is the presence of crosslinks.[7,9,10] Crosslinking of the first formed polymer (as in IPN or semi-1-

IPN) is thought to limit phase separation of the second polymer. If the linear polymer is formed first (as in semi-2-IPN) the morphology has been found to be irregular and coarse, producing poor mechanical properties. Comparisons between blends, semi-IPNs and IPNs from different polymers have generally shown that mechanical properties become inferior as the morphology of the system becomes more heterogeneous.[1,9,10] The morphology of a semi-2-IPN was not significantly affected by the extent of crosslinking in the second component.[11]

Several models exist which describe the mechanical behavior of IPNs. Three models representing a simple logarithmic rule of mixtures,[1] the Davies equation[12] and the Budiansky equation,[13] eqs. (1), (2), and (3), respectively

$$\log E = \phi_1 \log E_1 + \phi_2 \log E_2 \qquad (1)$$

$$E^n = \phi_1 E_1^n + \phi_2 E_2^n \qquad (2)$$

$$2 = \frac{G_1 - G}{G(G_1 - G_2)} (3/5\, G + 2/5\, G_2) \qquad (3)$$

where E_i and G_i are, respectively, the Young's and shear moduli of the different components, and ϕ_i is the volume fraction of the ith component. A fit of the experimental data to eq. (1) indicates simple additivity of properties without significant interaction between the two components. Eq. (2), with the exponent $n \geq \frac{1}{5}$, implies dual phase continuity, whereas a decrease in the exponent (i.e., $n \leq \frac{1}{5}$) is an indication of poor mixing.[4,13] The S-shaped curve which results from eq. 3 suggests the presence of phase inversion.[4] Thus a fit of the modulus data to one of these equations is indicative of a distinct morphology.

Recent work with both transmission electron microscopy[14] and small-angle neutron scattering[15] has indicated that "mixing" in IPNs may not take place on a molecular level. Microphase separation with dual phase morphology has been proposed in which colloidal structures are interconnected[15] and both polymers contribute to mechanical properties. This type of morphology could be represented by the Davies equation with n of $\frac{1}{5}$.[16–19]

Some IPN research has involved natural (plant) materials.[17–19] Castor (and other plant-extracted) oils have been used to prepare polyurethanes and polyester elastomers which were then used as the first component in both sequential and simultaneous IPNs. The thermal and mechanical properties were found to vary with composition and method of preparation; and so did the morphology. Properties were found to vary in a predictable and controllable manner.

With the successful preparation of polyurethanes from lignin-based polyols,[20,21] an investigation of IPN properties using the polyurethane/polymethyl methacrylate (LPU/PMMA) combination seemed appropriate. In this study the material properties of LPU/PMMA IPNs were to be studied in relation to changes in composition, network density, and method of preparation.

EXPERIMENTAL

Materials

With the exception of the hydroxypropyl lignin (HPL) polyol,[21] all IPN components were obtained from commercial sources (Table I).

Material	Description	Supplier
BPO	Benzoyl peroxide	Aldrich Chemical Co.
CEHPL	Chain-extended hydroxypropyl lignin	See Ref. 21
EDMA	Ethylene dimethacrylate	Polysciences, Inc.
HDI	Hexamethylene diisocyanate	Eastman Kodak Co.
MMA	Methyl methacrylate	Aldrich Chemical Co.
T-12	Dibutyltin dilaurate	Pfalz and Bauer

Prepolymer Preparation-Polymethyl Methacrylate (PMMA). Inhibitor was removed from methyl methacrylate (MMA) by washing with 0.1 N NaOH and water.[5] The MMA was kept over molecular sieves. Ethylene dimethacrylate (EDMA) was used as purchased.

A PMMA oligomeric mixture was prepared in a 250 mL round-bottom flask equipped with a nitrogen purge, stirrer, reflux condenser and thermometer. The flask was charged with 40 g of MMA and 0.15 g of benzoyl peroxide (BPO) which was stirred until it dissolved. The reaction was heated to 60°C under nitrogen for 90 min and then quenched in an ice bath. The mixture was stored in a freezer and used within two weeks. The crosslinked MMA prepolymer was prepared following the same procedure except 39 g of MMA and 1 g of EDMA were used with 0.15 g of BPO.

Chain-Extended Hydroxypropyl Lignin (CEHPL). The synthesis and properties of CEHPL are described elsewhere.[21] CEHPL can be viewed as an aromatic center with multiple, OH-terminated radiating propylene oxide arms of variable degree of polymerization (DP). DP is related to the molar substitution (MS) which is the number of propoxy repeat units which comprise the chain attached to a single reactive site on lignin. The CEHPL used in this study had a molar substitution of 4.5. The polyurethane network was a flexible elastomer at room temperature.[21]

Preparation of IPN Composites. Composites were prepared by weighing CEHPL into a flask and adding PMMA oligomer mixture. This combination was stirred until it was completely dissolved. Hexamethylene diisocyanate (HDI) was added with stirring to give an NCO/OH ratio of 1.8.[21] Finally, dibutyltin dilaurate catalyst (3 wt % based on NCO component) was added with rapid stirring. The mixture was degassed and poured into Teflon molds which were sealed with a rubber plate.

The mixture was held at room temperature for 2 h, 55°C for 16 h, and 105°C for 4 h. The covers were removed, and the IPNs were postcured at 135°C for 2 h. This preparation allowed for the formation of the polyurethane followed by curing of the MMA[5] above the T_g of the polyurethane.[21]

Lignin polyurethane (LPU) controls were prepared as described above, but stabilized MMA was used without BPO initiator. The residual MMA was removed at 135°C under vacuum. Crosslinked and branched LPUs were prepared with NCO/OH ratios of 1.8 and 0.66, respectively. Pure PMMA samples were prepared using the curing conditions described above. The stoichiometric molecular weight between crosslinks (M_c) for the crosslinked PMMA (X-PMMA) was 1670 d.

Methods

Thermal and mechanical properties of the IPNs were characterized by dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC), and stress/strain testing as described previously.[21]

RESULTS AND DISCUSSION

The sample nomenclature is used to designate composite type and lignin content. Four "types" of IPNs were prepared: simultaneous full-IPN, (IPN); simultaneous semi-1-IPN, (S-1); simultaneous semi-2-IPN, (S-2); and simultaneous linear blend, (B). The number following the IPN type indicates the weight percent of the lignin-based polyurethane (LPU) used in the composite. All the composites are described in Table II.

TABLE II
Nomenclature of LPU/PMMA Composites

Composite type	Code	Weight fraction		Lignin content (%)[a]
		PMMA (%)	LPU (%)	
Simultaneous IPN[b]	IPN (1.0)	0	100	30
	IPN (.75)	25	75	22.5
	IPN (.5)	50	50	15
	IPN (.25)	75	25	7.5
	IPN (0)	100	0	0
Semi-1-IPN[c]	S-1 (1.0)	0	100	30
	S-1 (.75)	25	75	22.5
	S-1 (.6)	40	60	18
	S-1 (.5)	50	50	15
	S-1 (.4)	60	40	12
	S-1 (.25)	75	25	7.5
	S-1 (0)	100	0	0
Semi-2-IPN[d]	S-2 (1.0)	0	100	30
	S-2 (.75)	25	75	22.5
	S-2 (.6)	40	60	18
	S-2 (.5)	50	50	15
	S-2 (.4)	60	40	12
	S-2 (.25)	75	25	7.5
	S-2 (0)	100	0	0
Blend[e]	B- (1.0)	0	100	30
	B- (.75)	25	75	22.5
	B- (.5)	50	50	15
	B- (.25)	75	25	7.5
	B- (0)	100	0	0

[a] True lignin content of composite.
[b] Lignin polyurethane crosslinked, polymethyl methacrylate crosslinked.
[c] Lignin polyurethane crosslinked, polymethyl methacrylate linear.
[d] Lignin polyurethane branched, polymethyl methacrylate crosslinked.
[e] Lignin polyurethane branched, polymethyl methacrylate linear.

Dynamic Mechanical and Thermal Behavior

The DMTA results for the IPN, S-1, S-2, and B-series of composites are presented in Figures 1–6. Common to all materials were changes in the magnitude of the tan δ peak temperature in response to composition. In general, the magnitude of the high temperature peak increased while the intensity of the low temperature peak decreased as the acrylate content of the materials increased. For most of the composites, two separate tan δ peaks were identified, although the peak temperature varied for several of the compositions. The log E' response for the composites also showed several consistent trends in relation to acrylate content. As the acrylate content increased, the room temperature log E' response increased and the abruptness of the low-temperature log E' drop diminished.

All materials were also analyzed by DSC. Both the DMTA and DSC results are given in Table III. DSC analysis allowed for an independent observation of T_g, and in some cases resulted in the resolution of a transition temperature that was not clearly observed by DMTA. Differences in the transition temperatures observed by DMTA and DSC are due to heating rate and frequency effects.
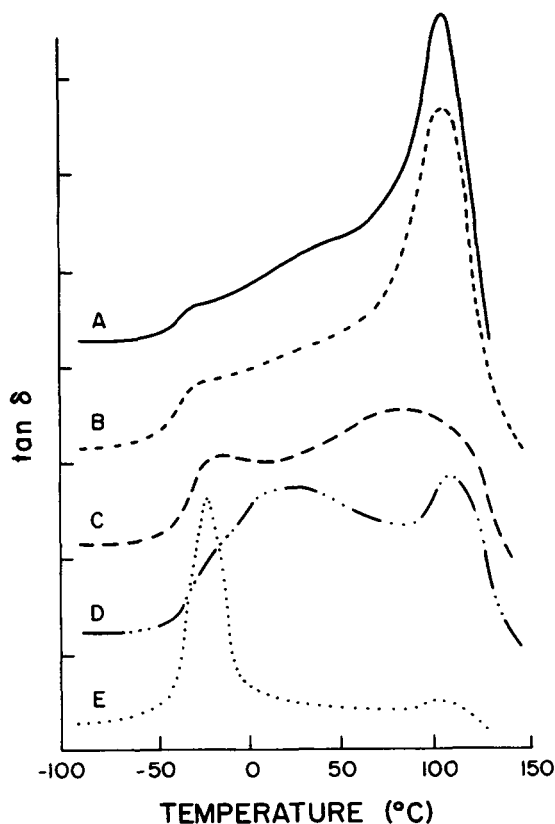

Fig. 1.   Dynamic mechanical properties (tan δ tracings) of S-1s with varying LPU/PMMA compositions: (A) S-1(.25), (B) S-1(.4), (C) S-1(.5), (D) S-1(.6), and (E) S-1(.75). The T_g of the LPU was $-37°$C and the T_g of the PMMA was 116°C. (Traces are offset for clarity; tick marks are at 0.2 intervals.)
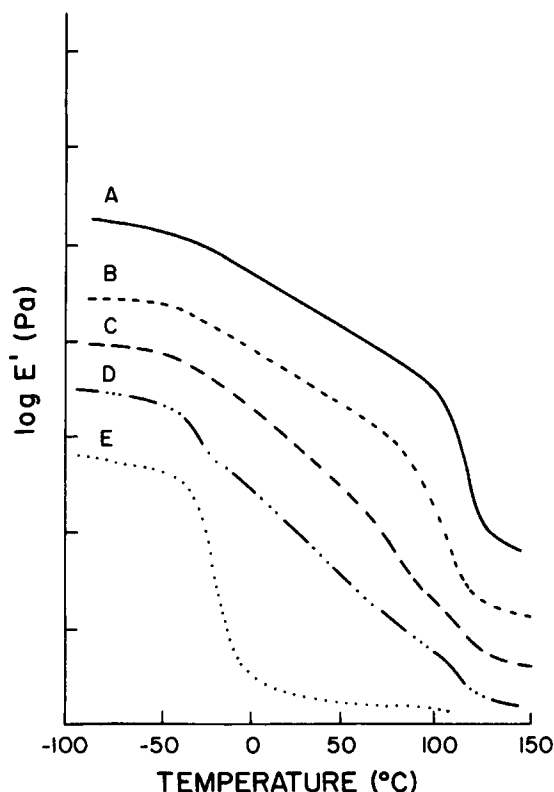
Fig. 2. Dynamic mechanical properties (log E' tracings) of S-1s with varying LPU/PMMA compositions: (A) S-1(.25), (B) S-1(.4), (C) S-1(.5), (D) S-1(.6), and (E) S-1(.75). The T_g of the LPU was $-37°C$ and the T_g of the PMMA was $116°C$. (Traces are offset for clarity; tick marks are at 1.0 intervals.)

Glass Transitions. Analysis of DMTA data focused on the temperature, shape and magnitude of the tan δ peaks. DSC analysis was used to corroborate the changes in T_g observed by DMTA. Observation of two separate T_gs indicated that the two components (LPU and PMMA) were phase separated, and interaction was indicated by changes in peak temperature and shape of the transition. Significant interaction between the polymer pair causes the tan δ peak to shift to different temperature.[18] In the absence of interaction the tan δ peak temperature (or T_g) does not depend on the amount of a second component. It was apparent from both techniques (DMTA and DSC) that for all composites, at all weight fractions, the T_gs of both components were shifted toward one another. This is an indication of at least limited interaction between the two components.

This T_g shift typically amounted to 10 to 15°C for the IPN and S-1 composites, and to 10 to 20°C for the S-2 and B materials. With a few exceptions, this shift was not strongly dependent on composition (wt fraction) or method of preparation. The most notable exceptions were those of IPN(.5), S-1(.6), and S-1(.5), each of which showed that one of the two peaks had broadened and peak temperature had shifted substantially (see Figs. 1 and 3). For IPN(.5) and S-1(.5) an extraneous broad peak was seen at low temperature (ca. 20°C),
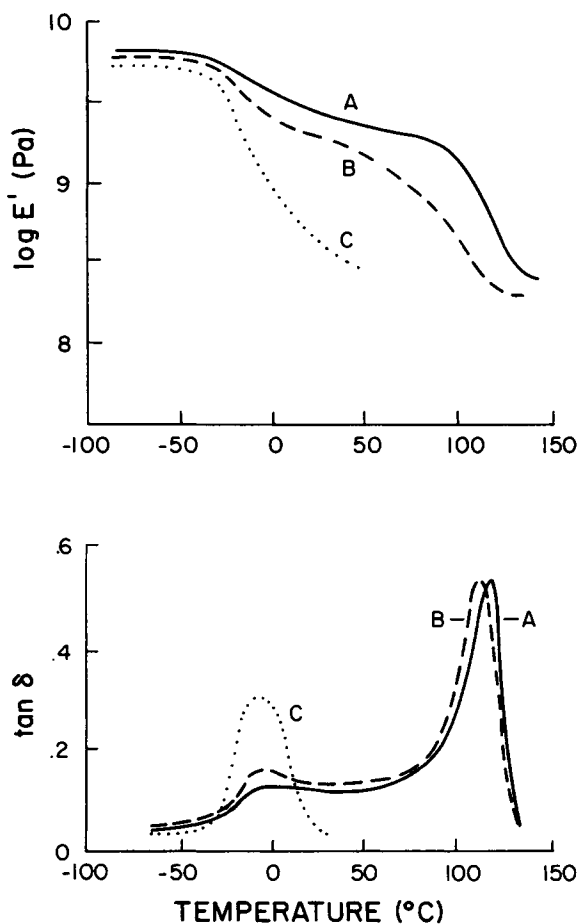
Fig. 3. Dynamic mechanical properties of IPNs with varying LPU/PMMA compositions: (A) IPN(.25), (B) IPN(.5), and (C) IPN(.75). The T_g of the LPU was $-37°C$ and the T_g of the PMMA was 126°C.

while for S-1(.6) the extraneous peak was seen at high temperature (ca. 80°C). These unusual transitions were only observed in the systems which contained crosslinked LPU. Broadening of tan δ peaks has been observed previously with conventional polyurethane/PMMA IPNs[22] where the behavior was attributed to small fluctuations in composition on a very local scale. Thus each region would undergo a transition temperature which was dependent on the behavior of the nearest neighbors. A second interpretation for tan δ peak broadening[9,22] was advanced based on interphase behavior. This idea postulates the presence of an interphase that gives rise to a transition, on a local scale, intermediate to the transition of the two original components.

A convergence of all transition peak temperatures implies interaction between the component pair. Partial or complete miscibility between polymers has been noted for mixtures where each component possesses similar solubility parameters (usually due to similar chemical composition), or in mixtures which develop strong specific interactions.[23-25] For the LPU/PMMA system there was
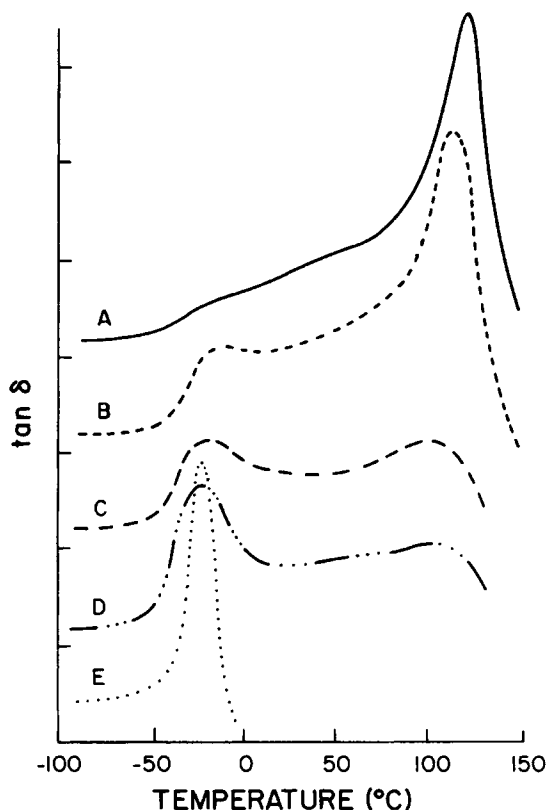
Fig. 4. Dynamic mechanical properties (tan δ) of S-2s with varying LPU/PMMA compositions: (A) S-2(.25), (B) S-2(.4), (C) S-2(.5), (D) S-2(.6), and (E) S-2(.75). The T_g of the LPU was ca. $-52°C$ and the T_g of the PMMA was $126°C$. (Traces are offset for clarity; tick marks are at 0.2 intervals.)

potential for a specific interaction between the aromatic electrons of the LPU and the electrons of the PMMA ester side group. Such interaction could be responsible for some mixing of IPN components independent of method of preparation.

Specific interactions between PMMA and aromatic systems have been previously noted[25,26] for the PMMA/polycarbonate (PC) system in which limited miscibility was detected. The extent of interaction was promoted by the orientation of the aromatic ring which lies in a plane parallel to the polymer backbone. Similar circumstances may be responsible for the alignment of the aromatic rings of lignin in LPU/PMMA materials. Partial miscibility was observed in related work for hydroxypropyl lignin (HPL)-PMMA blends.[26] The extent of interaction was found to depend on the characteristics of the solvent from which the blends were cast. Interactions between the HPL and PMMA were noted for compositions up to 40% HPL.

These results made it appear likely that specific interactions between LPU and PMMA had an effect on the dynamic mechanical and thermal properties of the IPNs. It was surprising that the magnitude of the interaction (judged by T_g shifts) was not correlated to composition. Shifts in T_g also appeared to be relatively independent of composite type. The slightly larger shifts in the
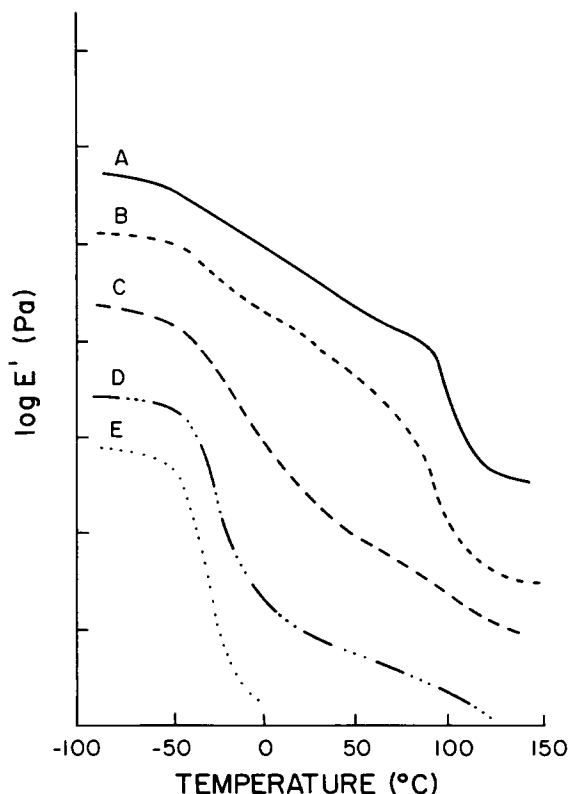
Fig. 5.   Dynamic mechanical properties ($\log E'$) of S-2s with varying LPU/PMMA compositions: (A) S-2(.25), (B) S-2(.4), (C) S-2(.5), (D) S-2(.6), and (E) S-2(.75). The T_g of the LPU was ca. $-52°$C and the T_g of the PMMA was $126°$C. (Traces are offset for clarity; tick marks are at 1.0 intervals.)

LPU T_gs seen in the S-2 and B materials were attributed to large differences in the T_gs of the original components rather than to differences in the composite type. The observation of an anomalous peak in three composites [IPN(.5), S-1(.6) and S-1(.5)] may be related to further differences in morphology or the presence of an interphase.[22,23]

   Activation Energies. A second indication of interaction between two IPN components may emanate from T_g activation energies (E_a). The E_a values for the transitions in the S-1 series (where they could be reliably determined) indicated a decline of the PMMA transition E_a as the LPU content of the IPN increased (Table IV). If there were no interactions between the LPU and PMMA components, the E_a of the PMMA should not depend on LPU content. The observed substantial decrease in the E_a of the PMMA T_g-transition could not be explained, in a simple manner, with an increase in free volume of the system since the T_g of the material remains relatively constant over this same composition range. Thus, some interaction between the components on a molecular level appears to be responsible for the observed change in E_a in relation to composition. Whereas the gradual change in E_a with composition is reasonable for systems which interact, this is not consistent with the relatively constant T_g observed over the same range. No explanation is available for this apparent discrepancy.
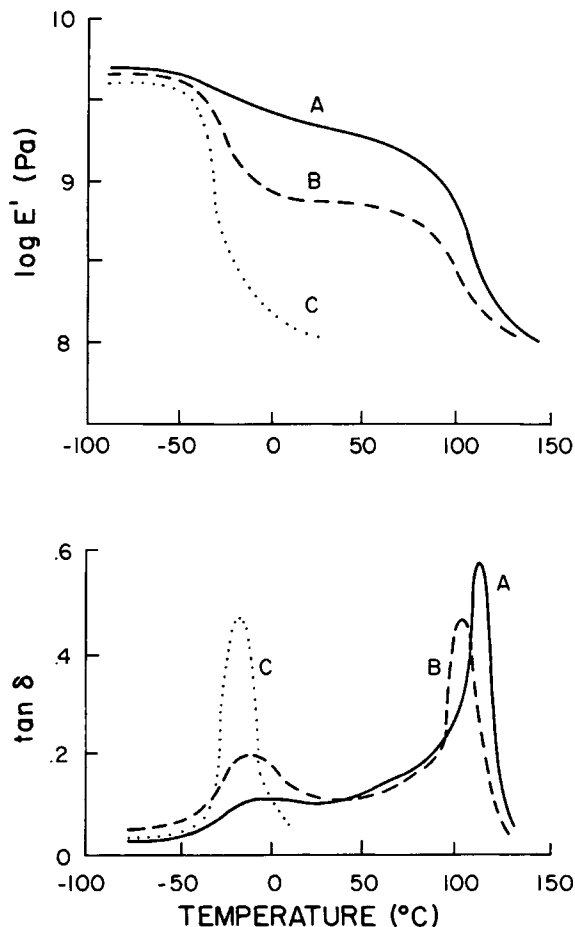
Fig. 6. Dynamic mechanical properties of blends with varying LPU/PMMA compositions: (A) B(.25), (B) B(.5), and (C) B(.75). The T_g of the LPU was ca. $-52°C$ and the T_g of the PMMA was 116°C.

Log E' Behavior. The storage modulus (log E') of a composite in which both components are continuous should not decrease substantially in the temperature range between the two T_g transitions. Materials comprised of a dispersed glassy domain in a continuous elastomeric matrix would be expected to exhibit a large decrease in log E' at the T_g of the elastomer because discrete glassy domains would not be able to contribute a substantially to the material's log E'. However, if the glass component were to form a continuous structure, the log E' would remain high.

The log E' response for the different composites varied consistently (Figs. 2, 3, 5, and 6). In particular the log E' response for the IPN and S-1 materials differed from that of the S-2 and blend systems. The log E' declined sharply at low temperature (ca. $-25°C$) for all composites with an LPU content of 75%. For the IPN (.5), S-1(.6), and S-1(.5), the log E' did not sharply decline at the temperature which corresponded to the tan δ peak for the LPU component (ca. 20°C). A complete drop in log E' was not observed until the temperature

TABLE III
Thermal Transitions by DMTA and DSC of IPN, S-1, S-2, and B-Composites

Composite type	DMTA Tan δ peak temperature (C)		DSC T_g (C)	
	LPU	PMMA	LPU	PMMA
IPN (1.0)	−37	—	−41	—
IPN (.75)	−18	NR[a]	−30	NR[a]
IPN (.5)	22	108	19	100
IPN (.25)	−23	110	−26	104
IPN (0)	—	126	—	118
S-1 (1.0)	−37	—	−41	—
S-1 (.75)	−22	112	−34	NR
S-1 (.6)	−24	88	−30	84
S-1 (.5)	21	109	10	100
S-1 (.4)	NR[a]	105	−20	101
S-1 (.25)	NR[a]	110	−18	104
S-1 (0)	—	116	—	108
S-2 (1.0)	—	—	−59	—
S-2 (.75)	−31	NR[a]	−39	NR[a]
S-2 (.6)	−28	NR[a]	−34	NR[a]
S-2 (.5)	−26	96	−32	91
S-2 (.4)	NR[a]	110	−25	101
S-2 (.25)	NR[a]	108	NR[a]	100
S-2 (0)	—	126	—	118
B (1.0)	—	—	−59	—
B (.76)	−34	NR[a]	−47	NR[a]
B (.5)	−28	91	−40	86
B (.25)	NR[a]	102	NR[a]	99
B (0)	—	116	—	108

[a] Transition was not resolved.

TABLE IV
Effect of S-1 Composition on the Activation Energy (E_a) of the Glass Transition (T_g)

Composite type	LPU (%)[a]	LPU		PMMA	
		T_g (C)	E_a (kJ/mol)	T_g (C)	E_a (kJ/mol)
S-1 (1.0)	1.0	−37	196	—	—
S-1 (.75)	0.75	−22	218	112	183
S-1 (.6)	0.60	−24	NR[b]	88	203
S-1 (.5)	0.50	21	NR[b]	109	224
S-1 (.4)	0.40	NR[b]	—	105	253
S-1 (.25)	0.25	NR[b]	—	110	276
S-1 (0)	0.0	—	—	116	308

[a] Weight fraction of LPU in composite.
[b] Transition was not resolved.

rose above the T_g of PMMA. This indicates the presence of a continuous PMMA phase. However, the log E' response of S-2(.6), S-2(.5), and B(.5) reflected a large decrease at the T_g of LPU above which it was essentially complete. This may be explained with PMMA domains acting as filler particles in the rubbery LPU, thereby making a relatively small contribution to the log E' of the composite above the T_g of LPU.

The log E' reached a plateau at temperatures above the LPU T_g for both the IPN and S-1, but not for the S-2 or B. Both of these behaviors, the presence of a plateau for the IPN(.75) and S-1(.75) and the absence of a distinct low temperature decrease in the IPN(.5), S-1(.6), and S-1(.5) indicate differences in morphology between the IPN and S-1 group and the S-2 and B series.

One of the basic tenets behind the concept of IPN materials is that a high level of crosslinking of one polymer will limit phase separation of the second component as it is being polymerized. By limiting phase separation the material will possess a more homogeneous morphology which may lead to synergistic behavior.[1,27] In some cases, differences in a material's morphology should be reflected to a greater extent by the log E' response than the tan δ behavior. The IPN and S-1 composites, with their limited phase separation, may form a more continuous supermolecular network throughout the composite than comparable linear blends. The branched LPU of the S-2 materials and B might allow for substantial phase separation, and thus form the more common heterogeneous morphology, depending on composition. The two groups of materials (IPN and S-1 vs. S-2 and B) would be expected to have very different log E' behavior above the T_g of the LPU. This concept is supported by the observed major differences in log E' behavior between the two LPU/PMMA groups different in regard to crosslinking. The calculated M_c value for the LPU component (i.e., 770 d) indicates a highly crosslinked network which is not likely to possess sufficient mobility for substantial phase separation.

The log E' data thus support the concept of a supermolecular PMMA structure which is continuous throughout the IPN and S-1 composites, while the dispersion of glassy (PMMA) domains in a continuous rubbery (LPU) matrix is indicated for the S-2 and B materials.

Mechanical Properties

Effects of Crosslinking. The Youngs modulus (MOE), ultimate strength and ultimate strain data for the different LPU/PMMA composites* (Table V) reveal that the composition of the composites affected the mechanical properties. In general, MOE and ultimate strength declined while ultimate strain increased as the LPU content increased. Differences between the MOE of the IPN, S-1, and S-2 at 25%, and of the IPN, S-1, and S-2 at 40%, were not significant. However, as the LPU content increased to above 50%, significant differences became apparent for the IPN and S-1 group, and S-2. The IPN and S-1 group of materials (with crosslinked LPU) exhibit a higher MOE than the S-2 group (with only a branched LPU component).

Differences between the various composites were also supported by ultimate strength data. The S-2 series, which at high LPU contents may be comprised

* The blends (i.e., B-series of materials) were too brittle to allow for sample preparation and testing.

TABLE V
Effect of Composition on Mechanical Properties of IPN, S-1, and S-2 Composites

Composite type	LPU/PMMA	Young's modulus (MPa)	Ultimate strength (MPa)	Ultimate strain (%)
IPN (1.0)	1.0	8	3.8	34.9
IPN (.75)	.75	80	11.3	33.9
IPN (.5)	.5	500	16.6	28.4
IPN (.25)	.25	1,740	33.5	6.2
IPN (0)	0.0	3,200	35.0	2.4
S-1 (1.0)	1.0	8	3.8	34.9
S-1 (.75)	.75	80	10.5	29.9
S-1 (.6)	.6	150	14.9	30.0
S-1 (.5)	.5	490	23.5	22.8
S-1 (.4)	.4	600	29.4	21.1
S-1 (.25)	.25	1,630	38.0	17.7
S-1 (0)	0.0	2,850	36.2	4.2
S-2 (1.0)	1.0	—	—	—
S-2 (.75)	.75	5	1.2	31.2
S-2 (.6)	.6	17	4.8	24.0
S-2 (.5)	.5	80	8.3	25.1
S-2 (.4)	.4	550	24.1	20.3
S-2 (.25)	.25	1,840	37.0	16.8
S-2 (0)	0.0	3,200	35.0	2.4

[a] The blends (i.e., B-series of materials) were too brittle to allow testing.

of a rubbery matrix, produced lower strength values than either the IPN or the S-1 materials. Even at LPU contents of 75%, the IPNs and S-1s showed good strength properties while the S-2 materials were quite weak. This indicates that the high strength PMMA made a greater contribution to the mechanical properties of the IPN and S-1 composites than to those of the S-2s at low PMMA contents.

Differences in the ultimate mechanical properties were similar to those of the log E' response, which reflected distinction between the morphology of the IPN and S-1 materials compared to the S-2s (Table V).

Several models have been developed that predict a material's mechanical properties for different molecular morphologies.[1,12,13] Although these models commonly use the log E' values as the material response, the Young's modulus (MOE) was selected for the interpretation of LPU/PMMA data because the MOE values were felt to more accurately reflect the material's characteristics and could be easily replicated. The MOE values predicted from eqs. (1), (2), and (3) are shown in Figure 7. Eq. (1)[12] predicts a MOE value which is the sum of the individual parts. This model is appropriate for random copolymers. Eq. (2)[12] predicts for a positive interaction between the two polymer components, and this is thought to be appropriate for materials which possess dual phase continuity.[4] The Budiansky equation [Eq. (3)][13] is used to model materials which undergo phase inversion. Possible differences in the morphology of the various LPU/PMMA materials may be discussed on the basis of these models. The MOE values, which were measured at room temperature, for both
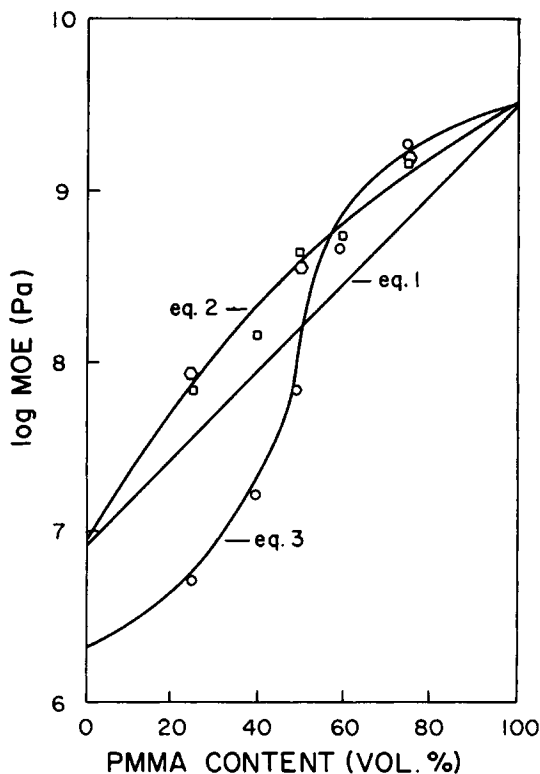
Fig. 7. Effect of composition and IPN type of the Youngs modulus (MOE): (○) IPNs, (□) S-1s, and (○) S-2s. The lines represent eqs. (1), (2), and (3) in the text. These equations are the logarithmic rule of mixtures [eq. (1), Ref. 12], the equation of Davies with $n = \frac{1}{5}$ [eq. (2), Ref. 12] and the equation of Budiansky [eq. (3), Ref. 13].

the IPN and S-1 materials substantially follow the behavior predicted by the Davies equation, while the Budiansky equation provided a good fit for the MOE values of the S-2 composites (Fig. 7). The fit of the experimental data to the models corresponds to predicted differences in morphology based on different methods of synthesis. Both the IPN and S-1 materials were prepared with the tightly crosslinked LPU formed first. This limits phase separation of PMMA, and allows for a material with dual phase continuity. The S-2 composites, by contrast, were prepared with a branched rather than a crosslinked LPU component. Thus, the first formed component (the rubbery LPU) retains significant mobility at room temperature, which allows for phase separation during MMA polymerization. These differences are consistent with the log E' and ultimate strength results of the IPNs. The dual phase continuity of the IPN and S-1 composites allows the stronger PMMA to support the rubbery LPU, while in the S-2s the continuous LPU matrix is not substantially reinforced by PMMA domains.

CONCLUSIONS

LPU/PMMA composites can be prepared by several different reaction sequences. The polymerization sequence, and the presence or absence of cross-

linking, allows for the preparation of IPN, semi-1-IPN, semi-2-IPN, and blend composites over a wide range of compositions. The dynamic mechanical, thermal, and mechanical properties of these materials were found to vary with composition.

Dynamic mechanical and thermal analysis of these composites revealed separate T_gs for both the LPU and PMMA components. These T_gs were shifted towards each another, away from the T_g of the pure components. This modification in T_g, which did not appear to be related to the material's composition, indicated partial interaction between the two components. Previous work with similar systems has noted the possibility of secondary interactions between the aromatic system and n-π electrons in the PMMA side chain. A substantial broadening of the tan δ response indicated some mixing for the systems where the LPU was crosslinked (IPN and S-1) and comprised 50 to 60% of the material. The log E' response also appeared to depend on the presence of crosslinks in the LPU. These differences in log E' were substantiated by tensile tests.

Both MOE and ultimate strength increased while ultimate strain decreased as the PMMA content increased. The mechanical properties proved to be sensitive to the presence (or absence) of crosslinking in the LPU. In particular, the MOE values for both the IPN and S-1 materials were greater than predicted by a simple logarithmic rule of mixtures. The MOE values for both the IPNs and S-1s followed the behavior predicted by the model developed by Davies. This model is appropriate for materials which possess dual phase continuity. The MOE values for the S-2s follow behavior predicted by a model developed by Budiansky; this model is appropriate for materials which undergo phase inversion. Thus it was concluded that the presence of crosslinking in the IPN and S-1 composites allowed each component to form continuous structures throughout the material.

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