Interpenetrating Polymer Networks Based on Thermoplastic Polyurethanes (TPUs) and cis-1,4-Polyisoprene

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SYNOPSIS

Semi-interpenetrating polymer networks based on two elastomers, cis-1,4-polyisoprene (PI) and thermoplastic polyurethane elastomers (TPUs) were prepared in varying compositions. The PI component was cross-linked using peroxide initiators. Modulus and mechanical properties were investigated as a function of composition and temperature. Slight synergisms were observed in mechanical properties, particularly for compositions containing 10% PI by weight. Little or no molecular mixing is shown by differential scanning calorimetry (DSC) for these two-phase materials. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The fields of polyurethanes and polyurethane-based interpenetrating polymer networks (IPNs) have had many important advances in recent years. There are several classes of the polyurethanes: Some are used in foams; others make outstanding fibers. A particularly interesting class of the polyurethanes are the so-called segmented elastomers, which are a type of multiblock copolymer.[1-3] These materials usually contain a polyether or polyester elastomeric block alternating with a urethane linkage. The elastomeric block is frequently made so that it crystallizes on extension, providing a certain degree of self-reinforcement. Polyurethane materials have been used in numerous industrial and commercial applications.[4] In the medical field, e.g., applications have included medical-grade tubing.[5-7]

A polyurethane may serve as network I in a sequential IPN synthesis[8] or in prepolymer form as one component of simultaneous interpenetrating networks (SINs).[9,10] One of the more interesting developments has been made by Meyer and co-workers,[11,12] who investigated compositions based

on cross-polyurethane-inter-cross-poly(methyl methacrylate) (PMMA). In general, the synthesis involved an aromatic triisocyanate and a poly(ether glycol). The PMMA network resulted from an AIBN-initiated free radical polymerization with a trimethacrylate cross-linker. The resulting IPNs exhibited two loss peaks in tan δ temperature studies, but the glass transitions were shifted inward significantly, with broadening. This inward shifting of the T_g indicates a certain extent of molecular mixing. More recently, Jin and Meyer[13] studied the kinetics of reaction of these IPNs. Other workers interested in polyurethane-based IPNs and SINs include Frisch et al.,[14,14a] Hourston and Huson,[15] Allen et al.,[16] and Klempner et al.[17]

Each of these IPNs or SINs was made with an elastomeric polyurethane and a rigid plastic of some sort, PMMA or polystyrene being the most popular. Up to this time, few IPNs or SINs have been made where both components are elastomeric.[14a] Some of the questions that may be raised are: What is the stress–strain behavior of an elastomer–elastomer IPN? What are the effects of crystallization on the mechanical behavior?

In this article, IPNs based on polyurethanes and cis-polyisoprene are described. Both the components are elastomeric, their glass transition temperatures lying in the range −65 to −40°C. Both components are known to crystallize on extension.

An IPN is a combination of two polymers in network form, at least one of which is synthesized and/ or cross-linked in the immediate presence of the other.[18,19] Semi-IPNs are those in which only one polymer component is cross-linked, the other being linear.[19] There is another type of IPN called "thermoplastic IPN," in which the chemical cross-links are replaced by physical cross-links, e.g., the crystallites in semicrystalline polymers and the ionic portions of ionomers.[19] In the present system, only one component, cis-polyisoprene, contains chemical cross-links. The polyurethane component is crystallizable and, hence, contains physical cross-links.

EXPERIMENTAL

Materials

Two series of IPN compositions were prepared, each using a different polyurethane: (1) Elastollan® (MP-100) from BASF Corp. and (2) Morthane® (PE90-100) from Morton International. Both of these polyurethanes (obtained as pellets or granules) fall into the category of polyether-based thermoplastic polyurethanes (TPUs) and are approved for medical use as USP Class VI materials. Linear, synthetic cis-1,4-polyisoprene (PI) was obtained from Aldrich Chemical Co. Benzoyl peroxide (BPO) and dicumyl peroxide (Dicup) initiators were obtained from Aldrich and tetrahydrofuran (THF) solvent from Fisher Scientific Co.

Synthesis

The method of synthesis was to blend the PI and one of the TPUs with a peroxide (BPO for the Elastollan series and Dicup for the Morthane series), followed by compression molding at an elevated temperature to cross-link the PI, forming a network. Approximately 10 × 10 cm films were prepared for each composition in thicknesses of about 1-2 mm.

Elastollan Series

Solutions of PI and Elastollan were prepared in THF solvent with ca. 15% polymer (by weight). Prior to mixing with THF, the PI was masticated in a Brabender mixer at 120°C for 10 min.[20] Otherwise, it was very difficult to form solutions, due to the high physical gel content in PI (the possibility of a slight chemical cross-linking in PI cannot be ruled out either). BPO initiator was added to the PI solution (1.0% of PI). The two polymer solutions were mixed using vigorous stirring in predetermined proportions

and poured into silicone-coated molds. The solution in the mold was degassed in a vacuum chamber to remove the air that was dissolved and trapped during the mixing step. The THF solvent was removed by evaporation (usually required 70–80 h). The polymer film obtained was kept in a vacuum chamber for 90–100 h to remove any residual THF. This film was compression-molded at 120°C for 15 min to cross-link the PI component.

Morthane Series

Morthane was processed in a Brabender mixer at 120°C at 50 rpm. A small quantity of THF was added (ca. 10% on Morthane) to plasticize the polyurethane. After 10 min, PI was added in predetermined proportions and the blending continued for another 10 min. Finally, the Dicup initiator was added as a 10% solution in THF and the mixing continued for 10 more min. The mixture of Morthane, PI, Dicup, and THF was compression-molded in 10 × 10 cm molds at 145°C for 90 min to cross-link the PI component. Most of the THF is evaporated during this step. However, the film was kept in a vacuum chamber for 60–70 h to ensure complete removal of THF. The recipes and the various compositions synthesized are described in Tables I and II.

Characterization

Mechanical testing of all materials was done at room temperature (25°C) on an Instron testing machine (Frame 1011) using a 5000 Newton load transducer. Microtensile test specimens were used for all samples. The specimens had gauge lengths of about 16.8 mm and widths of about 4.8 mm (except for sample nos. 7 and 12, for which the gauge lengths were 33.6 mm and the width 6.3 mm). A constant strain rate of about 150%/min was used for all samples (the crosshead speeds were 25 mm/min for samples with gauge length 16.8 mm, and 50 mm/min for those

Table I   Elastollan Series Recipes

Sample No.	Composition: PI/Elastollan Ratio	BPO (% on PI)
1	0/100	1.0
2	10/90	1.0
3	20/80	1.0
4	30/70	1.0
5	40/60	1.0
6	100/0	1.0

Table II   Morthane Series Recipes

Sample No.	Composition: PI/Morthane Ratio	Dicup (% on Total)
7	0/100	1.0
8	10/90	1.0
9	20/80	1.0
10	30/70	1.0
11	40/60	1.0
12	100/0	1.0

with the gauge length 33.6 mm). A minimum of two specimens were used for each composition.

A Mettler TA-3000 differential scanning calorimeter (DSC) was used to determine the glass transition behavior of the IPNs and the homopolymers. Each sample was quenched from room temperature to $-150°C$ and maintained at that temperature for 2 min, after which it was heated at a rate of 20°C/min under a nitrogen atmosphere.

A Rheometrics dynamic analyzer (RDA-II) was used to determine the dynamic modulus–temperature behavior of a selected composition from the Morthane series. Approximate specimen dimensions were 35 × 12 × 2 mm. A strain of 1.0% was applied at a frequency of 1 rad/s.

A Gehman torsional stiffness tester was also used in accordance with the ASTM-D1053-85 to determine the modulus–temperature behavior of selected compositions from the Morthane series. The samples were held in a stainless-steel Dewar flask filled with air cooled by liquid nitrogen and the whole apparatus allowed to warm up at the rate of about 1–3°C/min. The modulus calculated from a 10 s relaxation is reported.

Extraction experiments were conducted in THF to determine the soluble fractions of the IPNs. Total swelling was also recorded. A Brabender mixer was used to estimate the melt viscosities of the linear homopolymers Morthane and PI. The Brabender measures the torque needed to process a given polymer at a given temperature, which can be converted to viscosity units by using the empirical equations developed by Goodrich and Porter.[21]

RESULTS AND DISCUSSION

Mechanical Properties

Results of mechanical testing are shown for all the materials in Table III. Representative stress–strain plots for each of the compositions are shown in Figures 1 and 2. It was found that the 10% PI composition in the Elastollan series has an elongation to break higher than that for either of the two homopolymers. In the Morthane series, the elongation to break for all compositions prepared is greater than the value for the parent polyurethane, but less than that for the pure PI of the same series.

Table III   Mechanical Characterization of Elastollan- and Morthane-Series IPNs

Sample No.	% PI	Modulus (MPa)	Strain at Break	Tensile Strength (MPa)[a]		Toughness (MJ/m³)
				(Eng.)	(True)	
1	0	18.2	8.1	50	457	147
2	10	13.8	9.7	38	407	140
3	20	12.2	8.0	29	261	92
4	30	10.0	7.7	19	165	60
5	40	8.3	7.3	11	91	38
6[b]	100	—	7.1	—	—	—
7	0	10.0	8.2	27	246	110
8	10	8.6	10.3	30	339	135
9	20	5.9	9.5	17	179	74
10	30	5.5	9.9	16	174	67
11	40	4.1	9.2	16	163	57
12	100	0.6	14.5	5	78	22

Samples 1–6 represent the Elastollan series, and samples 7–12 represent the Morthane series.
[a] 1 MPa = 145 psi.
[b] The load required to pull sample no. 6 was too small to be accurately determined by the load transducer used.

The curves shown in Figures 1 and 2 are of *engineering stress* vs. strain, i.e., the load is divided by the initial cross-sectional area. However, since all these materials undergo a very large strain, at the time of rupture, the cross-sectional area of a sample is reduced by a large fraction. So, the tensile strength was calculated by using the final cross-sectional area, i.e., calculating the *true stress*. Table III shows both *engineering* and *true* stress values for the tensile strengths, the relation between the two being

$$\sigma_{\text{true}} = \sigma_{\text{engg}}(1 + \epsilon) \qquad (1)$$

where ϵ is the strain at the breakpoint.

Glass Transitions by DSC

Results of a typical DSC scan are shown in Figure 3 for the 30% PI sample from the Morthane series (sample no. 10). The glass transition for pure PI occurs at $-62°C$. For pure Morthane, a segmented polyurethane, the primary glass transition occurs at $-46°C$ (due to its soft polyether segment). The semicrystalline hard segment of Morthane melts between 145 and 180°C and goes through a faint secondary glass transition at 50°C. Since the primary glass transitions for the two pure polymers are very close, it is difficult to identify them separately in the normal DSC plots (heat flow vs. temperature). A plot of "derivative heat flow" vs. temperature indicates each T_g as an inverted peak. (The lowest point of such a peak is taken as the glass transition temperature. In the normal DSC plot, this refers to the temperature at the point of steepest
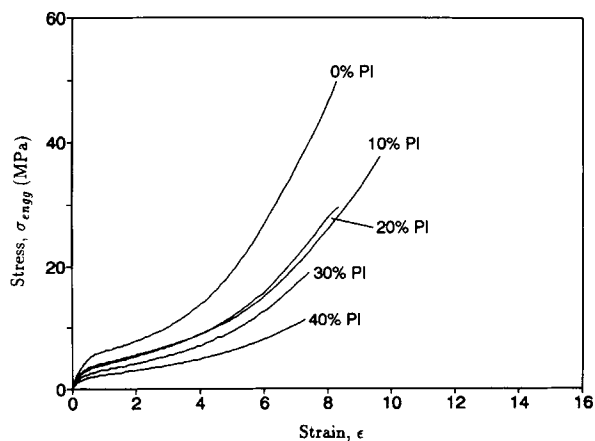

Figure 2 Engineering stress vs. strain plots for IPN samples based on Morthane and PI. Percentage PI in each sample is shown along with its curve. Samples were crosslinked using 1.0% Dicup initiator based on the total mass (PI + Morthane).

slope in the glass transition region.) In Figure 4, each of the two glass transitions for sample no. 10 is seen quite distinctly, which indicates the two-phase nature of these materials. Combining this information with the optical clarity of these materials hints toward a microheterogeneous morphology. DSC results also show faint shifts in the two individual glass transitions (1–2°C), indicating little or no mixing between the two components of the IPNs at the molecular level.

Modulus–Temperature Behavior

Dynamic shear modulus vs. temperature behavior of sample no. 10 (Morthane series, 30% PI) as obtained from RDA-II is shown in Figure 5. Although the storage modulus G' does not show two T_g's, the loss tangent shows two peaks, whereas the loss modulus (G'') shows a shoulder in addition to one peak. The polyurethane soft segment glass transition has a more prominent loss tangent peak than the PI peak, opposite of the DSC result (Fig. 4). This indicates that the polyurethane soft segment might lie in the continuous phase and that the polyurethane forms the continuous (or "more" continuous) phase.

Shear modulus–temperature behavior of sample no. 10 as obtained from the Gehman torsional stiffness tester is also shown (Fig. 6). Once again, the small difference in the two primary T_g's in the sample renders them indistinct. The glass transition covers a slightly broader temperature range of about 80°C as compared to a range of about 60°C for the

Figure 1 Engineering stress vs. strain plots for IPN samples based on Elastollan and PI. Percentage PI in each sample is shown along with its curve. Samples were crosslinked using 1.0% BPO initiator based on the mass of PI.
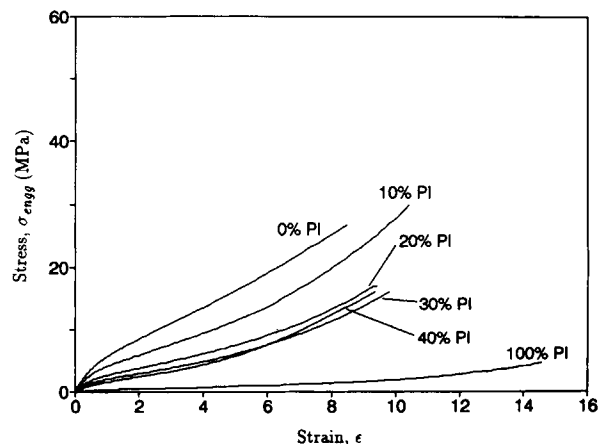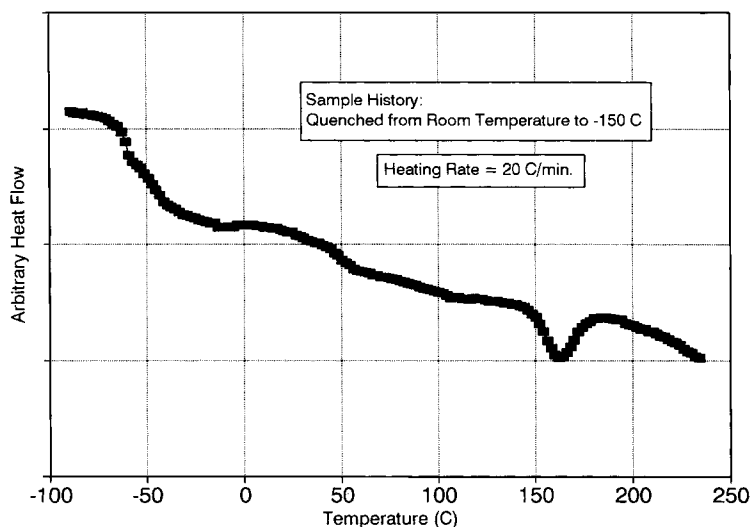
Figure 3 Differential scanning calorimetry scan on sample no. 10 (from the IPN series based on Morthane and PI. The sample contained 30% PI and was cross-linked using 1.0% Dicup initiator based on the total mass (PI + Morthane).

curve from RDA-II. This is not surprising, noting that the specimen temperature may not have been as uniform in the Gehman experiment as in the RDA-II experiment, which has a highly sophisticated specimen chamber.

Comparison of Moduli Values

Table IV compares the values of the room temperature Young's modulus for sample no. 10 as obtained from the three different techniques. RDA-II yields the highest value and the Instron yields the lowest

value. It must be noted that the RDA-II yields E^*, whereas the other two yield E values.

Figure 7 compares the Instron moduli of the Morthane series IPNs (samples 7–12, Table III) with several theoretical models. The top and bottom curves represent the upper- and lower-bound moduli (as predicted by the Takayanagi parallel and series models), respectively.[22] Curves for two models based on dual-phase continuity, the Davies and the Budiansky models, are also shown.[22] It is clear that within the range of experimental error the experimental modulus values lie much closer to the Davies
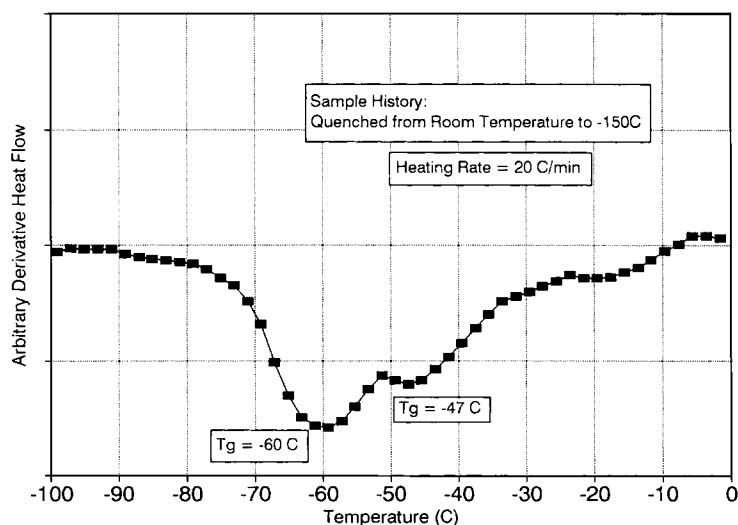

Figure 4 Derivative heat flow vs. temperature curve for the data of Figure 3 showing the primary glass transitions of sample no. 10.
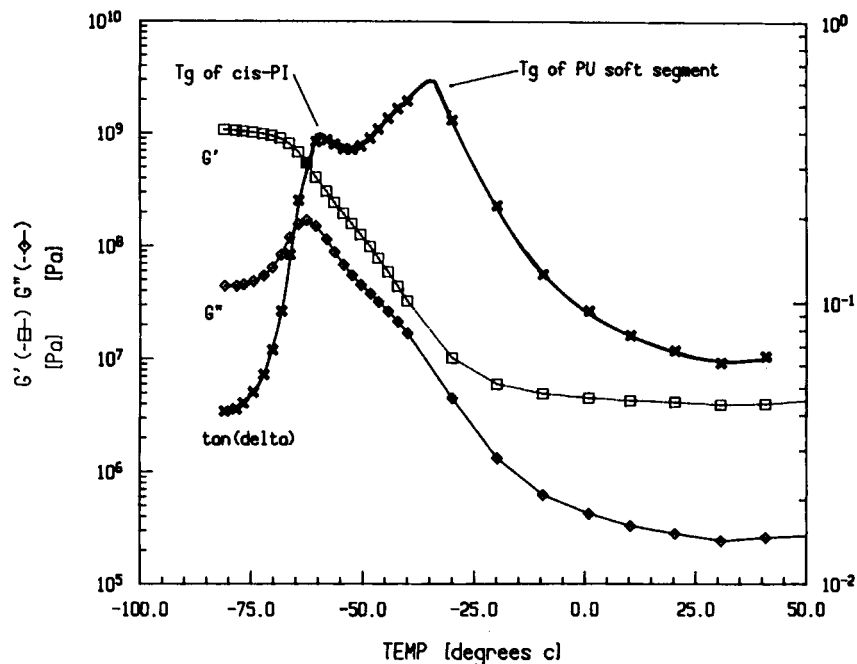
Figure 5   Dynamic shear modulus vs. temperature behavior using RDA-II of sample no. 10 (from the IPN series based on Morthane and PI). The sample contained 30% PI and was cross-linked using 1.0% Dicup initiator based on the total mass (PI + Morthane).

and the Budiansky curves than do the upper and lower bound curves based on the Takaynagi models. This indicates that these IPNs may have dual-phase continuity characteristics.

Swelling and Extraction Experiments

All samples of the Elastollan series, except the 100% PI (sample no. 6), disintegrated when soaked in

THF, meaning that the cross-link density of the PI phase was too low to firmly hold the linear polyurethane in the solvent. The cross-link density of the PI component was higher in the Morthane series. Results from swelling and extraction studies in THF for the Morthane series are shown in Table V. Since PI is the main component chemically cross-linked, the percentage of solubles increases as the percent-
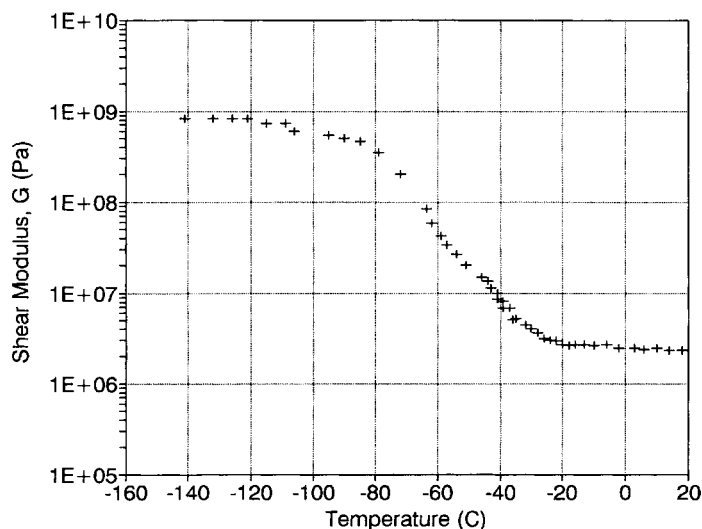

Figure 6   Gehman-shear modulus vs. temperature behavior of sample no. 10 (30% PI + 70% Morthane).

Table IV   Comparison of the Rubbery Moduli Obtained by Different Techniques for Selected Samples

Sample	Instrument/Technique	E (or E^*)[a] (MPa)
Sample no. 6	Theory[b]	0.08
(100% PI; Elastollan series)	Instron	c
Sample no. 12	Theory[b]	0.8
(100% PI; Morthane series)	Instron	0.6
Sample no. 10	RDA-II	12
(30% PI; Morthane series)	Gehman	7
	Instron	5.5
Sample no. 1	Instron	18.2
(100% Elastollan)		
Sample no. 7	Instron	10.0
(100% Morthane)		

[a] For RDA and Gehman, E is calculated as $E = 3G$.

[b] Theory; $E = 3nRT$; n determined from Flory–Huggins equation and swelling data.

[c] The load required to pull sample no. 6 was too small to be accurately determined by the load transducer used.

age of Morthane increases in the sample. However, the 0% PI (100% Morthane) sample is not completely soluble, which indicates that the some cross-linking is also introduced in the polyurethane component, possibly by a hydrogen-abstraction mechanism. The 100% PI sample (no. 12) has a soluble fraction of less than 4%.

The number of network chain segments per cm^3, n, were calculated for the 100% PI samples from both series (i.e., sample nos. 6 and 12) using the Flory–Rehner equilibrium swelling equation[23]:

$$-[\ln(1 - v_2) + v_2 + \chi_{12}v_2^2]$$

$$= V_1 n \left[v_2^{1/3} - \frac{(v_2)}{2} \right] \quad (2)$$

The polymer–solvent interaction parameter χ_{12}, for PI and THF, was calculated by the equation[24]:

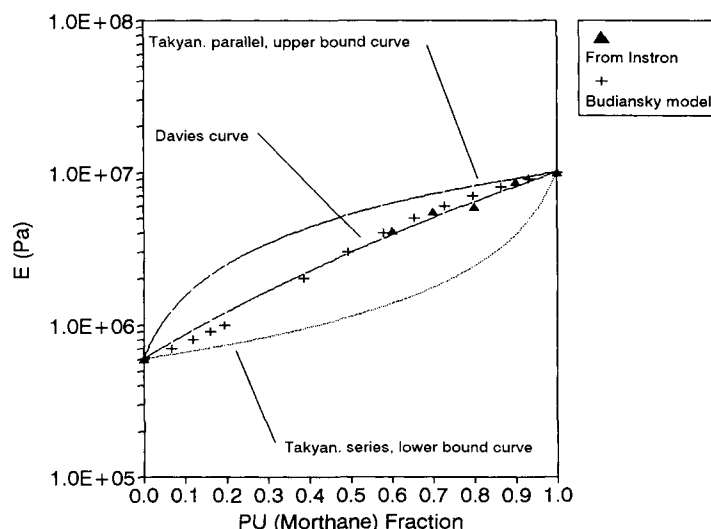$$\chi_{12} = \frac{V_1(\delta_1 - \delta_2)^2}{RT} \quad (3)$$

Figure 7   Instron moduli for the Morthane series samples vs. Morthane content (solid triangles). The upper and lower curves represent the Takayanagi parallel (upper bound) and series (lower bound) models, respectively.

Table V   Results of Swelling and Extraction Studies on Morthane Series IPNs Using THF Solvent

Sample No.	% PI	% Morthane	Equilibrium Polymer Volume Fraction (v_2)	% Solubles
7	0	100	0.07	69.9 ± 2.3
8	10	90	0.13	80.0 ± 0.8
9	20	80	0.12	68.1 ± 3.2
10	30	70	0.12	65.7 ± 1.6
11	40	60	0.13	53.8 ± 0.3
12	100	0	0.10	3.4 ± 1.7

where V_1 is the molar volume of the solvent; the δ's, the solubility parameters of the solvent and the polymer; R, the universal gas constant; and T, the absolute temperature. The parameters involved were assigned the following values:

$$V_1 \text{ (THF)} = 81.36 \text{ cm}^3/\text{mol};$$
$$\delta_1 \text{ (THF)} = 9.1 \text{ (cal/cm}^3)^{1/2}; \quad \text{(from Ref. 25)}$$
$$\delta_2 \text{ (PI)} = 7.9 \text{ (cal/cm}^3)^{1/2}; \quad \text{(from Ref. 26)}$$
$$R = 1.986 \text{ cal/mol K};$$
$$T = 298 \text{ K}.$$

The value of χ_{12} for this system was calculated to be 0.20.

For sample no. 12 (the 100% PI sample from the Morthane series), eq. (2) then provides a value of $n = 1 \times 10^{-4}$ mol/cm^3. Using the rubber elasticity equation[27]:

$$E = 3nRT, \tag{4}$$

this predicts a modulus of 0.8 MPa at room temperature (25°C), which is within the experimental error of the Instron-determined modulus, 0.6 MPa (see Table IV), noting the sensitivity of the Instron transducer.

For sample no. 6 (the 100% PI sample from the Elastollan series), the cross-link density is calculated as $n = 1 \times 10^{-5}$ mol/cm^3, which is an order of magnitude lower than for the corresponding composition in the Morthane series. Equation (4) then predicts a modulus of 0.08 MPa at room temperature (note that for this sample the Instron modulus could not be determined due to instrument limitations, Table IV).

It should be noted that at room temperature (25°C) linear PI, natural rubber, has an average molecular weight between entanglements, M_e: value of 6100 g/mol.[28] Thus, the effective physical cross-link level, n_p, can be estimated as approximately 1.5 $\times 10^{-4}$ mol/cm^3 ($n_p = \rho/M_e$; where ρ, the PI density = 0.91 g/cm^3). This indicates that in all the samples

of this study the level of physical entanglements for the PI component is higher than that of chemical cross-linking.

Melt Viscosities of Morthane and PI

Torque measurements on the PI and Morthane polymers yield their melt viscosities at 145°C. The following relation was used[21]:

$$\eta \text{ (poises)} = 450 \frac{M \text{ (meter-grams)}}{S \text{ (rpm)}} \tag{5}$$

where η is the melt viscosity of the polymer; M, the torque as read by the Brabender; and S, the rpm of Brabender operation. The torque read from the instrument at 20 min from the start was used: 2300 meter-grams for Morthane and 1800 meter-grams for PI, respectively (both at $S = 50$ rpm) (Table VI).

Thus, the ratio of the viscosities of PI and Morthane is roughly 0.78. Based on the equation

$$\frac{\eta_1}{\eta_2} \cdot \frac{\phi_2}{\phi_1} = 1 \tag{6}$$

for dual-phase continuity,[18,29] this means that a composition with approximately 44% PI + 56% polyurethane (Morthane) would form the theoretical center of the dual-phase continuity region on

Table VI   Melt Viscosity Calculated from Brabender Torque Measurements for PI and Morthane[21]

Polymer	Rpm, S	Torque, M (meter-grams)	Viscosity, η[a] (Pa-s)
PI	50	1800	1620
Morthane	50	2300	2070

Operating temperature = 145°C.
[a] 1 Pa-s = 10 poise.

the composition scale. Samples with significantly lower than 44% PI might be expected to have polyurethane as the continuous phase. However, there is some evidence from Figure 7 that samples with 10–40% PI might have dual-phase continuity in this system.

DISCUSSION

Two series of semi-interpenetrating polymer networks were prepared using two thermoplastic polyurethanes and cis-1,4-polyisoprene (PI). The PI component was chemically cross-linked using a free-radical initiator. The cross-link density in the Elastollan series was an order of magnitude lower than that in the Morthane series (10^{-5} vs. 10^{-4} mol/cm^3). Swelling and extraction experiments show that some cross-linking is also introduced in the polyurethane component along with the cross-linking in the PI component.

Several factors need to be considered in determining the approach to equilibrium in phase-separated systems:

1. If the polymers are linear and amorphous, then interdiffusion is limited by the value of the free energy of mixing, usually positive, opposing mixing. Kinetic aspects include the position of the glass transition temperature, molecular weight, and the time alloted to diffusion. If the polymer blend is held above T_g, then the polymers ought to approach equilibrium reasonably rapidly, albeit only slightly mixed.
2. If both polymers are chemically cross-linked, then the system is physically locked together. Phase separation will always be nonequilibrium, with some trapped chains.
3. If only one polymer is cross-linked, then phase equilibrium may still be attained, but the time frame may be longer.

In the present system, formed by blending, then chemically cross-linking one component, with the other component physically cross-linked via crystalline regions, phase equilibrium may be approached very slowly. However, both polymers being above their glass transition temperatures may lead to a rapid attainment of phase equilibrium on a microscopic level. On the other hand, at the macroscopic level, the system may be permanently "locked" a bit short of the true phase equilibrium, due to cross-links. For IPNs, such a state might be called a "metastable-phase equilibrium" in order to differentiate it from the true phase equilibrium, which might be attained in the absence of cross-links.

DSC data shows the phase-separated nature of the IPNs with little or no mixing at the molecular level. The phase-separated nature of these IPNs, combined with their optical clarity, suggests a microheterogeneous morphology. However, firm conclusions cannot be made in the abscence of transmission electron microscopy (TEM) studies. Although the degree of chemical cross-linking in the polyurethane component is low, there is a significant degree of "physical cross-linking" owing to its semicrystalline polyurethane hard segments. In this respect, these compositions have structures intermediate between semi-IPNs and thermoplastic IPNs.

Synergistic behavior was observed in mechanical properties for the 10% PI compositions in both series of semi-IPNs. Although the mechanism responsible for these slight synergisms has not been investigated, it is believed that crystallization of both polymers plays an important role. The hard segments of the polyurethanes are crystalline initially. PI undergoes crystallization on stretching via strain-induced crystallization (SIC),[30,31] possibly creating a micromechanism for mutual reinforcement.

CONCLUSIONS

IPNs based on polyurethanes and cis-1,4-polyisoprene constitute a new class of material, where both components are elastomeric, with characteristics of dual-phase continuity. Mechanical property improvements may result from strain-induced crystallization.

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