

Polyurethane Interpenetrating Polymer Networks.

V. Engineering Properties of Polyurethane-Poly(methyl Methacrylate) IPN's

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Synopsis

The engineering properties of polyurethane-poly(methyl methacrylate) simultaneous interpenetrating networks (SIN's) were evaluated. The hardness behavior reflected the observed phase inversion in the electron-microscopic studies. The maximum ultimate tensile strength was observed at 85% polyurethane-15% poly(methyl methacrylate) IPN and was due to the filler-reinforcing effect of the rigid poly(methyl methacrylate) phase. The ultimate tensile strength of the 75/25 polyurethane-poly(methyl methacrylate) IPN was higher than that of the corresponding pseudo-IPN's (only one network crosslinked) and the linear blend. The leathery and glassy compositions did not show any reinforcement in the ultimate tensile strength. This indicated that the reinforcement in the ultimate tensile strength was not *directly* related to interpenetration (by increased physical entanglement crosslinks), but *indirectly* related by reducing the rigid phase domain sizes and increasing the adhesion between the two phases, thus enhancing the filler-reinforcing effect similar to that observed in a carbon black-filled rubber. The tear strengths of the polyurethane-rich IPN's pseudo-IPN's, and linear blends were found to be higher than that of the pure polyurethane as a combined result of increased modulus and tensile strength. The weight retentions in the thermal decomposition of the IPN's, pseudo-IPN's, and linear blends were higher than the proportional average of the component networks. The results seemed to indicate that this enhancement was related to the presence of the unzipped methyl methacrylate monomer. It was suggested that the monomers acted as radical scavengers in the polyurethane degradation, thus delaying the further reaction of the polyurethane radicals into volatile amines, isocyanates, alcohols, olefins, and carbon dioxide.

INTRODUCTION

The engineering properties of interpenetrating polymer networks (IPN's) (as well as other properties) are largely dependent on the morphology. In homogeneous IPN systems, the effect of interpenetration was shown to be due to the increased physical entanglement crosslinks. Frisch et al.¹ observed a maximum in the ultimate tensile strength versus composition, a maximum which was significantly higher than the ultimate tensile strengths of the constituent networks. It was also observed that the ultimate tensile strength was dependent on the level of interpenetration (no significant enhancement was observed when

the network crosslink density was high, thus limiting the probability of interpenetration).

The nature of intermolecular forces existing in the constituent network also plays an important role in affecting the mechanical properties. Strong hydrogen bonding in the constituent network would be reduced if the network was interpenetrated by other network chains, thus reducing the ultimate tensile stress until the increased physical entanglement effect becomes significant.

In heterogeneous systems, however, the effect of interpenetration has not been clearly identified. Whether the effect of interpenetration on the morphology (reducing the phase domain sizes and thus indirectly affecting the mechanical properties) is significant or the direct effect of interpenetration on engineering properties (increased physical entanglement crosslinks and increased adhesive bonding between the continuous and dispersed phase) is significant, for each particular system, has not been determined. It is generally believed that the filler-reinforcing effect (when the rubbery component assumes the continuous phase) and the rubber-reinforcing effect (when the glassy component assumes the continuous phase) plays a major role in determining the engineering properties in addition to the interpenetration effect.^{2,3} The comparative analysis of the IPN's with the corresponding pseudo-IPN's (only one network crosslinked) and linear blends could enable one to distinguish the effect of interpenetration in a heterogeneous IPN system.

The thermal stability of IPN's has been measured by thermogravimetric analysis. Although in some cases enhanced thermal stability has been observed in IPN's compared to each component network,⁴ indications are that this is not a general phenomenon applicable to all IPN's.

In this paper, we report the hardness, tensile, and tear strengths and the thermogravimetric analyses of polyurethane-poly(methyl methacrylate) IPN's.

EXPERIMENTAL

Synthesis

The preparation of polyurethane-poly(methyl methacrylate), simultaneous IPN's, pseudo-IPN's, and linear blends were reported elsewhere.⁵ Briefly, the linear prepolymers were combined in bulk in various proportions along with their crosslinking agents, sheets molded, and thermally crosslinked. Pseudo-IPN's (one component linear) and linear blends were prepared in a similar fashion, omitting the appropriate crosslinking agents. The sample compositions were coded for the convenience of presentation. The first letter denotes the polymer type [U for polyurethane and M for poly(methyl methacrylate)], the second letter denotes the nature of the polymer (L for linear and C for crosslinked), and the third numeral denotes the weight percentage of the polymer.

Measurements

The durometer hardness was measured at room temperature using a Shore A hardness tester according to ASTM D 2240. The ultimate tensile strength, elongation at break, and tear strength were measured on an Instron tensile tester

Model 1130 at room temperature. All the samples were conditioned according to ASTM D 618, procedure A. The samples for the tensile measurements were cut in a dumbbell shape of $\frac{3}{16}$ in. in width, $\frac{3}{4}$ in. in span, and 0.05–0.08 in. in thickness. ASTM D 638 procedure was followed employing a cross-head speed of 2 in./min. The samples for the tear measurements were cut with a Graves tear die with a 90-degree angle and 0.5 in. in width at the tearing point. ASTM D 1004 procedure was followed employing a cross-head speed of 2 in./min.

TGA thermograms were obtained on a du Pont Model 950 thermogravimetric analyzer. The samples, ranging between 10 and 15 mg in weight, were placed in platinum sample pans under a continuous nitrogen flow of 1.5 cubic feet/hr. The weight retention as a function of temperature was recorded when the samples were subjected to continuous heating of 20°C/min.

RESULTS AND DISCUSSION

Hardness

The indentation hardness, which reflects the resistance to local deformation, is a complex property related to the modulus, strength, elasticity, and plasticity.⁶ However, in the case of elastic materials, the depth of penetration of the spherical indenter has been shown to be related to Young's modulus E , Poisson's ratio ν of the polymer, and the total force F on the spherical indenter of radius R by the following equation:⁷

$$h = \left[\frac{3}{4} \left(\frac{1 - \nu^2}{E} \right) \right]^{2/3} F^{2/3} R^{-1/3}$$

The hardness–composition curve (Fig. 1) agrees well with the modulus behavior.⁸ The hardness of the 75% polyurethane–25% poly(methyl methacrylate) IPN is lower than the corresponding pseudo-IPN's and linear blend, and even slightly lower than the 100% crosslinked polyurethane. This is due to the reduced crystallinity of the polyurethane phase in IPN's because of the interpenetration of poly(methyl methacrylate) chains (more completely described in ref. 8). The plot also reflects the phase inversion process where the hardness increases rapidly at 60–70% polyurethane concentration.

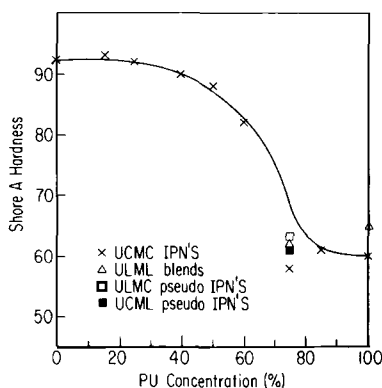


Fig. 1. Hardness vs. composition for IPN's, pseudo-IPN's, and linear blends.

TABLE I
Tensile and Tear Strengths^a

Composition	Ultimate tensile strength, psi	Elongation at break, %	Tear resistance, lb/in.
Homopolymers			
UC100	5159	780	252
UL100	5629	815	339
MC100	4106	4.9	—
IPN's			
UC85MC15	6096	767	294
UC75MC25	5127	833	355
UC60MC40	3265	300	381
UC40MC60	2592	43	—
Pseudo-IPN's			
UC75ML25	4072	728	364
UL75MC25	4157	749	369
Linear polyblends			
UL75ML25	4280	853	341
Average error range	500	71	16

^a Cross-head speed, 2 in./min.

Tensile and Tear Strength

The tensile and tear strength results are shown in Table I. The ultimate tensile strength, elongation at break, and tear strength measurements are rather rough estimates of the real property, particularly for the rigid specimens, since all of the measurements depend critically on local irregularities as governed by specimen preparation.

The leathery samples (UC60MC40, UC40MC60) showed stress whitening during elongation. The samples with the linear polyurethane became opaque at high elongation due to crystallization induced by orientation.

The ultimate tensile strength reached a maximum at the IPN composed of 85% polyurethane–15% poly(methyl methacrylate). Maximum tensile strength was also observed in the polyurethane–polystyrene IPN's.⁹ The electron micrographs⁵ showed that the polyurethane phase is continuous at this concentration. The increased tensile strength is due mostly to the filler-reinforcing effect of the dispersed glassy poly(methyl methacrylate) phase, since the other compositions did not show such an increase. Thus, the increased physical entanglement due to interpenetration did not contribute directly to increasing tensile strength in this IPN system, in contrast to the significant effect observed in previous studies on homogeneous IPN's.^{10,11} However, the interpenetration at the phase boundaries apparently does enhance the filler-reinforcing effect by reducing the domain sizes and increasing the adhesion between the phases.^{12,13}

The fact that the ultimate tensile strength of the 75% polyurethane–25% poly(methyl methacrylate) IPN is higher than that of its corresponding pseudo-IPN's, and the linear blend reflects the previously discussed interpenetration effect well, since the domain sizes of the pseudo-IPN's and the linear blend were significantly greater than those of the full IPN.⁵ The elongation-at-break results show a rapid drop at around 75–60% polyurethane concentration

TABLE II
TGA Results

Composition	Temperature at weight loss, °C					
	5%	10%	20%	30%	40%	50%
Homopolymers						
UC100	335	349	366	377	387	398
UL100	321	338	361	381	395	403
MC100	264	278	297	317	343	360
ML100	255	278	303	332	354	367
IPN's						
UC85MC15	335	349	367	385	398	407
UC75MC25	347	363	384	403	413	420
UC60MC40	325	348	372	387	398	406
UC40MC60	327	344	362	375	386	396
UC25MC75	318	339	358	369	380	388
UC15MC85	247	278	320	338	352	362
Semi-IPN's						
UC75ML25	345	362	385	407	420	429
UL75MC25	338	362	378	406	418	427
Linear polyblends						
UL75ML25	339	361	378	404	417	426

and seem to reflect the phase inversion. The Graves tear resistance results show increased tear resistance in most of the elastomeric samples. There is no difference in the tear resistance among IPN's, pseudo-IPN's, and the linear blend at the 75% polyurethane-25% poly(methyl methacrylate) composition. The Graves tear resistance is complicated in nature, and the relation to other properties is difficult.

Thermogravimetric Analysis

The thermogravimetric analysis (TGA) results are shown in Table II and Figures 2 and 3. The maximum experimental error range was $\pm 5^\circ\text{C}$. The

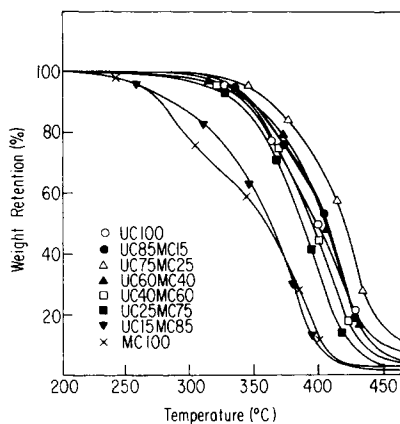


Fig. 2. TGA thermograms for IPN's.

polyurethane–poly(methyl methacrylate) IPN's all show enhancement of the weight retention compared to the proportional average of the weight retentions of the pure components (Fig. 2). In particular, the 75% polyurethane–25% poly(methyl methacrylate) IPN exhibits maximum weight retention.

The comparison between the IPN, the pseudo-IPN's, and the linear polyblend at 75% polyurethane concentration (Fig. 3) indicates that there is no significant difference in the degradation behavior and that the enhancement of the weight retention is not related to interpenetration. The weight retention enhancement could be explained by comparing the thermal degradation behavior of the component polymers. Belyakov et al.¹⁴ detected small amounts of carbon monoxide in the thermal degradation of polyurethane based on toluene diisocyanate and ethylene glycol at 250°C in vacuum. He also observed the presence of the radical component in the electron-paired magnetic resonance spectrum.

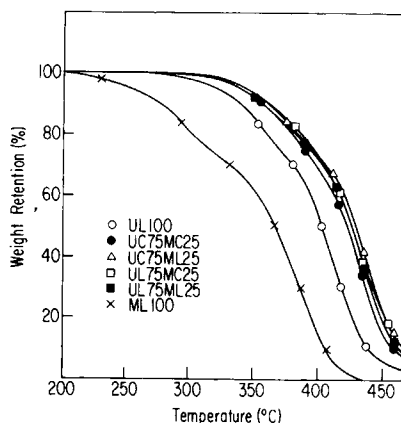


Fig. 3. TGA thermograms for 75/25 (PU/PMMA) IPN, pseudo-IPN's, and linear blends.

He suggested that a radical mechanism plays an important role in the thermal degradation of polyurethanes. The thermal degradation of the poly(methyl methacrylate) in the temperature range of about 150–500°C has been shown to yield almost 100% monomer by the stepwise unzipping process.¹⁵ The TGA thermograms seem to indicate that the enhancement of the weight retention is related to the presence of the unzipped methyl methacrylate monomer. One possible explanation is that the unzipped monomers act as radical scavengers for the radicals produced from the polyurethane degradation, thus delaying the further reaction of the radicals into volatile amines, alcohols, isocyanates, olefins, and carbon dioxide.

The previously reported TGA analysis of polyurethane–polystyrene IPN's⁹ also showed weight enhancement above 400°C. This agrees well with the above hypothesis, since in the polystyrene thermal decomposition the unzipped monomer appears only in the later stages of decomposition.^{16,17}

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