

The Effects of Functional Azo Initiator on PMMA and Polyurethane IPN Systems. I. Synthesis, Characterization, and Thermal Effects

M. ROHA* and B. WANG†

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106

SYNOPSIS

The use of functional azo initiators and the thermal history of the materials have been shown to exert significant effects on the properties of interpenetrating polymer networks (IPNs). The IPNs prepared with a reactive azo initiator from MDI and 1,2-PBD (1,2-polybutadiene diol) with PMMA have been found to exhibit greater ductility, lower rigidity, and lower moduli than IPNs prepared with AIBN. This probably resulted from the attached PMMA blocks modifying the properties of the PU matrix phases. Increasing thermal treatment of IPNs prepared from either the reactive or the normal azo initiators exhibited increased T_g values in both DSC and DMTA scans. These results have been explained by increased association from chemical reactions between the hard segments of the polyurethane and poly(methyl methacrylate) ester groups.

INTRODUCTION

An IPN (interpenetrating polymer network) is formed when a pair of intimately mixed polymeric networks is prepared in which at least one network is synthesized and/or crosslinked in the presence of the other. Several review papers¹⁻⁶ have been published covering the literature up to 1985. The chemical and physical combinations of IPN have provided convenient ways to meet specific material requirements: processing, flexibility, tensile and impact strength, chemical resistance, weatherability, flammability resistance, or other properties.

IPN structures have been synthesized by several methods. These included *sequential* IPNs, where the networks were made sequentially and *simultaneous* IPNs (SINs), where both monomers were mixed together and polymerized simultaneously by independent and noninterfering routes. If both polymers of the IPN were crosslinked, the material was called a *full IPN*. If only one polymer was crosslinked, it

was a *semi-IPN*. In a *semi-1-IPN* the first formed polymer was crosslinked and the second polymer was not. In a *semi-2-IPN* the second formed polymer was crosslinked and the first one was not. This paper discusses the characteristics of a *semi-1 1,2-PBD-PU/PMMA sequential IPN*.

For many years, there has been interest in sequential and simultaneous semi-1-IPNs of PU and PMMA prepared by the polymerization of polyurethanes in methyl methacrylate as solvent. Allen and co-workers⁷⁻¹¹ studied in detail the chemical and physical aspects of the PMMA-polyurethane system. They reported extensive studies of the effects of reactant ratios and of gelation and polymerization times and conditions on the physical properties and the structures of the IPN products. Allen and co-workers demonstrated the formation of highly transparent products containing microphases of PMMA domains in a polyurethane matrixes. Later, Frisch et al.¹²⁻¹⁶ studied the mechanical properties, viscoelastic properties, morphologies, densities, and volume resistivity behavior of both full and semi PU/PMMA IPNs by the simultaneous technique. Hur, Manson, and Hertzberg¹⁷ have studied the fatigue and energy absorption behavior of acrylic simultaneous interpenetrating networks based on crosslinked poly(propylene glycol)-MDI/PMMA

* To whom correspondence should be addressed.

† Present address: Chemical Engineering Department, Beijing Institute of Technology, P.O. Box 327, Beijing 100081, People's Republic of China.

systems. The fatigue fracture surfaces showed that the dominant factor for the energy dissipating deformations was shear yielding rather than crazing.

More recently, Tabla, Widmaier, and Meyer¹⁸ have studied the kinetics of the octyl tin catalyzed formation of polyurethanes in ethyl acetate as solvent as models for the first step in the PU/PMMA IPN systems. This work was extended by Robinet¹⁹ in a study on the casting of acrylic sheets from the *simultaneous* polymerization of polyurethanes and PMMA. He used octyl tin to catalyze the formation of the poly(propylene oxide) glycol and triisocyanate polyurethane systems and AIBN to catalyze the production of MMA and trimethylol propane triacrylate acrylic copolymer. The kinetics of the polymerizations and the morphologies of the products were strongly influenced by the reactants. Robinet found that low levels of tin⁺² gave incomplete polyurethane formation with little PU reaction continuing while the PMMA was being formed. The product contained large PMMA particles and the DMTA showed peaks of both the polyurethane rubber and the PMMA plastic. Increasing Sn⁺² concentrations progressively increased the polyurethane formation rates and conversion with only minor effects on the PMMA reaction. The greater amounts of PU formed before PMMA formation resulted in the progressive loss of the polyurethane peak in the DMTA and the successive formation of, first, a broad peak above that of PMMA and, with more tin, of a very broad peak below PMMA. The photomicrographs showed progressively smaller PMMA particles with increasing tin catalyst. This chemistry appears to be used commercially in France²⁰ to produce high impact resistant cast acrylic sheets.

In an effort to increase the intermolecular interactions between the PU and the PMMA phases, Klempler²¹ has introduced opposite-charged groups (tertiary amines and carboxylic acids) into PU/PMMA IPNs prepared from poly(1,4-oxybutylene)glycol and MDI. These IPNs exhibited increased tensile strengths and moduli compared to the IPNs containing similar polymers without the ionic charges. Single phase morphology was observed for these IPNs. Khanna²² has reported the addition of hydroxyethyl methacrylate (HEMA) to polystyrene-polyurethane IPN systems to enhance the chemical bonding between the IPN phases. The use of increasing HEMA increased the moduli and tensile strengths and decreased the elongations of the polymer mixtures. Recently, a patent application²³ has been filed by Edison Polymer Innovation Corp. describing the production of IPNs by the use of azo initiators that contain functions which are reactive

in the polyurethane system. This combination was expected to bind segments of PMMA to the ends of the polyurethane segments.

It was of interest to understand the effects of these functionalized azo initiators, which are capable of combining into the polyurethane structure and how they effected the PU-PMMA materials and the structures and properties of the resultant IPN products. Of special interest was how a reactive azo initiator, capable of producing PMMA blocks at the ends of polyurethane structure, would alter the IPN reaction and the structures and properties of the resultant products.

1,2-Polybutadienediol-based PU/PMMA was one of the systems studied by Allen and co-workers.⁹ Similar 1,2-PBD-PU/PMMA IPNs were selected for this study because of the known and defined difunctionality of the oligomeric diol, the absence of polar functions in the backbone and inherent low water content.

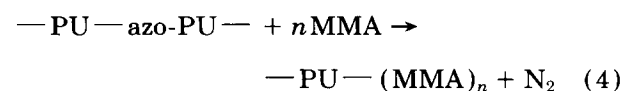
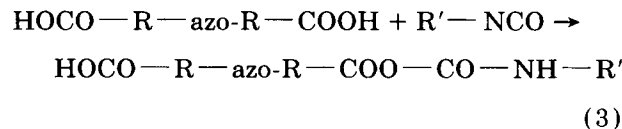
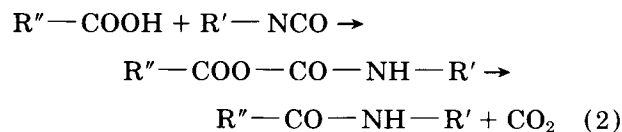
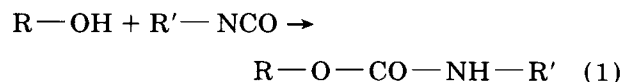
CHEMISTRY

A study of PU/PMMA IPN systems requires the understanding of several facets of these systems: (1) the compositions of the polyurethane and of the PMMA phases, (2) the miscibility of the PU and the PMMA materials in each other, (3) the nature of the interfaces between the PU and the PMMA phases, and (4) possible interactions and chemical reactions between the PU and the PMMA materials.

Compositions of PU and PMMA Phases

PU/PMMA IPN systems contain several reactants. The *polyurethane* materials are produced during the IPN formation by reactions of hydroxyl and carboxyl functions with isocyanates with the formation of urethanes and of amides. The bulk properties of polyurethanes are significantly influenced by the presence or absence of *hard segments* and on the *ratios* of hard segments to soft segments. Hard segments are usually produced by the coupling of the urethane functions by relatively short diol and triol segments while soft segments result from the introduction of long oligomer chains, which have lesser tendencies to bond to the other polymers segments. The use of a reactive azo initiator introduces a *new* segment into the polyurethane, an amorphous PMMA block. Generally, increased *hard segments* produce products with higher moduli, higher strengths, and lower elongations at break while in-

creased *soft segments* increase the flexibility of the polyurethane. The reactions which produce these structures in these systems are:



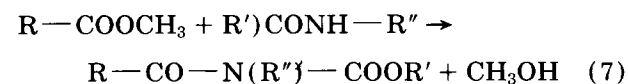
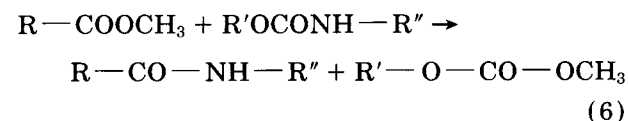
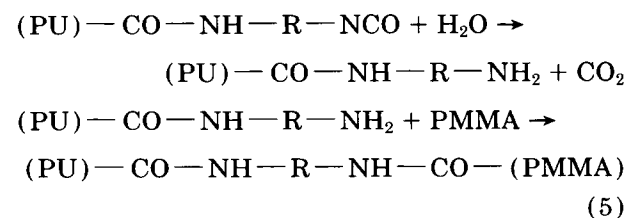
The reaction of diisocyanates with the carboxy-azo initiator (ABC) that would introduce azo functions only at the terminal *ends* of the polyurethane chains, would subsequently polymerize *amorphous* PMMA segments onto the polyurethane. These PMMA blocks could be effective *soft segments* in disrupting the usual association of the *hard segments* of the polyurethane chains. The carboxy-containing azo initiator would be bound by amide functions into the polyurethane chains. In most of the studies reported here, equivalent amounts of amide functions have been introduced into the reference system by the use of adipic acid (AA) in the nonreactive initiator (AIBN) systems. However, adipic acid can also introduce into the reference IPN materials, new *hard segments* consisting of two amide groups separated by the short $\text{-C}_4\text{H}_8\text{-}$ segment. The *hard segment/soft segment* ratios should appear differently in the different initiator systems. The normal AIBN initiator would produce the normal ratios of *hard* and *soft segments* whereas the AIBN-AA initiator could produce increased *hard* amide segments. This became most obvious in the data from products with lower PU contents where the initiator/PU ratios are highest. ABC-AA initiators could produce both increased *hard segments* derived from the adipic acid, and increased *soft segments* derived from the PMMA blocks.

The *poly(methyl methacrylate)* results from the free radical polymerization of MMA through the radicals produced by elimination of nitrogen from the azo initiators. The use of the normal nonfunctional initiator (AIBN) produces IPNs without this chemical bonding between the PMMA and the

polyurethane segments. With the reactive initiator (ABC) that initiates the MMA polymerization, a certain amount of bonding occurs by the direct chemical linkage of the a portion of the azo compound to the ends of the PU chains. These differences were expected to influence the characteristics of the interface between the PMMA and the PU.

Chemical Reaction between PU and PMMA

It was shown²⁴ that the reaction of amines with PMMA produced amides that were converted to glutarimide structures which resulted in a significant increase in the Vicat softening temperature of the PMMA to 134°C. This significant increase resulted from only 16% reaction of the PMMA monomer units. Studies²⁵ in this laboratory have demonstrated that the addition of 10 meq of amines, or of water that would convert diisocyanates into amines, to 800 meq MMA, resulted in a sharp increase of the T_g of the PMMA phase to 128–130°C in a PU/PMMA IPN based on poly(propylene glycol). Additional heat history made the T_g peak sharper. This increase in T_g from the introduction of amines to PU/PMMA IPNs paralleled the reactions of simple amines with PMMA and the formation of glutarimide structures. In addition, it is also possible that a direct chemical metathesis reaction between the PU and the PMMA materials could also occur from the intimate contact between PU and PMMA during the present preparative conditions.



The amide produced in reactions (5) and (6) would react further to produce the imide structure. Reaction (7) would produce an imidelike structure directly.

Recent research by Kim et al.²⁶ have shown that the miscibility of PMMA with immiscible polystyrene was increased by the introduction of active hy-

drogen functions (hydroxyl) into the polystyrene. Hydrogen bonding to the carbonyl of the PMMA was demonstrated. In a like manner, hydrogen bonding between PU and PMMA could result from the —NH of the urethane function bonding to the carbonyl of the PMMA in parallel manner.

Interfaces

Allen et al. had shown that PU/PMMA IPN materials were composed of particles of PMMA within the PU elastomer matrix. The introduction of *particulate* materials, such as carbon black and plastic phases, into elastomeric matrixes generally are known to increase the moduli and the resistance to failure of the elastomer. The nature and strength of the interface between the particulate and the elastomeric phases have significant influences on the properties of the *reinforced* blend. The strong chemical bonding by the imidization reaction between the PMMA-rich particulate and the PU-rich matrix of these IPN materials could influence the reinforcement performances.

Model

It is proposed that the functional azo initiator influenced the character of the PU-rich continuous matrix of the PU/PMMA system whereas thermal treatment influenced the microstructures of both the continuous PU-rich and discontinuous PMMA-rich phases. The properties of the PU-rich *matrix* resulted from the different *hard segments and soft segments* along with the presence of the *PMMA blocks* that were produced by the carboxy-azo initiator. This model for the PU/PMMA IPN systems with PMMA-rich *dispersed phases* within PU-rich continuous phases contain similar associated PU/PMMA materials but at different weight ratios. The composition of each phase was determined at the point of phase separation during the polymerization of the MMA in the gel state. The compositions of these phases are controlled by the ratios of PU/PMMA during the gel polymerization step. This model has been evaluated in the present studies.

EXPERIMENTAL

Reagents

All chemicals, listed in Table I, were carefully dried, and free from water and inhibitor.

Table I Chemicals

Name	Supplier
Methyl methacrylate (MMA)	Aldrich
1,2-Polybutadiene diol (1,2-PBD), $M_n = 2500$; $F = 2.00$	Colorado Chemical Co.
Methylene bis 4,4'-(isocyanato phenyl) (MDI)	BASF
Azo-bis-isobutyronitrile (AIBN)	Kodak
Azo-bis(4'-cyanovaleic acid) (ABC)	Aldrich
Dibutyltin dilaurate (DBTDL)	Aldrich
Tri-methanol propane (TMP)	Aldrich
Adipic acid (AA)	Aldrich
<i>N,N</i> -dimethyl formamide (DMF)	Aldrich

Preparation

Semi-1-IPNs were synthesized according to the procedure of Allen and co-workers.⁷ The reaction was carried out in a one-shot, two-step procedure. In the standard synthesis procedure all of the reactants were dissolved in the required amount of MMA. DBTDL (0.05 wt %) was used as the PU catalyst. The azo initiator (0.01 mmol/g) was dissolved in 2 g DMF, and added to the mixture under nitrogen. The reactant molar ratios were: $[NCO]/[OH] = 1.1$, and $[tri\text{-function}]/[di\text{-function}] = 0.45$. IPN compositions with weight ratios of 20/80 and 50/50 PU/PMMA were prepared. After allowing gelation to proceed to yield a viscous syrup, the mixture was degassed and poured into molds (170 × 32 × 3 mm), then sealed and maintained at room temperature (23°C) for 2 days to allow the PU network to form completely. The temperature was then raised to 55°C for 2 days followed by a further 4 h at 120°C to complete the MMA polymerization by the azo initiator. To determine whether additional curing effected the properties of the composites, materials were also heated to 140°C for 4 h and for 10 additional hours, and then quenched to room temperature. After polishing the surfaces, all of the materials were quite clear and transparent.

Pure PU was also prepared as in the first stage above using inhibited MMA, which was subsequently removed slowly under vacuum. Pure PMMA

was prepared in bulk under the conditions described above.

Test Procedures

The engineering properties of the materials were obtained on an Instron 1123 machine using a strain rate of 100%/min at 23°C according to the ASTM procedure.²⁷ Dynamic mechanical measurements were run on an IBM PC controlled Polymer Lab DMTA, using a tensile head. Specimens cut to the approximate dimensions of 20 × 3 × 1 mm were evaluated. The temperature was controlled to ±1°C over the range from -100 to +150°C. Five frequencies (0.33, 1, 3, 10, 30 Hz) were used under the heating rate of 1°C/min.

Thermal analyses were run on a Perkin-Elmer 7 series system DSC. The scan was carried out at 20°C/min over the temperature range from -70 to +180°C. A second scan was run after the specimen was held at 180°C for 2 min, and then quenched to -70°C.

The ATR infrared spectra were collected on a Nicolet 800 FTIR system by using a 45° angle KRS-5 crystal. Specimens were polished, washed with THF, and dried.

Electron microscopy was run on 1,2-PBD-PU/PMMA blocks that had been stained in 2% OsO₄ solution for 2 weeks. The samples were washed and cut into sections about 60 nm thick from the top surface with an RMC MT-6000 ultramicrotome at room temperature. A JEOL EM 100SX-1 TEM was used for morphology observation.

The densities of the IPNs were determined by an ASTM procedure²⁸ at 23°C by measuring the apparent weight of the specimens in air and in water on a analytical balance with a precision within 0.1 mg.

RESULTS AND DISCUSSION

The goal of the studies reported in the three publication of this series is to elucidate how the compositional changes in the PU-rich matrix and the PMMA-rich dispersed phase and how the chemical reactions between the polyurethane and the PMMA polymers influence the morphologies, structures, and properties of the PU/PMMA sequential IPN systems.

Morphologies

The electron micrographs of 1,2-PBD-PU/PMMA IPN are shown in Figure 1. These figures show that

the morphology of the IPN system was influenced only by the PU/PMMA ratios. The same morphology had also been found by Allen et al.⁸ The sizes of these domain structures were calculated by using the Ruan²⁹ equation,

$$D = 1.5 \langle l \rangle \quad (1)$$

where D is the particle mean diameter and $\langle l \rangle$ is the mean chord length. The accuracy of this measurement is usually within 15%, but smaller domains and poorer micrographs yield less accuracy. The 50/50 domains were diffuse clumps ($D = 450 \text{ \AA}$) embedded in a continuous phase. Table II shows that with both the 50/50 and 20/80 compositions, identical structures were observed in both ABC and AIBN initiated samples. The 20/80 compositions were made up of PMMA domains, with a mean size $D = 1460 \text{ \AA}$, which were mostly distorted or elongated, but uniformly dispersed within the PU matrix. The gaps between the larger domains were occupied by the smaller ones. Yeo and Sperling³⁰ also observed similar distorted domain shapes (cylindrical and ellipsoidal). In the present sequential systems, the PU networks were completely formed before the MMA polymerization began.

It is likely that the PMMA domains were established by the onset of phase separation during the polymerization of MMA in the PU gel. The domain sizes of the PMMA were mainly governed by the crosslink density of the PU, which was identical in both the ABC and the AIBN samples and varied only with composition. The morphology was not modified by the ABC bound onto the PU network, which acted only to chemically bind the PMMA blocks to the PU segments. Thermal treatment also produced no detectable morphological changes, indicating that the imidization reaction occurred within each phase and involved no transport of material across phase boundaries. Thus the physically interlocked and interpenetrating structure in both IPNs were thermally stable with time.

In their study, Yeo and Sperling³⁰ developed a theory for predicating the domain size of polymer 2. The basic assumptions in their theory were (1) achievement of thermodynamic equilibrium, (2) a spherical domain shape, and (3) a monodispersed domain size.

The diameter of a domain in IPN was expressed as

$$D_2 = 4\gamma^0 / [RT(A\nu_1 - \rho_2 \ln \phi_2/M_2)] \quad (2)$$

where D_2 is the domain diameter of polymer 2, ν_1 and ν_2 are the crosslink densities of polymers 1 and

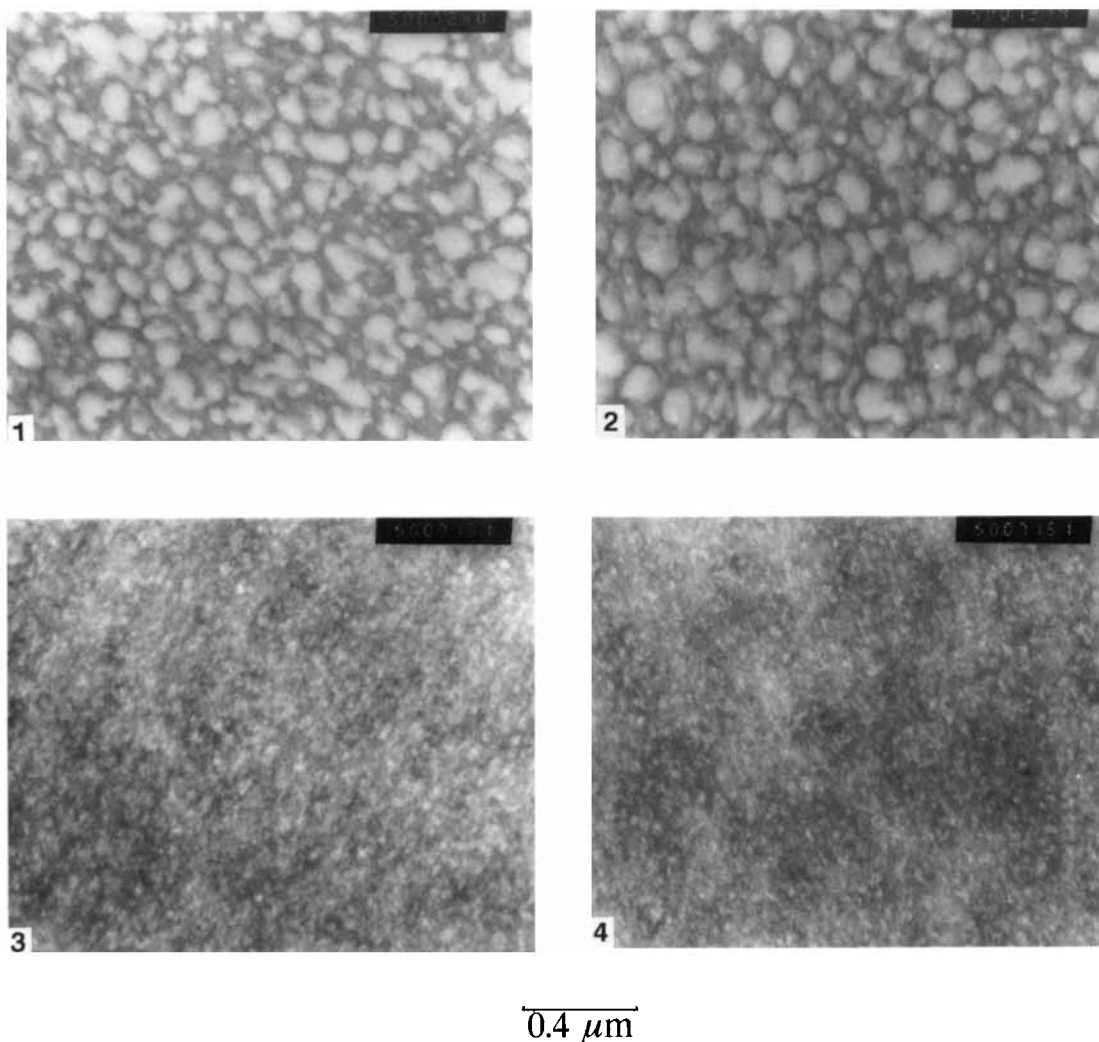


Figure 1 TEM micrographs of 1,2-PBD-PU/PMMA IPNs: (1) 20/80; AIBN + AA; (2) 20/80; ABC; (3) 50/50; AIBN + AA; (4) 50/50; ABC.

2, γ^0 is the interfacial tension between polymer 1 and 2, M_2 and ρ_2 are the molecular weight and density of polymer 2, ϕ_1 and ϕ_2 are the volume fractions of polymers 1 and 2, and R and T represent the gas constant and absolute temperature, respectively.

Table II lists the domain sizes of the measured

Table II Theoretical and Experimental Domain Sizes

Composition	Domain Diameter D (Å)		
	Experimental		
	ABC	AIBN	Theory
50/50	460 ± 90	450 ± 80	459
20/80	1520 ± 210	1460 ± 180	1636

values from micrograph and calculated values using eq. (2). The interfacial tension γ^0 was calculated as 8.27 dyn/cm, using the Good and Girifalco³¹ empirical equation. The crosslink density of the PUs, ν_1 , were calculated as 18.85 and 7.54×10^{-5} mol/cm³ for 50/50 and 20/80 compositions, respectively, using the equation of Yeo et al.^{32,33} $G = \nu RT$. The density (ρ_2) and molecular weight (M_2) of PMMA, 1.184 g/mL and 1×10^6 g/mol, respectively, were determined from the above density data and from GPC measurements by Dong.³⁴ Within the experimental error, the Yeo-Sperling theory predicts domain size, agreeing very well with the experimental values. This agreement further supports the assumption that the sizes of the PMMA particles were established in the gel state when the basic assumptions were valid.

Table III Densities of PBD(1,2)-PU/PMMA IPNs^a

Material	50/50		20/80		PU	PMMA
	ABC	AIBN + AA	ABC	AIBN + AA		
Final conditions						
120°C, 4 h	1.040	1.045	1.127	1.133	0.911	1.184
140°C, 4 h	1.046	1.048	1.134	1.141		
140°C, 10 h	1.041	1.046	1.130	1.138		
Additive values		1.047		1.129		

^a All experimental values \pm 0.001–0.002.

Densities

Frisch et al.¹³ studied the density–composition behavior of PU/PMMA full IPNs. The higher densities than predicted by simple additivity were claimed to be the result of *extensive mixing* of the components. On the other hand, decreased values were observed by Hourston and Zia³⁵ in their PU/PMMA semi-1-IPN study. Table III lists the experimentally determined densities and the densities calculated by volume additivity. In both 50/50 and 20/80 compositions, the AIBN materials were more dense than the corresponding ABC materials. In the ABC systems, the lower densities were explained by the presence of *soft segment* PMMA blocks on the PU chains that disrupted the normal PU hard segments. Heating to 140°C resulted in increased den-

sities in all compositions, thus demonstrating the effect of the imidization reaction. Additional times at 140°C resulted in a drop in densities in all cases, possibly the result of some thermal decomposition.

The 50/50 compositions showed densities lower to only slightly higher than the calculated values while the 20/80 compositions showed higher to slightly lower values than calculated. Although the higher densities for the imidized PU/PMMA systems are apparent at low PU compositions, it appeared that the increased amounts of PU in the IPNs progressively disrupted the imidized structures.

Extraction

IPNs prepared with ABC and AIBN were extracted with refluxing THF for 40 days. The weight losses

Table IV DMTA T_g and DSC Determined T_g ^a

	PU	50/50		20/80		PMMA
		ABC	AIBN + AA	ABC	AIBN + AA	
DMTA						
120°C, 4 h	10	11 ^b 59	15.5 ^b 62	11 ^b 106 ^c 131	16 ^b 113 ^c 129	115
140°C, 4 h		101 ^c 15.5 ^b 89	105 ^c 18 ^b 86	15.5 ^b —	18 ^b —	
140°C, 10 h		128 ^c 18 ^b 93 133 ^c	125 ^c 20 ^b 91 130 ^c	136 18 ^b — 137.5	134 20 ^b — 134.5	
DSC						
120°C, 4 h	10	12	12	112	109	107
140°C, 4 h		13	15	125	121	
140°C, 10 h		13	15	125	123	

^a Major peaks in bold.

^b Broad peak.

^c Shoulder peak.

of all materials were less than 0.5%. A GPC study³⁴ of the extract identified only low molecular polyurethane materials mixed with some degradation products. Allen et al.⁹ had shown that the polymerization of MMA in the presence of 1,2-polybutadiene diol produced a crosslinked system from which the diol could not be extracted. Thus, the chemical binding of the PMMA to the crosslinked PU did not permit extraction of the PMMA material by a good PMMA solvent.

Dynamic Mechanical and Thermal Properties

The dynamic mechanical properties (storage modulus E' and the loss tangent, $\tan \delta$) of the controls (pure PU and PMMA) are represented in Figure 2. The typical atactic PMMA sharp α -relaxation was observed at 115°C with a broad β -process around 30°C. The 1,2-PBD-PU α -transition was found at 10°C.

Figure 3 shows the corresponding data for the 1,2-PBD-PU/PMMA IPNs. There were no qualitative difference between ABC- and AIBN-initiated materials, in either the 50/50 or the 20/80 compositions. However, the ABC-initiated samples showed much more pronounced shoulders at 11°C in 50/50 and in 20/80 materials. These differences indicate that there was more PU phase separation in the ABC samples. This may have resulted from the PMMA block on the PU chain producing the less dense structure. The higher, undisrupted association of a typical PU remained in the AIBN case.

The transition temperatures, measured both by DMTA and by DSC (Table IV) show the effects of thermal history on the T_g of the PU/PMMA IPNs. In all cases, the samples had a polyurethane glass transition temperature (11°C) that is very close to that of the pure PU (10°C). However, the DMTA study of 20/80 compositions made with either initiator showed a transition temperature (130°C),

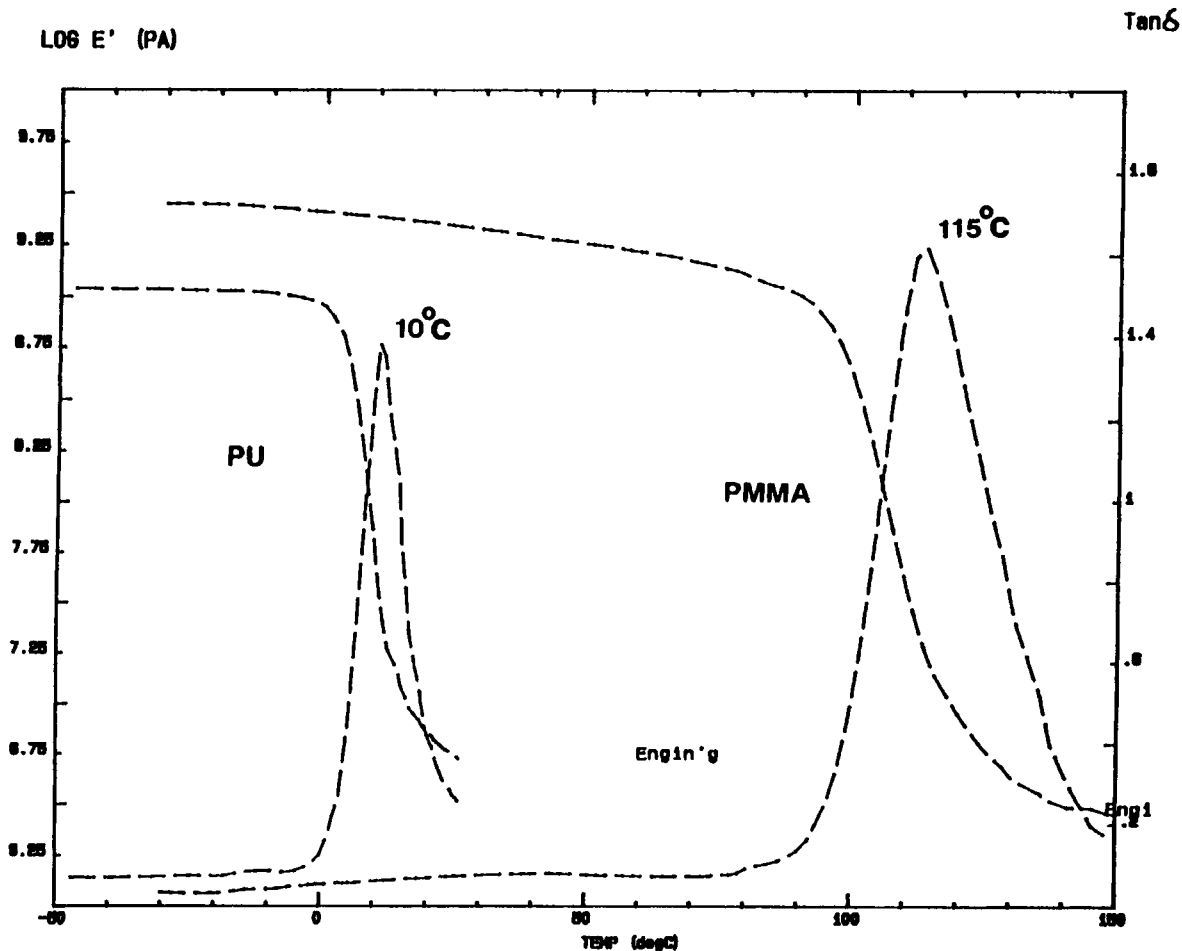


Figure 2 Thermal dynamic mechanical behaviors of PU and PMMA.

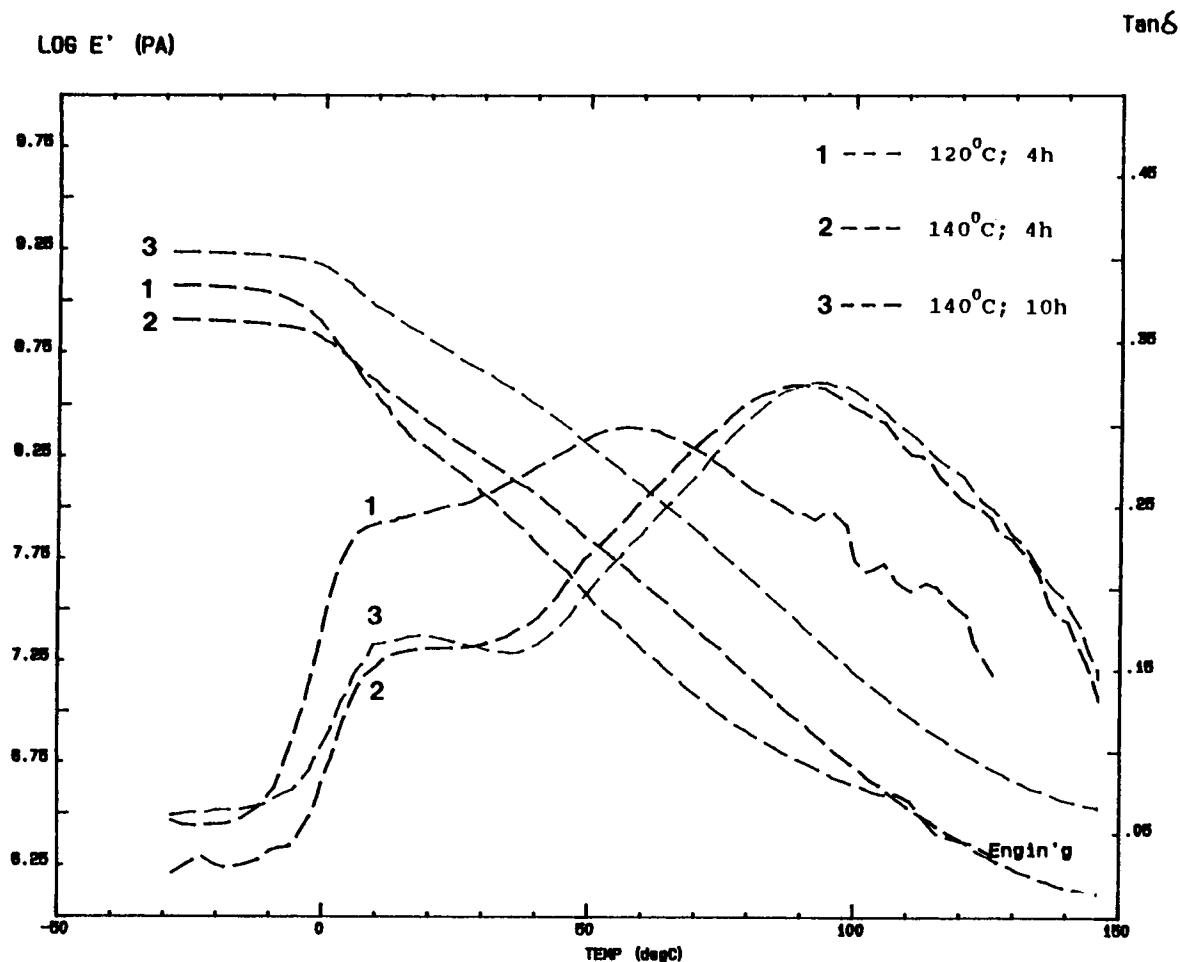


Figure 3a The effect of thermal history on the IPN's thermal dynamic mechanical behavior: 50/50 PU/PMMA with ABC.

higher than the typical PMMA peak (115°C), along with a lower temperature shoulder (110°C). This is contrary to the normal glass transitions observed in polymer blend systems. This unusual phenomena has also been reported by Hermant et al.³⁶ with PPG-PU/PMMA IPN studies and by Robinet¹⁹ with PPG-PU/PMMA IPN studies. On the other hand, Hourston and Zia³⁷ studied the semi-1 (PPG-PBD)-PU/PMA IPN system. Various composition ratios showed no shifts in the T_g peaks from those of the corresponding PU or the PMA polymers. These blends had not been heated higher than 90°C for 6 h. Theocaris and Kefalas³⁸ found a 4°C increase in the T_g when 10% PU was added to a polystyrene blend. This was explained by interactions between the P bonds of the aromatic rings in the PU and in the polystyrene phases. These authors demonstrated

that crosslinking of the PU phase had no effect on the T_g of the blend.

The present studies have indicated that these PU/PMMA materials have a higher interaction between the PMMA and the polyurethane structures. The imidization reaction probably occurred between the PU and PMMA polymers producing the enhancement of the PMMA glass transition temperature. The increase in T_g paralleled the similar increase in densities noted earlier for the same materials.

With the 50/50 compositions, a broad transition with a maximum at about 60°C was observed with both initiators. With these compositions, further thermal treatment (140°C for 4 h) was found to advance the positions of both the lower temperature transition shoulder and the higher peak. The broad

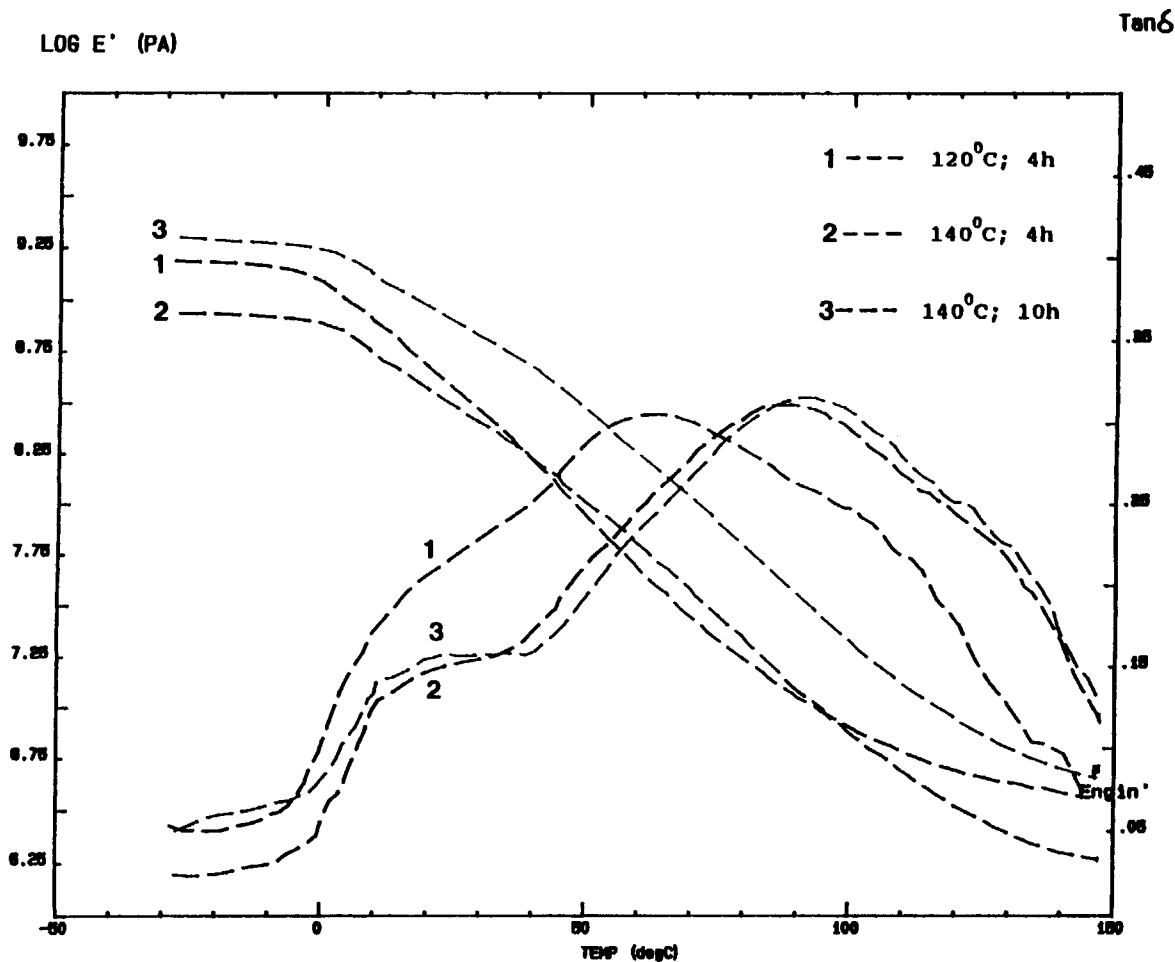


Figure 3b 50/50 PU/PMMA with AIBN + AA.

peak moved upward to about 87°C and the lower shoulder to about 19°C. This higher peak appeared to be that of an alloy with wide PU-PMMA composition ratios.

With 20/80 compositions, the high temperature peak also moved higher and became sharper with loss of the PMMA shoulder. With even longer thermal treatment (10 h at 140°C), no additional changes occurred. This effect, probably from the imidization reaction paralleled changes in the IR spectra and the storage moduli E' .

Infrared Studies

Figure 4 shows the C=O stretching vibration bands of PU, PMMA, and the PU/PMMA IPNs. The spectrum of PU shows a band that is the overlapped combination of the free C=O band (1737 cm^{-1})

and a higher intensity hydrogen bonded C=O band (1709 cm^{-1}). The spectrum of PMMA shows a strong C=O stretching vibration at about 1723 cm^{-1} . The C=O band of the 50/50 IPN (initiated by ABC and heating at 120°C for 4 h) showed a single sharp C=O band at 1727 cm^{-1} with a slight tailing off towards the low frequency region. This appeared to be the PMMA carbonyl, which is the dominant C=O component of system. Both the hydrogen bonded and free C=O bands of the urethane PU and imide structures (expected³⁹ to be at 1725 cm^{-1}) would be hidden under the PMMA band.

Figure 5 shows that 1,2-PBD/MDI polyurethane had a strong hydrogen bonded N—H stretching vibration band at 3325 cm^{-1} and a free N—H band at 3442 cm^{-1} . The PU/PMMA IPN blends showed a relatively higher intensity of *bound* N—H relative to the *unbound* N—H than in the pure PU. This

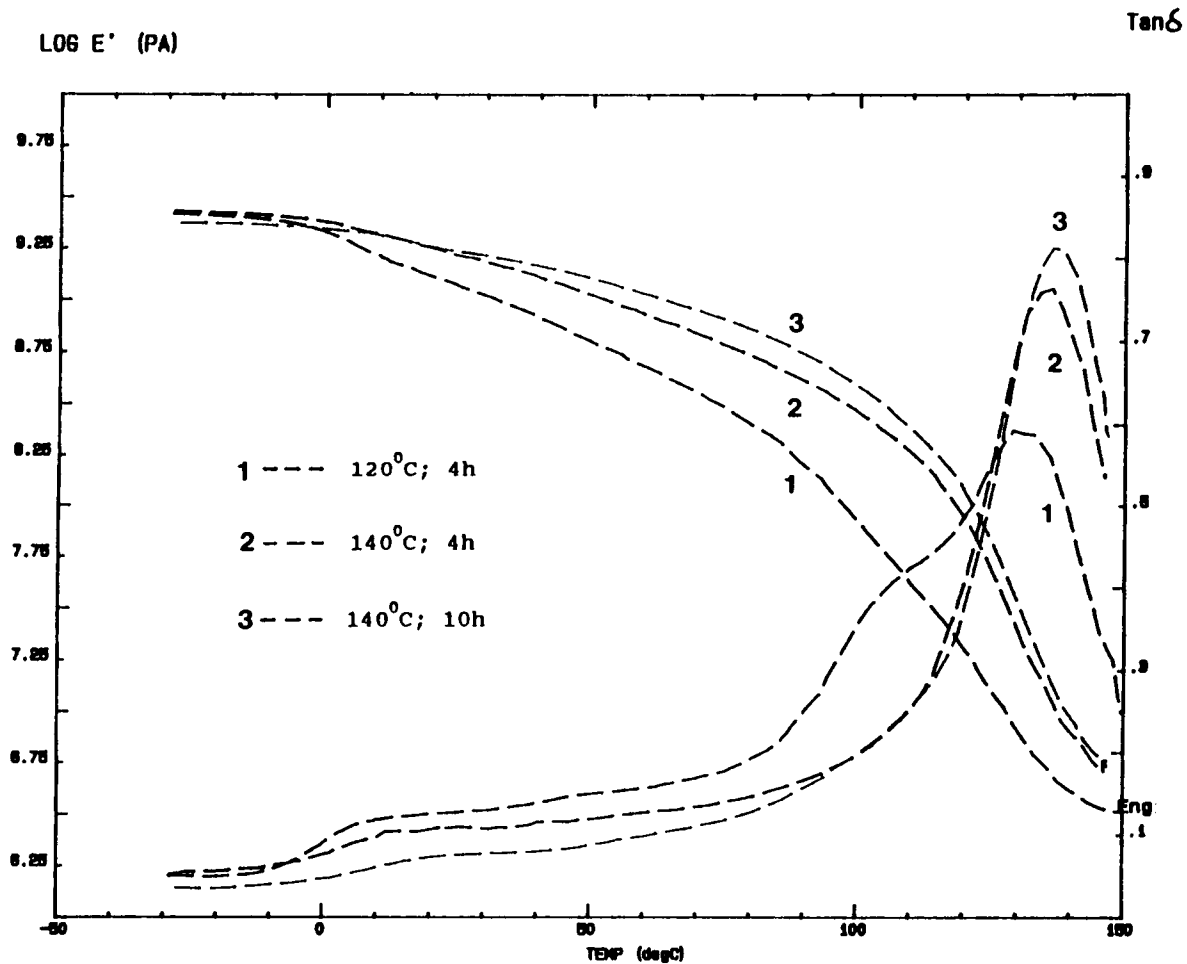


Figure 3c 20/80 PU/PMMA with ABC.

was probably the result of the contribution of bonding to the carbonyls present in the PMMA similar to the O—H bonding to PMMA observed by Kim, Kwei, and Pierce.²⁶ Additional changes in the N—H stretching vibration of the PU were also observed on thermal treatment at 140°C for 4 h and for 10 h. The relative intensity of the *bonded* N—H band decreased further. This indicated that the imidization reaction between the PU and the PMMA involved the N—H that was bonded to a carbonyl, probably that of PMMA. With the 20/80 samples, the relative intensity of bonded N—H band (3100–3500 cm^{-1}) also decreased. This, again, indicated the occurrence of the same type of reaction between the PU/PMMA that has been noted with the 50/50 materials.

Physical and Mechanical Properties

Physical property measurements have shown effects from both the functional initiator and from the thermal history of the samples. Figure 6 shows the typical stress-strain curves of 1,2-PBD-PU/PMMA IPNs, where the 50/50 composition sample showed rubbery behavior while the 20/80 showed ductile behavior. A quasiyield point could also be seen in the 20/80 samples. Allen⁷ had reported brittle behavior for composites containing less than 10% PU.

Table V and Figure 7 show the effects of composition, initiator, and thermal history on the properties of the IPN. In all cases, the AIBN-initiated IPNs exhibited higher initial moduli, strengths, and lower elongations and recoveries than the ABCs.

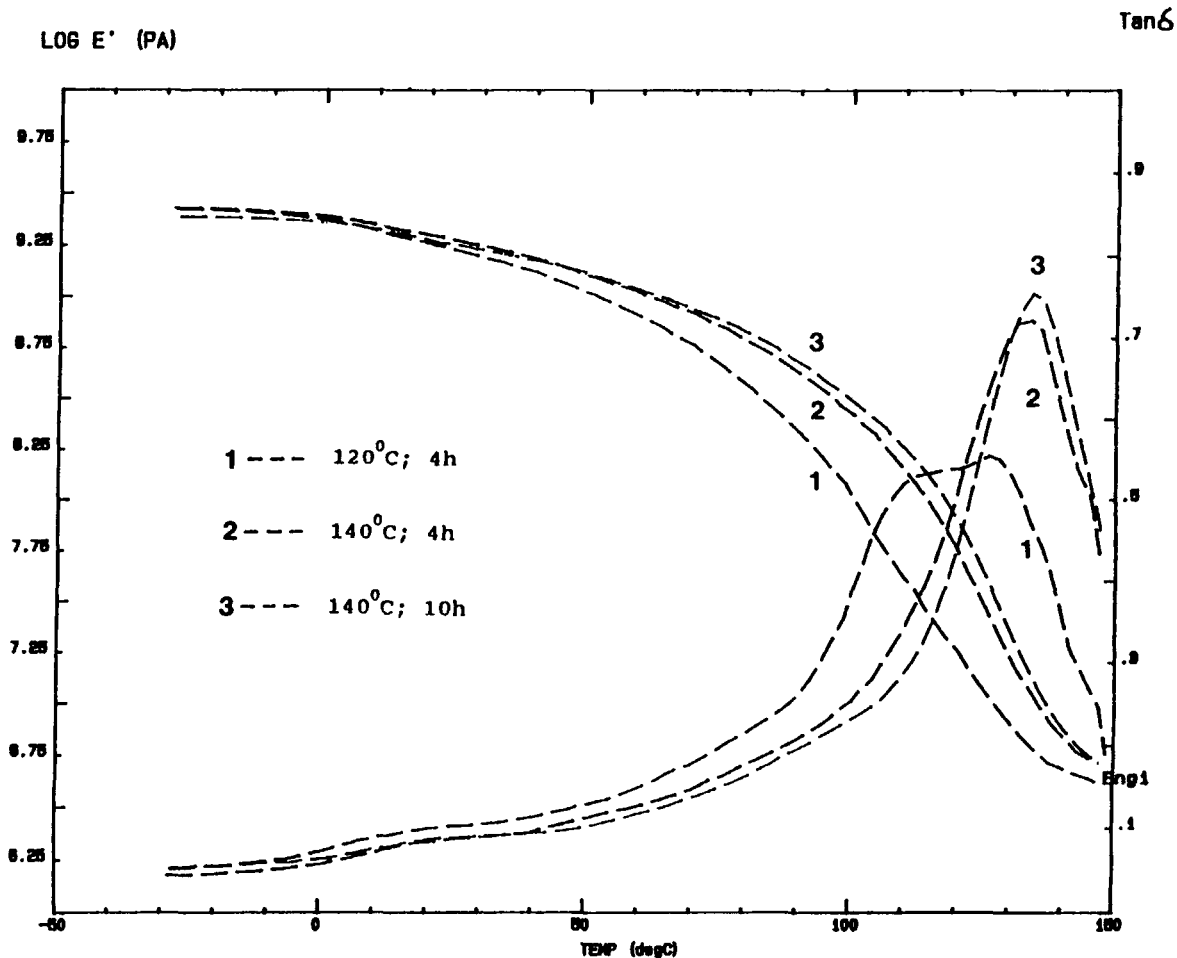


Figure 3d 20/80 PU/PMMA with AIBN + AA.

The use of ABC made the material much more ductile. This was the result of the presence of PMMA blocks on the chains of the PU matrix material. Increased imide content by the thermal treatment of all samples produced increased moduli and strengths, and decreased elongations and recoveries with all initiators and compositions. However, this heat treatment increased the strengths of the ABC products to nearly those of the AIBN products while retaining the significantly higher elongations at break that ABC products exhibited.

Moduli

To understand more about the present IPN systems, the storage modulus E' was measured by DMTA. Data, obtained at 1 Hz and 25°C are tabulated in Table VI. The storage moduli E' for PU and PMMA are 1.02 and 2.88 MPa, respectively. Allen et al.¹⁰ and Hur, Manson, and Hertzberg¹⁷ had found in PPG-PU/PMMA systems that the best fit to the experimental points was obtained by the Davies^{40,41} equation:

$$E_1^{1/5} = \phi_1 E'^{1/5} + \phi_2 E_2'^{1/5} \quad (3)$$

However, the experimental data in Table VI were generally slightly higher than those calculated by this equation and increased with increased thermal treatment. This equation was derived from theories considering particle-particle interactions. It has been suggested by Davies that this equation is best suited to morphologies which have continuity of both phases at the complete $0 < \phi_2 < 1$ range. This indicates that there was some phase continuity in the PMMA phase which is not directly observed in the morphological studies as was discussed above. Such a continuity could possibly have been caused by the an enhanced interaction between the PU and the PMMA phases due to the imidization of PMMA by the PU, which made an increasing chemical connection of PMMA domains to each another.

OTHER SYSTEMS

Observations similar to the 1,2-PBD-PU/PMMA systems have been noted^{42,25} in our studies of ABC

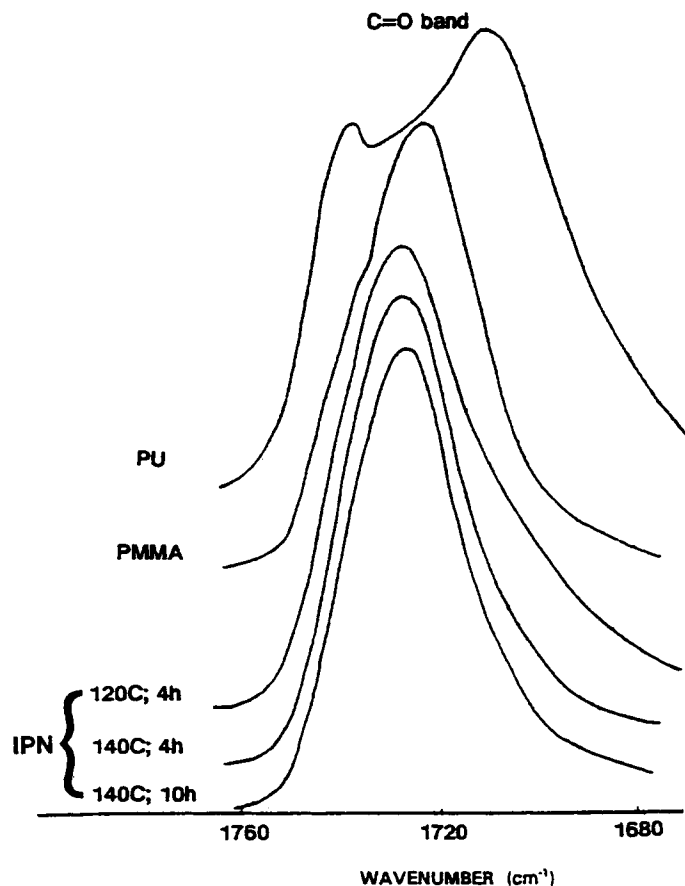


Figure 4 IR spectra of C = O stretching vibration of PMMA, PU, and ABC initiated 50/50 1,2-PBD-PU/PMMA IPNs.

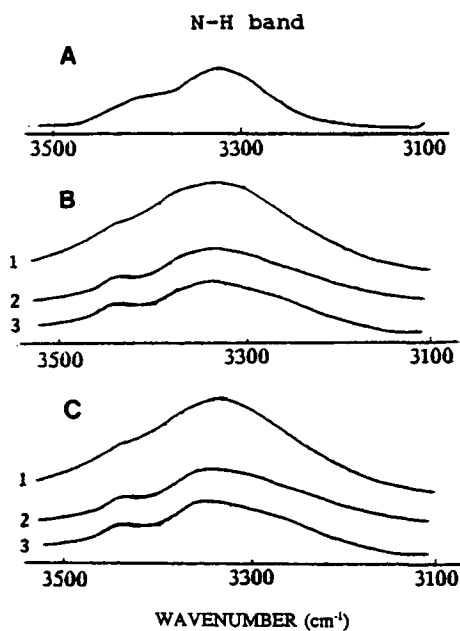


Figure 5 The effect of thermal history on N—H bonds: (A) polyurethane; (B) 20/80 PU/PMMA; (C) 50/50 PU/PMMA; (1) 120°C, 4 h; (2) 140°C, 4 h; (3) 140°C, 10 h.

versus AIBN with IPNs derived from polyurethanes based on the other diols studied by Allen et al. These included 1,4-polybutadiene diol ($M_n = 2800$, $F = 2.33$) from ATOCHEM, and mixtures of polypropylene glycol ($M_n = 2000$, $F = 2.00$) and poly(propylene glycol) ($M_n = 3000$, $F = 3.00$), both from Union Carbide. However, these materials were not studied extensively and only preliminary conclusions were drawn.

CONCLUSIONS

Functional azo initiator (ABC) and thermal history have been found to influence the properties of PU/PMMA IPNs. The IPN materials made with ABC were much more ductile than those made with AIBN. This was the result of introducing PMMA blocks onto the ends of PU chains, which modified the *hard segment/soft segment* character of the PU-rich matrix.

Heating PU/PMMA IPNs at 140°C for 4 h re-

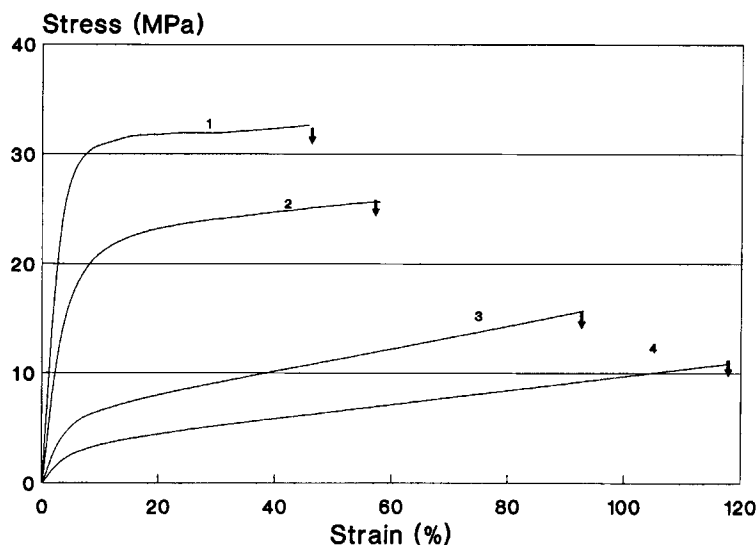


Figure 6 Stress-strain curves of 1,2-PBD-PU/PMMA IPNs: (1) 20/80; AIBN + AA; (2) 20/80; ABC; (3) 50/50; AIBN + AA; (4) 50/50; ABC.

sulted in materials with increased tensile, moduli, and lower elongation. The T_g 's of the 20/80 products were significantly higher than that of PMMA.

The heating step appeared to produce imide structures that were responsible for the improved properties. Loss of N—H bonds during heating were observed in the IR.

The effects of differences in initiators were even more marked after annealing at 140°C, where nearly

equivalent tensiles and significantly higher elongations were observed with the functional ABC IPNs.

The microstructures of the IPNs were mainly controlled by composition. There was similar phase separations in IPNs initiated by either ABC and AIBN. The PMMA existed as PMMA-rich domains in continuous PU-rich phases. These structures did not change with thermal history.

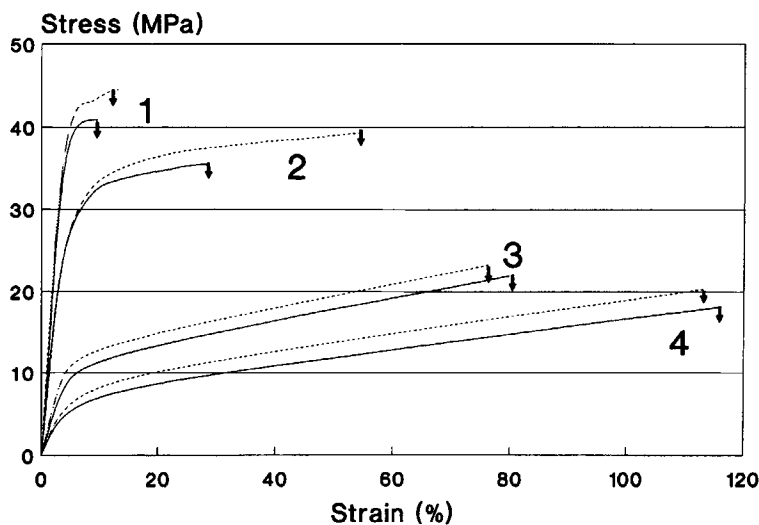


Figure 7 The effect of thermal history on the IPNs mechanical behaviors: (1) 20/80; AIBN + AA; (2) 20/80; ABC; (3) 50/50; AIBN + AA; (4) 50/50; ABC; (—) 140°C, 4 h; (---) 140°C, 10 h.

Table V Physical Properties of 1,2-PBD-PU/PMMA IPNs

Material (Ratio, Initiator)	Initial Modulus (MPa)	Strength at Break (MPa)	Elongation at Break (%)	Recovery (%)
50/50, ABC				
120°C, 4 h	75 ± 5	10 ± 1	118 ± 5	87 ± 3
140°C, 4 h	154 ± 5	18 ± 1	116 ± 4	70 ± 5
140°C, 10 h	190 ± 6	20 ± 2	112 ± 4	69 ± 3
50/50, AIBN + AA				
120°C, 4 h	145 ± 8	15 ± 1	92 ± 2	81 ± 2
140°C, 4 h	268 ± 5	22 ± 2	79 ± 3	69 ± 2
140°C, 10 h	310 ± 6	23 ± 1	76 ± 5	66 ± 4
20/80, ABC				
120°C, 4 h	500 ± 9	25 ± 2	58 ± 2	51 ± 4
140°C, 4 h	726 ± 7	35 ± 3	30 ± 3	32 ± 3
140°C, 10 h	765 ± 9	37 ± 2	35 ± 2	34 ± 5
20/80, AIBN + AA				
120°C, 4 h	900 ± 10	33 ± 4	35 ± 4	36 ± 6
140°C, 4 h	1025 ± 8	40 ± 3	10 ± 2	13 ± 2
140°C, 10 h	1120 ± 11	44 ± 3	12 ± 3	15 ± 3
Poly(methyl methacrylate)	1380 ± 14	52 ± 3	6 ± 1	<4
1,2-PBD-polyurethane	1.5 ± 0.5	3 ± 0.5	>200	—

Table VI Comparison of Theoretical Moduli with Experimental Moduli, log E' (MPa)

	50/50		20/80	
	ABC	AIBN + AA	ABC	AIBN + AA
Calculated Davies Equation	2.26		2.97	
Experimental (1 Hz, 25°C)				
120°C, 4 h	2.18	2.55	3.06	3.22
140°C, 4 h	2.33	2.45	3.20	3.28
140°C, 10 h	2.72	2.88	3.23	3.27

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