

Uralkyd and Poly (Butyl Methacrylate) Interpenetrating Polymer Networks

VILAS ATHAWALE AND SURESH KOLEKAR

Department of Chemistry, University of Mumbai, Vidyanagari, Mumbai-400 098, India

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ABSTRACT:: Hydroxyl terminated alkyds synthesized from castor oil, glycerol, and different dibasic acids were used to develop uralkyds and their interpenetrating polymer networks (IPNs) with polybutyl methacrylate (PBMA). Glass transition temperature measurements gave the evidence of interpenetration. The IPNs were characterized for their physicochemical properties and their phase morphology was studied by scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). As the concentration of the uralkyd in IPNs increases, a gradual increase in elongation, density, and swelling with a consequent decrease in the hardness were observed for all IPNs. Swelling is relatively more prominent in methyl ethyl ketone (MEK) and toluene than in water. From SEM it was observed that IPNs of PBMA-uralkyd containing phthalic anhydride (UA-P) as an acid part showed greater compatibility than those containing dimethyl terephthalate (UA-D). From thermogravimetric analysis (TGA) no significant change was observed in the degradation behavior of the IPNs. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 825–832, 2000

Key words: interpenetrating polymer networks; poly (butyl methacrylate); uralkyd.

INTRODUCTION

Interpenetrating polymer networks (IPNs) have been one of the fastest growing areas in the field of polymer blends during the last two decades. There are many applications in variety of technologies for IPNs where blends of linear polymer may not be suitable. IPNs are defined as a combination of two network polymers, at least one of which is prepared or cross-linked in the immediate presence of other. The multicomponent systems thus obtained display a broad range of properties, from toughened elastomers to high-impact plastics. The physical nature of the constituent network, their relative proportion in the blends, and so on, control the ultimate performance of the resulting IPNs.^{1–3}

Syntheses, analyses, and characterization of IPNs based on various polymers have been extensively reported.^{4–10} However, no report is available on the synthesis of IPNs based on urethane alkyd and poly (butyl methacrylate) (PBMA). The central concept of choosing the uralkyd and PBMA pair is to combine the coating properties of urethane alkyd and elastomeric nature of PBMA to get a polymer with these desired properties. Hence, it was felt necessary to carry out a systematic investigation to study the properties of uralkyd and PBMA IPNs.

EXPERIMENTAL

Materials

British standard specifications (BSS) grade castor oil (Acid value, 2.0 mg KOH/g, hydroxyl value 162 mg KOH/g and iodine value [Wij method] 82–90)

Correspondence to: V. Athawale.

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Table I Composition and Characterizations of Castor Oil Alkyds in Moles

Ingredients	D^a	P^b
Castor oil	1	1
Glycerol	2	2
Phthalic anhydride	—	0.3
Dimethyl terephthalate	0.3	—
Acid and Hydroxyl Values in mg KOH/g		
Acid value	3.3	4.2
Hydroxyl value	337.0	288.9

^a Hydroxy terminated alkyd containing DMT as an acid moiety.

^b Hydroxy terminated alkyd containing Phthalic anhydride as an acid moiety.

was procured from M/s Jayant Oil Mill (India). Castor oil is a triglyceride of various fatty acids. However, it contains very high (87–90 wt %) content of ricinoleic acid, $C_{18}H_{34}O_3$ structurally cis-12-hydroxyoctadeca-9-enoic acid. The detailed composition (in wt %) is as follows: ricinoleic acid (89.5), dihydroxystearic acid (0.7), palmitic acid (1.0), stearic acid (1.0), oleic acid (3.0), linoleic acid (4.2), linolenic acid (0.3). Isophorone diisocyanate (IPDI), polyethylene glycol (PEG -200), and benzoyl peroxide were obtained from E. Merck (India) and Thomas Baker Co. (India), respectively. Butyl methacrylate (BMA) and ethylene glycol dimethacrylate (EGDMA) were purchased from E. Merck (India) and Fluka (Switzerland) and were freed from stabilizer prior to use. Phthalic anhydride, dimethyl terephthalate were procured from s. d. fine chemicals (India). Dibutyltin dilaurate (DBTL) was obtained from local market. All other reagents were of analytical grade and have been used without further purification.

Synthesis of Hydroxyl-Terminated Castor Oil Alkyds

The compositions for castor oil alkyds are given in Table I. A reaction kettle equipped with thermometer, water condenser, stirrer, and nitrogen inlet was charged with castor oil, glycerol, and either dimethyl terephthalate or phthalic anhydride, along with litharge as a catalyst (0.05 wt % based on oil). Temperature was then raised to 240°C and maintained between 240–250°C, with constant stirring in an atmosphere of nitrogen for 6 h (acid value < 4 mg of KOH/g of sample). The

water formed during the course of reaction was removed with the aid of Dean-stark apparatus. The castor oil alkyds thus synthesized were tested for their hydroxyl value and acid values,¹¹ which appear in Table I.

Synthesis of Uralkyd Network (UA)

A reaction kettle equipped with stirrer and nitrogen inlet was charged with one equivalent of 50% solution of castor oil alkyd in dioxane, followed by addition of two equivalents of IPDI along with catalyst DBTL (0.01 g/g of IPDI) and was kept in a thermostated water bath. The temperature was then raised to 40°C ± 2 and maintained for 2 h with continuous stirring. After completion of 2 h a mixture of polyethylene glycol and castor oil (4:1 equivalent ratio) (for chain extension and cross-linking) was added and mixed thoroughly for 5 min. The solution was then poured into the mold, where it was kept initially at 78°C for 24 h and then at 120°C for 6 h.

Interpenetrating Polymer Networks

One equivalent of the urethane prepolymer was added to one equivalent of the polyethylene glycol and castor oil mixture (4:1 equivalent ratio) followed by the addition of predetermined amount of

Table II Glass Transition Temperatures (T_g s) of Homopolymers and IPNs

Sample Code	Compositions UA/PBMA (wt %)	T_g (degree Kelvin)	
		Low	High
Homopolymers			
UA-D ^a	100/0	247	—
UA-P ^b	100/0	253	—
PBMA	0/100	—	300
UA-D IPNs			
I-1	20/80	259	297
I-2	40/60	263	291
I-3	60/40	257	282
I-4	80/20	256	283
UA-P IPNs			
I-5	20/80	270	294
I-6	40/60	268	293
I-7	60/40	268	296
I-8	80/20	264	291

^a UA-D: uralkyd containing dimethyl terephthalate as an acid moiety.

^b UA-P: uralkyd containing phthalic anhydride as an acid moiety.

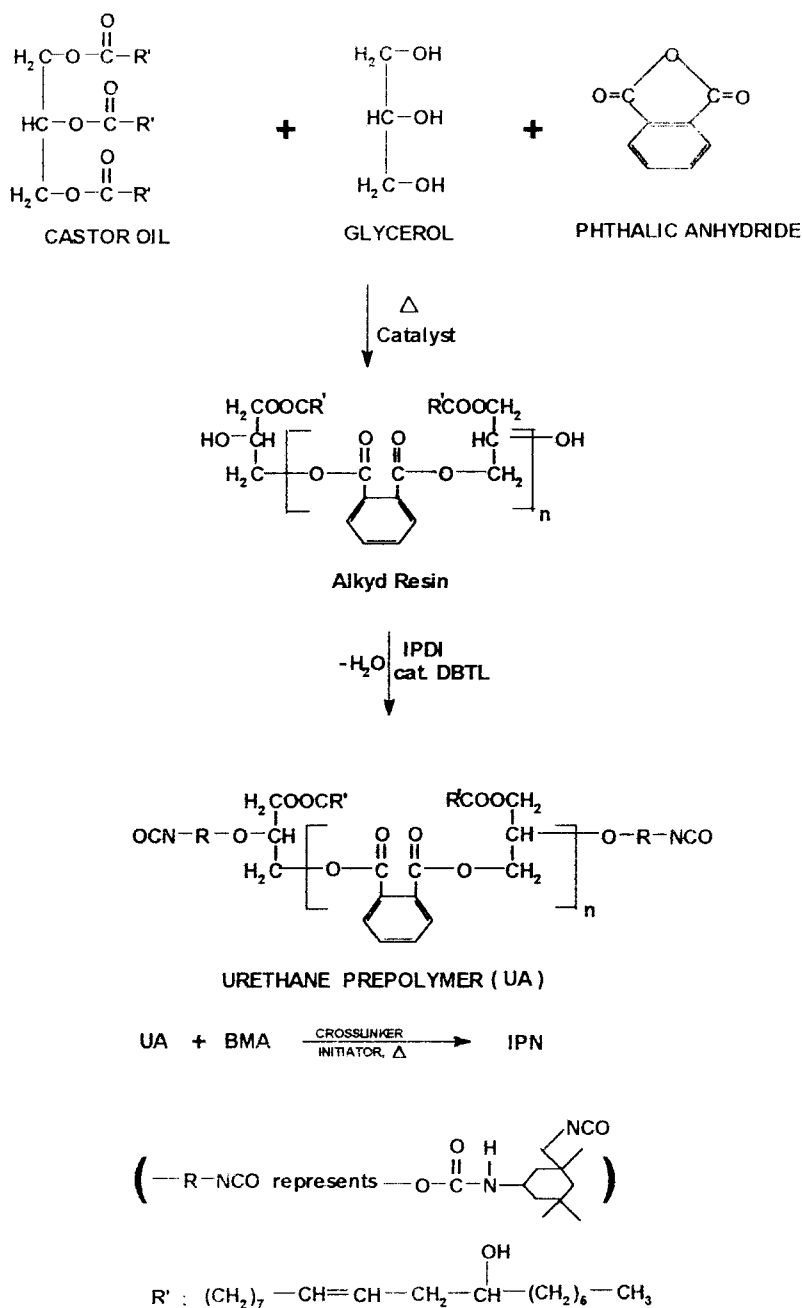


Figure 1 Synthesis of urethane alkyd and IPN.

BMA along with EGDMA (5 wt % based on BMA) and benzoyl peroxide (0.5 wt % based on BMA) and were intimately mixed for 3 min at 40°C. The temperature was then subsequently raised to 75–78°C and the reaction was further continued for 30 min. After that, the reaction mixture was poured into the mold and cured initially at 75–78°C for 24 h and later at 120°C for 6 h.

The general reaction scheme for the synthesis of uralkyd and IPN is given in Figure 1.

Characterizations

The glass transition temperatures were determined on DuPont 9900 differential scanning calorimeter at a heating rate of 10°C/min in the temperature range from –60 to +100°C under nitrogen atmosphere. Electron micrographs were obtained on Cameca (France) Model SU-30 scanning electron micrograph (SEM). Samples were prepared for SEM by freeze fracturing them in

Table III Mechanical and Physical Properties of Homopolymers and IPNs

Sample Code	Composition UA/PBMA (wt %)	Tensile Strength MPa	Elongation (%)	Hardness Shore A
Homopolymers				
UA-D ^a	100/0	4.1	180	80
UA-P ^b	100/0	7.9	284	70
PBMA	0/100	6.9	230	65
UA-D IPNs				
I-1	20/80	6.1	74	80
I-2	40/60	3.8	138	72
I-3	60/40	4.9	200	62
I-4	80/20	4.5	245	60
UA-P IPNs				
I-5	20/80	6.3	84	80
I-6	40/60	1.6	265	72
I-7	60/40	6.4	283	65
I-8	80/20	2.5	308	56

^a UA-D: uralkyd containing dimethyl terephthalate as an acid moiety.

^b UA-P: uralkyd containing phthalic anhydride as an acid moiety.

liquid nitrogen and applying a gold coating of approximately 200Å°. Tensile strength and elongation were measured using computerized tensile testing machine "Tensilon" (R&D Electronics, India) as per ASTM D 638, and hardness was determined with a Shore A durometer using ASTM D 2240-75 standard. The apparent densities of the films were obtained by weighing strips of the film of measured volume.¹² The swelling study was carried out in water, methyl ethyl ketone (MEK), and toluene.¹³ Thermogravimetric measurements were made on a Mettler TA 4000 thermogravimetric analyzer (TGA) at a heating rate of 10°C/min in air and activation energies were computed using Broido method.¹⁴

RESULTS AND DISCUSSION

Glass Transition temperatures

The glass transition temperatures (T_g s) of the samples are listed in Table II. The low T_g corresponds to the uralkyd phase transition and the high T_g is related to the polybutyl methacrylate phase transition. However, they were shifted inwards, which indicates that some extent of interpenetration has occurred between UA and PBMA. The shift was more prominent in low T_g than in the high T_g . The shift was more prominent in UA-D (uralkyd consisting of DMT as an acid

part)/PBMA IPNs than in UA-P (uralkyd consisting of phthalic anhydride as an acid part/PBMA). The shifting of glass transition temperatures was difficult to be correlated with the compositions of IPNs because of wide range of phase domain sizes and of the complexity of the morphology of the heterogeneous systems.

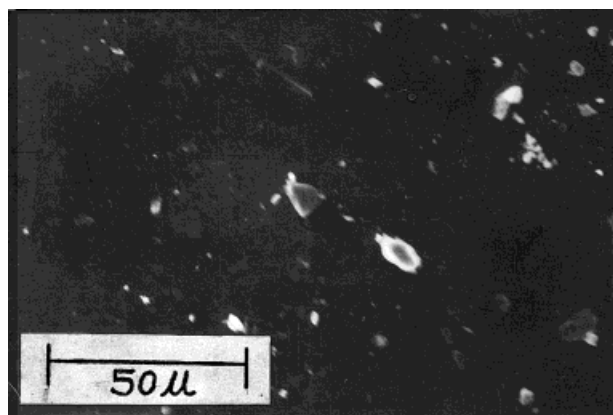
Morphology

The morphology of the IPNs is revealed by the electron micrographs (Fig. 2). In all the micrographs the polyurethane was present as the continuous phase with large globules of acrylate dispersed within it, indicating phase separation. The domains of the dispersed phase were clearly irregular, rather than spherical in shape. It is interesting to note that the phase separation between two polymers appeared to be more pronounced, in the case of I-2 (domain size 3-12 μ) than in I-5 (domain size 1-8 μ), indicating low compatibility of former over that of the latter two. This clearly proves the relatively high degree of cross-linking density in UA-P/PBMA IPNs.

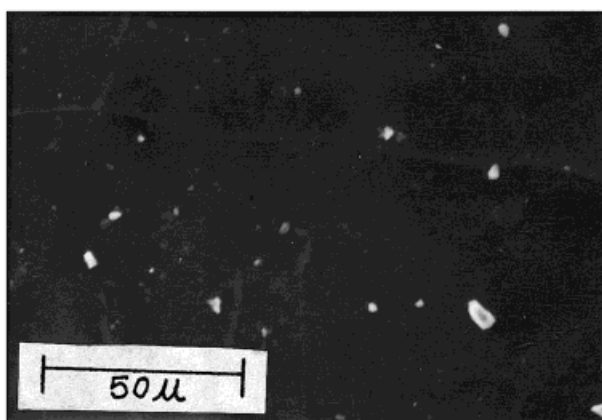
Mechanical Properties

The effect of the variation of the blend ratio on tensile strength, percentage elongation, and hardness (Shore A) are listed in Table III.

In all the cases, the tensile strength data of IPNs were so diverse that no trend can be seen.



(a)



(b)

Figure 2 Scanning electron micrographs of (a) I-2 (UA-D40/PBMA60) and (b) I-5 (UA-P40/PBMA60).

All the values are intermediate between those of the constituent networks. This may be due to the fact that tensile strength of UA and PBMA were comparable to each other owing to elastomeric nature of both the polymers. However, elongation showed systematic variation with respect to the blend ratio. Elongation decreased with the increasing PBMA content in the (UA)/PBMA IPNs. This is possibly due to the fact that PBMA has relatively less free volume as compared with UA and the observations were made in the vicinity of transition temperature of PBMA; thus, there was less scope for threading (easy mobility of chains) as more and more UA was substituted by PBMA. Further, it is interesting to note that, in all UA/PBMA IPNs, composition UA 80 PBMA 20 showed higher elongation than that of the component network, which can be ascribed to reinforcement of interpenetration. Among all the newly synthesized IPNs (UA-P)/PBMA IPNs exhibited

higher tensile strength and elongation. This increase in tensile strength is due mostly to the filler effect of the UA phase.

Hardness data of IPNs (Table III) revealed that UA-D/PBMA and UA-P/PBMA exhibited similar hardness. However, in both the cases the hardness decreased with increasing UA content in the IPNs. This behavior is difficult to explain.

Apparent Density

The density-composition curves of IPNs (Figs. 3 and 4) show that the densities of UA-D/PBMA and UA-P/PBMA IPNs increased with the corresponding increase in the UA contents. This is because UA is denser than PBMA, and hence density of IPN system increased as more and more PBMA was substituted by UA. Interestingly, it was observed that the density-composition curve of all IPNs (Fig. 4) were above that of the corresponding curves representing the theoretical densities based on the additivity principle that states that $[d = w_1d_1 + w_2d_2]$ where, d is the density of the IPN sample, w_1 and w_2 are the weight fractions of the constituents, d_1 and d_2 are the corresponding densities, respectively. It can be observed from Figures 3 and 4 that in the case of UA-P/PBMA IPNs (Fig. 4) the theoretical and actual density curves are well separated for all concentrations, whereas in the case of UA-D/

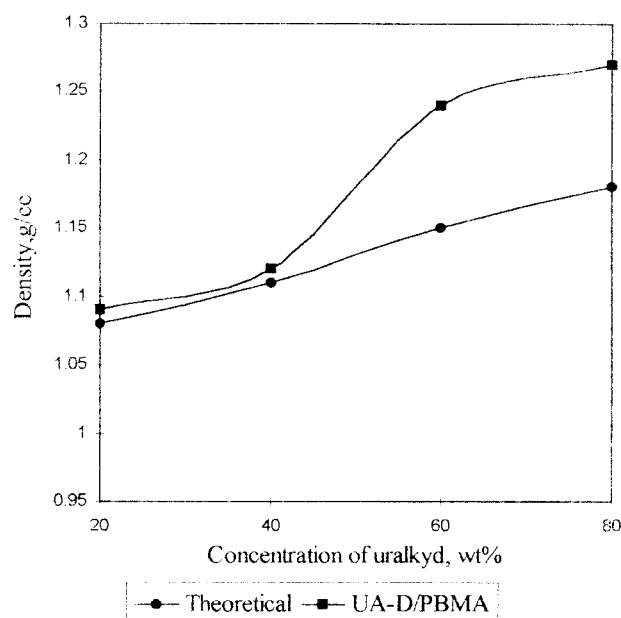


Figure 3 Density vs uralkyd concentration (in wt %) of UA-D/PBMA IPNs.

PBMA IPNs (Fig. 3) these curves are much closer to each other up to 40% UA, and concentration of UA above 40% showed significant enhancement in the densities. The enhancement in actual density is explained by considering the fact that since measurements were made at near T_g , a few short-lived "holes" between molecules become large enough that an adjacent molecule or segment of polymer molecule can fit between two molecules.¹⁵

Swelling Behavior

The percentage swelling data of IPNs in nonpolar solvent toluene, polar solvents, MEK, and water are presented in Table IV. It is evident from the data that very slight swelling occurred in water, whereas significant swelling was observed in MEK and toluene; this is because of the greater solvent penetration into the IPN matrix with less resistance, thereby increasing the swellability. Percent swelling increased in both solvents with increase in PBMA in the UA/PBMA IPN systems. The extent of swelling in MEK is much greater. This is because of the polar nature of MEK. Both the IPN systems behave in similar manner in toluene and MEK. Comparing the swelling of PBMA and IPNs, it was found that IPNs showed highly improved solvent resistance, indicating increasing degree of cross-linking.

Thermal Analysis

Clustering of the UA/PBMA curves in Figure 5 indicate that there was no significant difference

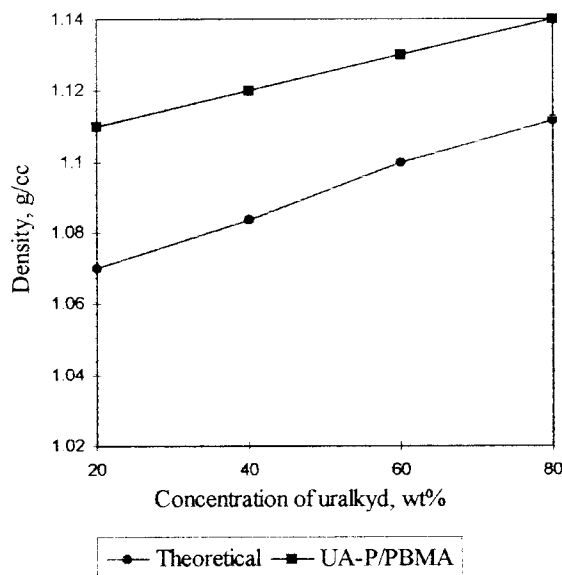


Figure 4 Density vs Uralkyd concentration (in wt %) of UA -P/PBMA IPNs.

Table IV Swelling of Homopolymers and IPNs

Sample Code	Composition UA/PBMA (wt %)	% Swelling		
		Toluene	MEK	Water
Homopolymers				
UA-D ^a	100/0	66	114	1
UA-P ^b	100/0	79	101	2
PBMA	0/100	190	179	1
UA-D IPNs				
I-1	20/80	149	170	1
I-2	40/60	121	124	2
I-3	60/40	89	119	3
I-4	80/20	50	119	3
UA-P IPNs				
I-5	20/80	148	154	1
I-6	40/60	147	147	1
I-7	60/40	136	120	1
I-8	80/20	121	104	1

^a UA-D: uralkyd containing dimethyl terephthalate as an acid moiety.

^b UA-P: uralkyd containing phthalic anhydride as an acid moiety.

in the degradation behavior of IPNs. All IPNs were stable up to 270°C, followed by substantial loss in weight at around 300–420°C. Finally, the IPNs showed a complete weight loss at around 500°C. The weight loss of about 50% in the temperature range of 275–375°C can be attributed to the breaking of —NH bond in the uralkyd and de-cross-linking of the two network forms of the IPNs. In this region the monomer attached to the backbone of the UA network is most probably detached by a free radical mechanism from the trunk of the main constituent polymer. The final weight loss that occurred in the range 375–500°C can be ascribed to the breakage of the bonds of the homopolymer PBMA and polyol decomposition of uralkyd, which is bound to be a slow process.¹⁶ For all IPNs the activation energy values (Table V) are considerably higher in the temperature 275–375°C than in the range 375–500°C. This clearly indicated that the degradation process is slower in the first stage than in the second stage. Thus, the thermal degradation pattern of the IPNs was more or less similar and the variation of acid moiety in uralkyd has not influenced the thermal stability.

CONCLUSIONS

The following concluding remarks emerged from this work.

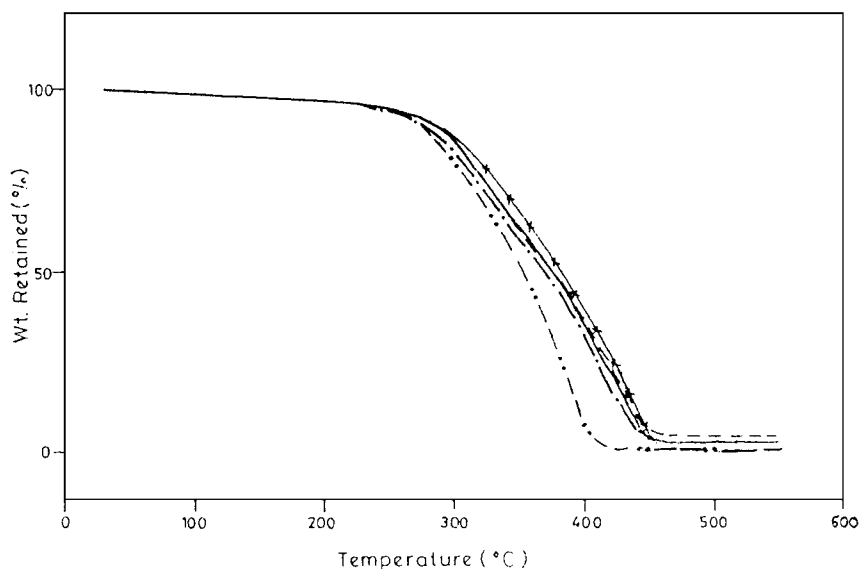


Figure 5 Representative thermograms for UA/PBMA IPNs: I-2 (—); I-5 (—•—•—); UA-P (- - -); UA-D (—•—•—); PBMA (—×—×—).

- Both the IPN systems UA-P/PBMA and UA-D/ PBMA exhibited phase separation. However, slight shift in T_g s of the constit-

Table V Activation Energy of Homopolymers and IPNs

Sample Code	Composition UA/PBMA (wt %)	Temperature Range (°C)	Activation Energy (kcal/mol)
Homopolymers			
UA-D ^a	100/0	275–375	36
		375–500	89
UA-P ^b	100/0	275–375	34
		375–500	86
PBMA	100/0	275–450	37
UA-D IPNs			
I-2	40/60	275–375	38
		375–500	88
I-3	60/40	275–375	40
		375–500	89
UA-P IPNs			
I-6	40/60	275–375	35
		375–500	82
I-7	60/40	275–375	35
		375–500	87

^a UA-D: uralkyd containing dimethyl terephthalate as an acid moiety.

^b UA-P: uralkyd containing phthalic anhydride as an acid moiety.

- uent polymers indicated some extent of interpenetration has taken place.
- Comparing the different properties of the IPNs it was evident that UA-P/PBMA IPNs are more compatible. This phenomenon enhanced the mechanical properties.
- Interpenetration of PBMA with uralkyd increased the solvent resistance of IPN system.
- Thermal properties of IPNs were independent of acid part in the urethane alkyd backbone.
- The IPN systems under study showed good solvent resistance, hardness, elongation (flexibility), tensile strength, and excellent overall film properties as well, which render them as potentially useful in coatings and rubber industries.

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