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INTERPENETRATING POLYMER NETWORKS BASED ON OIL MODIFIED CASTOR OIL URETHANE AND POLY(METHYL METHACRYLATE)

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Key Words: Interesterification, Poly(methyl methacrylate)/Polyurethane Interpenetrating Polymer Networks

ABSTRACT

Castor oil was initially subjected to an interesterification reaction with linseed and tung oils and the resulting intermediate was used for the preparation of polyurethanes and their IPNs with poly(methyl methacrylate). They were characterized for their physico-mechanical, swelling, and thermal properties. The morphologies of IPNs were studied with the aid of scanning electron microscopy and differential scanning calorimetry. On comparing the mechanical properties of castor oil polyurethane (CU) and their IPNs (C-IPNs) with those of the castor oil modified with linseed and tung oil (L-IPN and T-IPN, respectively) it was found that L-IPNs showed higher tensile strength, hardness, and better compatibility than C-IPNs. All IPNs showed synergistic effect in elongation and exhibited similar thermal behavior with no significant change with respect to their composition. However, the castor oil polyurethane and their IPNs showed relatively higher elongation and better resistance to solvents.

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INTRODUCTION

The efforts of both industrialized and developing countries to use and cultivate natural oils as a renewable source for polymer manufacture have led to a high growth in the world-wide production of natural oils. Multiple hydroxyl functionality is required for the natural oils to be used as convenient raw material for polyurethane production. Hydroxyl functionality occurs naturally in castor oil. Thus, castor oil acts as a polyol which reacts with polyfunctional isocyanates to form polyurethanes whose properties range from rigid polymers to elastomers [1, 2]. Presently, the synthesis of interpenetrating polymer networks (IPNs) from natural products (mainly from castor oil) has attracted the attention of many researchers worldwide [3-9]. The materials known as IPNs contain two or more polymers each in a network form. A practical restriction requires at least one of the polymer networks being polymerized or crosslinked in the immediate presence of the other.

The central concept of the present communication is to investigate the effect of increasing unsaturation in castor oil, on the physical, swelling and thermal properties of its resulting polymers (IPNs). Polyols were prepared by interesterification of castor oil with linseed and tung oil. These oils had a constant hydroxyl number, and exhibited different degree of unsaturation. The present paper reports the synthesis and characterisation of modified castor oil polyurethane, which is elastomeric in nature and its IPNs using poly (methyl methacrylate) as a plastic component.

EXPERIMENTAL

Materials

British Standard Specifications (BSS) grade castor oil [hydroxyl value, 162 mg KOH/g, acid value, 2.0 mg KOH/g and iodine value (Wij method), 82-90] was procured from M/s Jayant Oil Mill, India. Isophorone diisocyanate (IPDI) and benzoyl peroxide were obtained from Fluka, Switzerland and Thomas Baker Co., India, respectively. Methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA) purchased from Sisco-Chem., India and Fluka, Switzerland, respectively were washed with 2% NaOH, dried over CaCl₂ and distilled under reduced pressure prior to use. Dibutyltin dilaurate (DBTL), Fascat 4100 (tin catalyst for interesterification), alkali refined linseed oil [iodine value (Wij method) 180 and acid value, 6.0 mg KOH/g] and tung oil [iodine value (Wij

method) 165, acid value, 4.0mg KOH/g] were obtained from the local market. All other reagents were of analytical grade and have been used without further purification.

Synthesis (Figure 1)

Synthesis of Castor Oil-Linseed Oil/Tung Oil Interesterification Intermediate (IP)

Castor oil and linseed oil/tung oil, in a predetermined proportion were placed in a reaction kettle equipped with thermometer, water condenser, stirrer, and nitrogen inlet. The mixture was heated to 200°C and Fascat 4100 catalyst (0.05 wt% based on castor oil) was added. The temperature was then raised to 230°C and maintained between 230 to 235°C, with constant stirring in an atmosphere of nitrogen for 2 hours. The reaction was monitored by thin layer chromatography (solvent system: petroleum ether, diethyl ether and acetic acid in a ratio of 85:15:1 by volume, respectively). In the later stage, traces of water in the resin were removed by adding a small amount of xylene to the kettle and dis-

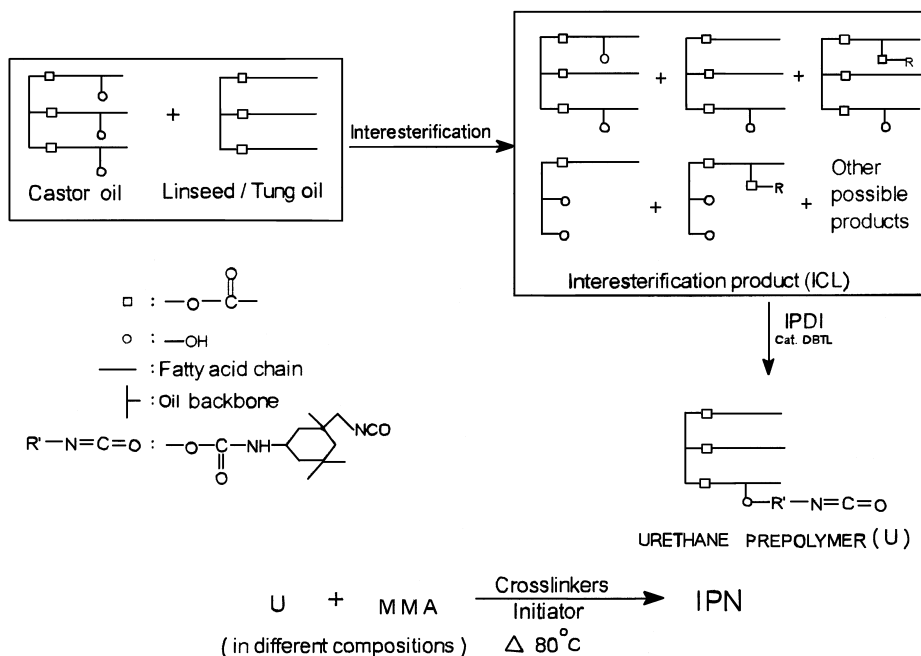


Figure 1. Synthesis of modified castor oil urethane and IPNs with PMMA.

TABLE 1. Acid and Hydroxyl Values for ICL Intermediates in mg KOH/g of Sample

ICL Intermediates Based on ^a			
Property	70% CO 30% LO	70% CO 30% TO	100% CO
Acid value	6.4	5.0	2.0
Hydroxyl value	133.18	110	162

^a composition based on total weight of the mixture in wt%

tilling it under vacuum. Hydroxyl and acid values of the resulting product were determined using American Oil Chemists' Association (AOCS) official method and reported in Table 1.

Synthesis of Polyurethane Network (U)

A reaction kettle equipped with a stirrer and nitrogen inlet, was charged with one equivalent of 50% solution of castor oil-linseed oil/tung oil interesterified product in dioxane. Then, two equivalents of IPDI along with catalyst DBTL (0.01 g/g of IPDI) was added to it and the mixture was kept in a thermostated water bath, which was maintained at $40 \pm 2^\circ\text{C}$ for 2 hours with continuous stirring. After completion of 2 hours, triethanolamine (1.0 wt% of the resin for chain extension and curing) was added and mixed thoroughly for 5 minutes. The solution was then poured into the mold, where it was kept initially at 78°C for 24 hours and later on at 120°C for 4 hours.

Interpenetrating Polymer Networks (IPNs)

The reaction kettle containing urethane prepolymer was charged with triethanolamine (1.0 wt% based on polyurethane), predetermined amount of MMA along with EGDMA (1.0 wt% based on MMA) and benzoyl peroxide (0.5 wt% based on MMA) and thoroughly mixed for 3 minutes at 40°C . The temperature was raised to 75 to 78°C and reaction was continued for 60 minutes. Finally, the reaction mixture was poured into the mold and cured initially at 75 to 78°C for 24 hours and later at 120°C for 6 hours.

Characterizations

Infrared spectra of the IPNs were obtained from Shimadzu FTIR 4200 series spectrophotometer using KBr pellets, whereas, in the case of polyurethane

prepolymer, being highly viscous in nature, a thin film was cast over NaCl block. Tensile strength and elongation at break 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 the strips of the films of measured volume [10]. The swelling study was carried out in water, methyl ethyl ketone (MEK) and toluene [11]. Thermogravimetric measurements were made on a Mettler TA 4000 thermogravimetric analyzer (TGA) at a heating rate of 10°C/min in a nitrogen atmosphere and the energy of activation was computed by using Broido method [12]. Sample morphology was studied by scanning electron microscopy. Samples were prepared for SEM by freeze fracturing them in liquid nitrogen and applying a gold coating of approximately 200 Angstrom units. The gold coated samples were mounted on the SEM stubs with Ag adhesive paste. And glass transition temperatures were determined by differential scanning calorimetry on DuPont 9900 thermal analyzer at a heating rate of 10°C/min in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Infrared Spectroscopy (IR)

IR spectra of polyurethane prepolymer showed characteristic absorption bands at 1740 cm^{-1} and 3400 cm^{-1} corresponding to urethane and amide II (-NH stretching), respectively. As the prepolymer is isocyanate terminated, an intense and sharp band due to NCO was observed at 2270 cm^{-1} . IR spectra of IPNs showed all bands corresponding to polyurethane and methacrylate network and no additional bands were observed, thereby ruling out the possibility of any chemical interaction between the component networks.

Glass Transition Temperatures (T_g)

Table 2 shows that, C-IPNs exhibited two glass transitions, which indicated phase separations. However, there was an inward shift of T_g corresponding to polyurethane and PMMA phase, implying a small amount of polyurethane mixed with the polyacrylate phase. All the other IPNs showed a single glass transition intermediate between those of their parent networks ensuring better interpenetration. In the case of L-IPNs and T-IPNs, the latter showed relatively less deviation of T_g from theoretically calculated T_g , suggesting a high degree of interpenetration. It is difficult to correlate the composition of IPNs with the shift-

TABLE 2. Glass Transition Temperatures (T_g s) of Homopolymers and IPNs

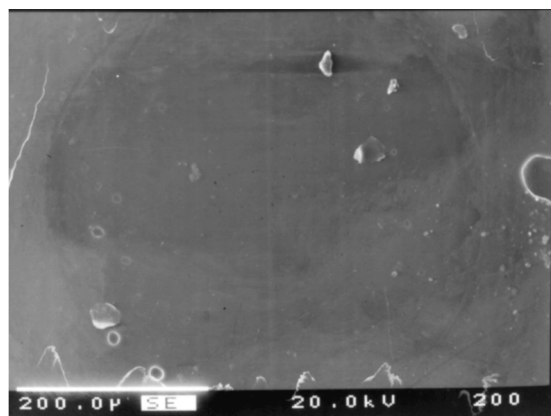
Sample Code	Composition U/PMMA (wt%)	No. of Glass Transitions	T_g (K) by DSC	$T_{g (avg)}^*$ (K) (calculated)
C-IPNs				
Homopolymer (CU)	100/0	1	244	-
IPN-1	25/75	2	245, 379	-
IPN-2	50/50	2	249, 377	-
IPN-3	75/25	2	249, 373	-
L-IPNs				
Homopolymer (ICLU)	100/0	1	266	-
IPN-4	25/75	1	358	353
IPN-5	50/50	1	331	324
IPN-6	75/25	1	303	295
T-IPNs				
Homopolymer (ICTU)	100/0	1	253	-
IPN-7	25/75	1	343	345
IPN-8	50/50	1	313	317
IPN-9	75/25	1	285	285
Homopolymer (PMMA)	0/100	1	382	-

$T_{g (avg)} = W_1 T_{g1} + W_2 T_{g2}$; W_1, W_2 are the weight fractions of urethane and PMMA, respectively

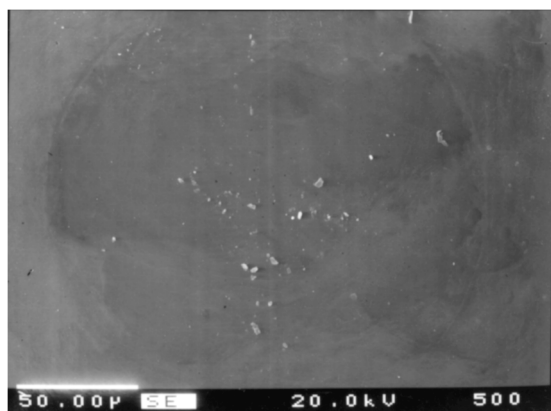
ing in glass transition temperatures because of wide distribution of phase domains and complexity of the morphology.

Morphology

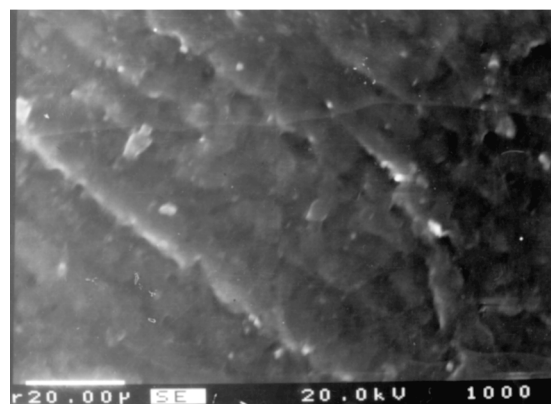
Morphology of the IPNs is revealed by electron micrographs [Figure 2 (a, b, c)]. All IPNs showed microphase dispersion of PMMA phase in the polyurethane matrix, indicating heterophase morphology. However, in the case of T-IPNs [Figure 2(c)] continuous phase of urethane network was observed clearly along with the dispersion of some small particles of domain sizes ranging between 0.9-3.0 μm , suggesting less separation of the phases. In the L-IPNs, the domain size (3 μm) is small, indicating good mixing of the constituent polymers. Figure 2(a) shows that in C-IPNs along with microphase dispersion, large globules of acrylate having domain sizes ranging from 8 μm to 30 μm have also



(a)



(b)



(c)

Figure 2. Representative Scanning Electron Micrographs of (a) IPN-2, CU50/PMMA50, (b) IPN-5, ICLU50/PMMA50, (c) IPN-8, ICTU50/PMMA50.

been dispersed. This behavior indicated higher compatibility of L-IPNs and T-IPNs than C-IPNs.

Mechanical Properties

Tensile strength, elongation at break and shore A hardness of homopolymers and their corresponding IPNs are given in Table 3. PMMA is characterized by high tensile strength and low elongation compared to polyurethane networks. It can be noted from Table 2, that tensile strength decreased and elongation increased with increasing polyurethane content in all the IPNs. In all the cases, variation of blend ratio resulted in considerable change in the elongation but, only nominal change occurred in tensile strength. Thus, interpenetration of polyurethane and poly (methyl methacrylate) did not directly influence the tensile strength of these IPN systems. The critical observation of Table 2 showed that, among all the IPNs, C-IPNs exhibited relatively higher elongation. This is possibly due to the loosely packed structure in C-IPNs, as observed from the

TABLE 3. Mechanical Properties of Homopolymers and IPNs

Sample Code	Composition U/PMMA wt%	Tensile Strength Mpa	Elongation at Break %	Hardness Shore A
C-IPNs				
Homopolymer (CU)	100/0	0.85	142	72
IPN-1	25/75	1.91	48	92
IPN-2	50/50	1.63	242	76
IPN-3	75/25	1.02	310	71
L-IPNs				
Homopolymer (ICLU)	100/0	1.44	97	87
IPN-4	25/75	2.18	10	>100
IPN-5	50/50	2.06	91	100
IPN-6	75/25	1.57	188	92
T-IPNs				
Homopolymer (ICTU)	100/0	0.88	110	70
IPN-7	25/75	1.58	11	96
IPN-8	50/50	1.46	98	89
IPN-9	75/25	0.40	196	60
Homopolymer (PMMA)	0/100	62.00	8	hard

large domain sizes (8 μm - 30 μm) [Figure 2(a)] leading to an increase in the free volume and mobility of elastomeric urethane chains. In all the IPNs, the compositions having 75% urethane showed higher elongation than that of their constituent homopolymers. This is mainly due to reinforcement of interpenetration at this particular composition. Interestingly, T-IPNs did not show any enhancement in the tensile strength over that of the parent networks. This could be due to the plasticization effect of T-oil (without OH), reducing the mechanical properties and hardness.

Hardness

It was worth noting (Table 3) that, L-IPNs and C-IPNs showed higher hardness as compared to T-IPNs at 75% polyurethane content in the blend. This is due to the formation of more crosslinked and stiffer polyurethane networks in the L-IPNs and C-IPNs. However, this enhancement occurs to a lesser extent in C-IPNs. In all the cases, hardness increased with concentration of PMMA in the IPNs, which is because, soft and flexible polyurethane resin was being substituted by hard poly (methyl methacrylate). Interestingly, T-IPNs showed comparatively low hardness at 75% concentration of polyurethane. This is possibly due to the formation of relatively more linear network of ICTU during IPN synthesis which gave highly elastic polymer rather than plastic. Shore A hardness of C-IPNs ranges between 71 to 92 and T-IPNs between 60 to 96.

Apparent Density

The density-composition curves of all the IPNs [Figures 3(a-c)] showed that the densities of C-IPNs, L-IPNs and T-IPNs increased with the corresponding increase in the PMMA contents. PMMA is denser than urethane, hence, density of IPN system increased as more and more polyurethane was substituted by PMMA. It can be observed from Figures 3(c), that in the case of T-IPNs theoretical (calculated on the basis of additivity principle) and actual density curves are well separated for all the concentrations, whereas, in the case of C-IPNs [Figure 3(a)] these curves are much closer to each other up to 50% polyurethane concentration. The higher actual density exhibited by L-IPNs [Figure 3(b)] (50/50) and C-IPNs (75/25) than the theoretically calculated values, is possibly due to the increase of interpenetration at those particular compositions. T-IPNs [Figure 3(c)] showed lower densities than the C-IPNs and L-IPNs. In all the IPNs, (except L-IPN 50/50 and C-IPNs 75/25), the actual densities were lower than the theoretical densities. Disagreement of the actual and theoretical densi-

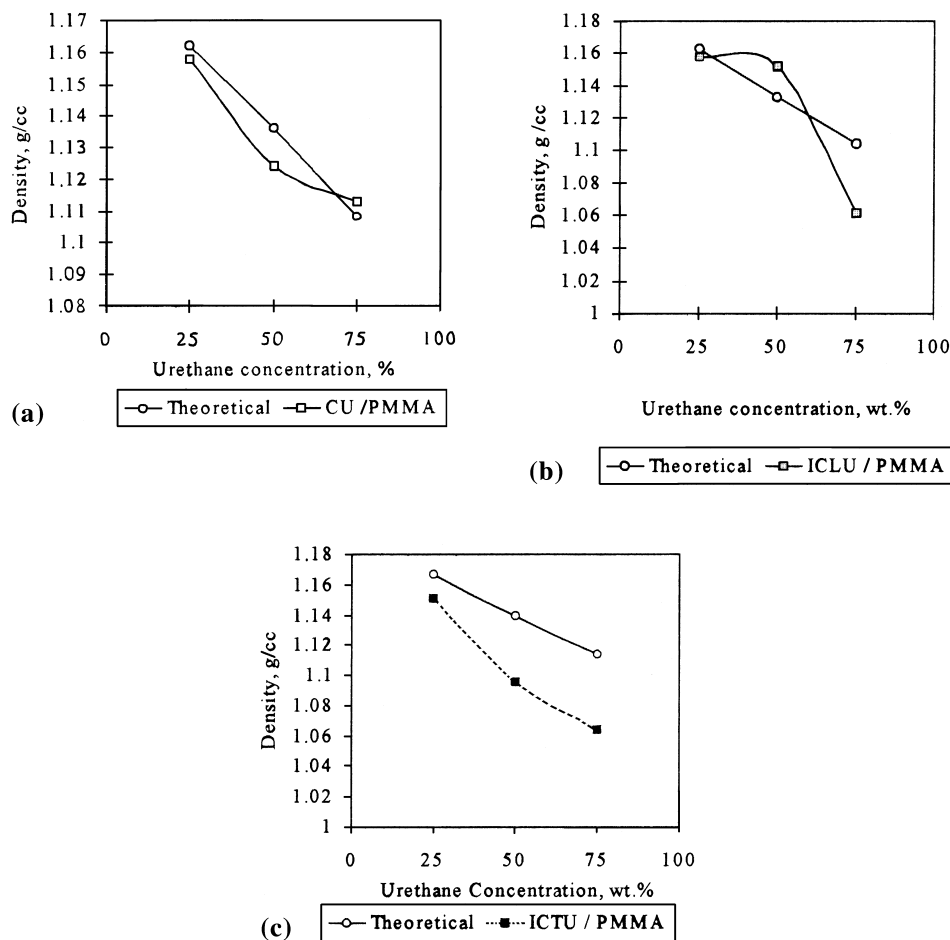


Figure 3. Density vs. polyurethane concentration (in wt%) of (a) CU/PMMA IPNs; (b) ICLU/PMMA IPNs; (c) ICTU/PMMA IPNs.

ties implies that, there seems to be a low density amorphous region at the interface between polyurethane and PMMA phases. Interpenetration of the two networks causes the low density amorphous region. The deviation between actual and theoretical densities is dependent on the amount of such an interpenetrated layer in the blends [13].

Swelling Study

Swelling experiments were carried out according to the procedure of Sperling and Mihalakis and the percentage of swelling was calculated for each IPN and homopolymers according to the following equation :

$$\% \text{ Swelling} = \frac{(\text{weight of swollen polymer} - \text{weight of dry polymer})}{\text{weight of dry polymer}} \times 100$$

Table 4 reveals the % swelling data of IPNs in MEK, toluene and water. Swelling was more prominent in MEK and toluene, possibly due to the ease of penetration of the solvents into the IPN matrix with less resistance. In contrast to the gradual increase in swelling with an increase in concentration of polyurethane in the case of C-IPNs and T-IPNs, the swelling was highest at 50% polyurethane composition for L-IPNs. C-IPNs exhibited relatively greater resistance to swellability than those of L-IPNs and T-IPNs. This is because castor oil forms relatively more crosslinked polyurethane network, which limits the swelling of PMMA network and hence that of the IPNs. Swelling of IPNs was more prominent in toluene, which proves that, toluene penetrates into core of the IPN matrix with less resistance. Among all IPNs, T-IPNs showed relatively greater swelling. This, was supported by the fact that due to the more linear nature of parent network (ICTU) [as observed from Figure 2(c)], which allows the solvents to penetrate in easily.

TABLE 4. Swelling of Homopolymers and IPNs

Sample Code	Composition U/PMMA (wt%)	% Swelling		
		Toluene	MEK	Water
C-IPNs				
Homopolymer (CU)	100/0	111	96	1
IPN-1	25/75	103	98	no change
IPN-2	50/50	118	103	no change
IPN-3	75/25	121	111	no change
L-IPNs				
Homopolymer (ICLU)	100/0	119	103	2
IPN-4	25/75	104	99	no change
IPN-5	50/50	128	114	no change
IPN-6	75/25	116	106	no change
T-IPNs				
Homopolymer (ICTU)	100/0	110	91	no change
IPN-7	25/75	114	101	no change
IPN-8	50/50	120	110	no change
IPN-9	75/25	150	140	no change
Homopolymer (PMMA)	0/100	96	101	1

Thermal Properties

Thermal behavior of the IPNs and homopolymers suggests that, the thermal stability of the IPNs falls intermediate between those of polyurethane and PMMA. Clustering of the TGA curves [Figure 4] indicated that there was no significant difference in the degradation behavior of all the IPNs. However, from the activation energy data [Table 5] it was observed that, polyurethane homopolymer (CU) is relatively more stable than ICLU, ICTU. In all the cases, generally, two stage decomposition was observed. Stage I corresponds to the urethane bond breaking in the case of urethane, whereas, in its IPNs, along with urethane bond breaking, unzipping of PMMA network also occurred, in the temperature range 330-340°C. Stage II corresponds to the polyol decomposition, which occurred at 450-455°C for both, polyurethane and their IPNs [14]. Finally, polyurethane showed complete weight loss at 500°C and its IPNs at 550°C. All the IPNs decomposed within 2-4% weight in the temperature range of 0-200°C, and about 10% weight loss occurred at 310°C-320°C. There was rapid weight loss from 30-90% at 355°C-475°C. This is because of decross-linking of the two

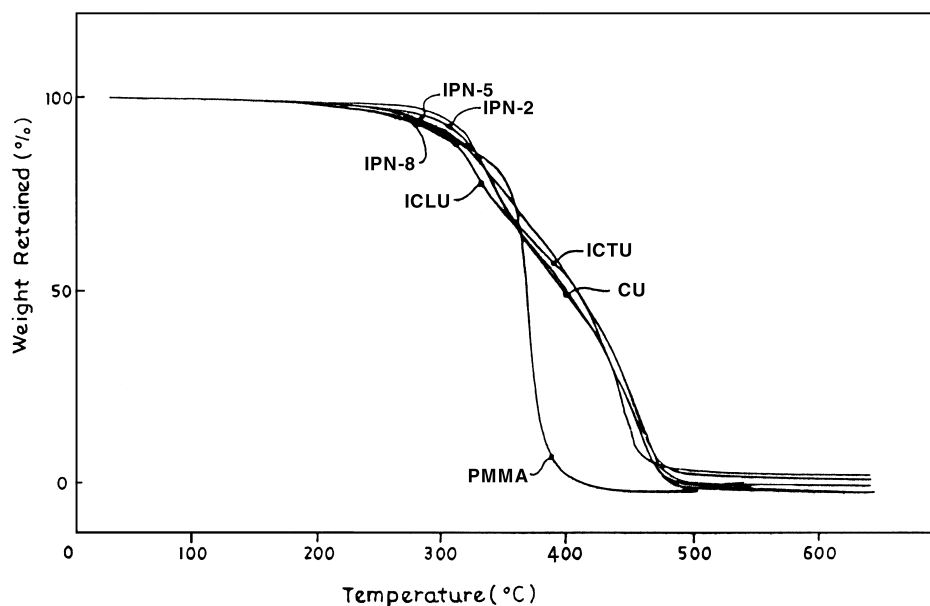


Figure 4. Representative thermograms for 50/50 (Urethane/PMMA) IPNs and homopolymers.

TABLE 5. Thermal Decomposition of Homopolymers and IPNs

Sample Code	Compositions	Decomposition Stages			
		Stage I (°C)	Activation Energy (kcal/mol)	Stage II (°C)	Activation Energy (kcal/mol)
Homopolymers					
CJ	100/0	254-391	36	391-502	44
ICLU	100/0	185-353	22	353-505	34
ICTU	100/0	250-380	31	380-500	39
PMMA	0/100	154-450	16	-	-
IPNs					
IPN-2	50/50	194-365	29	365-562	40
IPN-5	50/50	182-540	17	-	-
IPN-8	50/50	201-370	30	370-550	42

networks. Almost all IPNs decomposed completely from 475°C onwards up to 550°C. In this region along with the unzipped MMA monomer the polyol of the urethane network was detached by a free radical mechanism. For all the homopolymers and IPNs, activation energy values were lower in the first stage of degradation and higher in the second stage indicating that, the degradation process was relatively faster in the first stage. PMMA showed single stage decomposition and lower activation energy, implying that the chain scission of PMMA was a rapid process.

CONCLUSION

The insertion of double bond in castor oil (via interesterification with linseed oil /tung oil) gives a versatile and highly compatible polymer with MMA. The T-IPNs though, were quite weak with a low tensile strength as compared to those synthesised from castor oil based polyurethane yet, have a high potential for elastomer application L- IPNs offers a high tensile strength with relatively greater hardness. Hence, it can be put to use for various elastomeric as well as plastic applications. These results demonstrate the versatility of castor oil based polyurethane IPNs and highlight its adaptability by suitable incorporation of unsaturation for meeting specific end uses.

APPENDIX

Table 1

CO: Castor oil
LO: Linseed oil
TO: Tung oil

Tables 2-5

CU = unmodified castor oil urethane
ICLU= modified castor oil (using 30% linseed oil) urethane
ICTU= modified castor oil (using 30% tung oil) urethane

REFERENCES

- [1] K. T. Achaya, *J. Amer. Oil Chem. Soc.*, *48* (11), 758 (1971).
- [2] P. L. Nayak, S. Lenka, K. Santosh, Panda, and T. Pattnaik, *J. Appl. Polym. Sci.*, *47*, 1089 (1993).
- [3] G. M. Yenwo, J. A. Manson, J. Pulido, L. H. Sperling, A. Conde, and N. Devia, *J. Appl. Polym. Sci.*, *21*, 1531 (1977).
- [4] L. H. Sperling, "Interpenetrating Polymer Networks and Related Materials", Plenum Press, New York, 1981.
- [5] M. Patel and B. Suthar, *J. Polym. Sci., Polym. Chem. Ed.*, *25*, 2251 (1987).
- [6] Chakrabarty and B. Das, *J. Appl. Polym. Sci.*, *60*, 2125 (1996).
- [7] Vilas Athawale and Kolekar Suresh, *J. Macromol. Pure and Appl. Sci.*, *A35*, 1929 (1998).
- [8] Vilas Athawale and Suresh Kolekar, *Eur. Polym. J.*, *34* (10), 1451 (1998).
- [9] Vilas Athawale and Suresh Kolekar, *Polymer J.*, *30* (10), 813 (1998).
- [10] H. L. Frisch and D. Klemper, *Polym. Lett.*, *7*, 775 (1969).
- [11] L. H. Sperling and E. N. Mihalakis, *J. Appl. Polym. Sci.*, *17*, 3811 (1973).
- [12] A. Broido, *J. Polym. Sci., Polym. Phy. Ed.*, *7*, 1761 (1969).
- [13] J. Quin, F. Li, Z. Wu, and B. Qian, in "Advances in Interpenetrating Polymer Networks", K. C. Frisch and D. Klemper, Eds., Vol II, Technomic, p. 233, Lancaster, Pa., 1990.

- [14] P. D. Nair and M. Jayabalan, *J. Polym. Sci., Polym. Chem. Ed.*, 28, 3775 (1990).

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