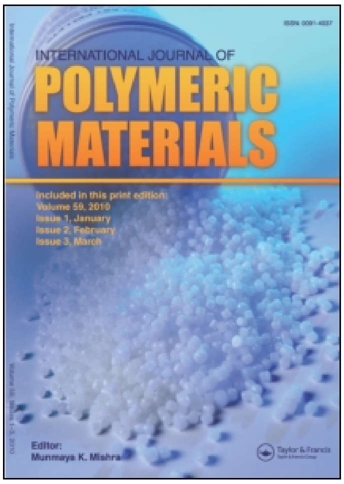

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Interpenetrating Polymer Networks from Castor Oil Based Polyurethanes and Poly(n-Butyl Acrylate). VI.

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Castor oil—a naturally occurring triglyceride of ricinoleic acid containing a special functionality of —OH group was reacted with hexamethylene diisocyanate to obtain liquid polyurethanes under different stoichiometric conditions varying NCO/OH ratio. These polyurethanes were then individually interpenetrated with n-butyl acrylate and ethylene glycol dimethacrylate as crosslinker by radical polymerization using benzoyl peroxide as initiator. The polyurethane/poly(n-butyl acrylate) interpenetrating polymer networks (IPNs) were obtained as tough films by transfer molding. These IPNs were characterized by their chemical resistance, thermal behavior (TGA, DSC), mechanical properties namely tensile strength, Young's modulus, elongation at break (%) and Shore A hardness. The morphological behavior was analyzed by scanning electron microscopy and dielectrical properties namely, electrical conductivity (σ), dielectric constant (ε'), dielectric loss (ε'') and loss tangent ($\tan\delta$) at different temperature were studied.

KEYWORDS Polyurethanes Poly(n-butyl acrylate) Ethylene glycol dimethacrylate Interpenetrating polymer networks scanning electron microscopy Mechanical properties Dielectric properties

INTRODUCTION

Interpenetrating Polymer Network, IPN, among the creations of modern polymer chemistry provides the more exciting polymer

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materials in terms of intellectual imagination and practical utility. Though youngest in the field of polymer blends and composites, they exhibit excellent engineering properties through the synergistic behavior of the individual polymers. Since the historical synthesis of IPN by Millar,[1] the pioneering works of Sperling,[2–5] Frisch,[6–9] Hourston[10,11] and, Meyer,[12,13] IPNs have proven to be of great importance from technological point of view for the fact that they are structurally novel, excellent in end-use properties and industrial applications. Survey of literature revealed the sparse reports regarding the use of castor oil for processable elastomers. These processable elastomers have been successfully utilized in the synthesis of IPNs.[14] In continuation of the work,[15–18] we report here the novel IPNs from liquid polyurethanes (castor oil + hexamethylene diisocyanate) and poly(n-butyl acrylate) of different compositions. A series of IPNs were prepared and characterized in terms of resistance to chemical reagents, thermal behavior (DSC, TGA), mechanical behavior namely tensile strength, Young's modulus, elongation at break (%) and Shore A hardness. The morphological behavior (SEM) was studied and the dielectrical properties such as electrical conductivity, dielectric constant (ε'), dielectric loss (ε'') and loss tangent (tan δ) were studied.

EXPERIMENTAL

Materials

Materials	Description	Source	Code
Castor oil	Triglyceride of recinoleic acid, hydroxyl value 124, $-OH = 2.27$ per mole of castor oil	Local	—
Hexamethylene diisocyanate	density 1.04 $g.ml^{-1}$	Fluka Switzerland	HMDI
n-Butyl acrylate	density 0.901 $g.ml^{-1}$	Schuchardt M Germany	nBA
Ethylene glycol dimethylacrylate	Acrylic crosslinker	Schuchardt M Germany	EGDM
Benzoyl Peroxide	initiator, recrystallized from chloroform	Aldrich USA	Bz_2O_2
Polyurethane	Polyurethane from castor oil and HMDI	Our Laboratory	PU

Synthesis of Polyurethane

Castor oil (50 g, 0.05 mol) was reacted with hexamethylene diisocyanate (15.25 g, 0.092 mol) in order to maintain NCO/OH ratio 1.6. The reaction was carried out at 45°C with continuous stirring for 1 h. The polymer was isolated as a thick syrup. Following the same procedure, the other polyurethanes (PU) with varying NCO/OH ratio were prepared.

Synthesis of IPNs

IPNs were prepared by charging PU in different proportions into a round bottom flask. To this, a mixture of n-butyl acrylate, 1% EGDM (ethylene glycol dimethacrylate) and 0.5% benzoyl peroxide was added. The mixture was stirred at room temperature for 5 min to form homogeneous solution. The temperature was then raised to 60°C to initiate polymerization of n-butyl acrylate and the cross-linker. After stirring for 1 h, the solution was poured into the glass mold kept in a preheated air circulating oven maintained at 60°C. It was kept at this temperature for 24 h and at 120°C for 4 h. The film thus formed was cooled slowly and removed from the mold. Nine different IPNs were synthesized with different composition (Table I). It is worth mentioning here that the percentage composition exceeding 45% of PU in the IPN formation did not yield IPN film.

TABLE I

Data on IPN synthesis

Sample	Polyurethane Wt%[a)]	n-Butyl acrylate Wt%	Density gm/ml
IPN-1	25	75	1.12
IPN-2	35(1.6)[B]	65	1.40
IPN-3	45	55	1.56
IPN-4	25	75	1.23
IPN-5	35(1.8)[B]	65	1.10
IPN-6	45	55	1.34
IPN-7	25	75	1.36
IPN-8	35(2.0)[B]	65	1.23
IPN-9	45	55	1.27

[a] Contents of polyurethane >45 wt% was not possible due to experimental difficulties.

[b] NCO/OH ratio of castor oil and HMDI.

Characterization

Resistance to chemical reagents was studied according to ASTM D 543-67 (1978). The mechanical properties were measured on universal Instron testing machine according to ASTM D 638 (1977). Hardness measurements were made according to ASTM D 785 (1965). Dielectric properties were studied according to ASTM D 1531 (1962). DSC measurements were made on a Du Pont 900 thermal analyzer at the heating rates of 10, 20 and 30°C/min. in air. The thermal stability was assessed on a Du Pont 951 thermal analyzer at a heating rate of 10°C/min in air. Scanning electron microscopy (SEM) was made with the Phillips EM-400 equipped with S(T) EM system PW-6585 the scanning attachment. The cryogenically fractured film in liquid nitrogen was mounted vertically on SEM stub by silver adhesive paste. The specimen was coated with gold using E P5/Carl Zeiss Vacuum system at about 10^{-5} torr.

RESULTS AND DISCUSSION

PU/PnBA IPNs

All the IPNs reported here were transparent tough films. The experimental details for the formation of IPNs is furnished in Table I. The polyurethanes were obtained from castor oil and HMDI and their structural features were established previously.[16] The densities of IPNs were measured using the hydrostatic technique at room temperature (Table I). The IPNs were insoluble in all the common organic solvents; acetone, methanol, chloroform, carbon tetrachloride, dimethyl formamide, dimethyl acetamide, tetrahydrofuran, dioxane, pyridine, benzene, toluene, and xylene. It was found that there was no weight loss of IPNs kept in these solvents.

Chemical resistance

The solvent resistance of PU/PnBA IPNs was made according to ASTM D 543-67 (1978) with a series of standard reagents namely 25% H_2SO_4, 15% HCl, 5% HNO_3, 5% NaOH, 10% NH_4OH, 25% CH_3COOH, 5% H_2O_2, 40% NaCl, methyl ethyl ketone, distilled water, carbon tetrachloride and toluene. The pieces of IPNs (20 mm × 20 mm × 0.8 mm) were put in 100 ml standard reagents for seven days. After exposure to chemical reagents, each of the IPN pieces was examined on the basis of physical appearance such as discoloration, loss of gloss, change in weight and change in thickness. These IPNs were stable in all these reagents while in methyl ethyl ketone, toluene, and carbon tetrachloride, the IPNs lost their gloss and became brittle. In 5% NaOH, IPNs showed swelling and considerable loss in weight and thickness.

Thermal behaviour

Frisch and coworkers[19–21] reported the thermal behavior of the various IPNs and found that these IPNs possessed greater thermal stability than their component networks. The thermal stabilities of the PU/PnBA IPNs were examined on the basis of percentage weight loss at different temperatures from the TG thermograms and compared with the homopolymer poly(n-butyl acrylate). The results are reported in Table II. It is evident that all the IPNs are stable up to around 250°C and rapidly lose weight around 350°C, and decompose completely beyond 550°C, (Figure 1). Only IPN-8 in the present study was analyzed by DSC at the heating rates of 10, 20

TABLE II

Thermogravimetric data of IPNs

	Percent weight loss (±2%) at different temperature, °C.						
Sample	250	300	350	400	450	500	550
IPN-1	—	3	23	41	63	83	92
IPN-2	—	3	24	41	62	83	91
IPN-3	—	3	24	41	64	83	92
IPN-4	—	2	22	40	62	85	92
IPN-5	—	3	23	39	62	85	92
IPN-6	—	4	22	41	63	82	94
IPN-7	—	3	24	40	62	84	95
IPN-8	—	2	23	40	64	83	92
IPN-9	—	2	23	38	63	82	91
Homopolymer Poly (n-butyl acrylate)	7.2	34	82	96.2	—	—	93 —

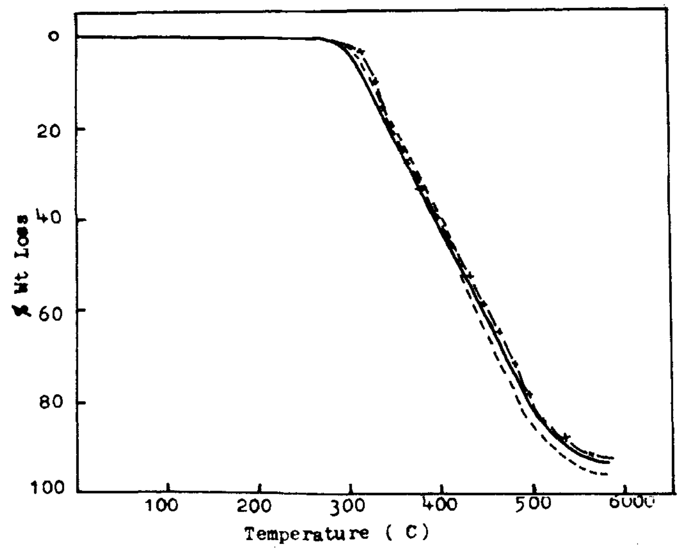

FIGURE 1 TGA thermograms, (—) IPN-1, (---) IPN-5, (-x-) IPN-8.

and 30°C/min. The values of the exothermic peak temperatures are reported in Table III. The data of exothermic peak temperatures were utilized for the application of the Ozawa,[22] the Kissinger[23] and the Crane[24] methods to estimate the kinetic parameters. The energy of activation (E), pre exponential factor (z), rate constant (k) and half life time ($t_{1/2}$) were computed on the basis of the Ozawa,[22] the Kissinger[23] and the Crane[24] methods and listed in Table III.

Mechanical properties and morphology

Table IV represents the mechanical properties of PU/PnBA IPNs in terms of tensile strength, Young's modulus, elongation at breaking point, and Shore A Hardness. These IPNs exhibit good mechanical properties compared to their homopolymer poly(n-butyl acrylate). This is because of the incorporation of polyurethane as a separate phase in IPNs which brings about the enhanced modification in the mechanical properties. The morphological evidence comes from their scanning electron micrographs and are shown in Figure 2 for selected IPNs namely IPN-1, IPN-5, and IPN-8. The observed

TABLE III

Kinetic parameter from DSC for IPN-8.

Heating rate °C/min	Exotherm peak temperature in °K	Ozawa method $E = 89.5$ KJ mole^{-1a} $Z = 8.5 \times 10^6$ min^{-1d}		Kissinger Method $E = 83.5$ KJ mole^{-1b} $Z = 2.5 \times 10^6$ min^{-1d}		Crane, Kaelble and Dynes method $E = 94.1$ KJ mole^{-1c} $Z = 2.1 \times 10^7$ min^{-1d}	
		k (min^{-1})	t 1/2 (min)	k (min^{-1})	t 1/2 (min)	k (min^{-1})	t 1/2 (min)
10	623	0.26	2.60	0.25	2.68	0.27	2.54
20	648	0.51	1.33	0.48	1.4	0.54	1.26
30	663	0.75	0.91	0.68	1.01	0.81	0.85

[a] 21.3 Kcal mole^{-1}.
[b] 19.9 Kcal mole^{-1}.
[c] 22.4 Kcal mole^{-1}.
[d] Z = pre exponential factor.

TABLE IV

Mechanical properties of IPNs

Sample	Tensile strength, MN/m^2	Young's modulus, MN/m^2	Elongation at break, %	Hardness shore A
IPN-1	0.62	0.69	68	73
IPN-2	1.00	1.54	56	74
IPN-3	0.64	0.92	66	41
IPN-4	1.06	2.13	39	74
IPN-5	0.97	2.20	35	75
IPN-6	0.79	2.02	26	73
IPN-7	1.25	2.04	46	76
IPN-8	1.30	2.12	48	76
IPN-9	1.20	2.22	39	75
Homopolymer Poly (n-Butyl acrylate)	60.4	2300	2–8	90

homogeneity in each specimen indicates the interpenetration of the phase domains of PU and PnBA.

Electrical properties

Polymer is becoming increasingly popular in engineering as dielectrics and their choice mainly depends on their dielectric properties. Frisch and coworkers[25] reported the dielectrical pro-

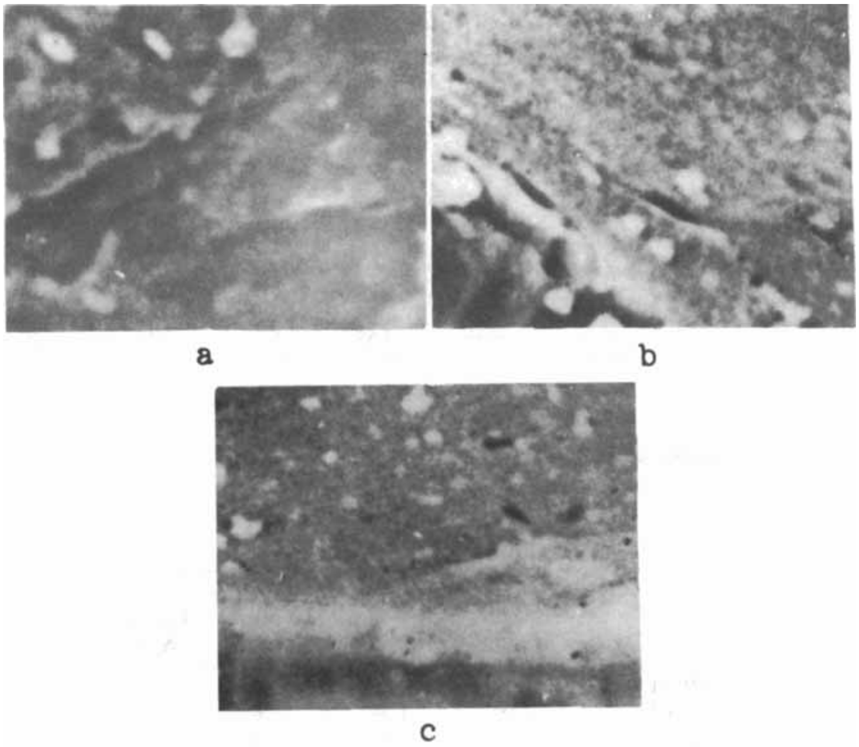

FIGURE 2 Scanning electron micrographs with 1200 magnification, (a) IPN-1, (b) IPN-5, (c) IPN-8.

TABLE V
Electrical properties

Sample	Electrical conductivity at room temp σ, ohm^{-1} cm^{-1}	Specific conductivity σ_0, ohm^{-1} cm^{-1}	Activation energy E KJ/mol.
IPN-1	3.8×10^{-13}	2.5×10^{-10}	59.8
IPN-5	4.1×10^{-13}	6.3×10^{-10}	67.1
IPN-8	5.0×10^{-13}	6.6×10^{-11}	44.5

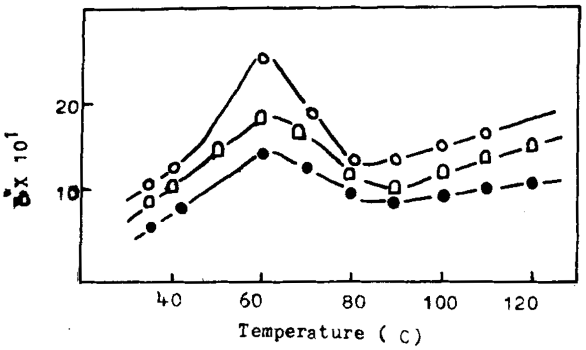

FIGURE 3 Dielectric constant (ε') versus temperature, (○) IPN-1, (●) IPN-5, (□) IPN-8.

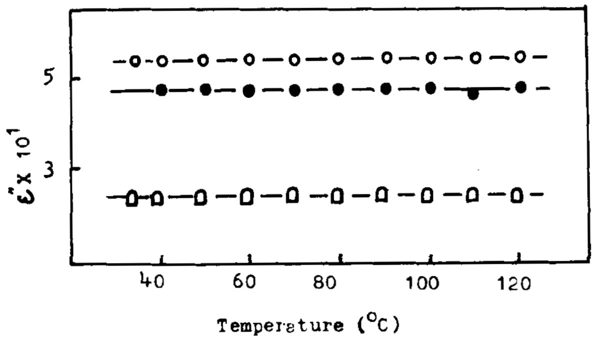

FIGURE 4 Dielectric loss (ε'') versus temperature, (○) IPN-1, (●) IPN-5, (□) IPN-8.

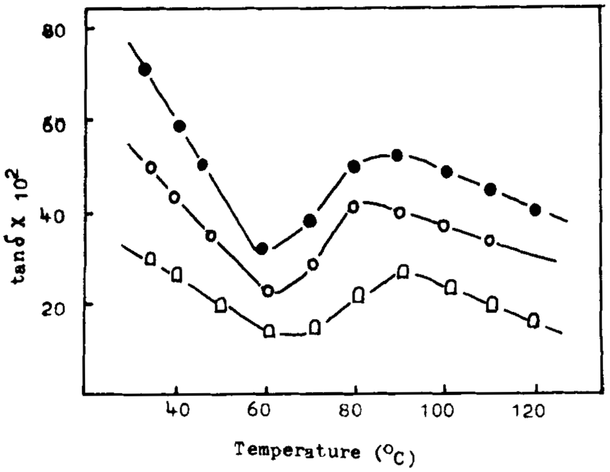

FIGURE 5 Loss tangent (tan δ) versus temperature, (○) IPN-1, (●) IPN-5, (□) IPN-8.

perties of three component network of IPNs. IPNs in present study have been studied in terms of dielectrical properties. The specific electrical conductivity (σ_0), electrical conductivity at room temperature (σ) and the activation energy (E) are reported in Table V. The dielectrical properties (ε', ε'' and $\tan\delta$) Vs temperature at 10 KHz are shown in Figures 3–5. From these dielectrical properties, these IPNs behaved like perfect insulators and have properties bordering on those exhibited by semi-conductors.[25]

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