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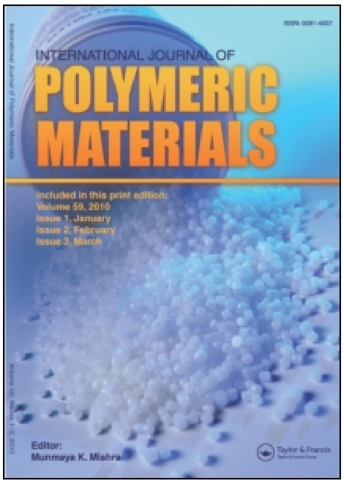

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Interpenetrating Polymer Networks from Castor Oil Based Polyurethanes and Poly(*n*-Butyl Acrylate)

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Castor oil was reacted with diphenyl methane diisocyanate under different experimental conditions and varying NCO/OH ratios to obtain liquid crosslinked polyurethanes. These polyurethanes were then subsequently interpenetrated with *n*-butyl acrylate monomer and ethylene glycol dimethacrylate as cross linker by radical polymerization using benzoyl peroxide as an initiator. This lead to the formation of novel interpenetrating polymer metworks PPU/PnBA IPNs films by transfer moulding technique. All these IPNs films were characterized by their resistance to chemical reagents, thermal behaviour (TGA), mechanical properties namely tensile strength, Young's modulus, elongation at break (%) and shore A hardness. The morphology of the IPNs was studied by scanning electron microscopy and dielectric properties namely electrical conductivity (σ), dielectric constant (ϵ'), dielectric loss (ϵ'') and loss tangent ($\tan \delta$) at different temperature were computed.

KEYWORDS: Castor oil, Diphenyl methane diisocyanate, Poly(*n*-butyl acrylate), Interpenetrating polymer networks, Transfer moulding, Thermal behaviour, Mechanical properties, Scanning electron microscopy, Dielectric properties.

INTRODUCTION

INTERPENETRATING POLYMER NETWORKS is defined as the crosslinked polymer composed of two chemically different polymer component networks. Such IPNs have been proved the

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possible candidates to replace the conventional polymers to meet the needs of present-day engineering material. The pioneering work of Millar,[1] Sperling[2-4], Frisch,[5-7] Meyer[8,9] and Hourston[10,11] has proved that IPNs are of the great importance from technological point of view. Castor oil—a natrually occurring triglyceride of ricinoleic acid, contains hydroxyl group. On the basis of its hydroxyl functionality, Sperling and his coworkers[12,13] reported the IPNs from polyurethanes based on castor oil and styrene monomer. They reported that IPNs behave like toughened elastomers or reinforced plastics depending on their composition of the two components. In the present investigation, the synthesis of IPNs from castor oil based polyurethanes from diphenyl methane diisocyanate (DMDI) and *n*-butyl acrylate monomer containing 1% ethylene glycol dimethacrylate is reported. A series of IPNs were prepared and characterized by their resistance to chemical reagents, thermal behaviour (TGA), mechanical behaviour namely, tensile strength, Young's modulus, elongation at break (%) and shore A hardness. The morphological behaviour (SEM) was studied and dielectric properties such as electrical conductivity, dielectric constant (ϵ'), dielectric loss (ϵ'') and loss tangent (tan δ) were studied at different temperature.

EXPERIMENTAL

Materials

Chemicals used in the present investigation are described and abbreviated in the following. Castor oil from local market contained hydroxyl value 127 corresponded to 2.30—OH groups per mole of castor oil. Diphenyl methane diisocyanate (DMDI), *n*-butl acrylate (nBA) and ethylene glycol dimethacrylate (EGDM) are purchased from Schuchardt M, Germany, Benzoyl peroxide from Aldrich, USA was recrystallized from chloroform.

Synthesis of Polyurethane

Castor oil (10 g, 0.01 mol) was reacted with diphenyl methane diisocyanate (5.75 g; 0.0230 mol) to maintain NCO/OH ratio 2.0.

TABLE I

Data on IPN synthesis

Sample	Polyurethane wt%[a]	*n*-Butyl acrylate wt%	Density gm/ml
IPN-1	15	85	1.07
IPN-2	25 (2.0)[b]	75	1.10
IPN-3	35	65	1.13
IPN-4	15	85	1.16
IPN-5	25 (2.2)[b]	75	1.15
IPN-6	35	65	1.12
IPN-7	15	85	1.14
IPN-8	25 (2.4)[b]	75	1.20
IPN-9	35	65	1.17

[a] Contents of polyurethane >35 wt % was not possible due to experimental difficulties.

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

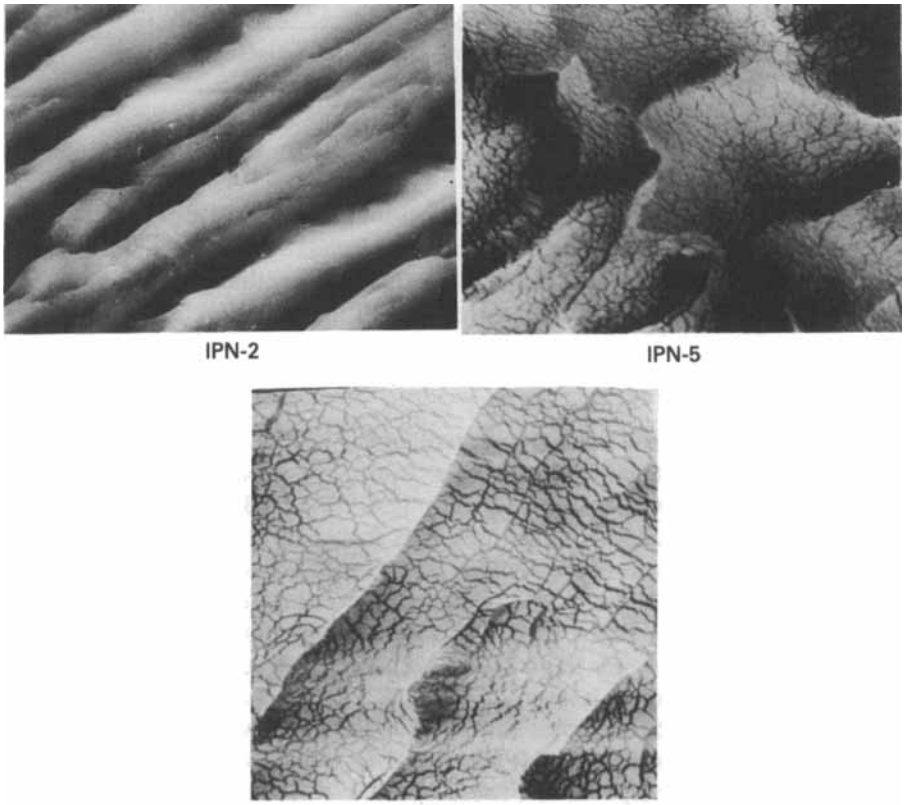
This reaction mixture was stirred continuously for 10 min at 35°C and for 1 h at 45°C. The polymer was isolated as a thick syrup. Following the above procedure the other polyurethanes (PU) with varying ratio of NCO/OH are prepared (Table I).

Synthesis of IPNs

IPNs were prepared by charging swollen PU in different proportions into a round bottom flask. To this, a mixutre of *n*-butyl acrylate, 1% ethylene glycol dimethacrylate (EGDM) and 0.5% benzoyl peroxide were 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 120°C for 4 h. The film thus formed was cooled slowly and removed from the mold. A series of IPNs (IPN-1 to IPN-9) were synthesized with different composition (Table I). It is worth mentioning here that the percentage composition exceeding 35% PU in the IPN formation did not yield IPN film.

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). The thermal stability was measued on a Du Pont 951 thermal analyzer at a heating rate of 10°C/min in air. Scanning electron micrographs (SEM) were made on Phillips EM-400 equipped with S(T) EM system PW 6585 the scanning attachment



IPN-2

IPN-5

IPN-9

FIGURE 1 Scanning Electron Micrographs with 12000 magnification.

(Figure 1). The cryogenically fractured film in liquid nitrogen was mounted vertically on SEM stub by silver adhesive paste. The specimen was coated with gold using EP 5/Carl Ziess Vacuum system at about 10^{-5} torr. Dielectric properties were measured according to ASTM D 1531 (1962) on 1620 A Capacitance Measuring Assembly, Gen Rad (USA) and electrical conductivity measured on Hewlett-Packard 4329 high resistance meter with temperature controlled furnace.

RESULTS AND DISCUSSION

The plyurethanes were obtained from castor oil and diphenyl methane diisocyanate and their structural features established previously.[14] However, detailed characterization could not be made for the fact that the condensation of the trifunctional (—OH) castor oil and DMDI yielded polyurethane of a cross-linked swollen mass. This swollen polyurethane was used immediately for further interpenetration with *n*-butyl acrylate; otherwise it continues to cross link that results into insolubility in organic solvents and consequently solution properties of the polyurethanes could not be studied. The interpenetration of PU and *n*-butyl acrylate was carried out under different experimental conditions as mentioned in Table I. Thus obtained PU/PnBA IPNs were tough films. These IPNs were insoluble in all the common organic solvents; methanol, ethanol, acetone, carbon tetrachloride, dimethyl formamide, dimethyl acetamide, tetrahydrofuran, dioxane, pyridine, benzene, toluene and Xylene. The densities of IPNs were measured by the hydrostatic technique at room temperature (Table I).

Solvent resistance

The PU/PnBA IPNs were subjected to the series of standard reagents to study chemical resistance quantitatively according to ASTM D 543–67 (1978) procedure. The pieces of IPNs (20 mm × 20 mm × 0.5 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, decrease in weight and change in thickness. The

TABLE II

Study of Resistance to Chemical reagents of IPNs according to ASTM D 543–67 (1978)

Solvent	IPN-2			IPN-5			IPN-9		
	% Change in weight	% Change in thickness	Physical Appearance	% Change in weight	% change in thickness	Physical Appearance	% Change in weight	% Change in thickness	Physical Appearance
25% H_2SO_4	3.24	0.87	NO CHANGE	5.54	0.83	NO CHANGE	3.38	0.63	NO CHANGE
25% CH_3COOH	6.12	0.67	NO CHANGE	4.37	0.37	NO CHANGE	5.64	0.48	NO CHANGE
15% HCl	2.26	0.80	NO CHANGE	3.05	0.41	NO CHANGE	2.07	0.72	NO CHANGE
5% HNO_3	2.32	1.38	NO CHANGE	1.87	1.70	NO CHANGE	1.89	1.11	NO CHANGE
40% NaCl	2.14	1.33	NO CHANGE	3.53	1.42	NO CHANGE	4.38	1.42	NO CHANGE
10% NH_4OH	6.25	0.83	NO CHANGE	2.56	0.76	NO CHANGE	5.11	0.95	NO CHANGE
5% H_2O_2	1.19	2.17	NO CHANGE	0.74	1.96	NO CHANGE	1.31	1.87	NO CHANGE
5% NaOH	1.15	0.94	NO CHANGE	0.63	0.76	NO CHANGE	1.01	0.82	NO CHANGE
Distilled water	3.57	1.80	NO CHANGE	4.31	1.76	NO CHANGE	3.81	2.00	NO CHANGE
MEK	37.30	16.36	*	46.45	19.20	*	50.37	15.71	*
CCl_4	57.05	11.51	*	57.14	9.42	*	52.33	14.85	*
Toluene	38.61	10.40	*	29.12	18.32	*	34.44	25.19	*

* In solvents like MEK, CCl_4 and Toluene, the IPNs become brittle, two phases are separated without dissolution, loses elasticity.

details of the results of some of the IPNs were reported in Table II. It is observed that these IPNs are stable in all the standard reagents while in methyl ethyl ketone, toluene and carbon tetrachloride the IPNs lost their gloss and became brittle.

Thermal behaviour

The thermal behaviour of the IPNs indicated that these IPNs possessed greater thermal stability than their component networks.[15–17] The thermal stabilities of the PU/PnBA IPNs were examined on the basis of percentage retention of weight at different temperatures from the TG thermograms and compared with the homopolymer poly(*n*-butyl acrylate). The results are reported in Table III. The IPNs are found to be stable up to 270°, lose weight rapidly around 450°C and decompose completely beyond 600°C (Figure 2). It is evident that thermal stability of IPNs is much greater than that of homopolymer component poly(*n*-butyl acrylate). This may be due to the interpenetration of the two component network polymers.

TABLE III

Thermogravimetric data of IPNs

	Percent weight loss (±2%) at different temperature, °C							
Sample	250	300	350	400	450	500	550	600
IPN-1	–	3	17	28	44	71	82	95
IPN-2	–	4	18	28	43	70	82	93
IPN-3	–	3	19	27	43	70	83	94
IPN-4	–	4	18	28	43	68	84	93
IPN-5	–	3	18	27	45	66	84	93
IPN-6	–	2	17	29	44	66	83	96
IPN-7	–	3	15	32	46	68	82	95
IPN-8	–	3	16	30	43	70	84	93
IPN-9	–	2	15	25	43	68	80	90
Homopolymer Poly(*n*-butyl acrylate)	7	34	82	96	—	—	—	—

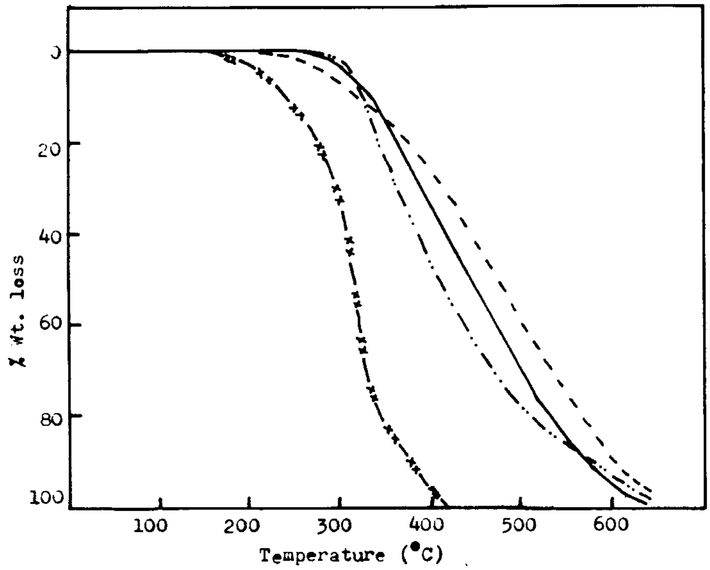


FIGURE 2 TGA Thermograms of IPN-2 (———), IPN-5 (– – – – – –), IPN-9 (—..—..—..—), Homopolymer (-xx-xx-xx-), Poly(*n*-butyl acrylate).

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	0.088	1.24	68	71
IPN-2	0.11	1.61	85	68
IPN-3	0.25	1.99	80	69
IPN-4	0.37	2.61	90	79
IPN-5	0.41	3.81	85	75
IPN-6	0.47	5.66	106	74
IPN-7	0.68	6.10	83	83
IPN-8	0.80	7.68	59	86
IPN-9	0.85	9.08	88	84
Homopolymer Poly(*n*-Butyl acrylate)	60.4	2300	2-8	90

Mechanical properties and morphology

Sperling and coworkers[18,19] reported the synergistic behaviour of IPNs from polystyrene (PS) and poly(*n*-butyl acrylate) (PnBA) component networks. The PS/PnBA IPNs have better mechanical properties and superior to their individual homopolymers.[17,18] Table IV reports the mechanical properties of PU/PnBA IPNs in terms of tensile strength, Young's modulus, elongation at break (%) and Shore A hardness. From the data among the IPN-1 to IPN-9, of different composition shows the variation in mechanical properties. It is evident that increased in polyurethane content, thereby increased crosslinking in the IPNs confers on their increased mechanical properties than their corresponding homopolymer—poly(*n*-butyl acrylate). The morphological behaviour of these IPNs was analyzed from their scanning electron micrographs with magnification as shown micrographs of IPN-2, IPN-5 and IPN-9 (Figure 1). It is observed that these IPNs have indicated the phase separation of individual domains of two component network polymers.

Electrical properties

The use of polymers in engineering as dielectrics is becoming increasingly important. Choice of the polymeric dielectric depends upon its dielectric and other physical properties over a wide range of temperatures and electric field frequencies. Frisch and coworkers[20] reported the dielectric properties of three component networks of IPNs. IPNs in present investigation studied in terms of dielectrical properties. The specific electrical conductivity (σ_0),

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/mole.
IPN-2	7.94×10^{-14}	1.0×10^{-10}	47.09
IPN-5	3.16×10^{-14}	3.63×10^{-12}	55.67
IPN-9	1.26×10^{-13}	1.99×10^{-11}	32.94

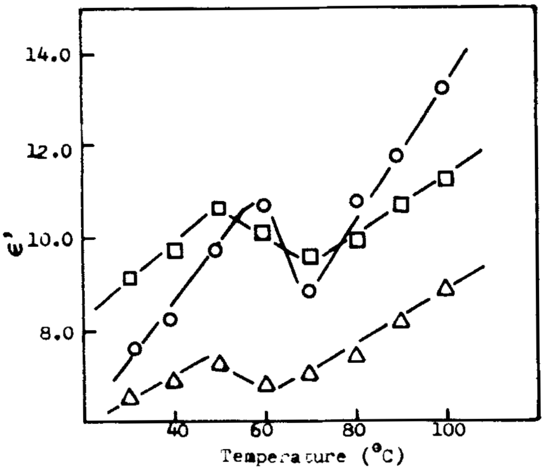


FIGURE 3 Dielectric constant (ε') Versus Temperature IPN-2 (○), IPN-5 (□), IPN-9 (△).

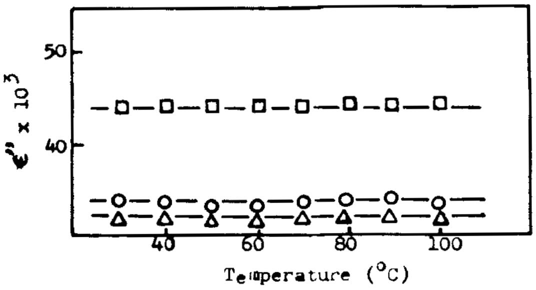


FIGURE 4 Dielectric loss (ε'') Versus Temperature IPN-2 (○), IPN-5 (□), IPN-9 (△).

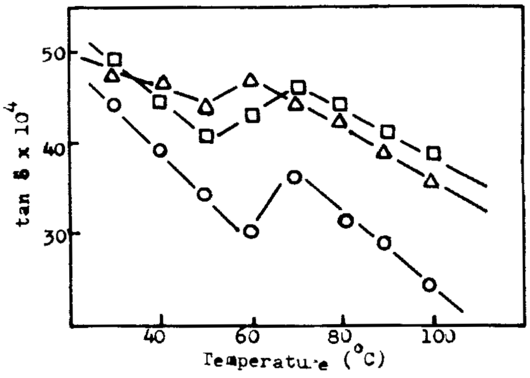


FIGURE 5 Loss tangent (tan δ) Versus Temperature IPN-2 (○), IPN-5 (□), IPN-9 (△).

electrical conductivity at room temperature (σ) and the activation energy (E) of some selected IPNs are shown in Table V. The dielectric properties (ϵ', ϵ'' and $\tan\delta$) Vs temperature at 10 KHz frequency for IPN-2, IPN-5 and IPN-9 are shown in Figures 3–5. From these dielectrical properties, it is found that the IPNs behave like insulators and have properties bordering on those exhibited by semiconductors.[20]

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