

Interpenetrating Polymer Network from Castor Oil-Based Polyurethanes and Poly(methyl Acrylate). XIV

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Synopsis

Castor oil containing hydroxyl functionality was reacted with 4,4'-diphenylmethanediisocyanate under different stoichiometric ratios of NCO/OH to obtain liquid polyurethanes. These polyurethanes were subsequently interpenetrated with methyl acrylate monomer using ethylene glycol dimethacrylate as a crosslinker by radical polymerization using benzoyl peroxide as an activator. The polyurethane/poly(methyl acrylate) interpenetrating polymer networks (PU/PMA IPNs) were obtained as tough films by transfer molding techniques. All IPNs were characterized by their resistance to chemical reagents, optical properties, thermal behavior, and mechanical properties: tensile strength, Young's modulus, elongation at break (%) and hardness Shore A. The morphology of the IPNs was studied by scanning electron microscopy and dielectric properties: electrical conductivity (σ), dielectric constant (ϵ'), dielectric loss (ϵ''), and loss tangent ($\tan \delta$) at different temperatures.

INTRODUCTION

Castor oil has been a successful candidate in the formation of industrially useful materials. Castor oil has been extensively used in reaction injection molding (RIM) and reinforced reaction injection molding (RRIM) processes¹⁻⁴ and interpenetrating polymer networks synthesis.⁵⁻⁹ Yenwo et al., Devia et al., and Sperling and Manson⁵⁻⁷ reported on a series of IPNs from castor oil-based polyurethanes derived from 2,4-toluene diisocyanate, and subsequent interpenetration was effected with styrene containing 5% divinyl benzene as crosslinker. From mechanical and morphological studies, IPNs behaved as a reinforced, highly extensible elastomer at low polystyrene levels and as a rubber-toughened plastic at high levels of polystyrene or crosslinking.⁵ Preliminary reports on IPNs showed high strength, good resiliency, and resistance to abrasion and hydrolysis.⁹

This work was undertaken to investigate the properties of elastomeric castor oil-based polyurethanes and vinyl monomers.¹⁰⁻¹² This article deals with the synthesis of IPNs by incorporating a swollen polyurethane (castor oil + 4,4'-diphenyl methane diisocyanate) and methyl acrylate containing crosslinker. These IPNs were characterized by their resistance to chemical reagents, optical properties, thermal behavior (TGA), and mechanical properties. The morphology by scanning electron microscopy (SEM) and dielectric properties at different temperatures was studied.

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EXPERIMENTAL

Chemicals

Castor oil was obtained locally and had a hydroxyl value 127 corresponding to 2.12 OH groups/mol of castor oil. 4,4'-Diphenylmethanediisocyanate (DMDI) and ethylene glycol dimethacrylate (EGDM) were purchased from Fluka AG, Basel, Switzerland. Benzoyl peroxide purchased from Aldrich USA, was recrystallized from chloroform and used. Methyl acrylate (MA) from Schuchardt M, Germany, was freed from stabilizer prior to use.

Polyurethane Synthesis

Castor oil (10.11 g; 0.0108 mol) was reacted with 4,4'-diphenyl methane diisocyanate (5.75 g; 0.023 mol) to maintain NCO/OH ratio of 2. This reaction mixture was stirred continuously for 10 min at 35°C and then for 1 h at 45°C. The polymer was isolated as a thick syrup. The other polyurethanes (PU) with varying ratios of NCO/OH were prepared (Table I) following the above procedure.

IPN Synthesis

The swollen polyurethane PU (DMDI + castor oil) was charged in different proportion into a round-bottom flask. To this, a mixture of methyl acrylate, EGDM (1% based on MA used) and benzoyl peroxide (0.5%) was added. The mixture was stirred at room temperature for 5 min to form a uniform mixture. The temperature was then raised to 60°C to initiate polymerization of methyl acrylate and added crosslinker. After stirring for 1 h, the solution was poured into glass molds kept in a preheated air-circulating oven maintained at 60°C. It was kept at this temperature for 24 h and then at 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) of different compositions was obtained (Table I).

TABLE I
Data on IPN Synthesis

Sample	Content of polyurethane (wt%) ^a	Content of methyl acrylate (wt%)	Density (g/mL)
IPN-1	15	85	1.12
IPN-2	25 (2.0) ^b	75	1.21
IPN-3	35	65	1.14
IPN-4	15	85	1.10
IPN-5	25 (2.2) ^b	75	1.20
IPN-6	35	65	1.17
IPN-7	15	85	1.22
IPN-8	25 (2.4) ^b	75	1.20
IPN-9	35	65	1.90

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

^b NCO/OH ratio of castor oil and DMDI.

CHARACTERIZATION

IPNs were characterized according to the following methods:

Property	ASTM specification
Resistance to chemical reagents	D 543 (1978)
Tensile properties	D 638 (1977)
Rockwell hardness	D 785 (1965)
DC conductance of materials	D 257 (1978)
AC loss characteristics at permittivity of solids	D 150 (1978)
Haze and luminous transmittance	D 1003 (1977)

Optical properties were measured using a visible light transmission and hazemeter of Suga Test Instrument Company (Japan) using dust- and grease-free films of IPNs. The thermal stability was measured on a Du Pont 951 thermal analyzer at a heating rate of 10°C/min in air. Scanning electron micrographs were made on Phillips EM-400 equipped with S(T)EM system PW 6585 as 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 vacuum system EPS/Carl Zeiss at about 10^{-5} torr. Dielectric properties were measured on 1620 A Capacitance Measuring Assembly, Gen Rad (USA) and Electrical conductivity was measured on Hewlett-Packard 4329, High Resistance Meter with temperature-controlled furnace.

RESULTS AND DISCUSSION

The polyurethanes obtained from castor oil and DMDI with different NCO/OH ratios were thick liquids. Initially, they are soluble in organic solvents like acetone, dioxane, toluene, and dimethyl formamide. But, upon standing at room temperature, they continue to crosslink, resulting in an insoluble mass due to the condensation of the trifunctional ($-OH$) castor oil and DMDI. However, the structural evidence comes from the infrared (IR) spectrum. It revealed that the polyurethane contained the characteristic group frequencies. The sharp bands around 3030 cm^{-1} may be assigned to aromatic C—H stretching vibrations and confirmed by the presence of a band around 1500 cm^{-1} and 1610 cm^{-1} due to C—H bending of aromatic moiety. A strong band easily discernible at 2260 cm^{-1} may be assigned to isocyanate group. In fact, the polyurethane is isocyanate-terminated polymer. A distinct, intense, but broad band is observed around $1730\text{--}1750\text{ cm}^{-1}$ which may be assigned as a group of bands concerning carbonyl groups: $\gamma_{C=O\text{ ester}} = 1746\text{ cm}^{-1}$, $\gamma_{C=O\text{ urethane}} = 1734\text{ cm}^{-1}$. The weak bands around 745 cm^{-1} and 815 cm^{-1} may be assigned to *p*-substituted aryl moiety (diphenyl methane moiety).

The polyurethane thus obtained was immediately swollen in methyl acrylate for further interpenetration. All the IPNs were obtained as tough transparent films. Solubility behavior of PU/PMA IPNs in a series of standard

reagents has been studied. It is observed that these IPNs are insoluble in all common organic solvents: methanol, ethanol, acetone, carbon tetrachloride, dimethyl acetamide, tetrahydrofuran, dioxane, pyridine, benzene, toluene, and xylene. The densities of IPNs were measured by the hydrostatic technique at room temperature (ASTM D 792 (1970)) (see Table I).

Solvent Resistance

The PU/PMA IPNs were subjected to a series of standard reagents to study chemical resistance quantitatively according to ASTM 543 (1978) procedure. The pieces of IPNs ($20 \times 20 \times 0.5$ mm) were put in 100 mL standard reagents for 7 days. After exposure to chemical reagents, each of the IPN pieces were examined on the basis of physical appearance such as discoloration, loss of gloss, decrease in weight, and change in thickness. The details of results of some of the IPNs were reported in Table II. It is observed that these IPNs are stable in all standard reagents, while in MEK, toluene, and carbon tetrachloride, the IPNs lost their gloss and became brittle. These results were compared with those of the individual component networks. Polyurethane (castor oil + DMDI) and poly(methyl acrylate) swell, lose weight, and change thickness in the stated reagents while in distilled water no change is observed.

Optical Properties

Results of the diffuse light, parallel light, total transmission, and haze measurements are presented in Table III. Results indicate that the percentage transmittance of light was very good in all the IPN films and was in the range of 49–81%. The difference is attributed to the contents of polyurethane in the IPN. Increase in the polyurethane content decreases the transmittance. This is similarly followed in the percent haze. Comparison of the optical properties of polyurethane and poly(methyl acrylate) component polymers indicated that poly(methyl acrylate) is a transparent film with 99% transmittance while polyurethane (castor oil + DMDI) is an opaque material with the transmittance of around 30% depending on the levels of NCO/OH ratios. Thus IPNs containing low contents of PU are good transparent films with minimum haze percentages.

Thermal Behavior (TGA)

Thermal gravimetric thermograms of IPNs indicated that these IPNs possessed greater thermal stability than their component networks.¹³⁻¹⁵ The thermal stabilities of PU/PMA IPNs were examined on the basis of percentage weight retention at different temperatures from the TG thermograms and compared with homopolymer, poly(methyl acrylate). The results are reported in Table IV. The IPNs are found to be stable up to 270°C, lose their weight rapidly around 450°C, and decompose completely beyond 600°C. It is evident that thermal stability of IPNs is greater than that of homopolymer component poly(methyl acrylate). This may be due to the interpenetration of two component networks polymers.¹⁶

TABLE II
Study of Resistance of IPNs to Chemical Reagents

Solvent	IPN-3			IPN-5			IPN-7		
	% 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 ₂ SO ₄	6.69	0.38	No change	1.20	1.37	No change	0.90	1.69	No change
25% CH ₃ COOH	6.33	1.12	No change	1.93	1.42	No change	2.02	1.52	No change
15% HCl	2.53	0.74	No change	0.63	1.34	No change	1.82	1.64	No change
5% HNO ₃	4.55	0.21	No change	0.58	1.41	No change	1.70	0.98	No change
40% NaCl	3.13	0.24	No change	0.24	1.78	No change	1.65	1.13	No change
10% NH ₄ OH	—	—	No change	0.22	1.38	No change	1.01	0.97	No change
5% H ₂ O ₂	5.10	0.56	No change	0.80	1.85	No change	1.60	0.92	No change
5% NaOH	4.52	0.37	No change	0.15	4.02	No change	1.85	0.62	No change
Distilled water	5.60	0.39	No change	0.57	1.64	No change	1.88	0.94	No change
MEK	26.01	18.13	^a	35.18	14.72	^a	38.12	24.72	^a
CCl ₄	58.40	37.10	^a	72.04	26.39	^a	68.33	34.08	^a
Toluene	27.50	23.13	^a	38.28	30.43	^a	56.82	39.82	^a

^a In solvents like MEK, CCl₄, and toluene, the IPNs become brittle, two phases are separated without dissolution, loses elasticity. Comparison with polyurethane and poly(methyl acrylate)-individual component networks indicated that PU and PMA swell, lose weight, and change thickness in the stated reagents, while in distilled water no change is observed.

TABLE III
 Optical Properties of PU/PMA IPNs

Sample	% Diffuse	% Parallel	Total % transmittance	% Haze
IPN-1	4.1	76.9	81.0	17.2
IPN-2	8.3	70.1	78.4	26.1
IPN-3	12.8	55.0	67.8	35.9
IPN-4	4.3	71.2	75.5	19.8
IPN-5	11.3	51.4	62.7	29.5
IPN-6	18.6	35.0	53.6	40.8
IPN-7	5.7	55.1	60.8	21.3
IPN-8	17.7	39.9	57.6	32.3
IPN-9	20.8	28.4	49.2	42.7

 TABLE IV
 Thermogravimetric Data of IPNs at Heating Rate of 10°C/min in Air

Sample code	Percent weight loss ($\pm 2\%$) at different temperature							
	250	300	350	400	450	500	550	600
IPN-1	—	2	18	28	45	70	85	96
IPN-2	—	3	17	27	46	71	84	95
IPN-3	—	2	17	28	44	71	83	96
IPN-4	—	3	18	25	45	72	84	95
IPN-5	—	2	17	26	46	70	85	94
IPN-6	—	2	16	28	44	72	83	93
IPN-7	—	3	18	27	43	70	82	93
IPN-8	—	2	17	26	42	70	84	92
IPN-9	—	2	16	26	43	71	83	90
Homopolymer poly(methyl acrylate)	7	10	15	24.5	51	99.5	—	—

 TABLE V
 Mechanical Properties of IPNs

Sample code	Tensile strength (MN/m ²)	Young's modulus (MN/m ²)	Elongation at break (%)	Hardness shore (A)
IPN-1	0.43	3.98	90	79
IPN-2	0.71	9.63	88	74
IPN-3	0.81	10.46	102	83
IPN-4	1.18	15.80	94	74
IPN-5	1.23	16.62	92	88
IPN-6	1.50	19.67	84	94
IPN-7	1.59	22.48	86	88
IPN-8	1.74	24.98	88	88
IPN-9	1.87	29.21	96	96
Homopolymer poly(methyl acrylate)	64.1	2200	2.8	90

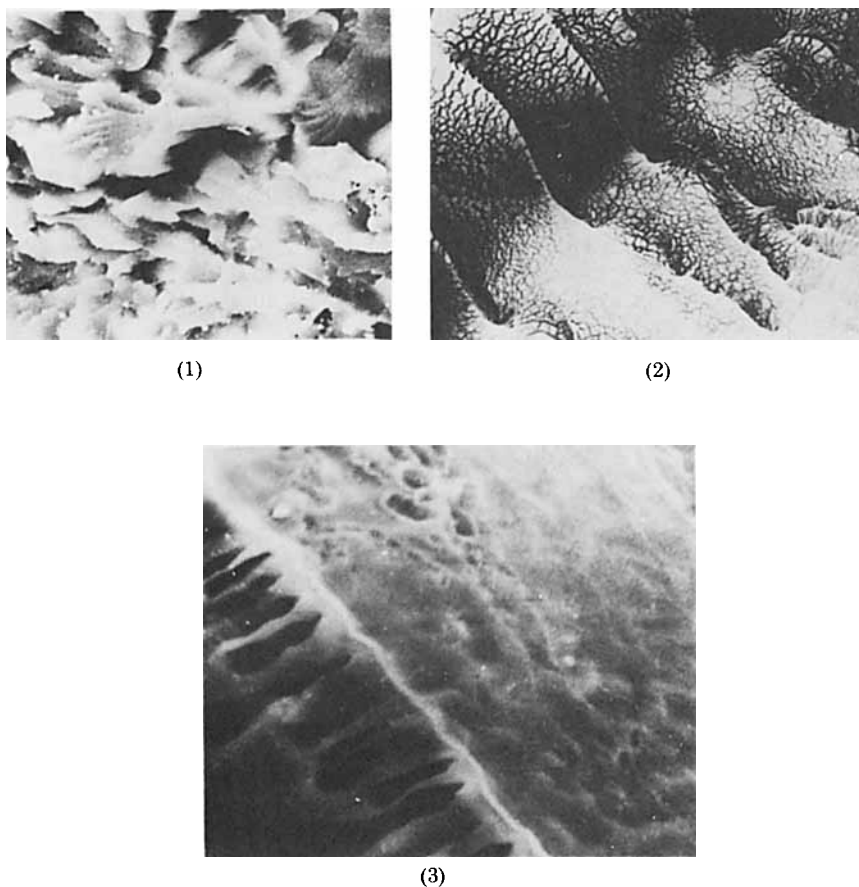


Fig. 1. SE micrographs with 12,000 magnification: (1) IPN-3, (2) IPN-5, (3) IPN-7.

Mechanical Properties and Morphology

Yeo and co-workers^{17,18} reported the synergistic behavior of IPNs from polystyrene (PS) and poly(*n*-butyl acrylate) (PnBA) component networks. The PS/PnBA IPNs have better mechanical properties and are superior to their individual homopolymers.¹⁴⁻¹⁶ Table V indicates the mechanical properties of PU/PMA IPNs in terms of tensile strength, Young's modulus, elongation at break (%), and Shore A hardness. The data showed that an increase in polyurethane content, and thereby increased crosslinking in the IPNs, confers increased mechanical properties as compared to their corresponding homopolymer, poly(methyl acrylate). The morphological behavior of these IPNs was analyzed from their scanning electron micrographs with magnification as shown in Figure 1. These IPNs show phase separation of two individual component networks.

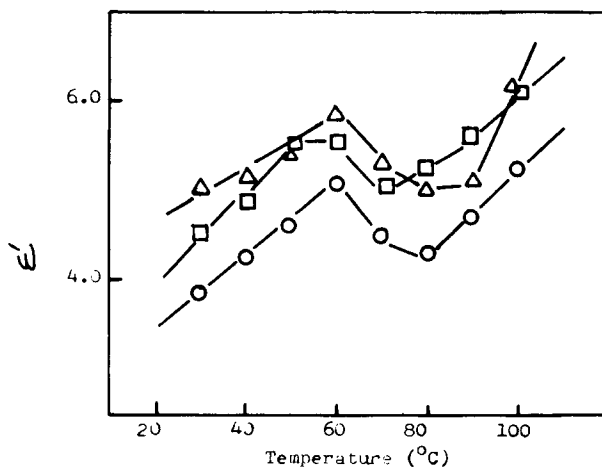
Electrical Properties

The use of polymers in engineering as dielectrics is becoming increasingly important. Choice of the dielectric material depends upon its dielectric and

TABLE VI
 Electrical Properties of IPNs

Sample code	Electrical conductivity at room temperature σ ohm ⁻¹ cm ⁻¹	Specific conductivity σ_0 ohm ⁻¹ cm ⁻¹	Activation energy E kJ/mol
IPN-3	2.51×10^{-13}	1.26×10^{-11}	46.7
IPN-5	7.94×10^{-14}	8.32×10^{-12}	42.1
IPN-7	2.51×10^{-13}	3.46×10^{-11}	41.9
PU (castor oil + DMDI)	3.16×10^{-16}	2.51×10^{-14}	45.6
PMA poly(methyl acrylate)	6.9×10^{-17}	6.3×10^{-17}	—

other physical properties over a wide range of temperature and dielectric field frequencies Cassidy and co-workers¹⁹ reported the dielectric properties of three component networks of IPNs. The specific electrical conductivity (σ_0), electrical conductivity at room temperature (σ), and the activation energy (E) of some selected IPNs and homopolymer-PMA and polyurethane components are shown in Table VI. The dielectric properties (ϵ' , ϵ'' , and $\tan \delta$) versus temperature at 10 kHz frequency for IPN-3, IPN-5, and IPN-7 are shown in Figures 2–4. Dielectric loss ϵ'' does not change with temperature, which implies that dielectric does not undergo energy attenuation when placed in dielectric field. Dielectric constant, ϵ' is frequency dependent as well as temperature dependent. Dielectric constant ϵ' shows a decrease (dip) in the temperature range around 70°C and a subsequent increase. This implies that the dielectric relaxation behavior of the material is observed. Similarly loss tangent ($\tan \delta$) would also exhibit the similar behavior as it is related to


 Fig. 2. Dielectric constant (ϵ') versus temperature: (1) IPN-3 (○); (2) IPN-5 (□); (3) IPN-7 (△).

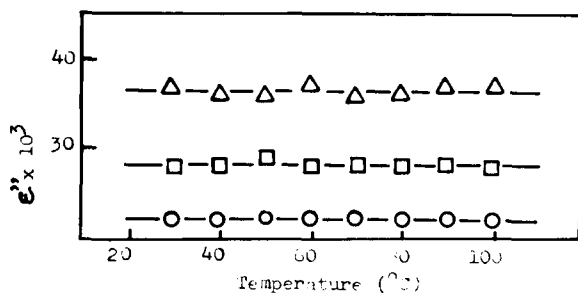


Fig. 3. Dielectric loss (ϵ'') versus temperature: (1) IPN-3 (○), (2) IPN-5 (□), (3) IPN-7 (Δ).

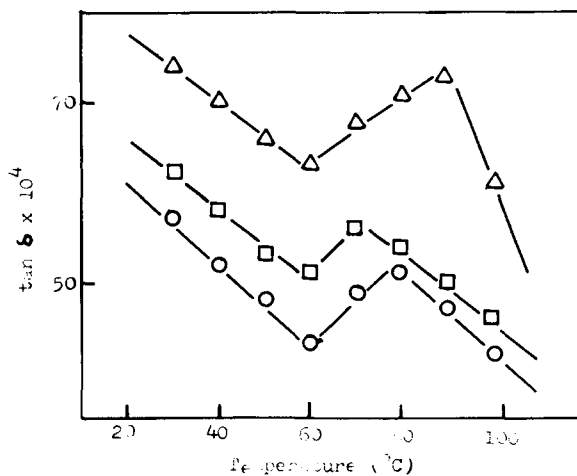


Fig. 4. Loss tangent ($\tan \delta$) versus temperature: (1) IPN-3 (○), (2) IPN-5 (□), (3) IPN-7 (Δ).

dielectric constant, $\epsilon'' = \epsilon' \times \tan \delta$. From these dielectric properties, it is found that the IPNs behave like insulators.¹⁹

CONCLUSION

Castor oil, a renewable resource, has been used in the novel synthesis of IPNs. The PU/PMA IPNs were tough films and have good resistance to chemical reagents, good thermal stability, and enhanced mechanical properties as compared to those of polyurethane and poly(methyl acrylate) component networks. These IPNs may find important applications for their dielectric behavior comparable to insulators.

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Received November 23, 1987

Accepted February 17, 1988