Interpenetrating Polymer Networks Based on Castor Oil, XVIII

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Synopsis

Castor oil—a renewable resource—is abundantly grown in tropical countries. It is a triglyceride of glycerol and ricinoleic acid containing hydroxyl functionality. These hydroxyls were reacted with 4,4'-diphenyl methane diisocyanate to form prepolyurethanes with different NCO/OH ratios. The prepolyurethane was swollen in ethyl methacrylate monomer containing 1% ethylene glycol dimethacrylate as crosslinker by radical polymerization initiated with benzoyl peroxide. The polyurethane/poly(ethyl methacrylate) interpenetrating polymer networks (IPNs) PU/PEMA were obtained as tough films by casting into glass molds. These IPNs were characterized by their resistance to chemical reagents, optical properties (% transmittance), thermogravimetric analysis and mechanical properties, dynamic storage modulus (ϵ'), loss modulus (ϵ''), and loss tangent (tan δ) by dynamic mechanothermal analysis, morphology by scanning electron microscopy, and dielectric properties (σ, ϵ', ϵ'', and tan δ) at different temperatures.

INTRODUCTION

Many plastics, such as acrylic plastics, are rather brittle as homopolymers. Even modest shocks, impact blows, or stresses may cause failure in application. Such plastics may be toughened by incorporation of judicious quantities of elastomeric material. The use of crosslinking in both components to form interpenetrating polymers networks (IPNs) leads to a novel engineering material.

Since historical synthesis of IPNs,[1] a tremendous amount of work of IPNs has emerged from the laboratories of Sperling,[2,3] Frisch et al.,[4,5] Hourston et al.,[6-8] and Hermant and Meyer.[9] Castor oil has been extensively used in the "one shot" reaction injection molding (RIM) or high pressure impingement mixing (HPIM) and reinforced RIM processes[10,12] and IPNs syntheses.[2,12] Sperling and co-workers[12,13] reported a series of IPNs from castor-oil-based polyurethane derived from 2,4-toluene diisocyanate and polymerizing styrene monomer in the presence of 5% p-divinyl benzene as crosslinker. From the mechanical and morphological studies, IPNs behaved as reinforced, highly extensible elastomer at low polystyrene content and as rubber toughened plastic as high content of polystyrene and/or crosslinking.[11] Preliminary reports on IPNs showed high strength, good resiliency, and resistance to abrasion and hydrolysis.[14,15]

With a view to investigating such potentialities, it was decided to undertake synthesis of IPNs based on castor oil. The present paper deals with the synthesis

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TABLE I
Data on Feed Composition (Individual) Polyurethane (PU) and Ethyl Methacrylate
for IPN Synthesis

Polymer code	NCO/OH ratio of MDI and castor oil	Content of polyurethane (wt %)[a]	Density (g/mL)
IPN-1	2.0	15	1.13
IPN-2	2.0	25	1.10
IPN-3	2.0	35	1.12
IPN-4	2.2	15	1.14
IPN-5	2.2	25	1.14
IPN-6	2.2	35	1.15
IPN-7	2.4	15	1.16
IPN-8	2.4	25	1.14
IPN-9	2.4	35	1.16
PU	—	100	1.07
PEMA	—	—	1.16

[a] Content of polyurethane > 35 wt % does not afford film formation as the islands of PU and PEMA are formed during IPN synthesis.

of PU/PEMA IPNs from a swollen crosslinked polyurethanes (castor oil + 4,4'-diphenyl methane diisocyanate) and poly(ethyl methacrylate) containing crosslinker and activator. These PU/PEMA IPNs were characterized by their resistance to chemical reagents, optical properties, thermal behavior, mechanical properties, dynamic mechanical thermal behavior, morphology by electron microscopy, and dielectric properties at different temperatures.

EXPERIMENTAL

Materials

Castor oil from local market was found to contain hydroxyl value 127 corresponded to 2.12—OH groups per mole of castor oil according to literature.[16]

TABLE II
Optical Properties of PU/PEMA IPNs

Sample code	% Diffuse	% Parallel	Total % transmittance	% Haze
IPN-1	9.2	77.5	86.7	14.3
IPN-2	13.8	65.0	78.8	21.5
IPN-3	22.5	47.8	70.3	29.1
IPN-4	14.5	68.8	81.3	19.6
IPN-5	19.3	54.2	78.5	27.4
IPN-6	27.6	39.5	67.1	36.8
IPN-7	17.9	60.5	78.4	28.3
IPN-8	23.3	46.0	69.3	38.6
IPN-9	38.7	26.1	64.8	43.7

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

	Percent weight loss (± 2%) at different temperature (°C)								
Sample code	250	300	350	400	450	500	550	600	650
IPN-1	—	3	20	39	51	64	70	90	92
IPN-2	—	4	20	30	50	64	72	89	93
IPN-3	—	3	22	40	51	66	73	88	92
IPN-4	—	4	21	38	52	70	74	87	95
IPN-5	—	3	20	36	54	69	76	85	96
IPN-6	—	4	21	34	54	69	76	88	96
IPN-7	—	3	20	43	56	70	81	90	97
IPN-8	—	4	22	45	59	74	81	94	98
IPN-9	—	4	19	41	57	72	80	92	96
Homopolymers:									
Polyurethane (PU)									
(castor oil + MDI)	15	67	77	90	98	—	—	—	—
Poly(ethyl methacrylate)									
(PEMA)	13	40	80	98	—	—	—	—	—

4,4'-Diphenyl methane diisocyanate (MDI) and ethylene glycol dimethacrylate (EGDM) from Fluka AG, Switzerland and 1,3-propane diamine from Reidel, Germany were purchased. Benzoyl peroxide (BzO) from Aldrich (U.S.A.) was recrystallized from chloroform. Ethyl methacrylate (EMA) from Schuchardt M, Germany was freed from stabilizer prior to use.

Synthesis of Polyurethane

A mixture of castor oil (10.11 g, 0.0108 mol) and 4,4'-diphenyl methane diisocyanate (5.75 g, 0.0230 mol) with NCO/OH ratio 2.0 was stirred for 10

TABLE IV
Mechanical Properties of PU/PEMA IPNs

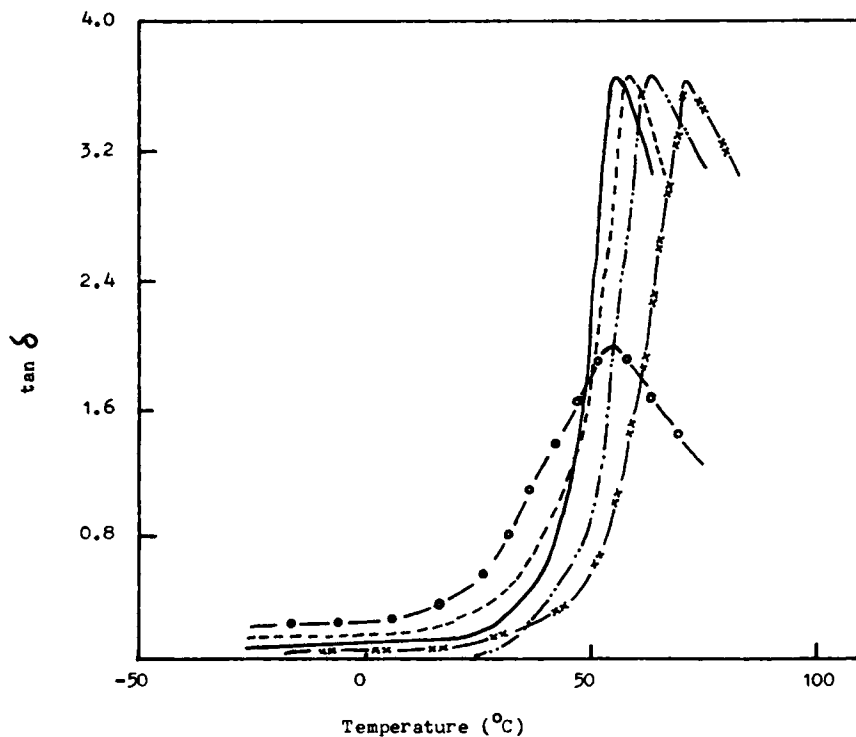| Sample code	Tensile strength (MN/m^2)	Young's modulus (MN/m^2)	Elongation at break (%)	Hardness shore A
IPN-1	0.45	4.02	82	74
IPN-2	0.75	7.69	96	77
IPN-3	0.78	10.73	80	79
IPN-4	0.81	12.61	92	88
IPN-5	0.86	13.81	96	85
IPN-6	0.88	4.50	90	93
IPN-7	1.03	19.21	92	88
IPN-8	1.14	24.99	90	96
IPN-9	1.21	39.06	88	98
Homopolymers:				
Polyurethane (PU)				
(castor oil + MDI)	1.08	5.52	56	88
Poly(ethyl methacrylate)				
(PEMA)	2.41	162.0	11	99

Fig. 1.   Loss tangent (tan δ) vs. temperature plots for IPN-3 (———), IPN-6 (- - -), IPN-9 (- · -), and homopolymers PU (-O-) and PEMA (-XX-).

min at 35°C and then for 1 h at 45°C. The polymer was isolated as a thick liquid. Following the above procedure, the other polyurethanes (PUs) with varying ratios of NCO/OH were prepared (Table I).

Synthesis of IPNs

A series of IPNs (IPN-1–IPN-9) of different compositions were obtained (Table I). Polyurethane was placed in different proportion into a round-bottom flask. To this, a mixture of ethyl methacrylate, EGDM (1% based on EMA), 1,3-propane diamine (1% based on PU), and benzoyl peroxide (0.5%) was added. The mixture was stirred at room temperature for 5 min to form homogeneous mixture. Still not gelled, the mixture was heated to 60°C to initiate ethyl methacrylate polymerization along with added crosslinker. After stirring for 1 h, the mixture, still not gelled, was poured into a glass mold kept in a preheated air circulating oven maintained at 60°C. It was held 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.

The optical properties were measured on a hazemeter of Suga Test Instrument Co. (Japan) using dust- and grease-free films (thickness ∼ 0.50–0.60 mm) of IPNs. The thermal stability was measured on a DuPont 951 thermal analyzer at a heating rate of 10°C min^{-1} in air. The dynamic mechanical behavior of the IPNs was examined on a dynamic mechanical thermal analyzer
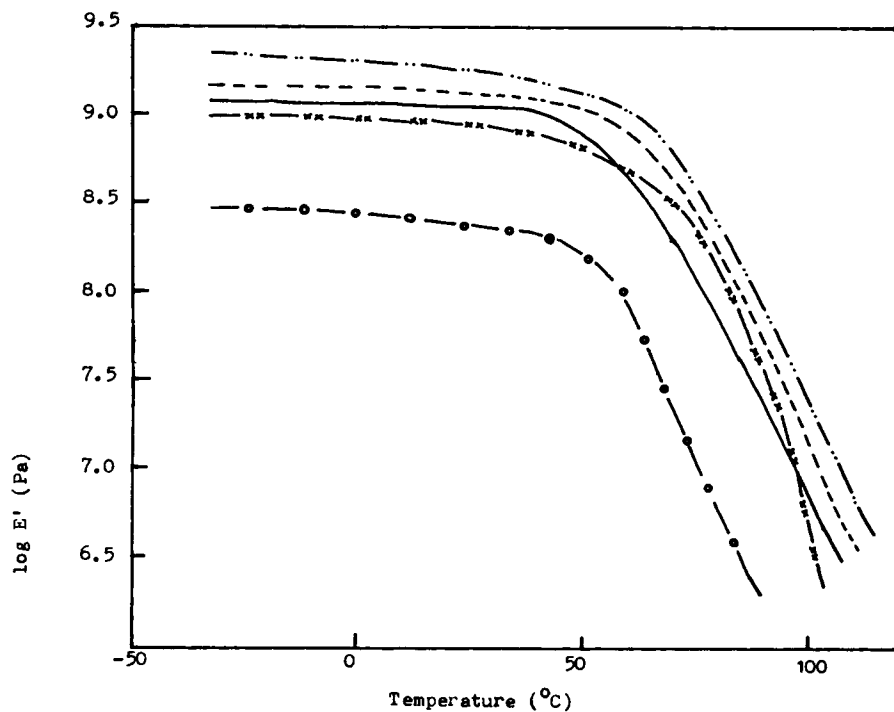
Fig. 2.   Dynamic storage moduli (E') vs. temperature plots for IPN-3 (——), IPN-6 (- - -), IPN-9 (- · -), and homopolymers PU (-O-) and PEMA (-✕✕-).
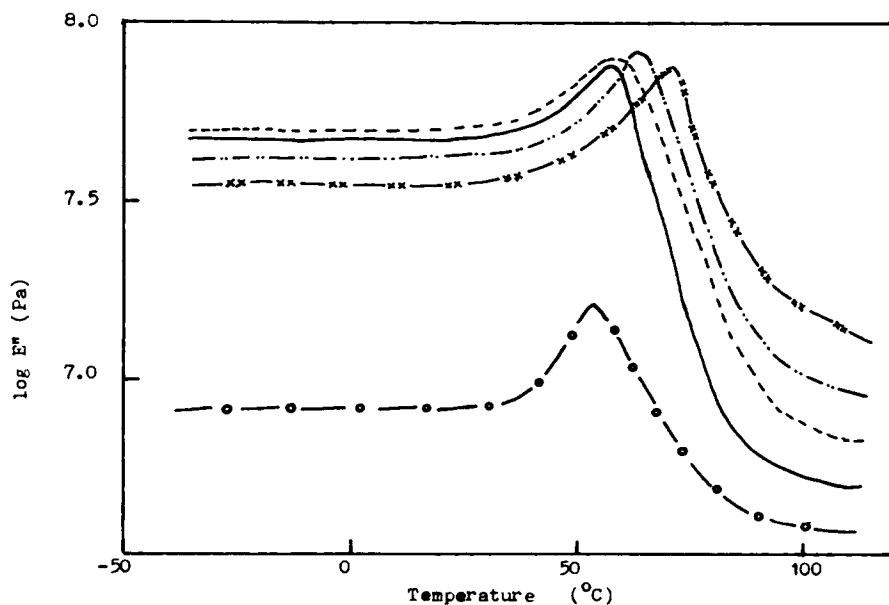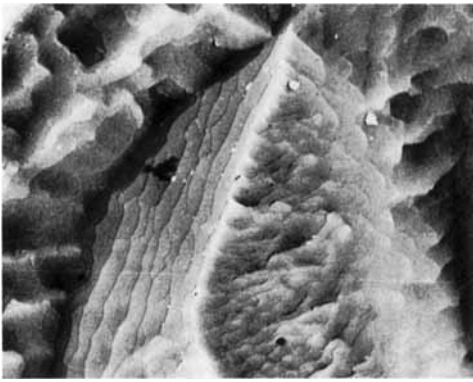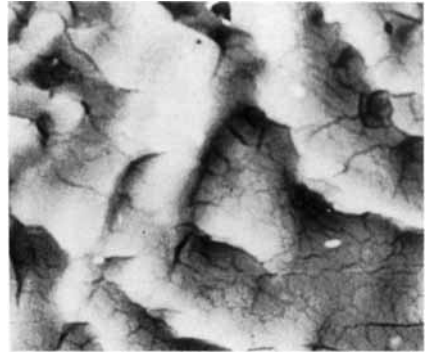

Fig. 3.   Dynamic loss moduli (E'') vs. temperature plot for IPN-3 (——), IPN-6 (- - -), IPN-9 (- · -), and homopolymers PU (-O-) and PEMA (-✕✕-).

Fig. 4.   Scanning electron micrographs with magnification 12,000 ×: (A) IPN-3; (B) IPN-6; (C) IPN-9.

(DMTA Mark II, Polymer Laboratories, U.K.) equipped with a Hewlett-Packard 200 series computer at a heating rate of 4°C min^{-1} and at a frequency of 10 Hz. Scanning electron micrographs (SEM) were made on Phillips EM 400 equipped with S(T)EM system PW 6585 as a scanning attachment. The cryogenically fractured film in liquid nitrogen was mounted vertically on a SEM stub using silver adhesive paste. The specimen was coated first with 200–250 Å carbon film in order to prevent cracking while imparting energetic electron beams and then gold 250–300 Å using an HBA/2 Carl Zeiss vacuum system at about 10^{-5} torr. Dielectric properties were measured on 1620 A capacitance measuring assembly Gen Rad (U.S.A.) and electrical conductivity measured on Hewlett-Packard 4329 A high resistance meter with temperature-controlled furnace using a chrome–alumel thermocouple.

TABLE V
Electrical Properties of IPNs

Sample code	Electrical conductivity at room temp (σ) (Ω^{-1} cm^{-1})	Intrinsic conductivity (σ_0) (Ω^{-1} cm^{-1})	Activation energy E (kJ mol^{-1})
IPN-3	3.16×10^{-13}	2.51×10^{-11}	63.75
IPN-6	3.98×10^{-13}	1.44×10^{-11}	66.98
IPN-9	2.51×10^{-13}	1.58×10^{-11}	44.62
PU (castor oil + MDI)	3.16×10^{-16}	2.51×10^{-14}	45.6
Poly(ethyl methacrylate) (PEMA)	4.2×10^{-16}	3.9×10^{-16}	[a]

[a] E is not computed as there is a negligible change in the electrical conductivity measurement over a temperature range of 30–120°C.

RESULTS AND DISCUSSION

Reaction of hydroxyl group of castor oil with 4,4'-diphenyl methane diisocyanate yielded liquid isocyanate terminated polyurethanes with different NCO/OH ratios. In the beginning they were soluble in organic solvents like acetone, dioxane, toluene, and dimethyl formamide. But, upon standing at room temperature, it would continue to crosslink, resulting in an insoluble mass in, but swollen by common organic solvents. However, structural evidence comes from the IR spectrum, indicating characteristic frequencies of ester linkage around $\dot{\nu}_{C=O}$ 1746 cm^{-1} and urethane linkage at $\dot{\nu}_{C=O}$ 1734 cm^{-1}. A sharp intense and easily discernible band around 2260 cm^{-1} may be assigned to an isocyanate group. The liquid polyurethanes in the presence of 1,3-propane–diamine as crosslinker were used immediately for further interpenetration with ethyl methacrylate. Thus obtained PU/PEMA IPNs were transparent brown films. They were insoluble in common organic solvents. The densities of the IPN films (Table I) were measured at room temperature by hydrostatic technique.
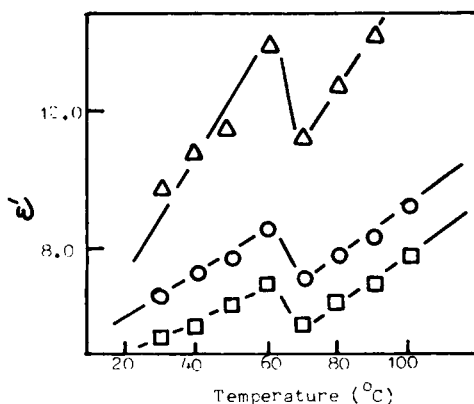

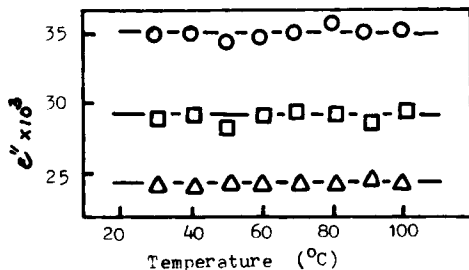Fig. 5. Dielectric constant (ϵ') vs. temperature plots for IPN-3 (O), IPN-6 ($\triangle$), and IPN-9 ($\square$).

Fig. 6. Dielectric loss (ϵ'') vs. temperature plots for IPN-3 (O), IPN-6 ($\triangle$), and IPN-9 ($\square$).

Resistance to Chemical Reagents

Solvent resistance of PU/PEMA IPN films to a series of standard reagents—25% H_2SO_4, 25% CH_3COOH, 15% HCl, 5% HNO_3, 40% NaCl, 10% NH_4OH, 5% H_2O_2, 5% NaOH, MEK, CCl_4, toluene, and distilled water—has been studied according to ASTM D 543 (1978). It was observed that these IPNs are stable in all standard reagents but become brittle and lose their gloss in methyl ethyl ketone, toluene, and carbon tetrachloride. The embrittlement was only a physical change and no soluble fraction of the IPN was isolated. Comparison with individual component networks, i.e., homopolymers PU and PEMA, indicated that PU and PEMA swell and lose weight in the stated reagents while in distilled water no change is observed.

Optical Properties

Results of diffuse light, parallel light, total light transmission and haze measurements are reported in Table II. Results indicate that the percentage transmittance of light was very poor in the range of 64–86% in all the IPN films. The difference is attributed to the content of polyurethane in IPN. Increase in PU content decreases the transmittance and percent haze. Comparison of the optical properties of polyurethane and poly(ethyl methacrylate) components indicated that poly(ethyl methacrylate) is transparent film with 99% trans-
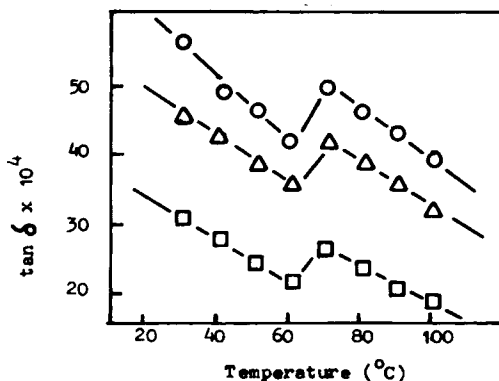

Fig. 7. Loss tangent (tan δ) vs. temperature plots for IPN-3 (O), IPN-6 ($\triangle$), and IPN-9 ($\square$).

mittance while polyurethane has transmittance around 43%, depending on the contents and NCO/OH ratios of PU. Thus IPNs with low PU are good transparent films with minimum haze percentage.

Thermal Behavior

The thermal behavior of IPNs indicated that some IPNs possess greater thermal stability than their component networks.[17-19] The thermal behavior of PU/PEMA IPNs were studied in terms of % loss in weight at different temperatures and compared with the homopolymer networks: PU and PEMA (Table III). The IPNs were stable up to 290°C, lose weight rapidly around 450°C, and decompose completely beyond 600°C. It is evident that the thermal stability of the IPNs is much greater than that of homopolymer components PU and PEMA. The enhancement in temperature for weight retention of PU/PEMA and PU/PS IPNs have been explained in the literature.[19] The unzipped PEMA monomer acts as free radical scavenger for PU degradation products, and thus the degree of intermixing of polyurethane/poly(ethyl methacrylate) networks may play an important role in the enhancement of thermal stability.

Mechanical Properties

Sperling and his co-workers[20] reported the synergistic behavior of IPNs from polystyrene (PS) and poly(n-butyl acrylate) PnBA component networks. The PS/PnBA IPNs exhibited modified properties of their individual component homopolymers.[18,19] Riordan and his co-workers[21] reported the improved impact strength of PU/PMMA IPNs compared to homopolymer PMMA. The mechanical properties of PU/PEMA IPNs in the present investigation were studied in terms of tensile strength, Young's modulus, elongation at break (%), and hardness Shore A. From the data among IPN-1–IPN-9 presented in Table IV show the variation in the mechanical properties to their homopolymer component networks, PU and PEMA, respectively. It is observed from the mechanical properties of these IPNs that incorporation of the plastic–poly(ethyl methacrylate) component into an elastomeric polyurethane has provided modest improvement in the Young's modulus from a value of 5.52 to 39.06 MN/m^2, depending upon the content of poly(ethyl methacrylate). Thus it may be concluded that, in the present set of IPNs, toughness in the elastomeric PU increases with the increase in the PEMA content of IPNs.

Dynamic Mechanical Behavior and Morphology

The dynamic mechanical behavior of these IPNs shown in Figures 1–3 present evidence of substantial miscibilities. The tan δ vs. temperature dispersion (Fig. 1) shows the transition of the IPNs which is only marginally higher than the glass transition of the PU but lower than the glass transition of PEMA. Figures 2 and 3 show dynamic storage moduli (E') and dynamic loss moduli (E'') vs. temperature of the IPNs. The IPNs show only one quite sharp transition region in the storage modulus spectra at a somewhat lower than the glass transition temperature of the component network PEMA. The E'' and tan δ vs. temperature plots show a sharp loss maximum intermediate with those of the component networks PU and PEMA.

From the above evidence, it is deduced that there is an appreciable mixing of PU and PEMA networks, but from scanning electron micrographs it is observed that there are two distinct phase domains due to phase separation of two component networks. However, PU network is formed first and interpenetrated with the PEMA component during IPN synthesis[12]; PU is a continuous phase in which second component PEMA is entangled in the matrix of polyurethane (Fig. 4).

Dielectric Properties

Use of IPN polymers in the field of dielectric materials has become of prime importance in the engineering materials; choice of material depends upon their dielectric and other properties over a wide range of temperature and dielectric field frequencies. Updated survey reveals that there are few reports about the dielectric behavior of the IPNs.[22] The IPNs in the present investigation were studied in terms of dielectrical properties. The intrinsic electrical conductivity (σ_0), electrical conductivity at room temperature (σ), and activation energy (E) of some selected IPNs and their control individual homopolymers namely polyurethane and poly(ethyl methacrylate) are presented in Table V. It is found that the intrinsic electrical conductivity of IPNs ranged from 1.44×10^{-11} to 2.51×10^{-11} Ω^{-1} cm^{-1} while their individual homopolymer networks have 2.51×10^{-14} (PU) and 3.9×10^{-16} (PEMA). It is evident from these observations that IPNs behave like semiconductors as compared to the insulating behavior of their individual homopolymers. The other IPNs in the present study were analyzed but indicated negligible variation in the series of particular NCO/OH ratio. The dielectric properties (ϵ', ϵ'', and tan δ) vs. temperature at 10 KHz frequency for IPN-3, IPN-6, and IPN-8 are shown in Figures 5, 6, and 7. The fact that dielectric loss (ϵ'') does not change with temperature implies that IPN does not undergo energy attenuation when placed in electric field. Dielectric constant (ϵ') is a property of insulation, which determines the electrostatic energy stored within the solid material. For all the IPNs, at a given test frequency, dielectric constant increases with increase in temperature due to softening of IPN. At a high temperature, dielectric constant reaches a plateau and then gradually decreases with increasing temperature. Dielectric constant (ϵ') shows a decrease (dip) at some temperature range around 70°C and, later on, it increases. The gradual decrease comes from a decrease in the orientation of the dipoles as the kinetic motion of the molecules opposes the orienting effect of the dielectric field, and from the decrease in density. Similarly loss tangent (tan δ) would also exhibit similar behavior as it is related to dielectric constant, $\epsilon'' = \epsilon' \times \tan \delta$. From these dielectrical properties, it may be concluded that these IPNs behave like semiconductors and have bordering properties of insulators.[22,23]

CONCLUSION

Castor oil—a renewable resource—has been used in the novel synthesis of IPNs. The PU/PEMA IPNs exhibited better resistance to chemical reagents and poor solubilities in organic solvents. These IPNs showed modification in

the percent weight retention at different temperatures and mechanical and electrical properties to their component networks PU and PEMA.

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