Interpenetrating polymer networks from castor oil-based polyurethane and poly(ethyl methacrylate) XVII

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Two-component interpenetrating polymer networks (IPNs) of castor oil-based polyurethane (PU) and poly(ethyl methacrylate) (PEMA) were prepared by sequential polymerization. The liquid polyurethanes were formed by reacting the hydroxyl group of castor oil with isophorone diisocyanate at different NCO/OH ratios. These polyurethanes were swollen in ethyl methacrylate monomer, which was subsequently polymerized by radical polymerization initiated with benzoyl peroxide in the presence of crosslinkers, ethylene glycol dimethacrylate and 1,3-propanediamine. A series of PU/PEMA interpenetrating polymer networks (IPNs) were obtained as tough films. These IPNs were characterized in terms of: resistance to chemical reagents, thermal behaviour and dynamic mechanical thermal analysis. The morphology was determined by scanning electron microscopy, and dielectric properties at different temperatures were studied.

(Keywords: castor oil; polyurethane, poly(ethyl methacrylate); interpenetrating polymer networks; crosslinker ethylene glycol dimethacrylate; dynamic mechanical thermal analysis; scanning electron microscopy; dielectric properties)

INTRODUCTION

Castor oil—a renewable resource—has been a successful candidate in the formation of industrially useful materials. Castor oil has been extensively used in reaction injection moulding (RIM) and reinforced reaction injection moulding (RRIM) processes[1–4], and interpenetrating polymer network (IPN) synthesis[5–10]. Sperling and coworkers[5–8] reported a series of IPNs from castor-oil-based polyurethanes derived from 2,4-toluene diisocyanate, subsequent interpenetration being effected with styrene containing 5% *p*-divinylbenzene as crosslinker. From mechanical and morphological studies, IPNs are found to be reinforced, highly extensible elastomers at low polystyrene content and rubber-toughened plastics at high contents of polystyrene and/or crosslinking[5]. Preliminary reports on IPNs showed high strength, good resilience and good resistance to abrasion and hydrolysis[9,10]. With a view to investigating such potentialities, it was decided to undertake the synthesis of novel IPNs based on castor oil[11–13]. The present communication reports the synthesis of polyurethane/poly(ethyl methacrylate) (PU/PEMA) IPNs. These IPNs were characterized by their resistance to chemical reagents, thermal behaviour and dynamic mechanical thermal behaviour. SEM morphology and dielectric properties at various temperatures were studied.

EXPERIMENTAL

Materials

Castor oil was obtained from a local market. Its hydroxyl value was estimated by the acetic anhydride-pyridine method[14] and found to be 127, corresponding to 2.12 –OH groups per mole of castor oil. Isophorone diisocyanate (IPDI) and ethylene glycol dimethacrylate (EGDM) were purchased from Fluka AG, Switzerland. 1,3-Propanediamine was purchased from Riedel, Germany. Benzoyl peroxide (BzO), from Aldrich, USA, was recrystallized from chloroform. Ethyl methacrylate (EMA), from Schuchardt, Germany, was freed from stabilizer prior to use.

Synthesis of polyurethanes

A mixture of castor oil (10.11 g, 0.0108 mol) and isophorone diisocyanate (4.817 g, 0.0218 mol), maintaining an NCO/OH ratio 2.0, was stirred continuously for 2 h at 45°C. The isocyanate-terminated polyurethane was isolated as a thick syrup. The other polyurethanes (PU) with varying ratios of NCO/OH were also prepared following the above procedure (*Table 1*).

Synthesis of IPNs

The polyurethane (PU) was placed in different proportions into a round-bottomed flask. To this, a mixture of

Table 1 Data on feed composition (individual polyurethane (PU) and ethyl methacrylate) for IPN synthesis

Sample code	NCO/OH ratio of IPDI and castor oil	Content of polyurethane (wt%)[a]	Content of ethyl methacrylate (wt%)
IPN-1	2.0	15	85
IPN-2	2.0	25	75
IPN-3	2.0	35	65
IPN-4	2.2	15	85
IPN-5	2.2	25	75
IPN-6	2.2	35	65
IPN-7	2.4	15	85
IPN-8	2.4	25	75
IPN-9	2.4	35	65
PU (castor oil +IPDI)	1.0	100	–
PEMA		–	100

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

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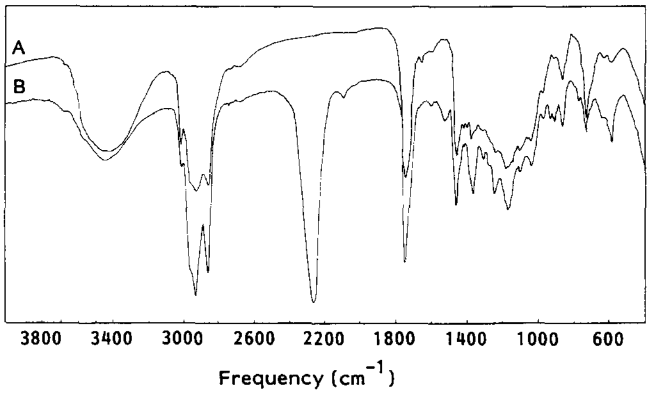

Figure 1 I.r. spectra of:, A, castor oil; B, prepolyurethane from castor oil and isophorone diisocyanate

ethyl methacrylate, EGDM (1% based on EMA), 1,3-propanediamine (1% based on PU) and benzoyl peroxide (0.5%) was added. The mixture was stirred at room temperature for 5 min to form a homogeneous mixture. The temperature was then raised to 60°C to initiate ethyl methacrylate polymerization along with the added crosslinker. After stirring for 1 h, the solution was poured into a glass mould 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 mould. A series of IPNs (IPN-1 to IPN-9) of different compositions were obtained following the above procedure (*Table 1*).

The homopolymer component networks of polyurethane and poly(ethyl methacrylate) were prepared under identical conditions to compare the properties of PU/PEMA IPNs.

Characterization

Dynamic mechanical properties were measured with a Dynamic Mechanical Thermal Analyser DMTA Mark II (Polymer Laboratories, UK) equipped with a Hewlett–Packard 200 series computer. The thermal stability was measured with a Du Pont 951 thermal analyser at a heating rate of 10°C min^{-1}. Scanning electron micrographs were obtained from a Phillips EM-400 equipped with scanning (transmission) electron microscope system PW 6585, the scanning attachment. The film was cryogenically fractured in liquid nitrogen and was mounted vertically on a SEM stub by silver adhesive paste. The specimen was coated with gold using an EPS/Carl Zeiss vacuum system at about 10^{-5} torr. Dielectric properties were measured with a 1620 A capacitance measuring assembly (Gen Rad, USA), and electrical conductivity was measured with a Hewlett–Packard 4329, a high-resistance meter with temperature-contolled furnace using a chrome–alumel thermocouple.

RESULTS AND DISCUSSION

The hydroxyl group of the castor oil was reacted with isophorone diisocyanate with different stoichiometric NCO/OH ratios. The resulting prepolyurethane was a thick liquid. It is clear from i.r. spectra that the prepolymer showed the characteristic polyurethane group frequencies. In addition to these, a strong band easily discernible at 2260 cm^{-1} may be assigned to isocyanate groups; in fact these polyurethanes are isocyanate-terminated polymers (*Figure 1*). A distinct but broad band was observed around 1750–1730 cm^{-1}, which may be assigned to carbonyl groups: $\nu_{C=O}$ ester at 1746 cm^{-1} and $\nu_{C=O}$ urethane at 1734 cm^{-1}. Freshly prepared samples of these polyurethanes were soluble in organic solvents like acetone, dioxane, toluene and dimethylformamide, but upon standing at room temperature they continued to crosslink, resulting in a product that was insoluble in common organic solvents. Thus, the polyurethanes were used immediately for interpenetration with ethyl methacrylate. The PU/PEMA interpenetrating polymer networks (IPNs) obtained were tough films and insoluble in all common organic solvents.

Resistance to chemical reagents

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

Thermal behaviour

The thermal behaviour of IPNs (*Table 2*) indicated that these IPNs possessed greater thermal stability than their component networks[15–18]. The probable explanation was provided[17,18] by the hypothesis that the unzipped EMA monomer produced during thermal degradation may act as a free-radical scavenger for PU degradation products, and thus the degree of intermixing of PU and PEMA networks may play an important role in the enhancement of thermal stability.

Dynamic mechanical behaviour and morphology

The dynamic mechanical behaviour of these IPNs, shown in *Figures 2–4*, presents evidence of substantial compatibility. The loss tangent (tan δ) vs. temperature dispersion (*Figure 2*) shows that the transition of IPNs is only marginally lower that the glass transition of the

Table 2 Thermogravimetric data of IPNs at a heating rate of 10°C min^{-1} in air

Sample code	Percentage weight loss (±2%) at various temperatures (°C)					
	250	300	350	400	450	500
IPN-1	–	7	21	43	74	97
IPN-2	–	5	20	46	77	98
IPN-3	–	7	22	47	75	99
IPN-4	–	9	23	56	81	97
IPN-5	–	12	30	50	83	98
IPN-6	–	10	28	48	85	97
IPN-7	–	12	24	50	81	99
IPN-8	–	10	23	51	82	97
IPN-9	–	11	26	48	80	96
PU (castor oil) +IPDI) (NCO/OH = 1.0)	11	52	88	94	–	–
PEMA	13	40	80	98	–	–

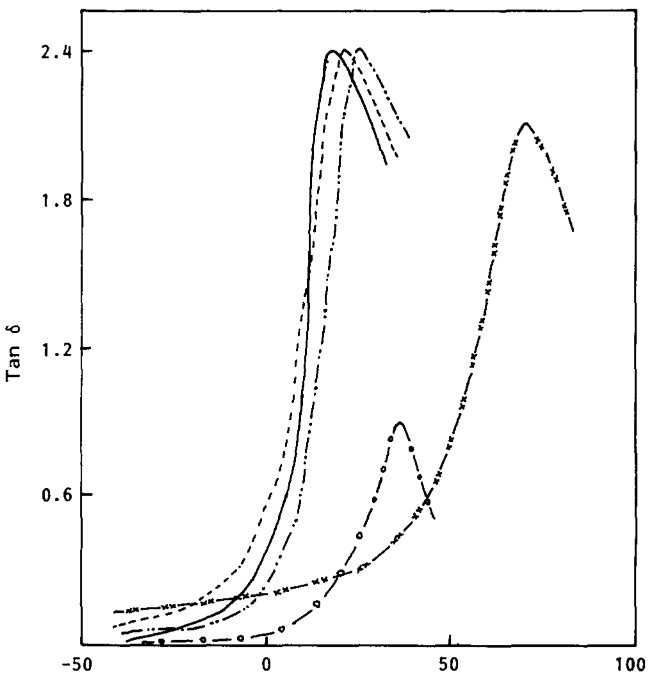

Figure 2 Loss tangent (tan δ) vs. temperature plots for IPNs and homopolymers: IPN-1 (——); IPN-4 (----); IPN-7 (—··—··—); PU (NCO/OH = 1.0) (—o—o—o—); PEMA (—× ×—× ×—)

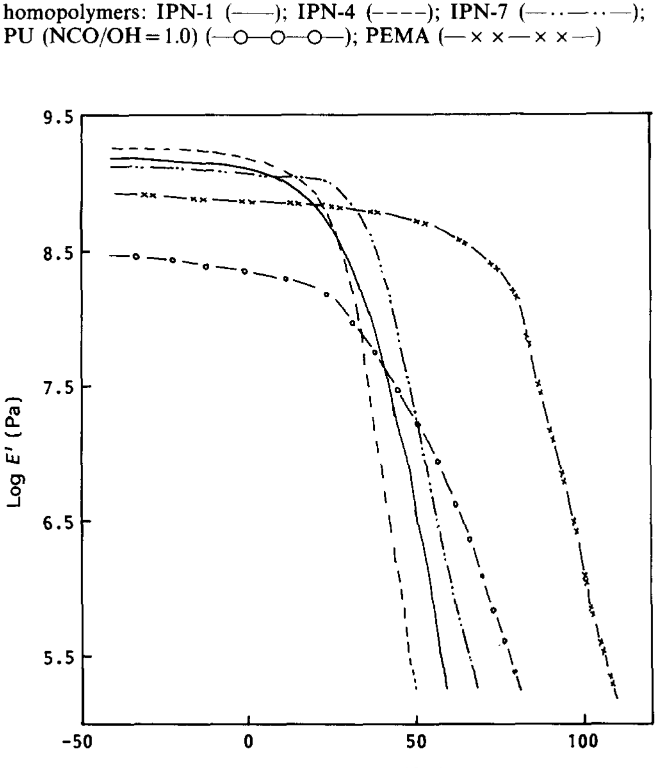

Figure 3 Dynamic storage moduli (ε′) vs. temperature plots for IPNs and homopolymers: IPN-1 (——); IPN-4 (----); IPN-7 (—··—··—); PU (NCO/OH = 1.0) (—o—o—o—); PEMA (—× ×—× ×—)

PU obtained at NCO/OH ratio 1.0 and much lower than the glass transition of PEMA. It is worth mentioning here that the polyurethanes with NCO/OH ratio 2.0, 2.2 and 2.4 respectively were prepared under identical conditions. The loss tangent dispersion of these PUs indicated that the glass transition temperatures were below −20°C. *Figures 3* and *4* show dynamic storage moduli (ε′) and dynamic loss moduli (ε″) vs. temperature of the IPNs. They show only one quite sharp transition region in the storage modulus spectra at a somewhat lower temperature than the glass transition temperature of the component network PEMA.

From the d.m.t.a. data, it appears that there is an appreciable mixing of PU and PEMA networks. Scanning electron micrographs show that there are two distinct phase domains due to phase separation of the two-component networks. The PU network is formed first and interpenetrated by the PEMA component during IPN synthesis[7,19–22]. PU is a continuous phase in which the second component, PEMA, is entangled (*Figure 5*).

Dielectric properties

A survey of the literature reveals that there are relatively few reports about the dielectric behaviour of IPNs[23–26]. 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 homopolymers, namely polyurethane and poly(ethyl methacrylate), are presented in *Table 3*. It is found that the intrinsic electrical conductivity of IPNs ranged from 1.0×10^{-9} to $2.08\times10^{-10}\,\mathrm{ohm^{-1}\,cm^{-1}}$ while their individual homopolymer networks have values of 1.12×10^{-11} (PU) and $3.9\times10^{-16}\,\mathrm{ohm^{-1}\,cm^{-1}}$ (PEMA). It is evident from these observations that IPNs behave like poor semiconductors as compared with the insulating behaviour of their individual homopolymers. The other IPNs in the present study were analysed 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-1, IPN-4 and IPN-7 are shown in *Figures 6–8*. Dielectric loss (ε″) does not change with temperature, which implies that the IPNs do not undergo energy attenuation when placed in an electric field. Dielectric constant (ε′) is a property of insulation, and 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 the IPN. At high temperature, the dielectric constant reaches a plateau and then gradually decreases with increasing temperature. Dielectric constant

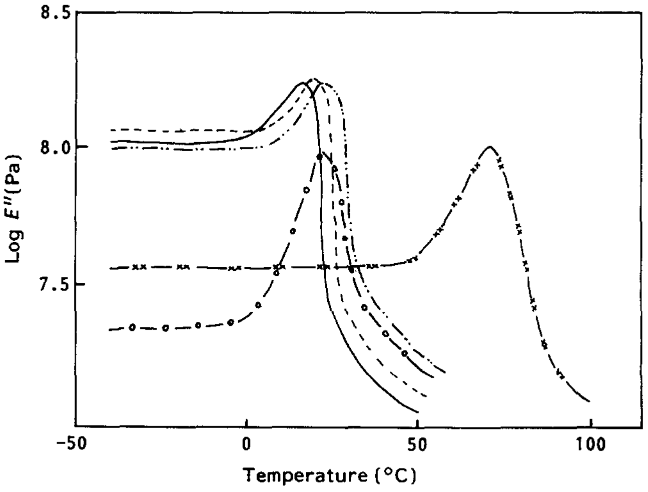

Figure 4 Dynamic loss moduli (ε″) vs. temperature plots for IPNs and homopolymers: IPN-1 (——); IPN-4 (----); IPN-7 (—··—··—); PU (NCO/OH = 1.0) (—o—o—o—); PEMA (—× ×—× ×—)

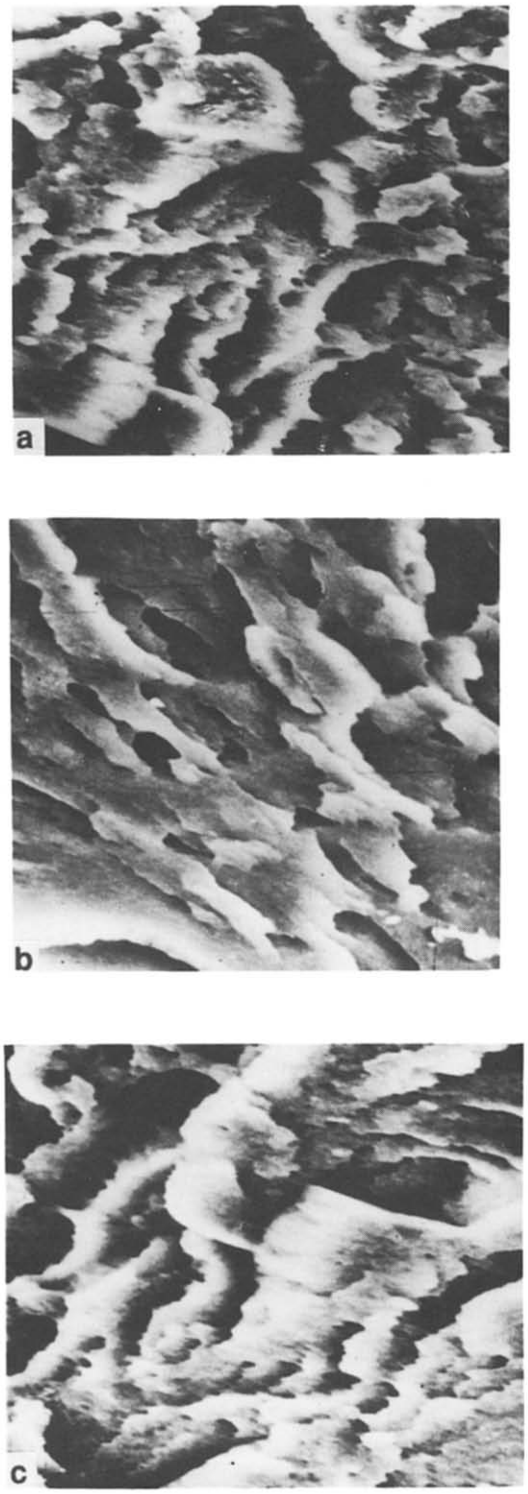

Figure 5 Scanning electron micrographs with magnification 12 000 × : IPN-1 (a); IPN-4 (b); IPN-7 (c)

(ε′) shows a decrease (dip) at some temperature range around 70°C and later it increases. The gradual decrease comes from a decrease in the orientation of the dipoles as the kinetic motion of the molecule opposes the orienting effect of the dielectric field, and from the decrease in density. Similarly, loss tangent (tan δ) would also exhibit similar behaviour as it is related to dielectric constant, $\varepsilon'' = \varepsilon' \tan\delta$. From these dielectric properties it may be concluded that these IPNs behave as semiconductors[23–26].

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 modifications of the thermal, mechanical and electrical properties as compared to their individual components.

Table 3 Electrical properties of PU/PEMA IPNs

Sample code	Electrical conductivity at room temperature, σ (ohm^{-1} cm^{-1})	Intrinsic electrical conductivity, σ_0 (ohm^{-1} cm^{-1})	Activation energy, *E* (kJ mol^{-1})
IPN-1	5.01×10^{-13}	1.78×10^{-10}	57.47
IPN-4	1.26×10^{-13}	2.08×10^{-10}	61.95
IPN-7	6.31×10^{-13}	1.0×10^{-9}	56.55
PU (NCO/OH = 1.0)	3.16×10^{-12}	1.12×10^{-11}	19.16
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

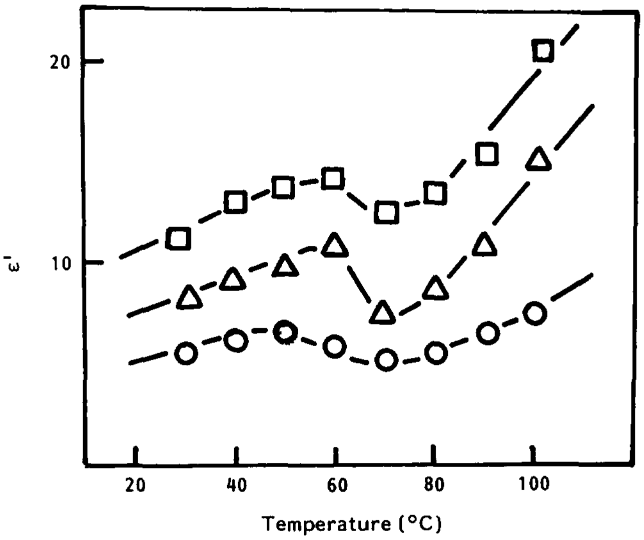

Figure 6 Dielectric constant (ε′) vs. temperature plots for: IPN-1 (○); IPN-4 (△); IPN-7 (□)

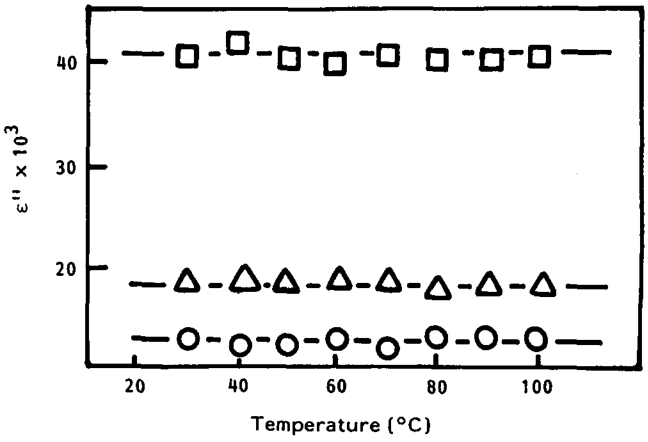

Figure 7 Dielectric loss (ε″) vs. temperature plots for: IPN-1 (○); IPN-4 (△); IPN-7 (□)

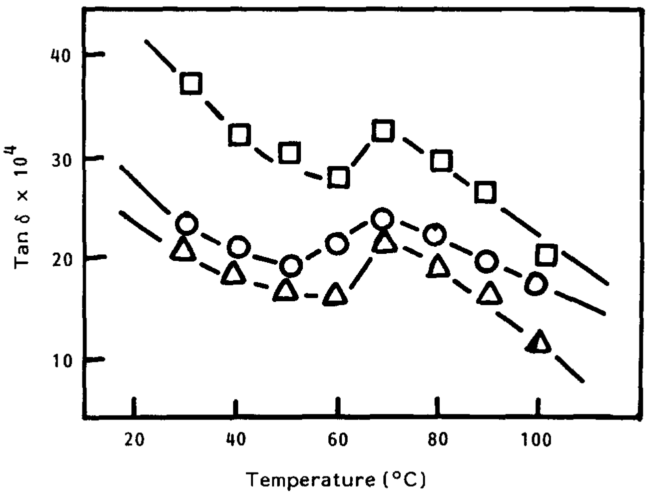

Figure 8 Loss tangent (tan δ) vs. temperature plots for: IPN-1 (○); IPN-4 (△); IPN-7 (□)

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