Novel Dielectrics from IPNs Derived from Castor Oil Based Polyurethanes

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SYNOPSIS

Three series of interpenetrating polymer networks (IPNs) based on a polyurethane (castor oil + toluene diisocyanate) with polystyrene, poly(methyl methacrylate), and poly(n-butyl methacrylate) were synthesized and characterized. Dielectric relaxation studies of these IPNs were carried out from −150 to 100°C in the 100 Hz to 100 kHz range. The effects of structural variables such as composition, type of vinyl monomer, as well as the effect of interaction of the phases on the dielectric properties were studied. A certain degree of phase mixing was observed to exist in all series as detected by the variation of the glass-transition temperatures of the IPNs. Maxwell–Wagner–Sillars polarization at the interface of the two phases was observed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Interpenetrating polymer networks (IPNs) are blends of cross-linked polymers that are unique in properties among the polymer alloys; they can display a more or less synergistic behavior depending upon the level of mixing of the component networks.[1,2] IPNs synthesized to date exhibit varying degrees of phase separation, dependent principally on the miscibility of the polymers. With highly immiscible polymers, the thermodynamic forces leading to phase separation are so powerful that it occurs substantially before the kinetic ramifications can prevent it. In these cases, only small gains in phase mixing occur. In cases where the polymers are more miscible, phase separation can be almost completely circumvented. Complete miscibility is not necessary to achieve complete phase mixing because the permanent entanglements can effectively minimize phase separation. With intermediate situations of miscibility, intermediate and complex phase behavior results. Thus, IPNs with completely distinct phase separation of the two networks are not clearly

observable because of the extreme variation in the intermolecular potentials in local regions caused by the topological entanglements of the two networks. Nevertheless, the IPNs can serve as a model for observing localized motions of chain segments within a matrix formed by the component networks possessing different glass-transition temperatures (T_gs). Several investigators have undertaken IPN studies employing various techniques to establish structure–property relationships: to name a few, the gelation technique was employed in a study of the reaction kinetics of simultaneous epoxy/poly(n-butyl acrylate) IPNs by Tousaent et al.[3] and polyurethane (PU)/acrylic copolymer IPNs by Klempner et al.[4] Density behavior, dynamic mechanical analysis, and scanning electron microscopy (SEM) were employed to observe the degree of phase mixing (interpenetration).[3,4] Meyer and coworkers[5-7] studied the kinetics and phase morphology of the PU/poly(methyl methacrylate) (PMMA) IPN systems in detail by the mechanical damping behavior. Optical laser diffractometry studies showed that phase separation follows the spinodal decomposition mechanism during IPN formation.[8] Differential scanning calorimetry (DSC) was used in a number of IPN studies to study the kinetics, energetics, thermal behavior, and glass transition. More recent

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Table I   Designation and Composition of IPNs

N1 series (PU/PS)							
Designation	N01	N11	N12	N13	N14	N15	N10
Composition, PU/PS	0/100	20/80	40/60	60/40	80/20	90/10	100/0
N2 series (PU/PMMA)							
Designation	N02	N21	N22	N23	N24	N25	N10
Composition, PU/PMMA	0/100	20/80	40/60	60/40	80/20	90/10	100/0
N3 Series (PU/PnBMA)							
Designation	N03	N31	N32	N33	N34	N35	N10
Composition, PU/PnBMA	0/100	20/80	40/60	60/40	80/20	90/10	100/0

Polyurethane is a common component in all series. N10 is a homopolymer; polyurethane (100%).

techniques, including small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) have provided additional information on the structural features of IPN.[9,10] Sound and vibration damping of IPNs has attracted the attention of several investigators.[11,12] The electrical behavior of IPNs can provide revealing information on the phase morphology and structure–properties relationship. Meyer and coworkers[13,14] studied the electrical behavior by the thermally stimulated depolarization technique. Mai and Johari[15] studied dielectric relaxation processes and aging effects in PU/PMMA IPNs. Two relaxation processes, α and β, were observed in the PMMA component network and a third process, γ, in the 10% PU/PMMA IPN. However at higher concentrations of PU, the γ process was removed from the temperature-frequency range.[15] Petrovic et al.[16-19] studied in detail the di-
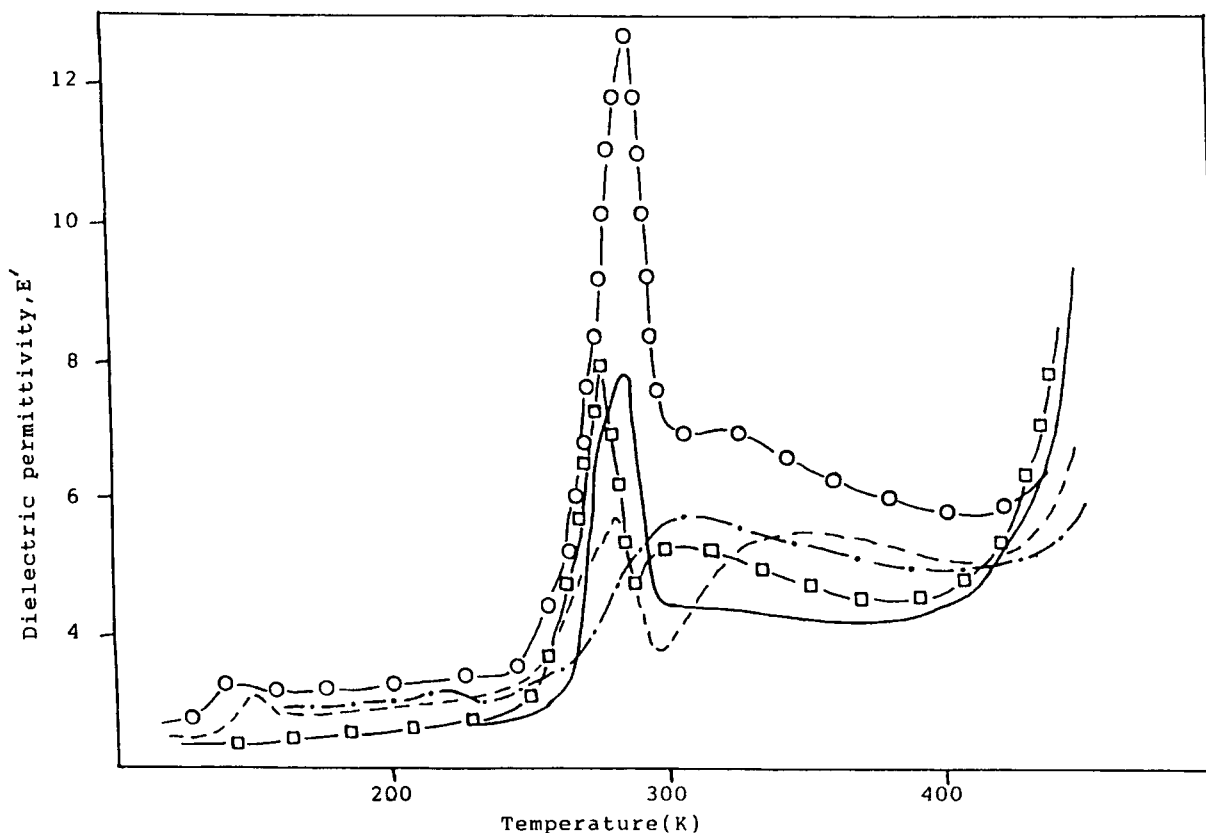

Figure 1   Dielectric permittivity, (E') vs. temperature for the N1 Series (PU/PS IPNs) at 100 Hz. (—) N11; (- - -) N12; (·····) N13; (– – –) N14; (- O - O -) N15.
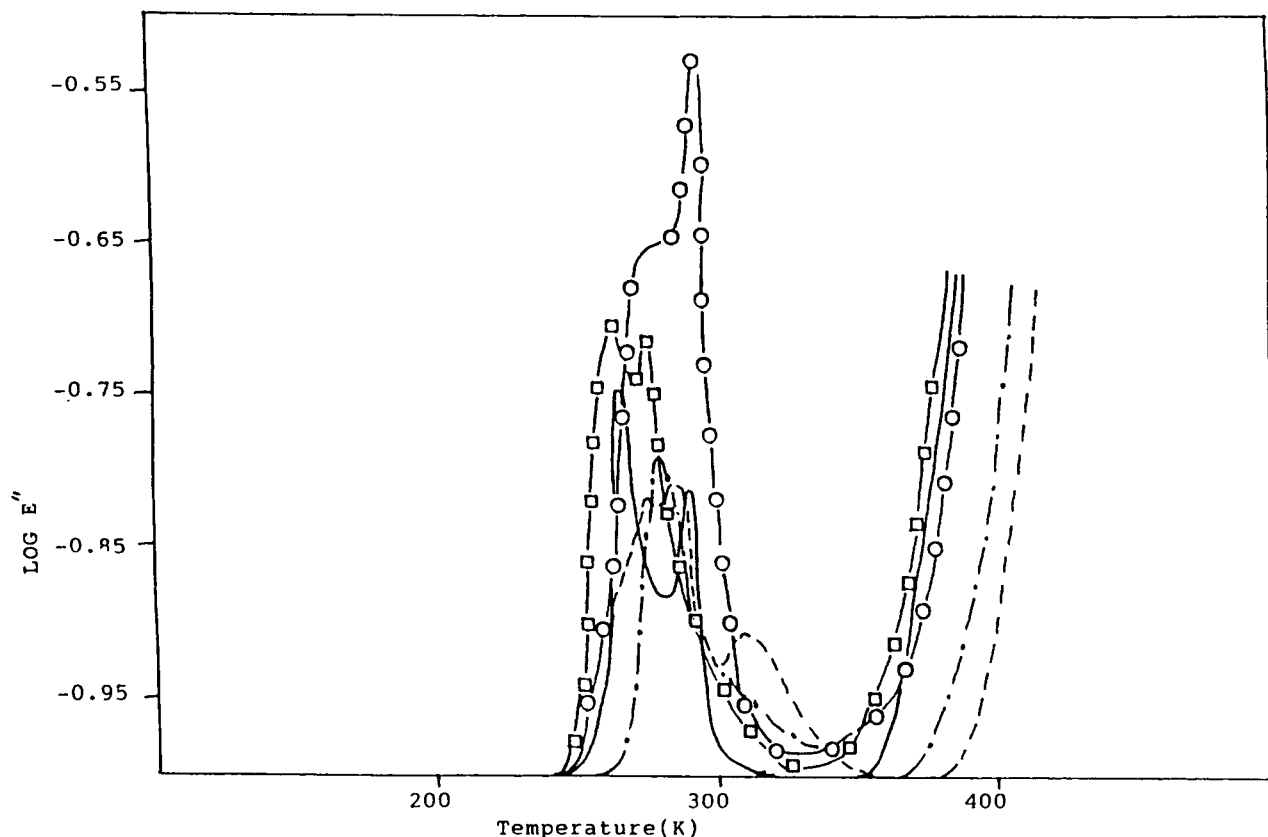
Figure 2 Dissipation factor, (E'') vs. temperature for the N1 Series (PU/PS IPNs) at 100 Hz. (—) N11; (- - -) N12; (· · · · ·) N13; (— — —) N14; (- O - O -) N15.

electric behavior of segmented PUs and observed that a certain degree of phase mixing existed; it appears that an interfacial polarization concerned with a two-phase structure exists. The experimental results were explained by the Maxwell-Wagner-Sillars (MWS) dielectric theory.[16-19]

In this study, we investigated the dielectric behavior of three series of interpenetrating polymer networks from castor oil based PU and polystyrene (PS), PMMA and poly(n-butyl methacrylate) (PnBMA). The effect of chemical structure and compositional variation of the PU were studied in terms of dielectric behavior and the structure–property relationship was developed.

EXPERIMENTAL

The preparation of the IPNs based on PU prepared from castor oil and toluene diisocyanate and PS, PMMA, and PnBMA has been described elsewhere.[20-22] The designation and composition of IPNs and homopolymers are given in Table I.

Samples for dielectric analysis were transfer-molded films formed at 120°C and dried under vacuum at 25°C prior to dielectric measurements. Test specimens were circular discs (d = 55 mm) ∼ 1 mm in thickness. The dielectric relaxation measurements were carried out with an Audrey dielectric wide frequency spectrometer (Tetrahedron, San Diego, CA) in the temperature range from −150 to +100°C and frequency range from 100 Hz to 100 kHz. The general procedure included cooling of samples to −150°C followed by heating at a programmed rate of 2°C/min while recording the dielectric properties.

RESULTS AND DISCUSSION

The present investigation on the dielectric properties of IPNs includes analysis of the effect of chemical structure and composition on phase separation of the component networks as determined by features of the dielectric permittivity, E', dissipation factor, E'', and loss tangent, tan δ vs. temperature
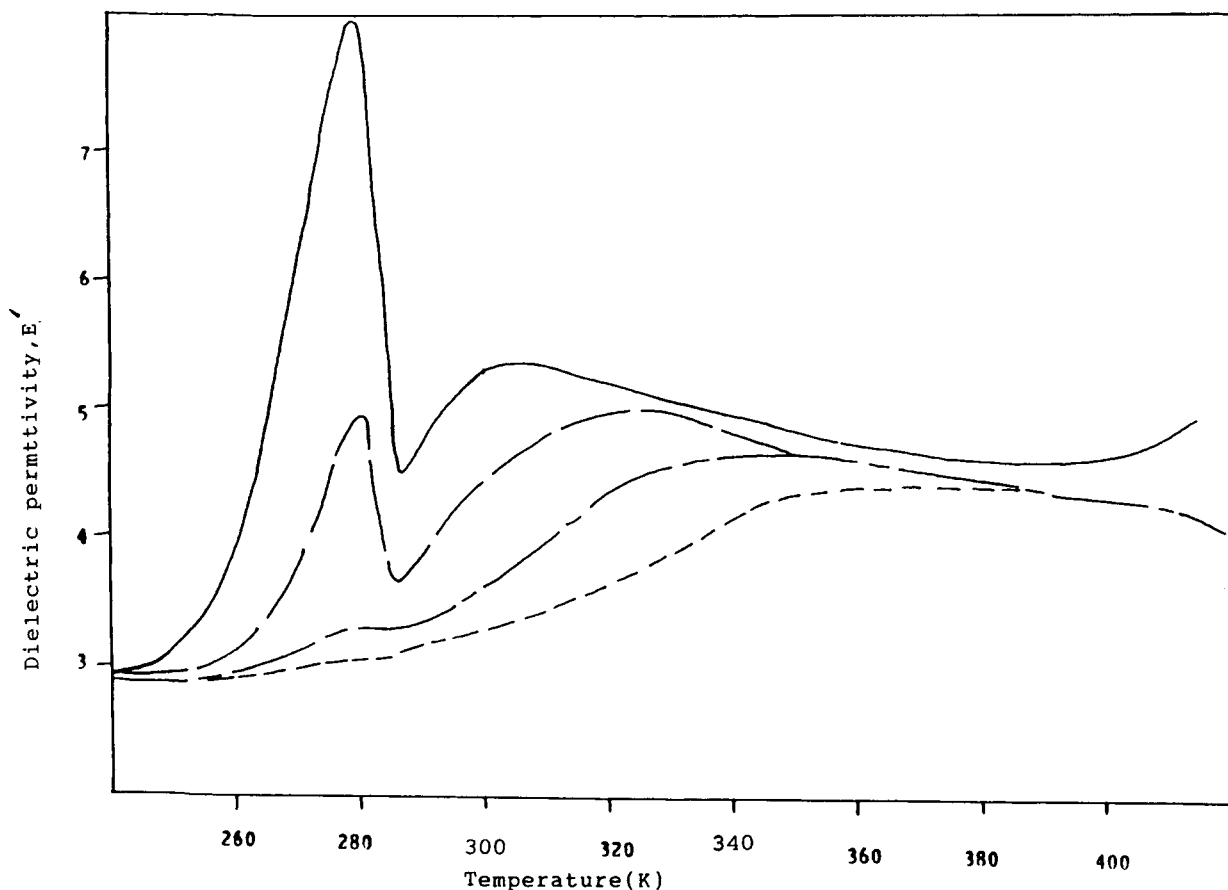
Figure 3 Dielectric permittivity, (E') vs. temperature for the N14 PU/PS IPN at different frequencies. (—) 100 Hz; (- - -) 1 kHz; (- · - · · -) 10 kHz; (– – –) 100 kHz.

curves. These IPNs all possessed two T_gs as measured by dynamic mechanical spectroscopy, around room temperature; it appears that there is appreciable phase separation of the castor oil based PU with PS, PMMA, and PnBMA similar to earlier studies on caprolactone based PU IPNs with PS and PMMA[23,24] in which two distinct T_gs occurred with large domains clearly visible under electron microscopy. SEM of the castor oil based IPNs showed that there were distinct but fine phase domains of vinyl polymer dispersed in a continuous PU network (forms first). This is also the observation made by other workers.[1,2,25]

Effect of Structure on E' and E'' at 100 Hz

The dielectric relaxation curves (E' and E'' vs. T) for the selected IPN series are shown in Figures 1 and 2 (E' and E'' at constant frequency; see Table I for the sample designations and description).

Figure 1 shows the change of dielectric permittivity, E', with temperature at 100 Hz for the N1

series of PU/PS IPNs. The figure shows the existence of only one transition at about 17°C. The magnitude of the transition is large when one of the components is in excess, but it is low in the case of approximately equal concentration of the components and does not even exist with the N13 IPN. It is interesting to note that the T_g of the PS network, expected well above 27°C, is observed with the sample containing 80% PS at about 115–120°C at 100-Hz frequency.

The dielectric relaxation curves (E' and E'' vs. T) at 100 Hz for PU/PMMA IPNs of the N2 series show that the transition region is from −23 to +27°C for the N21 and N22 series. The peak occurring in the transition region is the highest for the 60/40 PU/PMMA IPN. The value of permittivity E in the glassy state is 2.5, increasing to 14.5 in the rubbery region.

The dielectric relaxation curves (E' and E'' vs. T) at 100 Hz for PU/PnBMA IPNs of the N3 series show that transition region is about the same in the other two series, indicating that it is dominated by
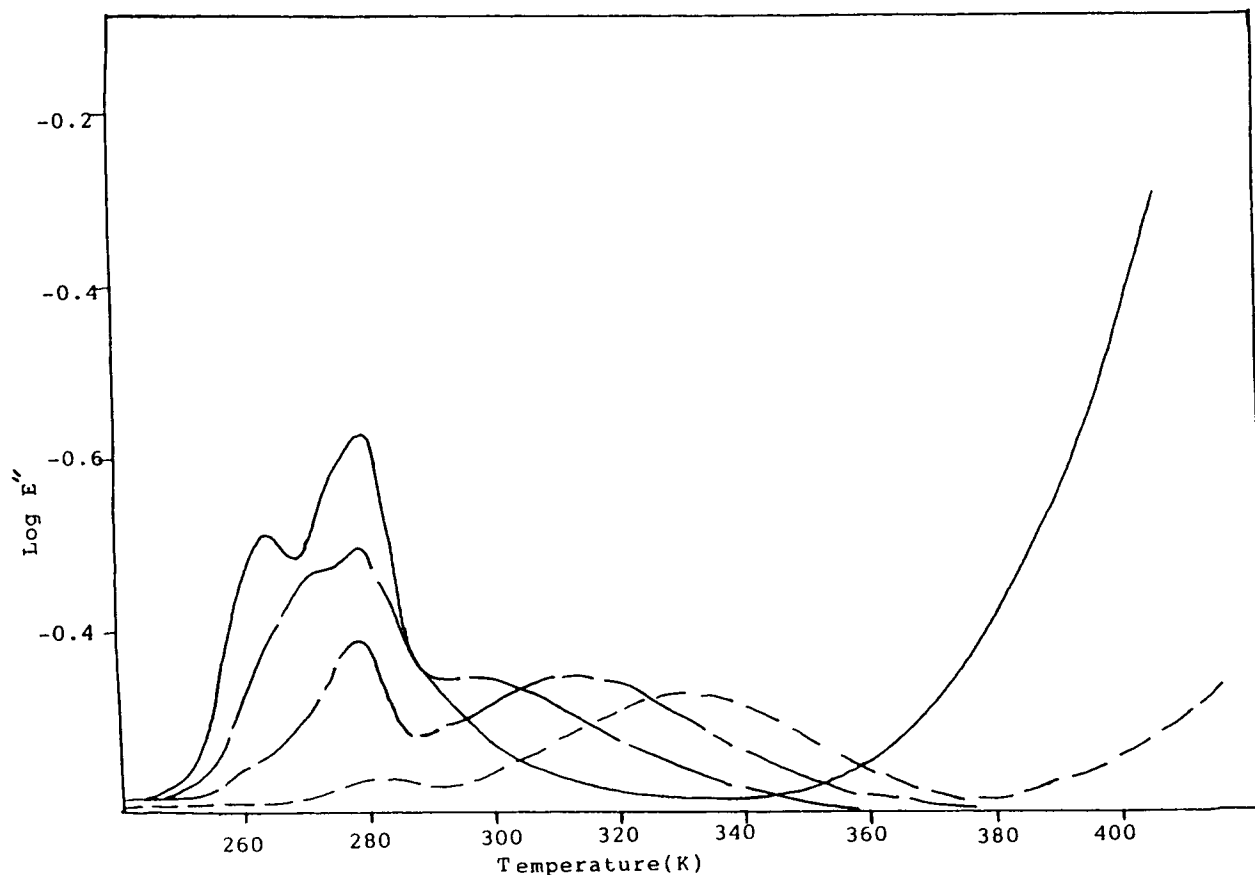
Figure 4   Dissipation factor, (E'') vs. temperature for the N14 PU/PS IPN at different frequencies. (—) 100 Hz; (---) 1 kHz; (-----) 10 kHz; (— — —) 100 kHz.

the rubbery PU continuous phase. The peak found in the middle of the transition appeared to increase the shift toward higher temperatures with the increase of the PU content in the IPNs.

The effect of chemical composition on the dissipation factor E'' in these series of IPNs has been studied at 100 Hz. Figure 2 shows the change of E'' with temperature for the PU/PS IPNs (N1 series). The two peaks occurring at about 3 and 17°C correspond to the existence of at least two relaxation processes in this temperature region. The peak at the higher temperature seems to increase in size with an increase of the PU content in the IPN. With the PU/PMMA IPNs and PU/PnBMA IPNs of (N2 and N3 series, respectively) a single of E'' peak is observed in the main transition region. The peak size, however, in these series does not vary regularly with composition. Asymmetry of the peaks reveals the existence of more than one relaxation process. The existence of two distinct peaks with the N1 series (PU/PS IPNs) indicates a lower degree of mixing of the PU with PS as compared to that of PU

with the other two components, PMMA and PnBMA. The glass transitions of PS, PMMA, and PnBMA, expected above 100°C, coincides with increasing conduction as observed in terms of continuous increase of E', E'', and tan δ rather than yielding clear sharp peaks as in the case of the neat polymers.

Effect of Frequency on E', E'', and Tan δ

The dependencies of E', E'', and tan δ on temperature as a function of frequency and composition were studied. Some of the selected figures show the effect of frequency on permittivity, E', of the three series of IPNs (Figs. 3, 4). The common feature of all dielectric relaxation curves is the existence of the glass transition region between −23 and +27°C, suggesting rubbery behavior of IPNs above room temperature. At low frequencies (100 Hz and 1 kHz) a peak in the middle of the transition region (at 2°C) is observed for N14 of PU/PS IPNs in the N1 series. At higher frequencies, the peak decreases in size or even disappears. The size of the peak decreases with
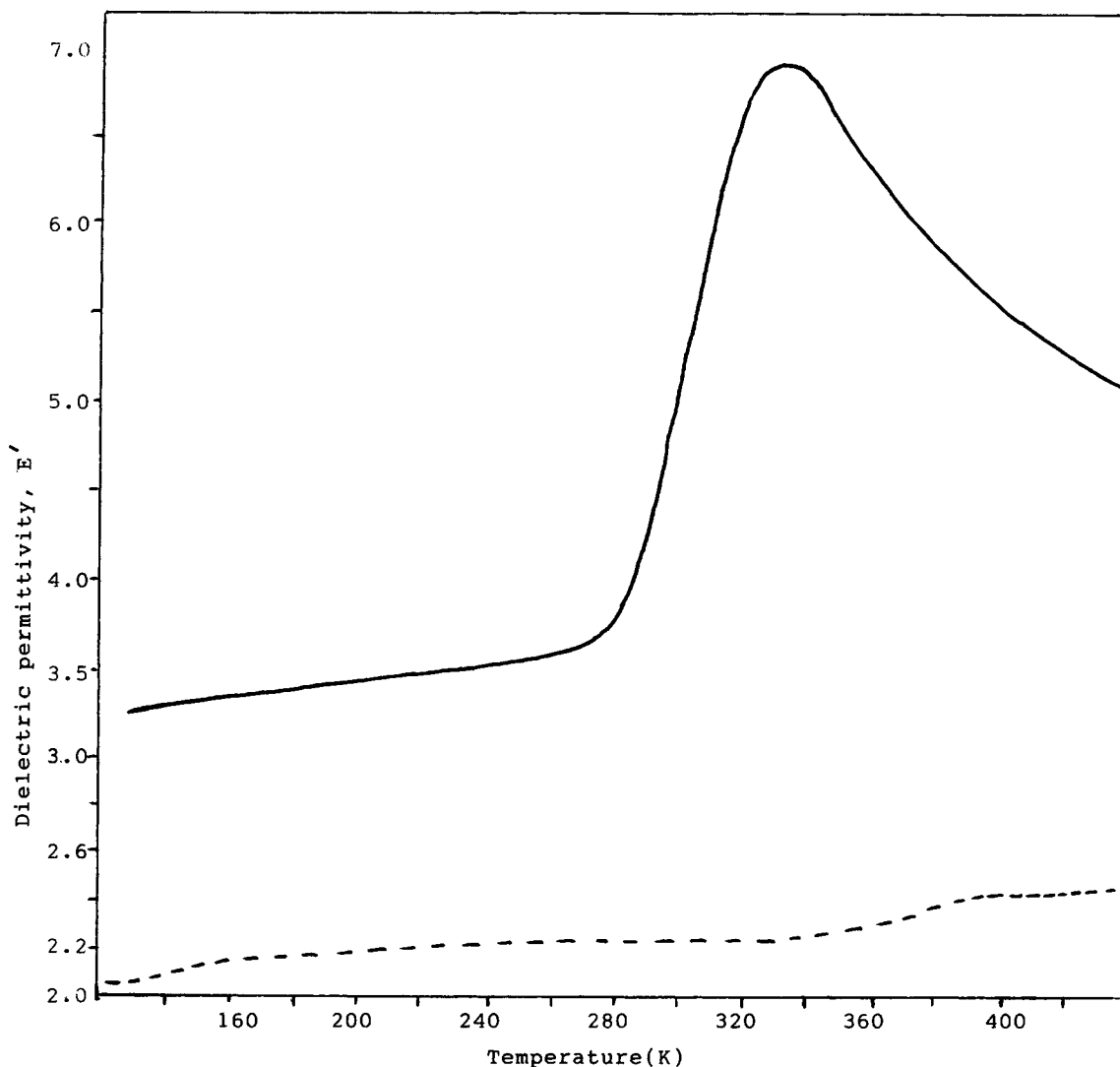
Figure 5 Dielectric permittivity, (E') vs. temperature for the controls (homopolymers) at 100 Hz; (– – –) polystyrene (100%); (—) polyurethane (100%).

a decrease of the PS content up to 40% PS, but a further decrease of PS causes a sharp rise of the peak again. Interpenetrating polymer networks of PU/PS are probably microseparated two-phased systems of a polar (PU) component in the nonpolar matrix of PS or vice a versa. Such conditions are suited for the appearance of the MWS polarization at the interface of two phases, causing the increase of permittivity.[26,27] Dielectric permittivity, E', is the result of several types of polarization, whose contributions are additives, namely induced polarization in the electric field and orientational polarization due to permanent dipoles in the polymer chain and side groups. At a higher temperature, the glass transition, major change takes place suddenly; the whole

segment-dipole can be oriented in the direction of the field. This orientational polarization is the whole contribution to E' which is usually dominant. In two-phased systems like IPNs, additional polarization at the phase interfaces arises due to the MWS mechanism. The frequency dependency of this peak also suggests such a possibility. For PU/PMMA IPNs in the N2 series, the glass transition was characterized by the jump from the low temperature value of $E' = 2.7$ to about 4.8 or 4.2 depending on the frequency. In this series, the peak in the middle of the transition region was observed with sample N23 and as a shoulder with N24. The absence of the peak in most of the samples seems to suggest better compatibility of PU with PMMA than PS, although
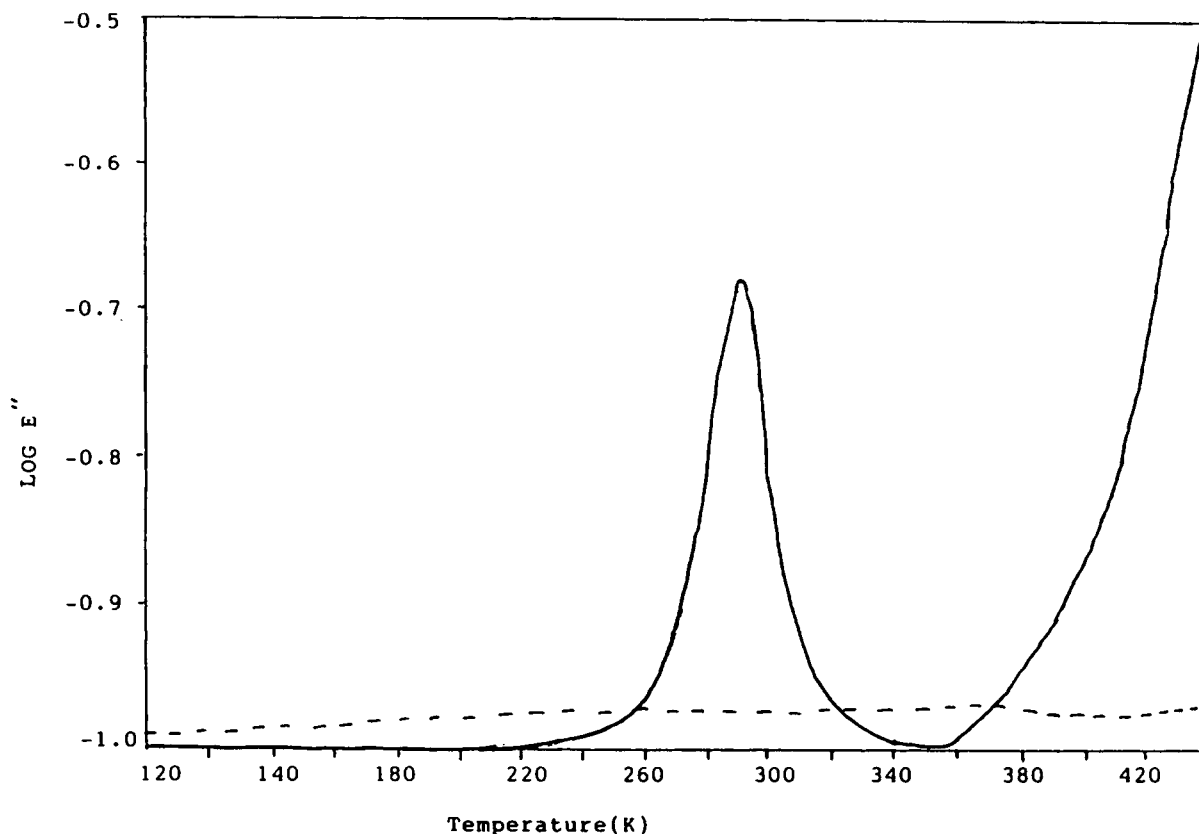
Figure 6 Dissipation factor, (E'') vs. temperature for the controls (homopolymers) at 100 Hz. (- - -) polystyrene (100%); (—) polyurethane (100%).

these systems are microphase separated. Only one peak was observed in PU/PnBMA IPNs at 100 Hz and 1 kHz. Alternatively, an additional E' peak probably explains the existence of some low molecular weight substances such as water.[28]

The effect of frequency on E'' and temperature is characterized by the existence of one or two maxima, depending on the frequency and composition of the IPNs in the series (Fig. 4). For PU/PS IPNs, usually two peaks, one at 4°C and the other at 90°C, are observed at 100 Hz. At higher frequencies, the peak at about −1 to +9°C becomes smaller, while a new one appears between 7 and 57°C. The position of the latter is strongly dependent on frequency, displaying a shift of about 10°C toward higher temperatures when the frequency is increased from 100 Hz to 100 kHz. For the N2 series PU/PMMA IPNs, a single peak at about 17°C or a shoulder at about 27°C of the main peak occurs between 47 and 67°C, when frequency is increased from 100 Hz to 100 kHz. By increasing the PU content, only one peak tends to be dominant. For PU/PnBMA IPNs of the N3 series, generally a single peak is observed on the E''

vs. the temperature curve. The size of the peaks decreases with increasing frequency. The dielectric relaxation curves $(E'$ and $E'')$ vs. temperatures for the homopolymers, PU, PS, PMMA, and PnBMA, are obtained for comparative study with the IPNs reported in the present study. The dielectric relaxation curves $(E'$ and $E'')$ for the selected homopolymers, PU and PS, are shown in Figures 5 and 6. Both of these spectra of homopolymers indicate broadening in glass transitions presumably due to several types of polarizations involved unlike dynamic mechanical spectra. Thus, the differences between dynamic mechanical and dielectric spectra arise due to an additional molecular mechanism, like the MWS mechanism, prevails. The activation energy of the transition process was measured from the shift of the E'' maxima with frequency. The values are presented in Table II. Variation of activation energy with composition of the IPNs seems to be at random within the series but the mean values for the series increase slightly going from series N1–N3 being 41.1 kJ/mol for PU/PS IPNs of the N1 series; 45.1 kJ/mol for PU/PMMA IPNs of the N2 series; and 48.5

Table II   Activation Energy of Glass Transition of IPNs

Sample	Activation Energy (kJ/mol)
N11	+111.2[a]
N12	+36.4
N13	+48.6
N14	+34.0
N15	+45.5
N21	+50.1
N22	+44.4
N23	+101.1[a]
N24	+38.4
N25	+47.5
N31	+43.8
N32	+51.2
N33	+52.8
N34	+43.6
N35	+51.0

[a] Correlation coefficient is less than 0.90.

kJ/mol for PU/PnBMA IPNs of the N3 series. The values are considerably lower than the values of activation energy, E_a (140 kJ/mol) for the α-process in poly(propylene oxide) based PU/PMMA IPNs, reported by Mai and Johari.[15]

CONCLUSIONS

In conclusion, dielectric relaxation studies showed that the IPNs prepared from castor oil based PU and PS, PMMA, and PnBMA, respectively, behave like homogeneous materials due to topological interpenetration (catenation) of the components during IPN formation. However, some microphase separation is observed in PU/PS IPNs, presumably because of the lower miscibility of the component networks.

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