Polymeric Thermoresistant Blends Based on Poly-SAN and Imidized PMMA: Thermal and Electrical Characterization

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SYNOPSIS

Blends of styrene/acrylonitrile copolymers (poly-SAN) with imidized PMMA exhibit increased thermoresistance in comparison with poly-SAN alone. The miscibility of two modified poly(methyl methacrylate) (PMMA) with poly-SAN has been evaluated with the aid of different techniques: isothermal calorimetry, through which mixing enthalpy and the Flory–Huggins χ parameter can be determined; dielectrical spectroscopy and thermally stimulated discharging currents (TSDC). The results obtained exhibit great consistency, thus supporting the usefulness of the applied methods for determining the mixing behavior of these polymer blends, which can be considered as model systems for thermoresistant ABS nowadays widely used in the automotive industry. Furthermore, the applied methods allow one to obtain useful data for the electrical application of the investigated blends. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymer blends have been studied extensively during the last decades both in industry and at universities. The cause of such an interest was the possibility to obtain new materials from existing polymers with "only" an extrusion step. Nowadays, the reality has been shown not to be so optimistic both for problems deriving from processing and incomplete knowledge of many aspects of polymers miscibility. Many techniques have been used to study polymer miscibility, especially, calorimetric and dynamic mechanical tests.

Many studies have been reported in the scientific literature on the miscibility of blends of styrene/acrylonitrile copolymers (poly-SAN) with other polymers, and of particular interest are those blends that exhibit increased thermal properties in comparison with those of poly-SAN alone. These blends can be considered as model systems for thermoresistant ABS nowadays employed in the automotive field. Polymers at least partially miscible with poly-

SAN, studied and developed to obtain these results, are poly(N-phenyl itaconimide-co-methyl methacrylate),[1] poly[styrene-co-(maleic anhydride)],[2] poly[styrene-co-(N-phenylmaleimide)],[2] and poly(methyl glutarimide-co-methyl methacrylate),[3] usually called imidized poly(methyl methacrylate) (PMMI).

DSC studies have already pointed out the immiscibility due to the presence of acid groups in PMMI blended with poly-SAN.[3] To compare the results obtained by differential scanning calorimetry, in the present study, we applied dielectric spectroscopy and thermally stimulated discharging currents (TSDC) to investigate miscibility. Moreover, isothermal calorimetry has been applied here to evaluate its consistency with other applied methods and its reliability in detecting the immiscibility of blends by mixing enthalpy measurements, which has never been applied before to immiscible systems.

THEORETICAL OVERVIEW

A direct and unambiguous determination of blend miscibility can be obtained by measuring the free energy of mixing (ΔG_{mix}). As is well known, a neg-

ative free-energy change is a necessary but not sufficient criterion of miscibility.[4]

Several schemes for the calculation of ΔG_{mix} have been proposed in recent years, but, in general, it may be written as the sum of a combinatorial and an interaction term.[5,6] The simplest expression for ΔG_{mix} is represented by the Flory–Huggins equation, which requires knowledge of the interaction parameter χ_{12}, as follows[7,8]:

$$\Delta G_{mix} = (RT_m)[(\phi_1/x_1)\ln \phi_1$$
$$+ (\phi_2/x_2)\ln \phi_2 + \phi_1\phi_2\chi_{12}] \quad (1)$$

where ϕ_1 and ϕ_2 are volume fraction of polymers 1 and 2 of degrees of polymerization x_1 and x_2, respectively, and m is the mass of a mole of mixture; eq. (1) predicts phase separation for nonzero (positive) values of χ_{12} when this outweighs the favorable combinatorial contribution to the free energy of mixing.[9] In general, this latter term is negligible for high molecular weight systems, and in these cases, small values of the enthalpy of mixing, obtained for a polymer–polymer mixture, are enough to cause incompatibility.

In this work, imidized poly(methyl methacrylate) (PMMI) (component 1)–poly-SAN (component 2) blends have been investigated by measuring the enthalpy of solutions ΔH_{mix}, related to the general expression for the free energy of mixing [eq. (1)]. In particular, for very diluted polymeric solutions, it is possible to obtain the pair interaction parameter χ_{12} directly from calorimetric data. The calorimetric measurements of the heats of solution of the 50 : 50 wt % blend and the pure polymers in a common solvent have been performed at a two different temperatures and the ΔH_{mix} has been obtained by the Hess law approach.[10-13]

The Hess law is given by the following expression:

$$\Delta H_{mix(1,2)} = a\Delta H_1^s + b\Delta H_2^s - (a + b)\Delta H_{blend}^s \quad (2)$$

where $a\Delta H_i^s$ is the heat of solution of a mole of the

Table I Binary Mixing Enthalpy and Flory–Huggins Interaction Parameters for the Poly-SAN/Paraloid EXL4150 (Blend A)

Temperature (°C)	$-\Delta H_{mix}$ (J/g)	χ_{12}
29.6	0.0158	0.0038
39.4	0.0157	0.0036

Table II Linear Correlation Coefficients and Related Slope for Data of Enthalpy of Mixing of Samples in MEK

| Samples | Linear Correlation Coefficients | | Slope | |
	29.6°C	39.4°C	29.6°C	39.4°C
SAN	0.9953	0.9702	0.325	0.320
EXL4150	0.9981	0.9838	0.360	0.323
Blend A	0.9807	0.9971	0.358	0.337

blend component i and $(a + b)\Delta H_{blend}^S$ is the heat of solution of a blend containing $(a + b)$ moles of components 1 and 2, respectively.[11-13] ΔH_{mix} is of relatively small magnitude in comparison with the terms on the right-hand side of eq. (2), so the availability of the method is limited by the precision attainable during the experimental procedure.[13,14]

This method has been applied to the PMMI/ poly-SAN blend in order to obtain the values of χ_{12} as a function of the experimental temperature T, using the following expressions[11,13]:

$$\chi_{12} = BV/RT \quad (3)$$

$$\Delta H_{mix} = (V_1 + V_2)B\phi_1\phi_2 \quad (4)$$

where $B = f(\Delta H_{mix})$ is a constant with respect to the temperature and V_i represents the molar volume of the polymeric unit.

Another powerful method to ascertain polymer miscibility consists of dielectric spectroscopy of the blends[6,15]: dielectric relaxation spectra of pure components can indeed be changed by molecular motion constraints due to the polymer mixing, thus supplying information on the miscibility behavior of the blend and specific molecular interactions; measurements can be performed either at constant frequency or temperature, and though less sensible than dynamic mechanical methods, this technique allows a wider range of frequencies to be investigated.

The thermally stimulated discharging current (TSDC) method provides another fast and versatile method based on the measurement of the relaxation of the polarized states on polymer electrects formed at high temperatures by a strong constant electric field, heating them at a constant rate after quenching at liquid nitrogen temperature.[16-18] Molecular motions give rise again to different relaxation spectra, related to the miscibility behavior of the system.
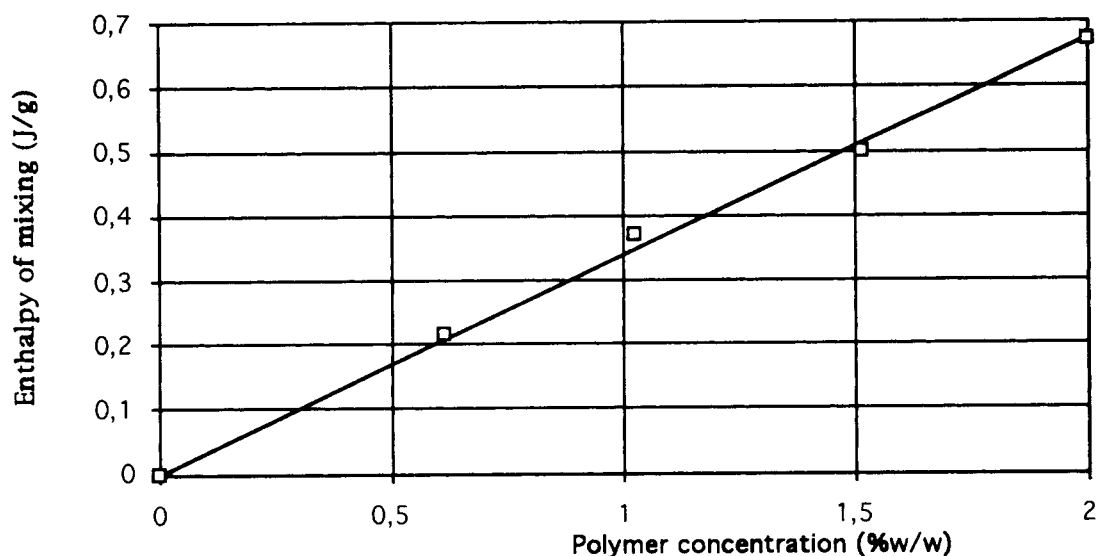
Figure 1 ($\square$) Mixing enthalpy of blend A in MEK at 39.4°C with regression curve (see Table II for regression parameters).

Although it is a rather efficient technique,[19] TSDC is not yet widely used in polymer blend routine analysis.

MATERIALS AND SAMPLES

The polymer systems used in this study are based on blends with poly(styrene-co-acrylonitrile) containing 24% w/w of acrylonitrile (SAN24) synthesized by suspension polymerization; its average weight molecular weight, M_w, determined by gel permeation chromatography (GPC), is 155,000 and the polydispersity M_w/M_n = 2.50. Imidized poly(methyl methacrylate)s (PMMI) Paraloid EXL4150 and EXL4241 were supplied by Rohm & Haas and their M_w's and polydispersity were determined respectively, by light scattering[20] and GPC. For EXL4150, M_w = 102,000 and M_w/M_n = 1.62, whereas for EXL 4241, M_w = 103,000 and M_w/M_n = 1.57. The two PMMI show comparable values of

imidization degree (76% mol EXL4150, 78% mol EXL4241), whereas EXL4150 is characterized by the presence of about 5% mol of acid groups that are completely absent in EXL4241.

Blends corresponding to the weight ratio 50 : 50 wt % were prepared by a Brabender mixer Plasti-Corder PL2000 at 220–230°C and 50 rpm. Blends are designated as Blend A (50% EXL4150) and Blend B (50% EXL4241).

Samples to be submitted to all electrical measurements were prepared as 0.3–0.8 mm-thick discs with a diameter of 30 mm, by hot pressing powdered materials at 250°C *in vacuo*. They were afterward coated with gold by evaporation *in vacuo* to provide a suitable three-terminal electrode configuration.

EXPERIMENTAL

The calorimetric measurements were performed on a Setaram C80 D heat flux calorimeter.[21] Reversal

Table III Physicochemical Data of Repeating Units: x = Polymerization Degree, m. wt. = Weight of the Repeating Unit

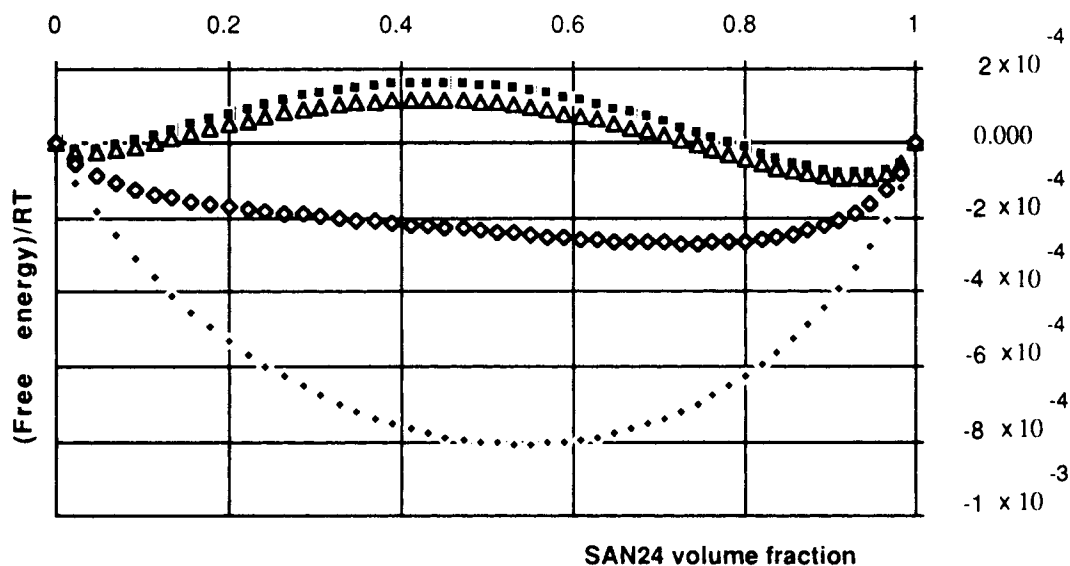| Samples	Density (g/mL)		Molar Volume (mL/mol)		m. wt.	x
	29.6°C	39.4°C	29.6°C	39.4°C		
SAN24	1.066	1.064	90.00	89.91	84.5	1200
EXL4150	1.190	1.180	179.69	178.18	151.0	695

Figure 2 Free energy of mixing of SAN24 (DP = 1200)/EXL4150 (DP = 695) (Blend A): (■) χ (29.6°C) = 0.0038; (△) χ (39.4°C) = 0.003; (◇) $\chi_{critical}$ = 0.0023; (◆) χ = 0.0000.

mixing cells, in stainless steel of 2.0 cm^3 with a pressure capacity of 20 bars, having two compartments separated by a PTFE membrane and provided with a rod whose bottom is threaded, were used. The rod is used to take a sharp-edged impeller that enables the membrane to be torn and, possibly, to agitate the two components.[13]

The glass transition temperatures, T_g, were measured using a Perkin-Elmer DSC-7; the samples were heated at a scanning rate of 20°C/min until a maximum temperature of 200°C, then cooled at 20°C/min until 40°C and reheated at 20°C/min in order to cancel the thermal history of the samples. Dielectrical measurements were performed in a dynamic vacuum (to eliminate any possible plasticizing effects of absorbed gases,[22] from room temperature to 175°C in the frequency range $10^{-2} \div 3 \times 10^5$ Hz; a three-terminal Schering Bridge technique was used according to ASTM D 150 by cell and instrumentation elsewhere described.[23-25]

TSDC measurements were carried out under vacuum using a three-terminal technique in the temperature range −120 to 175°C, with a constant heating rate of 5°C/min, via a PID regulator controlled by an on-line computer, with a system described elsewhere[25,26]; polarization was performed at 155°C under an electric field of 4 kV/cm for 2.5 h.

RESULTS AND DISCUSSION

Table I reports values of the Flory–Huggins interaction parameter χ_{12} reported together with the Hess

enthalpies from which they have been obtained [see eqs. (3) and (4)]. As far as the experimental enthalpies of solutions ΔH_1^s, ΔH_2^s, and ΔH_{blend}^S are concerned, the linear correlations calculated for 29.6 and 39.4°C are listed in Table II, with the corresponding slopes that enable calculation of the $\Delta H_{mix(1,2)}$ [see eq. (2)].

As one can see, the experimental data show a linear dependence of mixing enthalpy on concentrations up to 2% w/w, as appears for blend A as an example in Figure 1. This witnesses the power of the method, which, although requiring a very high accuracy and reproducibility of the experimental data for good reliability, at the same time gives a demonstration of the linear dependence of ΔH_i^s on concentration in the considered range.[13]

The measurements were performed at only two (and very close) temperatures because of the diffi-

Table IV Analysis of the $\Delta G_{mix}(T)$ Function for Blend A (Fig. 2)

	Φ_{SAN}	
	29.6°C	39.4°C
First minimum point	0.0255	0.0367
Second minimum point	0.9355	0.9356
Maximum point	0.4358	0.4333
First flexure point	0.1423	0.1533
Second flexure point	0.7750	0.7613
First zero setting point	0.0975	0.1088
Second zero setting point	0.7707	0.7377

Table V Glass Transition Temperature for the Measured Samples Obtained by DSC

Samples	T_g (°C)
SAN	104.9 ± 0.4
EXL4150	149.4 ± 1.3
EXL4241	146.7 ± 0.1
Blend A	109.3 ± 1.8
	147.5 ± 0.9
Blend B	121.8 ± 1.5

culty to make solutions under the solvent boiling point in order to avoid obnoxious interferences by detected heat fluxes. A suitable solvent must be chosen: The best one seemed to be methyl ethyl ketone (MEK), which allowed one to perform a complete solubilization of polymers and, consequently, to obtain very well shaped heat flux peaks. Table III summarizes the physicochemical data of the polymeric repeating unit used for the calculations of the $\Delta G/RT$ curves reported in Figure 2.

The $\Delta G/RT$ function is drawn vs. the poly-SAN volume fraction for blend A and its dependence on the binary interaction parameter χ_{12} is evident. This latter term can have different values for different temperatures, and if $\chi_{12} > \chi_{crit}$, the ΔG curve overcomes the zero-point line; this behavior is a direct consequence of the immiscibility status existing between the components of blend A. To make possible a comparison for different χ value curves, $\Delta G/RT$

corresponding to $\chi_{12} = 0$, which represents the athermal mixture situation, has also been drawn.

The meaningful points related to the free energy function, well represented in Table IV, make it possible to reproduce the boundary spinodal conditions for the considered SAN/PMMI; blend A. Measurements of blend B are still in progress[13]: however, the present work on blend A confirms the reliability of the calorimetric approach, already tested for some PMMA/poly-SAN blends,[13] whose miscibility at the same temperature conditions was observed.

A final confirmation of the immiscibility between poly-SAN (24% w/w) and EXL4150, at the normal conditions of temperature T and pressure P, can be found in Table V, which shows, for blend A, two distinct values of T_g, as well known in literature.[3] The immiscibility of the PMMI/poly-SAN system is principally ascribed to the presence of small quantities of acid groups.[3] The maximum amount of acid groups, which still allows miscibility, is about 1%. An esterification reaction during extrusion could, however, eliminate the majority of acid groups restoring miscibility.[27]

Figure 3 shows the loss factor of the measured poly-SAN: Both the α (related to the motion of large segments of the chain at the glass transition temperature) and β (corresponding to local molecular motions) peaks appear in this frequency range. The calculated activation energy for the α and β processes are 380 and 70 kJ/mol, respectively; both values are somewhat higher than those found in the literature,[28] which concern, however, lower T_g poly-SAN
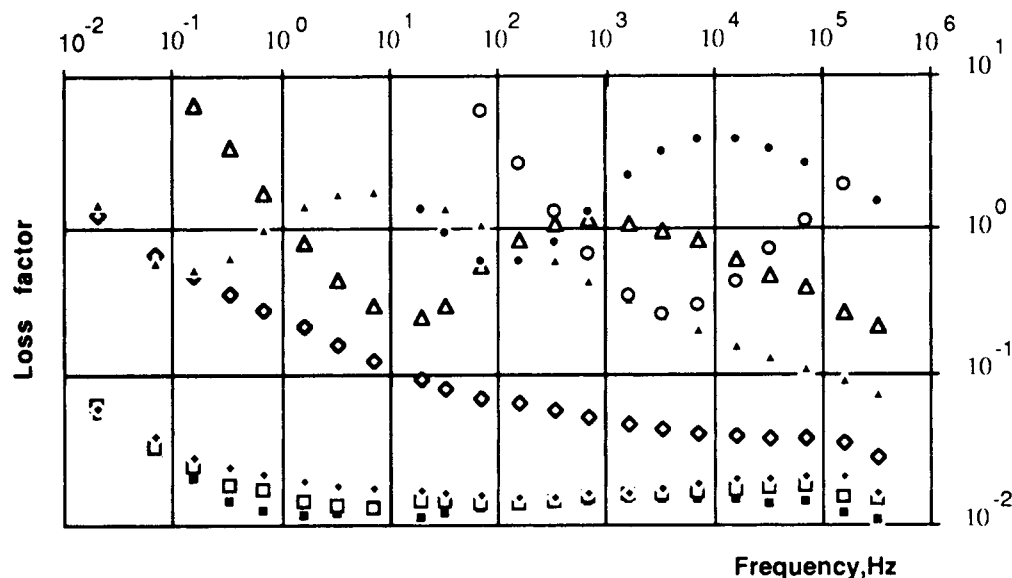

Frequency,Hz

Figure 3 Loss factor of poly-SAN as a function of frequency at different temperatures: (■) 25°C; (□) 55°C; (♦) 80°C; (◊) 105°C; (▲) 120°C; (△) 130°C; (●) 145°C; (○) 165°C.
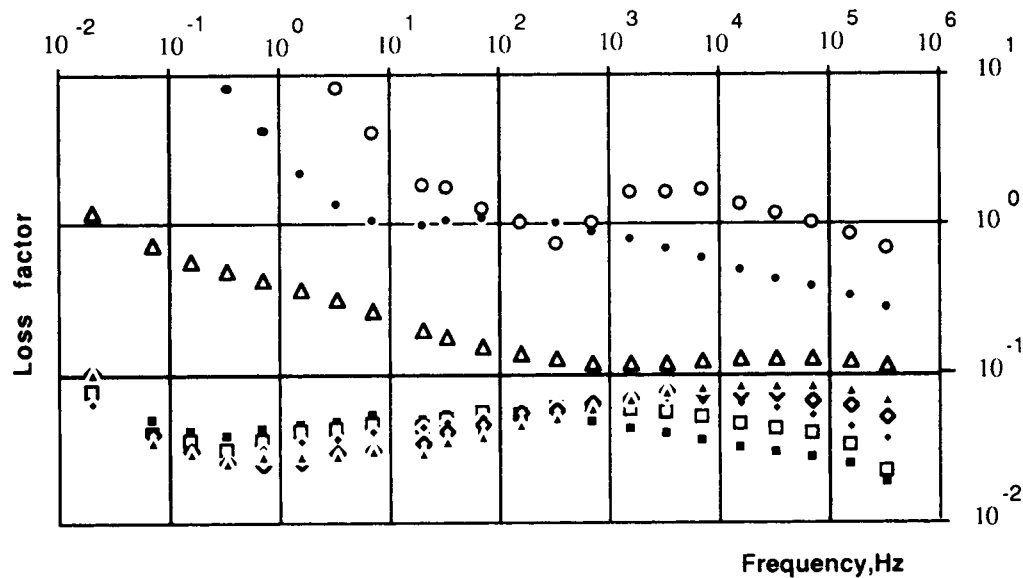
Figure 4 Loss factor of EXL4142 as a function of frequency at different temperatures: (■) 25°C; (□) 55°C; (♦) 80°C; (◊) 105°C; (▲) 120°C; (△) 145°C; (●) 165°C; (○) 175°C.

samples (95°C). A large increase of the loss factor occurs as frequency is lowered, particularly at temperatures higher than 80°C, probably related to the presence of ionic impurities in the material.

Figure 4 shows the loss factor of Paraloid EXL4241, whereas Figure 5, that of Paraloid EXL4150. In both polymers, α and β processes appear: the β process is less intense than in PMMA,

as a consequence of the reduced mobility of the imidized ester groups. The activation energy for the β process in both polymer is 67 for EXL4241 and 73 kJ/mol for the EXL4150, values close to that found for PMMA (76 kJ/mol); activation energies for the α process could not be determined because the above-mentioned strong absorption phenomena in the low-frequency range.
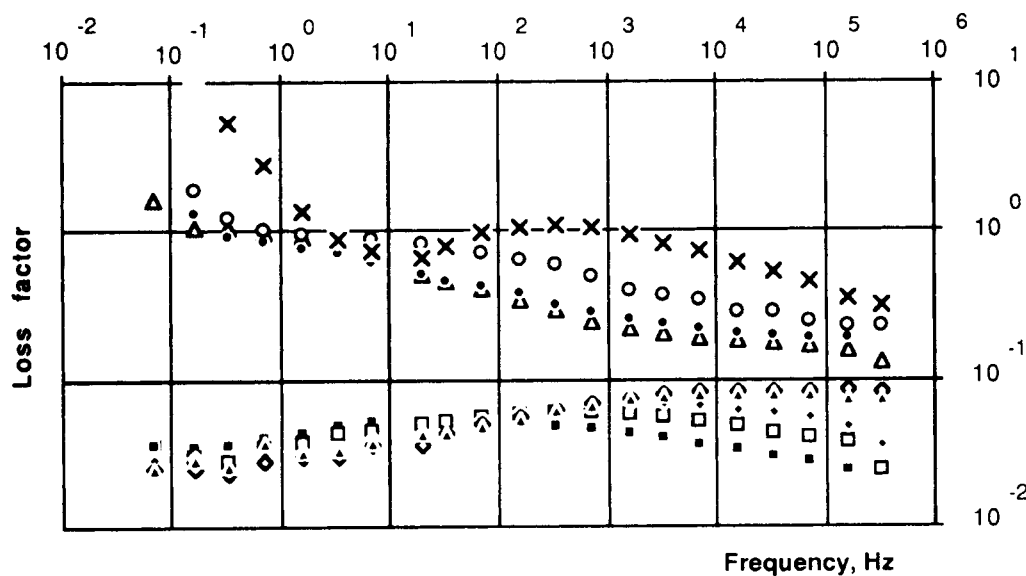

Figure 5 Loss factor of EXL4150 as a function of frequency at different temperatures: (■) 25°C; (□) 55°C; (♦) 80°C; (◊) 105°C; (▲) 120°C; (△) 145°C; (●) 155°C; (○) 160°C; (x) 165°C.
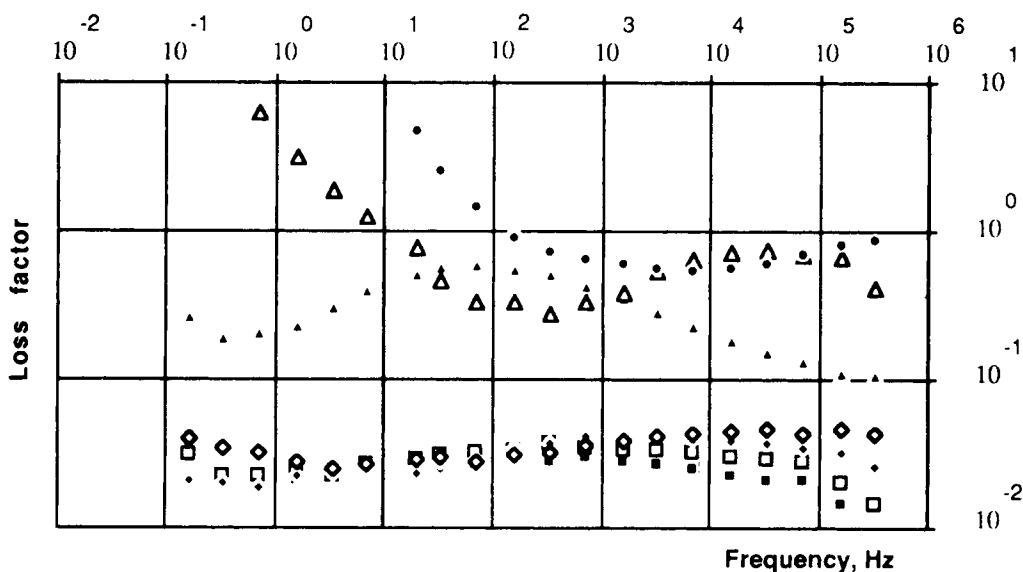
Figure 6 Loss factor of blend A as a function of frequency at different temperatures:
(■) 25°C; (□) 55°C; (♦) 80°C; (◊) 105°C; (▲) 120°C; (△) 145°C; (●) 165°C.

Figure 6 reports the dielectrical properties of blend A: α relaxation peaks are found at almost the same frequencies as those corresponding to pure poly-SAN, at temperatures lower than 145°C. Strong absorption phenomena, as frequency decreases, already present in both pure components but likely enhanced by interfacial polarization at the interfaces of the different phases, prevents the detection of the Paraloid EXL4150 α transition. These results again confirm the immiscibility of the two components, but the slight shift of peak frequencies related to the α relaxation of poly-SAN to higher values seems to hint to a sort of interaction between the chains, as found in other immiscible blends.[29] As to what concerns the β relaxation, it is not possible to separate the two contributions: The activation energy (73 kJ/mol) is similar to that of EXL4150 but maxima are shifted to higher frequencies, probably in virtue of the superposition of the peaks.
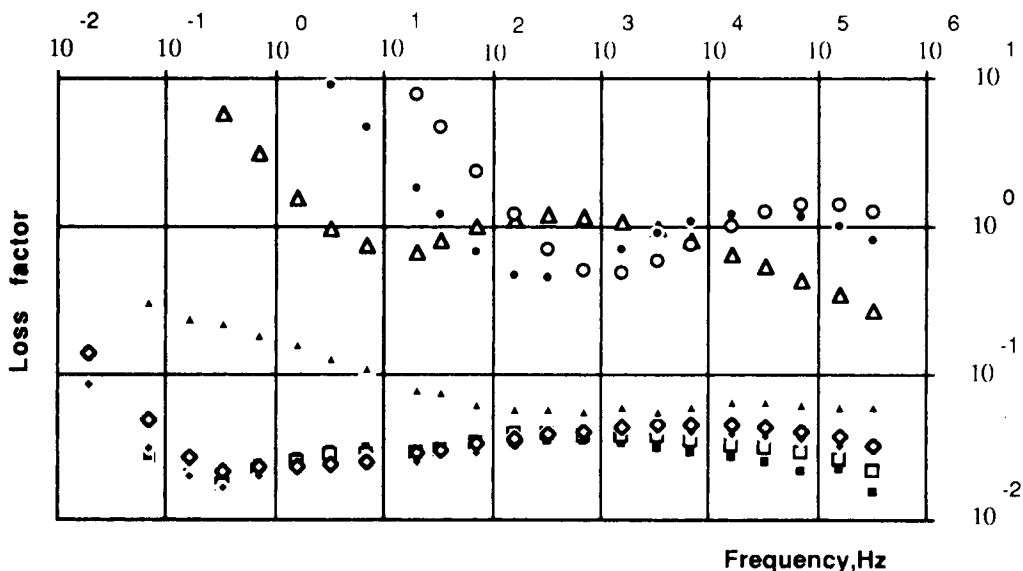

Figure 7 Loss factor of blend B as a function of frequency at different temperatures:
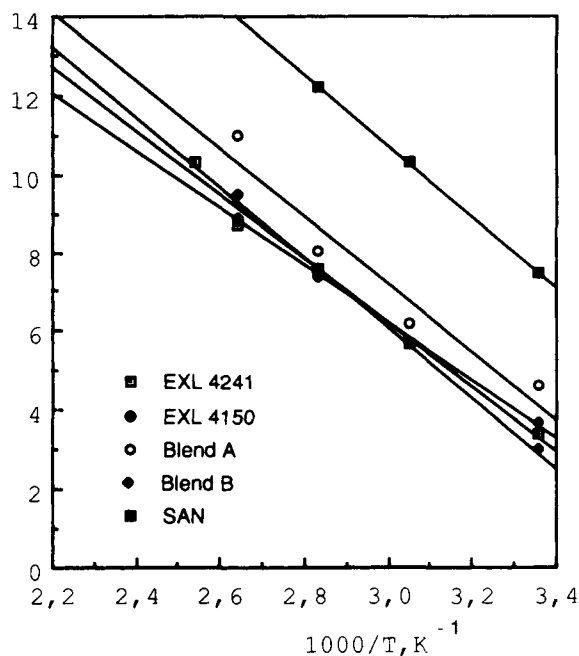(■) 25°C; (□) 55°C; (♦) 80°C; (◊) 105°C; (▲) 120°C; (△) 145°C; (●) 165°C, (○) 175°C.

Figure 8 Frequency of dielectric β maxima (Ln) vs. reciprocal temperatures $(1000/T)$.

Dielectrical characteristics of blend B are shown in Figure 7. α relaxations clearly appear at intermediate frequencies between those of the pure components, thus confirming polymer miscibility. The activation energies of the process are 304 and 65 kJ/mol for α and β process, respectively.

Figure 8 depicts the frequencies of the β maxima as a function of $1000/T$ (Kelvin degrees) for all

investigated materials. Figure 9 shows the TSDC spectra of pure components (Paraloid EXL4241 has been omitted for clearness sake, since its TSDC is very close to that of EXL4150) and blends for all investigated materials.

Poly-SAN TSDC curves show a broad peak from 60 to 135°C, in which two relaxation peaks coalesce, as found elsewhere.[30] Paraloid EXL4150 (the same situation is found in EXL4241) shows one intense peak corresponding to the α transition at 157°C (154°C for EXL4241); the β peak does not appear at the applied polarization field and time. Blend B shows only one peak, related to the glass transition, located at intermediate temperatures (130°C) between those of the pure components, whereas blend A shows two peaks, barely discernible, at temperatures close to the glass transition temperatures of poly-SAN and Paraloid EXL4150, respectively.

CONCLUSIONS

1. Dielectrical spectroscopy, TSDC, and isothermal calorimetry have been employed to confirm the thermal resistance of poly-SAN blended with PMMI, previously investigated by DSC data. Dielectrical measurements showed a lower loss factor for the miscible blend than that of poly-SAN alone at the higher investigated temperatures. This is of true interest for application in the automotive field, where good impact properties of ABS have, nowadays, to be combined with thermal
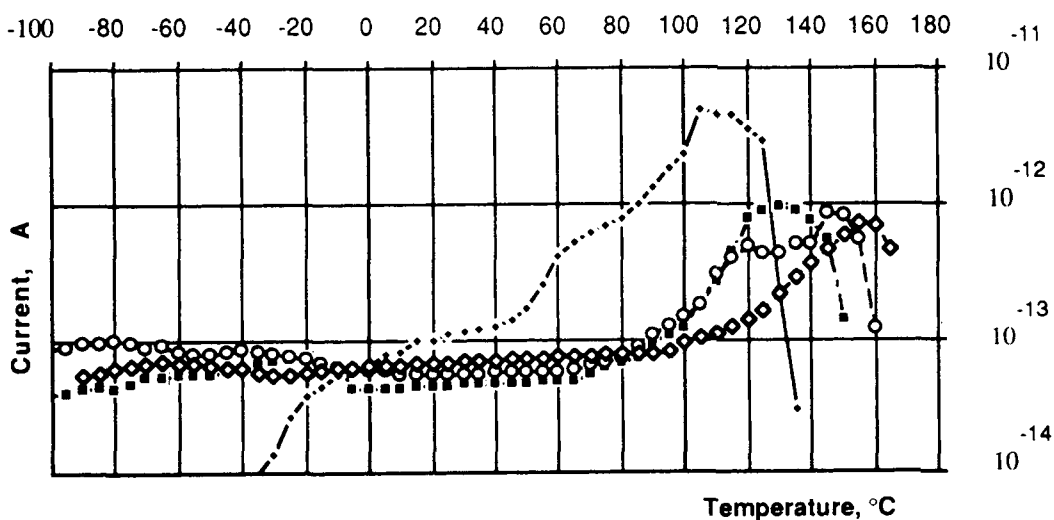

Figure 9 TSDC spectra of investigated polymers and blends: (O) blend A; (■) blend B; (◆) SAN24; (◇) EXL4150.

resistance or electrical applications where low dielectrical losses are required combined with thermal resistence.

2. Loss factor, permittivity, and TSDC measurement results agree well with miscibility results obtained by thermoanalysis data.

3. The isothermal calorimetric method seems to be a promising approach for the measurements of the mixing enthalpy of polymer blends: the mixing enthalpy and the Flory–Huggins X parameter have been determined for the poly-SAN and imidized PMMA (EXL4150) blend. The method allows one to determine both the immiscibility and miscibility[13] of thermoresistant blends, and its results again well confirm T_g measurements, thus allowing one to obtain a deeper knowledge of blend components' mixing behavior.

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