Structural Characterization of Polymer Blends Based on Polysulfones

A. Linares, J. L. Acosta

Instituto de Ciencia y Tecnología de Polímeros, C/ Juan de la Cierva, 28006 Madrid, Spain

ABSTRACT: A series of blends with various compositions was prepared on the basis of polysulfone, polyethersulfone, and polyimide. These blends were characterized by different techniques, including Fourier transform IR spectroscopy, differential scanning calorimetry, dynamic mechanical analysis, and tensile stress–strain measurements. The results obtained allowed for certain conclusions regarding blend compatibility. In addition, the mechanical properties were subjected to an experimental test design to measure the blends for tensile break strength and Young's modulus with a computer program, which eventually enabled us to obtain the surface response equations of both properties and also to predict the optimum composition presenting the best mechanical behavior. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3030–3039, 2004

Key words: polyimides; blends; compatibility: differential scanning calorimetry (DSC); mechanical properties

INTRODUCTION

Polymer blending as a property modification technique is an approach that is widely used to obtain cheap materials with improved properties. At first sight, polymer blends may be classed into homogeneous, or miscible, and heterogeneous, or immiscible, blends.

Homogeneous blends are relatively rare because the Gibbs free energy of mixing is positive because the change in entropy, as a consequence of high-molecular weight polymer blending, is practically negligible, with the enthalpy term being positive. The force accountable for miscibility is the existence of specific interactions between polymers.[1] There do exist certain blends, described as compatible, for instance, those consisting of polybenzoimidazols and aromatic polyimides,[2–4] polyimide blended with polyethersulfone,[5] and polysulfone,[6] and polysulfone with polyether sulfone.[7]

In this study, several blends consisting of polyimide (PI), polysulfone (PSU), and polyethersulfone (PES) were analyzed. The PI we used is a thermally stable thermoplastic that performs up to very high temperatures with good properties such as a dielectric, low inflammability, high radiation resistance, and low charge-induced deformation. Both PSU and PES are engineered high-performance thermoplastics that possess, thermally stable phenyl rings bonded to ether or sulfone groups. The delocalization of the structure is accountable for its good strength values against oxidative degradation and the stability of its mechanical properties, even at high temperatures. The presence of oxygen bonds of the ether group confers elasticity to the chains.

Because of the presence of aromatic rings in PSU, PES, and PI, these polymers are susceptible to a sulfonation reaction, through which they incorporate —SO_3H associations into their structure.

For several years, sulfonated polymers have been the object of intense research because of their potential applicability in many fields;[9] one specially interesting application is their use as ion-conducting membranes in batteries[10] or fuel cells.[11–13]

Our research integrates with this general context with this first article, which describes the preparation of blends based on the two aforementioned PSUs and PI, with the aim of improving the performance of conventional proton-conducting membranes. Subsequently, the blends were characterized by different techniques to assess their technological properties and to determine if they could be considered as base materials to be subjected to sulfonation and could then be applied as proton-exchanging membranes in fuel cells.

EXPERIMENTAL

Materials

All homopolymers and the methylene chloride used as a solvent were used as supplied without any previous purification.

The following were used as homopolymers: PSU was supplied by Aldrich (Madrid, Spain), with a weight-average molecular weight (M_w) of

Correspondence to: A. Linores (alinares@ictp.csic.es).

53,000–60,000 and a number-average molecular weight (M_n) of 26,000 PES was also supplied by Aldrich, and PI was supplied by Ciba Geigy (Basel, Switzerland) under the trade name Matrimid 5218 with the following characteristics: M_w = 80,000 and M_n = 11,000

The blends prepared in different compositions were obtained by dissolution of the respective homopolymer portions in methylene chloride. After solvent evaporation and vacuum drying for 2 days at 80°C, samples in the form of films were obtained, and then, the different tests and measurements were carried out.

Analytic techniques and procedures

Before the implementation of any test, all of the samples were carefully vacuum-dried for 2 days at a temperature close to 180°C.

The following tests were carried out:

Differential scanning calorimetry (DSC)

DSC was carried out with a Mettler TA 4000 differential scanning calorimeter (Barcelona, Spain). Before the tests, the samples were heated to a temperature close to their glass-transition temperature (T_g). Then, they were quenched, and finally, their respective thermograms were recorded. In this way, the recording method was standardized, with the elimination of any thermal antecedents. T_g was considered the point of inflexion of the variations of specific heat in that region.

Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy was carried out on a PerkinElmer FTIR spectrometer Spectrum One with the attenuated total reflection (ATR) technique (Massachusetts).

Dynamic mechanical analysis (DMA)

A DMTA V dynamic mechanical thermal analyzer from Rheometric Scientific (Piscataway, NJ) was used. The measurements were implemented between 50 and 250–320°C at a heating rate of 2°C/min. The frequencies chosen for test implementation were 0.1, 0.5, and 1 Hz. The technique was applied under bending, with single cantilever geometry.

Mechanical properties measured under tensile strain

The mechanical properties were measured on a universal Instron machine (model 4301) (Massachusetts) according to standard UNE 53510. The samples were small in size and of the Halterian type. The test was run at a rate of 10 mm/min and at room temperature. The measurements were carried out on five samples for each blend, with their arithmetical mean considered the values of tensile break strength and Young's modulus.

Statistical analysis

The equations for tensile break strength surface response and the elasticity module were calculated with NEMROD 3.1 software from LPRAI, Ltd.[14]

RESULTS AND DISCUSSION

FTIR spectroscopy

The homopolymers and the different experimental blends were characterized by FTIR spectroscopy with the ATR technique.

The measurements were taken from films obtained from the respective samples dissolved in methylene chloride solutions after the solvent was evaporated.

PES

Intense bands were observed. One at 1296 cm^{-1} was due to the asymmetric stress vibration of the S=O bond, and another at 1145 cm^{-1} corresponded to the symmetric stress vibration of the same bond. At 1933 cm^{-1}, a band, appeared also quite intense, that was attributable to the symmetric stress vibration of the aromatic ether, C—O—C. The absorption bands of the phenyl groups appeared at 687 and 758 cm^{-1}, and those due to the C—C bond vibration appeared at 1580, 1483, and 1405 cm^{-1}.

PSU

At 1234 cm^{-1}, the absorption band characteristic of the aromatic ether attributable to the symmetric stress vibration of the C—O—C bond appeared. The absorption bands, corresponding to the methyl group of the bisphenol group A, were situated at 1364 and 1387 cm^{-1}. The absorption due to the asymmetric stress vibration of the S=O bond appeared at 1294 cm^{-1}, and that of the symmetric stress appeared at 1148 cm^{-1}. Finally, the band at 699 cm^{-1} represented the phenyl group vibration.

PI

The carbonyl groups presented a characteristic peak at 1740 cm^{-1} (stress vibration), whereas the primary and secondary vibrations of the C—N bond generated bands at 1250–1350 cm^{-1}.

FTIR spectroscopy may constitute a direct route for the determination of the nature of a polymer blend, in such a way that the spectrum of a totally incompatible blend will be but the sum of the spectra corresponding
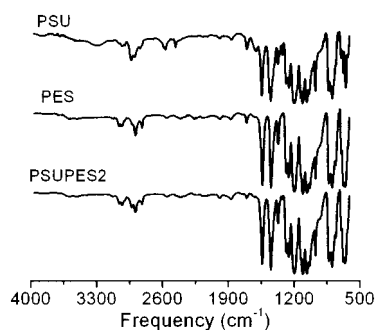
Figure 1 IR spectra of the PSU and PES homopolymers and their 50/50 composition.

to the constituent and pure homopolymers. In contrast, in the case of blends with at least a certain degree of compatibility, the shifts of certain significant bands to other frequencies generally point toward the existence of specific interactions taking place among the characteristic groups of the pure polymers.[15]

Figures 1–3 show the spectra attributable to PSU, PES, and PI, together with those of the binary blends resulting from their 50/50 combinations.

For the PSUPI2 and PESPI2 blends, if we subtracted, in either case, the PI spectrum and those of PSU or PES in the respective blends, the shift of the frequencies at which the absorption bands of certain groups of the pure polymers were usually situated become clearly visible. Although not significant as to its magnitude, the principal aspect to be highlighted was the shift in frequency undergone by the carbonyl group of the polyimide from 1716 to 1722 cm^{-1} in the case of the PSUPI2 binary blend and to 1721 cm^{-1} in the case of PESPI2. Other shifts were observed in the absorption bands of the aliphatic C—H bond vibrations that moved from 1365 to 1373 and 1372 cm^{-1} for PSUPI2 and PESPI2, respectively.

These spectral changes suggested, in some way, that the existence of specific interactions contributed to blend compatibility.
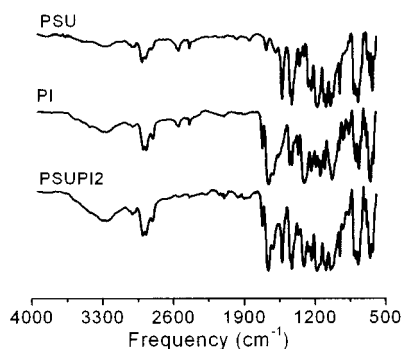

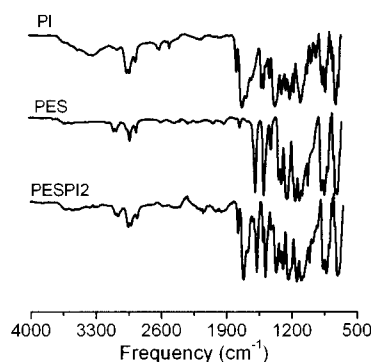**Figure 2** IR spectra of the PSU and PI homopolymers and their 50/50 composition.

Figure 3 IR spectra of the PES and PI homopolymers and their 50/50 composition.

DSC

The thermal properties of all of the blends were studied by means of DSC T_g determinations.

The films obtained through component dissolution in methylene chloride before DSC all showed aging phenomenon similar to what has been observed for other systems, such as polybenzoimidazol–PI blends.[16] So, before calorimetry, it was necessary to heat the different blends almost to their T_g's and subsequently quench them to room temperature. The aim of this treatment was to establish analogies in the thermal history of the whole sample series.

Table I summarizes the T_g values obtained, and Figure 4 shows the DSC thermograms. The values of T_g were obtained at the point of inflexion of the thermogram. Measurements were carried out three times for each sample, and the value assigned to T_g was the arithmetical mean of the respective measurements.

As observed in all cases, including the ternary blend, a single T_g was detected for each sample, which varied as a function of blend composition. This behav-

TABLE I
T_g and Specific Heat (C_p) Values of All of the Samples Under Study as Determined by DSC

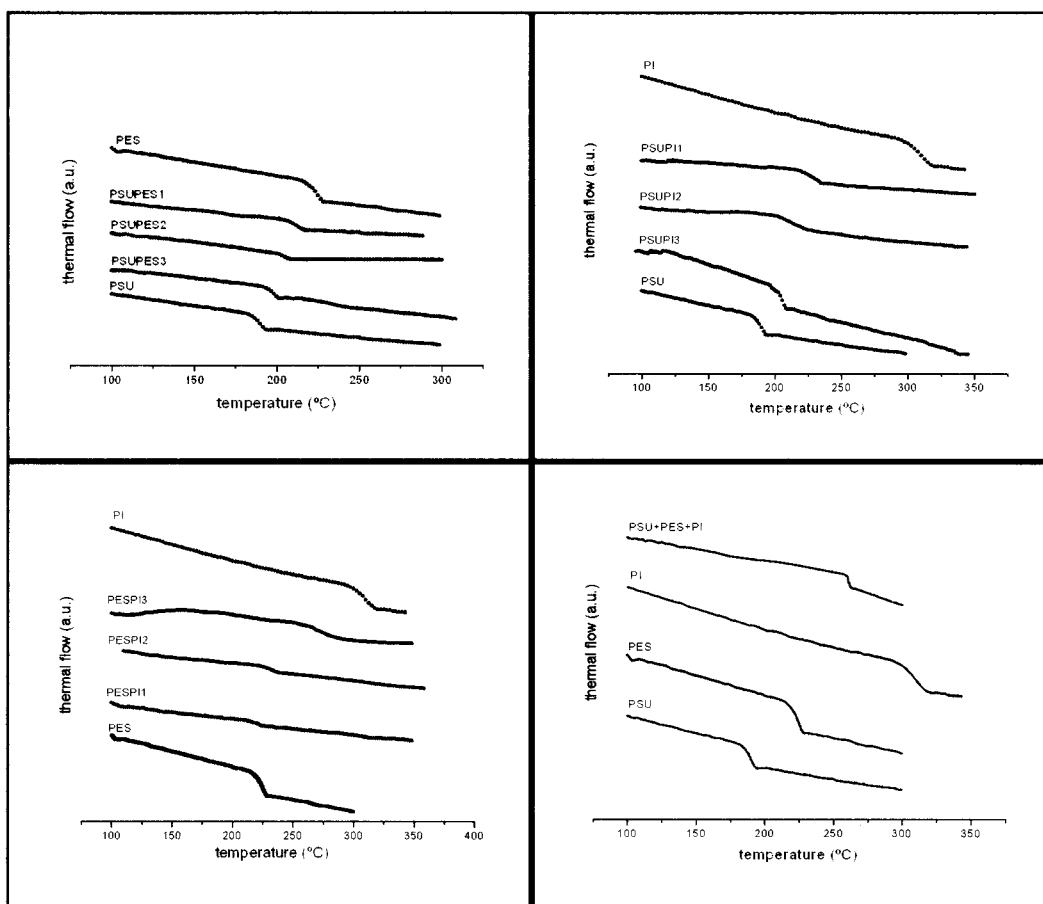| Sample	Composition (wt %)			T_g (°C)	C_p (J/g °C)
	PSU	PES	PI		
PSU	100	0	0	188.9	0.25
PES	0	100	0	222.9	0.23
PI	0	0	100	309.1	0.20
PSUPES1	75	25	0	197.5	0.16
PSUPES2	50	50	0	203.7	0.18
PSUPES3	25	75	0	212.4	0.12
PSUPI1	75	0	25	204.6	0.20
PSUPI2	50	0	50	212.5	0.15
PSUPI3	25	0	75	226.3	0.12
PESPI1	75	0	25	225.2	0.16
PESPI2	50	0	50	231.6	0.14
PESPI3	25	0	75	275.9	0.20
PSUPESPI	33.3	33.3	33.3	270.1	0.20

Figure 4 DSC thermograms for PSU, PES, PI, and their blends.

ior was *a priori* indicative of the fact that we were dealing with blends that at least from a macroscopic point of view, behaved like totally compatible blends.

When one examines the interdependence between T_g and the composition of a miscible blend on a theoretical plane, even if a universal relationship does not exist, it is perfectly possible to apply the equations available for random copolymers or plasticized systems, such as the so-called Wood[17] equation:

$$T_g = w_1 T_{g,1} + w_2 T_{g,2}$$

or the Fox equation[18]

$$1/T_g = w_1/T_{g,1} + w_2/T_{g,2}$$

or Pochan's[19]

$$\ln T_g = w_1 \ln T_{g,1} + w_2 \ln T_{g,2}$$

where w is the weight fraction and the subscripts 1 and 2 refer to the components, in this case those of a binary blend.

The three elementary models may be considered idealized equations and, hence, presuppose that the volume additivity rule is fulfilled consequential to the fact that there exists compensation between the energetic terms (interactions) and entropic configurations (free volume). Positive deviations from this rule (higher T_g values) suggest the existence of interactions, such as those occurring in the charge-transfer complexes or electron donor–receptor interactions vis-à-vis conformational reorganizations accompanied by changes in the free volume, which would give rise to negative deviations from the ideal values established by the volume additivity rule.[20,21]

With the aim of studying our series qualitatively, we compared the experimental data obtained with the respective theoretical values deriving from the previous equations. Figure 5 shows the respective graphs.

When we analyzed the binary blends constituted by PSU and PES, the experimental values adapted very well to the theoretical equations, with the adjustment to the Fox equation the most accurate when the PSU content was below 50%.

The other blend types, those made up by PI and PSU or PES, showed quite different behavior from the

one that could be theoretically predicted. Even if Fox's model was the one that best described their behavior, the discrepancies found to exist between their theoretical and real behavior were fairly significant. For both blend types and all of the compositions under study, the T_g values determined empirically were lower than their theoretical values calculated from the mathematical models. This was indicative of the fact that when the common component was the PI, the conformational restructuring taking place translated into an increase in free volume and, hence, into a drop in T_g.

DMA

The measurements were carried out under bending with single cantilever geometry on samples with a thickness greater than 3 mm. The experimental frequencies were 0.1, 0.5, and 1 Hz in the temperature range of 50 to 250–320°C. Before test implementation, the samples were vacuum-dried for 2 days at a temperature approaching 180°C.

The temperature at which glass transition occurred was determined from tan δ for both the pure homopolymers and the different blends. The results are compiled in Table II. By way of example, Figure 6 shows tan δ variation as a function of temperature for several samples.

In the light of the results presented, it is worth stressing some important aspects:

1. At low frequency, for the PI-containing binary blends, a single relaxation attributable to the blend's glass transition was detectable only when the PI content was no greater than 25%. This was indicative of the fact that we were dealing with miscible blends or at least compatible blends from a macroscopic point of view. With increasing PI content, however, more than one relaxation was detectable in the respective samples. Thus, when the PI content was 50%, two relaxations were observed: this increased to three at 75% PI. In the case of two relaxations, they could be associated to the glass transition of each of the constituents in the blend. In the case of three relaxations, we imagined the existence of an interface where the two polymers coexisted and which generated a third T_g, indicative of at least partial blend compatibility.
2. The binary PSU and PES blends generated three relaxations only in the presence of a high PES content; two of these were attributable to the glass transitions of each of the homopolymers, and the intermediate one corresponded to a potential interface. When PES content remained below 75%, the samples presented as totally compatible blends, in respect of the universally accepted criterion of a single T_g for the blend.
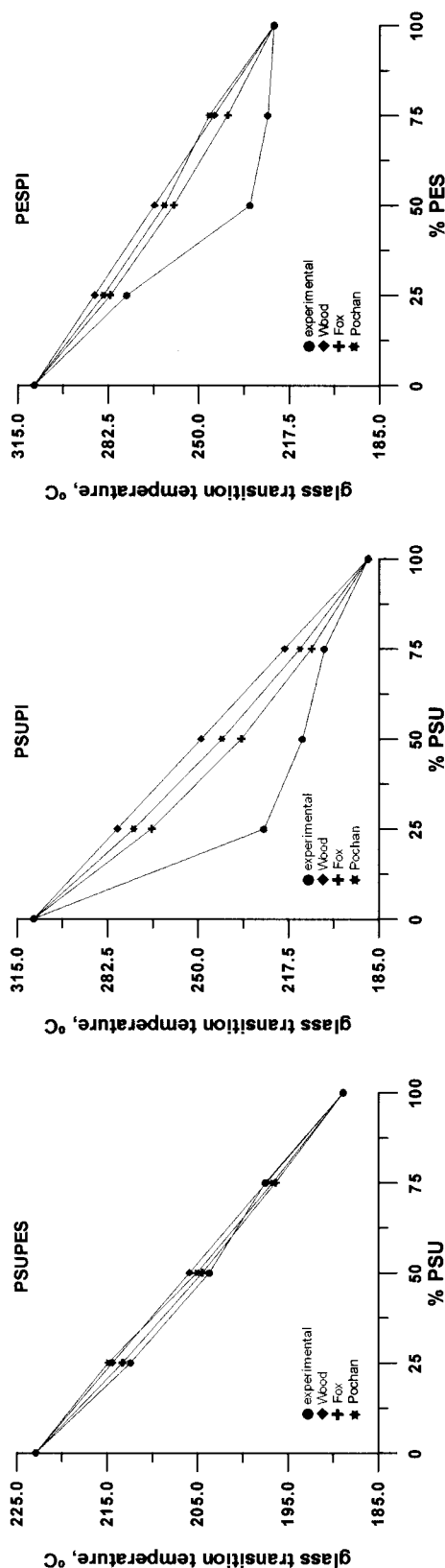

Figure 5 T_g behavior for the studied polymer blends. The experimental data were obtained through DSC analysis, and the theoretical points resulted from application of the discussed equations.

TABLE II
Temperature Values Obtained by DMA Analysis at Which the Multiple Relaxations Were Present in the Blends

Sample	Composition (wt %)			tan δ		
	PSU	PES	PI	0.1 Hz	0.5 Hz	1 Hz
PSU	100	0	0	194.8	197.1	199.9
PES	0	100	0	234.1	237.2	238.9
PI	0	0	100	325.8	331.3	334.1
PSUPPES1	75	25	0	198.9	201.3	202.2
PSUPES2	50	50	0	196.4	196.4, 203.5	196.7, 204.3
PSUPES3	25	75	0	188.3, 205.1, 232.5	191.8, 207.7, 238.4	193.0, 208.5, 239.2
PSUPI1	75	0	25	200.6	201.2	202.1
PSUPI2	50	0	50	189.8, 203.1	194.6, 204.9	195.3, 206.3
PSUPI3	25	0	75	207.6, 235.4, 312.2	207.3, 238.0, 321.2	208.4, 236.3, 326.1
PESPI1	0	75	25	245.1	246.7	249.4
PESPI2	0	50	50	226.7, 236.1	228.3, 240.6	229.5, 242.3
PESPI3	0	25	75	226.2, 237.1, 276.3	228.3, 243.4, 282.9	232.4, 245.6, 279.6
PSUPESPI	33.3	33.3	33.3	205.9, 234.1, 312.8	207.5, 235.3, 324.8	209.3, 237.4, 327.8

3. The ternary blend presented three transitions. The one presenting at the highest temperature was considered the T_g of the PI, whereas the assignment of the other two posed some problems. In principle, they could have been assigned each to one of the other components. Nevertheless, it was necessary to think about the possibil-

ity of an interface with either its own T_g or at least exerting an effect on the other polymers.

The fact that DSC only showed a single variation of the specific heat value as a function of temperature, that is, a single T_g for all of the experimental samples, both for the binary and the ternary blends, and that DMA de-
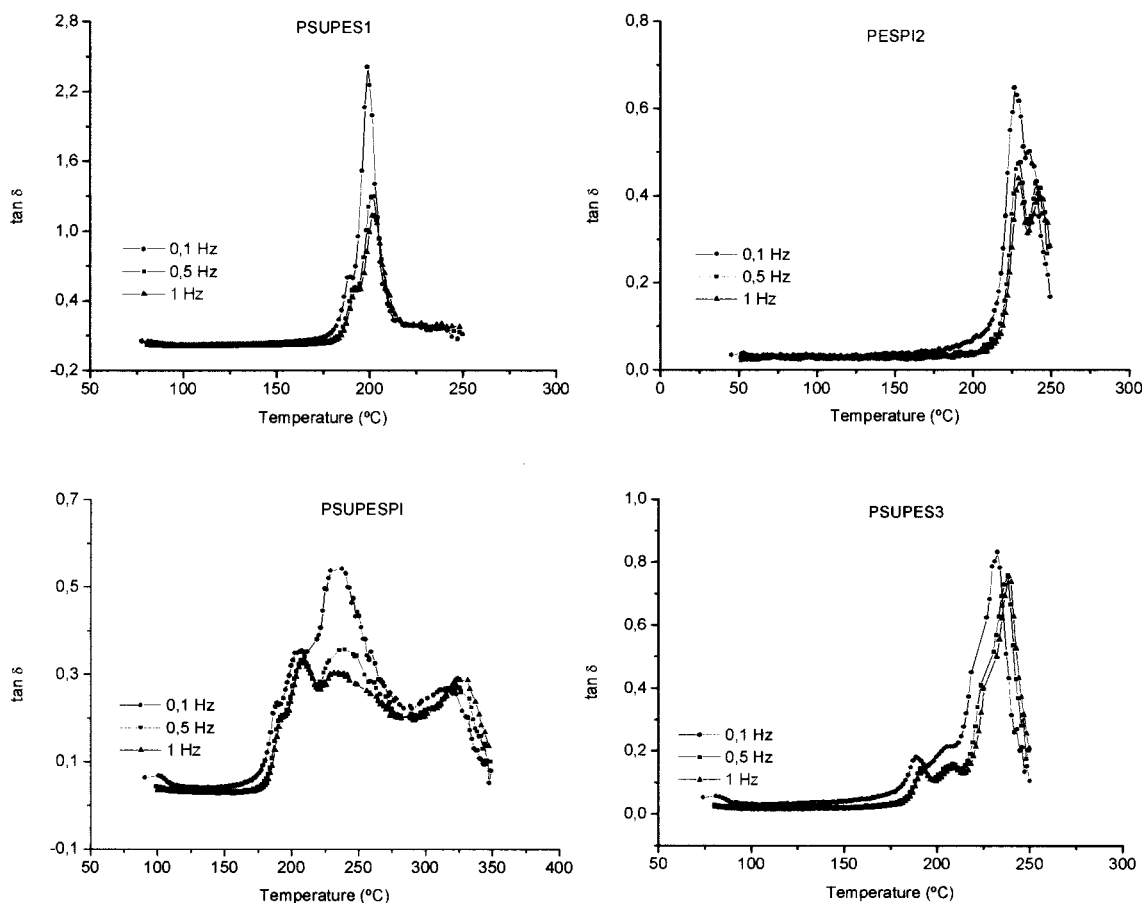

Figure 6 Dynamic mechanical measurements: tan δ as a function of temperature and frequencies for different blends.

TABLE III
Break Strength and Young's Modulus Measured Under
Tensile Strain

Sample	Composition (wt %)			Break strength (Mpa)	Young's modulus (Mpa)
	PSU	PES	PI		
PSU	100	0	0	26.28	1538.7
PES	0	100	0	46.18	1937.3
PI	0	0	100	65.46	2551.3
PSUPES1	75	25	0	44.72	2551.7
PSUPES2	50	50	0	57.31	2206.7
PSUPES3	25	75	0	46.09	2470.8
PSUPI1	75	0	25	63.22	2390.3
PSUPI2	50	0	50	76.69	2778.1
PSUPI3	25	0	75	86.02	3666.1
PESPI1	0	75	25	74.60	2952.7
PESPI2	0	50	50	82.88	3075.6
PESPI3	0	25	75	89.67	3484.8
PSUPESPI	33.3	33.3	33.3	89.81	3697.2

tected two or three relaxations, depending on blend composition, could be explained in terms of the different sensitivity of one and the other analytic technique.

It may be possible that the blends, prepared according to the procedure described in the Experimental section and treated before measurement as was described previously, could have formed systems that from a molecular point of view, were not totally homogeneous; that is, individual molecules of each of the constituent homopolymers may have joined to form small domains or microheterogeneities, detectable or not, depending on the sensitivity of the analytic technique. Thus, the molecular process accountable for the shift in specific heat, as observed through DSC, implied domain movements of a greater range than the dynamic mechanical response, which corresponded to micro-Brownian chain segment movements. Consequently, we could arrive at opposing conclusions.

When more than one relaxation presented in DMA measurements, we approached the compatibility by analyzing the different T_g shifts that occurred.

Mechanical properties measured under tensile strain

Standardized samples of the pure homopolymer and the different blends were examined for their mechanical properties.

The data obtained regarding break strength and Young's modulus are compiled in Table III. Figure 7 shows the respective stress–strain graphs.

As observed, in practically all of the tested blend samples the strength at the break point was greater than that of their constituent homopolymers in isolation, with the values obtained for the PES and PI

blends being especially good, together with that of the ternary blend.

However, except for the pure PI, the ternary blend, and the binary PES and PI blends, all of other blends and also the PSU and PES homopolymers exhibited the typical behavior of a material presenting with the cold creep phenomenon. In this case, stress variation as a function of strain reaches a peak at the so-called creep limit. With greater stretching efforts, the materials deform into a bottleneck or local narrowing, practically under constant stress conditions. Once the neckshape has covered the full length of the sample, the tensile stress goes up again if the stretching strain continues to increase until rupture eventually occurs. The creep limit usually presents for stretching strains between 5 and 20% when the test is run at room temperature and the stretching rate is moderate. Materials presenting with this behavior are considered especially stiff.

For PI, PESPI1, PESPI2, and the ternary blends, a drop in tensile strain was observed immediately before break. It was associated with a narrowing or softening due to plastic strain. This characteristic refers to stiff or hard materials. Finally, the stress–strain graph of PESPI3 was monotonic; that is, no cold stretch or thinning was observed. The only visible sign immediately before rupture was plastic yield. These latter materials were considered relatively hard or stiff.

The relevance that polymer blends have acquired in recent times, as an alternative to the chemical synthesis of new and advanced polymeric materials, need not be stressed at all. The problem arises when a blend or blends have to be chosen in which the desired property reaches optimum values. In principle, the number of compositions necessary to study the general behavior of a blend is unlimited; test series planning constitutes a tool of undeniable value if a functional relationship is to be established between the properties measured and the concentration of each polymer with a minimum number of tests.

Therefore, the results (tensile break strength and Young's modulus) were treated by means of a statistical method software once the levels of variables were proposed, that is, once the compositions of the experimental blends were established. Thus, insight was gained through the respective matrix development into the values of the coefficients in the equation of each of the responses, and it was possible to trace the respective isohyps or level lines with SW Logicel NEMROD 3.1.[14] So a first step in our research was to propose a model in which variables should comply with two conditions:

$$1°: 0 \leq X_{v,i} \leq 100$$
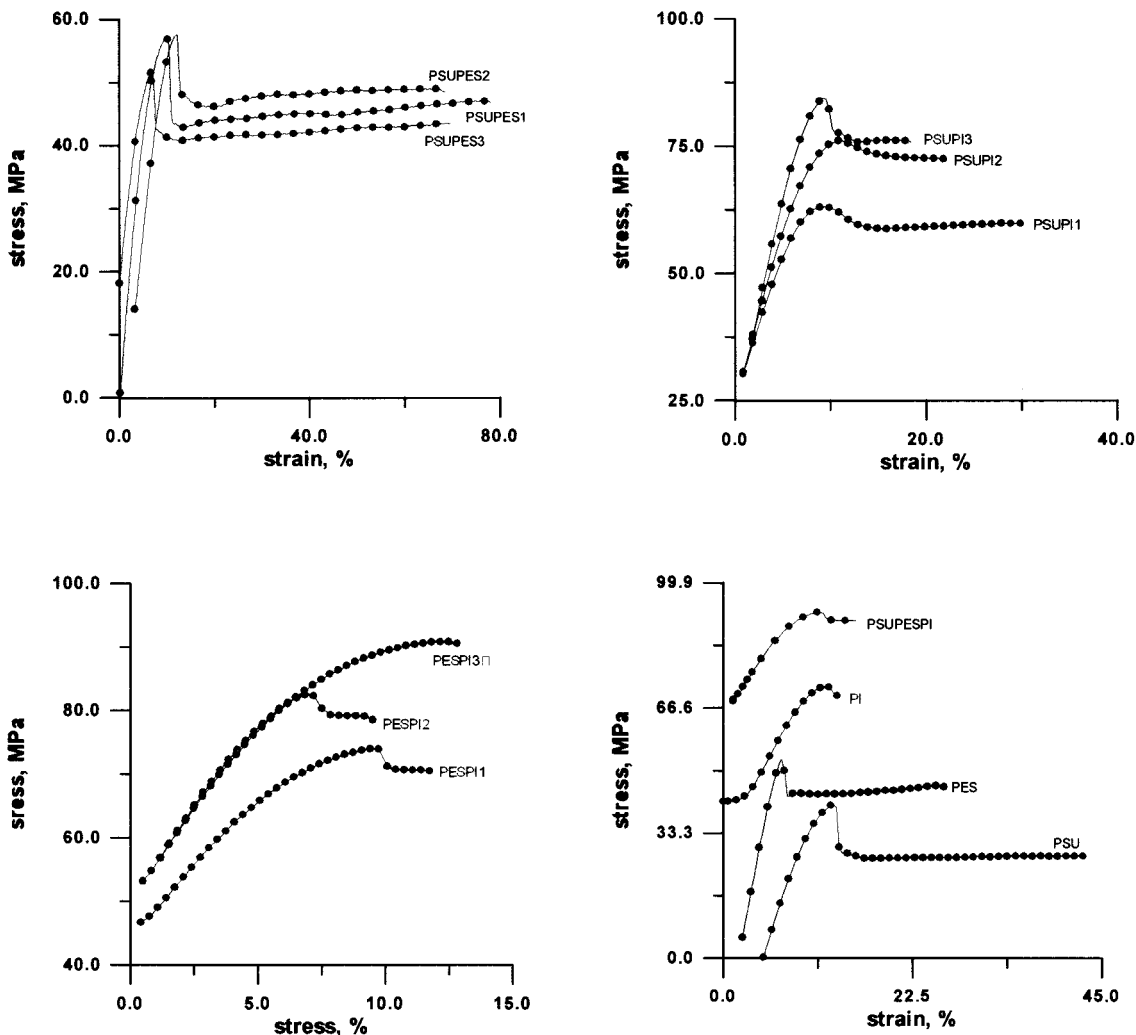
$$2°: \Sigma X_{v,i} = 100$$

Figure 7 Stress–strain behavior at 25°C for the different polymers and polymer blends.

where $X_{v,i}$ is the weight fraction of each polymer.

The experimental matrix proposed was the following:

X_1	X_2	X_3
1	0	0
0	1	0
0	0	1
0.5	0.5	0
0.5	0	0.5
0	0.5	0.5
0.75	0.25	0
0.75	0	0.25
0.25	0.75	0
0.25	0	0.75
0	0.75	0.25
0	0.25	0.75
0.33	0.33	0.33

The equation proposed for this model was

$$Y = b_1X_1 + b_2X_2 + b_3X_3 + b_4X_1X_2$$
$$+ b_5X_1X_3 + b_6X_2X_3 + b_7X_1X_2X_3$$

where Y is the property, X_i are the weight fractions, and b_i are the coefficients of the equation.

Once the blends were prepared according to the compositions detailed in the experimental matrix, that is, the compositions that were characterized by means of the different techniques described previously, they were tested under tensile strain to determine their break strength and elastic modulus values. The respective data are compiled in Table III.

The coefficients of the equation were obtained from the computed software for the two magnitudes measured:

$$\sigma_{\text{break}} = 27.25X_1 + 43.70X_2 + 68.09X_3 + 69.14X_1X_2$$
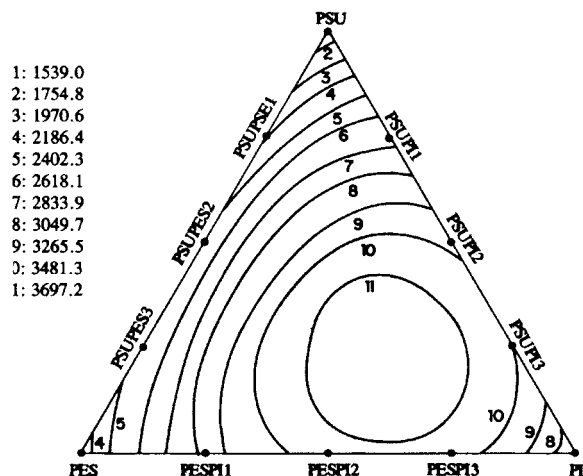$$+ 130.71X_1X_2 + 124.90X_2X_3 + 203.08X_1X_2X_3$$

Figure 8 Response–surface contours for Young's modulus obtained from tensile stress–strain measurements.

$$E = 1544.6X_1 + 1933.1X_2 + 2817.9X_3 + 3061.6X_1X_2$$
$$+ 3515.0X_1X_3 + 3698.7X_2X_3 + 12492.6X_1X_2X_3$$

where σ_{break} is break strength and E is the Young's modulus.

Subsequently, the surface responses were established as shown in Figures 8 and 9. When analyzing the elasticity modulus (Fig. 8) for the binary PSU–PES blend, we observed an increase proportionate to PES concentration up to a PES portion of slightly over 25% in the blend. Over a wide range of compositions, E remained constant yet diminished slightly for PES contents over 75%. A similar behavior was observed for the PSU–PI binary blends. However, in this latter case, the compositional range in which the modulus did not vary was much smaller, and the values obtained were much higher. Finally, the PES–PI binary blends also behaved in a similar way as described previously. In general terms, the Young's modulus variation as a function of composition was much more sensitive for high PSU content. For the ternary blends, the response plane indicated that the best modulus values were achieved with blends in a compositional environment around 25% PSU, 32% PES, and 43% PI.

For break strength (Fig. 9), the behavior observed was fully analogous to that described for Young's modulus. The aspects highlighted for E variation as a function of composition of the binary blends also applied to break strength behavior. However, here the optimum values of tensile break strength were slightly shifted toward the PI-rich ternary blends, that is, compositions around 21% PSU, 26% PES, and 53% PI.

CONCLUSIONS

Blends of different compositions were prepared based on three polymers: PSU, PES, and a PI. The blends were characterized by several analytic techniques.

The respective spectra were obtained by means of FTIR spectroscopy through ATR. For the PI-containing binary blends, shifts in their carbonyl group were observed, which however insignificant they were, were indicative of the existence of specific interactions between the homopolymer and PSU or PES.

DSC revealed a single peak for specific heat variation as a function of temperature for all cases, which shifted as a function of blend composition and could be attributed to glass transition. Following the universally accepted criterion, the single glass transition of these blends suggested that we were dealing with compatible blends.

The dynamic mechanical study, however, led to quite different conclusions. For binary blends with a PI content above 50%, more than one relaxation was observed. To be accurate, when the PI content was 75%, even three relaxations were detected. In principle, one would tend to think that two relaxations might correspond to the glass transition of each of the constituents, and for the third one, it seems legitimate to propose the existence of an interface at which both constituents coexisted. The ternary blend likewise presented three relaxations.

The differences found when the DSC and DMA data were examined could be explained in terms of the fact that these systems, under the experimental conditions for blend preparation and measurements, did not homogeneously mix at a molecular level, thus giving rise to certain minute domains or microheterogeneities, which depending on the degree of sensitivity of the analytic device, were detected or neglected. Thus, in conclusion, it was safe to assume that these systems were compatible from a macroscopic point of view, but from the molecular stance, they were immiscible. At this stage, the optical clarity of our sample series should also be highlighted.
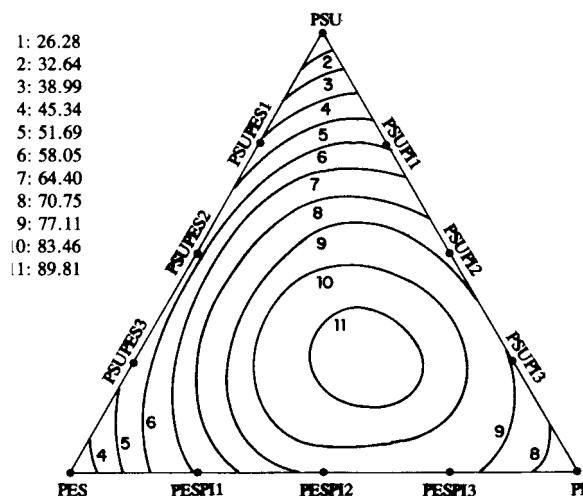

Figure 9 Response–surface contours for break strength obtained from tensile stress–strain measurements.

The study of the mechanical properties, in particular the determination of tensile break strength and the elastic modulus measured under tensile strain, revealed the excellent mechanical properties of the blends of our series. Through the application of an experimental design and by means of computing software, we were able to determine that the compositional range in which the mechanical properties presented optimum values moves around 25% PSU, 25% PES, and 50% PI. The identification of the conditions under which the mechanical properties achieved optimum performance is of vital importance in view of the potential application of these materials in fuel cells.

References

1. Flory, P. J. Discuss Faraday Soc 1970, 49, 27.
2. Leung, L.; Williams, D. J.; Karasz, F. E.; Macknight, W. J. Polym Bull 1986, 16, 1457.
3. Guerra, G.; Choe, S.; Williams, D. J.; Karasz, F. E.; Macknight, W. J. Macromolecules 1988, 21, 231.
4. Guerra, G.; Williams, D. J.; Karasz, F. E.; Macknight, W. J. J Polym Sci Part B: Polym Phys 1988, 26, 301.
5. Liang, K.; Grebowicz, J.; Valle, E.; Karasz, F. E.; Macknight, W. J. J Polym Sci Part B: Polym Phys 1992, 30, 465.
6. Kapantaidakis, G. C.; Kaldis, S. P.; Dabou, X. S.; Sakellaropoulos, G. P. J Membr Sci 1996, 110, 239.
7. Walsh, D. J.; Zoller, P. Makromol Chem 1987, 188, 2193.
8. Singh, V. B.; Walsh, D. J. J Macromol Sci Phys 1986, 25, 65.
9. Risen, W. M. In Ionomers: Characterization, Theory and Applications: CRC: Boca Raton, FL, 1996.
10. Pak, Y. S.; Xu, G. Solid State Ionics 1993, 67, 165.
11. Yeager, A. L.; Steck, A. J Electrochem Soc 1981, 128, 1880.
12. Scherer, G. G. Ber Bunsenges Phys Chem 1990, 94, 1008.
13. Savadogo, O. J. New Mater Electrochem Syst 1998, 1, 47.
14. NEMROD 3.1; LPRAI, Avenue Gaston Berger, F-13625 Aix-en-Provence, France, 1995.
15. Koenig, J. L. Spectroscopy of Polymers: ACS Professional Reference Book; American Chemical Society: Washington, DC, 1992.
16. Liang, K.; Banhegyi, G.; Grebowicz, J.; McKnight, W. J.; Karasz, F. E. J Polym Sci 1991, 29, 649.
17. Wood, L. A. J Polym Sci 1958, 28, 319.
18. Fox, T. G. Bull Am Phys Soc 1956, 1, 123.
19. Pochan, J. M.; Beatty, C. L.; Pochan, D. F. Polymer 1979, 20, 879.
20. Schneider, H. A. Polymer 1989, 30, 771.
21. Schneider, H. A.; Di Marzio, E. A. Polymer 1992, 33, 3453.