Miscibility behavior of polyamide 11/sulfonated polysulfone blends using thermal and spectroscopic techniques

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Abstract

Miscibility in a series of blends, derived from Polyamide 11 (PA 11) and sulfonated polysulfone (SPSF) with different sulfonation degrees, 20, 44 and 70% has been investigated using differential scanning calorimetry, dynamic mechanical analysis, Fourier transform infra-red (FT-IR) and Raman spectroscopy. The PA 11/SPSF(Na)$_x$ blends were prepared by solution casting from dimethyl formamide (DMF). Differential scanning calorimetry has shown a melting point depression of the equilibrium melting point of PA 11. From the melting point data of the blends of PA 11 with the SPSF with a 70% degree of sulfonation, the value of the polymer–polymer interaction parameter χ_{12} was found to be -1.1 at elevated temperatures where it was determined. Less negative values were obtained for the blends of SPSFs with lower degrees of sulfonation, indicating the role of the sodium sulfonate group to the observed miscibility. Dynamical mechanical analysis revealed a non single-phase system at lower temperatures, although the T_g of PA 11 phase is shifted to higher temperatures. FT-IR and FT-Raman spectroscopic techniques have been used to confirm the nature of the specific interactions involved. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: PA 11/sulfonated polysulfone blends; Miscibility behavior; Polymer–polymer interaction parameter

1. Introduction

The development of new useful blends is severely limited by the complete incompatibility of many polymer pairs of interest [1]. This is due to the inherent tendency of most polymers to demix because of the very small contribution from the entropy of mixing, resulting from the high molecular weight of components. One way to overcome this drawback is the development of specific interactions such as hydrogen bonding, dipole–dipole, ion–dipole, charge transfer and transition metal complexation by introducing specific functional groups to the polymers. Several studies have been carried out concerning the miscibility behavior of polymers bearing polar groups and polyamides [2–4].

In recent years a lot of scientific interest has been directed to ionomers, e.g. polymers containing a small amount of bonded ionic groups. Ionomers are attractive polymers for promoting miscibility with a wide range of other polymers. The ionic functional groups may be used to achieve interactions with complementary functional groups of another polymer. Such interactions are hydrogen bonding, dipole–dipole and ion–dipole. Polystyrene based ionomers (sulfonated polystyrene, SPS) have been extensively used in order to promote miscibility [5,6]. Sulfonated polyesters such as PET have also been used in blends [1,7–9]. In all the above cases, the observed miscibility was attributed to specific interactions between the ionic groups of the ionomer and polar groups on the other polymer. One prominent advantage of this approach is that the strength of the specific interactions and as a result the phase behavior of the resulting blends can be tailored by varying the structure of the ionomer, the functionality level, the acid group and the counterion used.

Polysulfone (PSF) is an engineering thermoplastic with exceptional mechanical properties [10]. Sulfonation of polysulfone resulted in materials bearing functional groups and having high glass transition temperatures. Since SPSF bears polar groups, it can be considered as an ionomer with functional groups that can participate in specific interactions. So, blends of these functionalized polysulfones

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Table 1
Melting point temperatures of PA 11 in its blends with SPSF(Na)$_x$ of different sulfonation degrees

Blend	T_m (°C) of PA 11		
	PA 11/SPSF(Na)$_{20}$	PA 11/SPSF(Na)$_{44}$	PA 11/SPSF(Na)$_{70}$
100/0	188.3	188.3	188.3
90/10	186.9	185.8	184.0
75/25	185.7	184.1	182.5
50/50	182.2	180.9	175.7
25/75	184.6	181.7	179.1

with polyamides are expected to be miscible, having enhanced mechanical properties as well.

In this study, we report on the miscibility behavior of the Polyamide 11/SPSF system. Various sulfonation degrees have been achieved by chemical modification of the polysulfone. Blends in the whole composition range were prepared by solution casting and studied using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), FT-IR and FT-Raman spectroscopy. Analysis of the observed melting point depression led to the estimation of the interaction parameter χ_{12} of the polymer pair studied.

2. Experimental

2.1. Materials and sample preparation

PA 11 was obtained from BDH and dried in a vacuum oven at 120°C for 24 h to remove sorbed water before processing. PSF with an average M_n ca 26 000, was obtained from Aldrich (Europe).

Sulfonated polysulfone was prepared according to the procedure described by Johnson [11] using as a sulfonation agent chlorosulfonic acid instead of a complex of SO$_3$ with triethyl phosphate. The sulfonation levels for the three
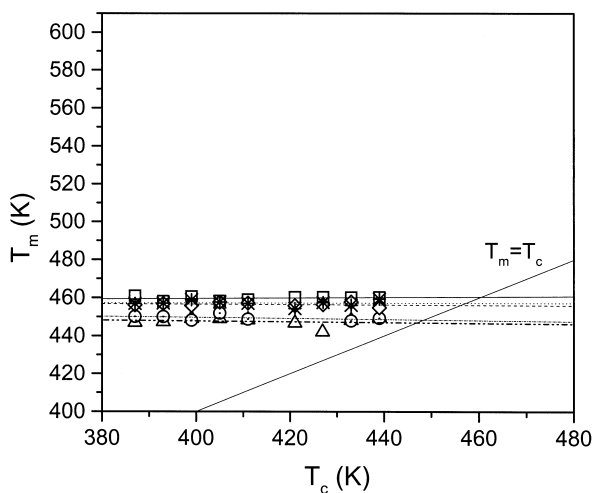
samples prepared were 20, 44 and 70 mol%, respectively, as determined by ^{1}H NMR measurements. The sodium salt (SPSFNa) was prepared by neutralizing the SPSF by sodium hydroxide/methanol solution under vigorous stirring. The precipitated product was filtered, washed several times with ethanol and dried at 120° under vacuum for 2 days. Blends of PA 11/SPSFNa were prepared by solution casting. PA 11 and SPSFNa were dissolved in DMF and stirred for 1.5 h at 160°C. Films of the blends were cast from solution at 100°C and dried at 120°C for 2 days.

2.2. Apparatus and procedures

DSC measurements were carried out in an inert atmosphere using the DSC plus of Rheometrics Scientific. Sample weight was ca 10 mg and heating rate 20°C min^{-1}.

DMA was performed with a solid state Analyzer RSA II, Rheometrics, at 10 Hz. Specimen dimensions were $3.0 \times 0.5 \times 0.01$ cm^3.

IR spectra were measured in the transmission mode on a Bruker Equinox 55 mid-IR spectrometer with sealed and desiccated optics. All spectra were measured at room temperature and represent the average of 50 scans at a resolution of 2 cm^{-1}.

Raman spectra have been recorded with the FT-Raman FRA-106-S module of the Equinox 55 FT-IR spectrometer of Bruker using NIR excitation at 1064 nm.

3. Results and discussion

3.1. Melting temperature

The melting temperatures of PA 11 in its blends with SPSF(Na)$_x$ of three different sulfonation degrees are reported in Table 1 where in all cases, a significant melting point depression is observed. In miscible blends, the melting point of a crystalline component is usually lowered with respect to pure polymer as a result of thermodynamically favorable interactions. The extent of the melting point depression in such systems provides means for measuring the polymer–polymer interaction parameter χ_{12} [12] as described by Nishi and Wang [13]. However, the melting point of a polymer is affected not only by thermodynamic factors but also by morphological parameters such as the crystal thickness. So, in order to eliminate the morphological effects in melting point depression analysis, the equilibrium melting points were estimated.

The equilibrium melting point of a polymer, T_m^0, is determined using the Hoffman–Weeks procedure [14]. This method involves isothermal crystallization of the sample at various temperatures T_c and plotting of the observed melting points T_m, as a function of T_c. The Hoffman–Weeks equation

$$T_m = \eta T_c + (1 - \eta)T_m^0 \qquad (1)$$

predicts a linear relation of T_m vs T_c. The equilibrium

Fig. 1. Hoffman–Weeks plots for PA 11 in its blends with SPSF(Na)$_{70}$ at various compositions: (△) PA 11; (∗) 90/10; (S) 75/25; (W) 50/50; (K) 25/75.

Table 2
Results of the Hoffman–Weeks analysis of the melting behavior of the PA 11 component in PA 11/SPSF(Na)$_{70}$ blends

Blend PA 11/SPSF(Na)$_{70}$	T_m^0 (°C) of PA 11
100/0	187.3
90/10	184.2
75/25	183.2
50/50	175.1
25/75	173.3

melting point T_m^0 is obtained from the intersection of this line with the $T_m = T_c$ equation. The slope of the Hoffman–Weeks plot, η, assumes values between 0 and 1 and may be regarded as a measure of the stability of the crystals undergoing the melting process. The obtained value for η of ca 0, implies that the crystals are perfectly stable ($T_m = T_m^0$ for all T_c), see Fig. 1. This figure shows the Hoffman–Weeks plots for pure PA 11 in the bulk as well as in its blends with SPSF(Na)$_{70}$ and the results are summarized in Table 2. It is seen that, in the blends the equilibrium melting point of PA 11 phase decreases steadily with SPSF(Na)$_{70}$ content. The maximum extent of this melting point depression is 14°C for the 25/75 (PA 11/SPSF(Na)$_{70}$) blend and the T_m^0 of PA 11 is determined to be 173.3°C.

As stated above the diluent effect causing the T_m depression can be treated by the equation of Nishi and Wang [13]:

$$\frac{1}{T_m^0(\text{blend})} - \frac{1}{T_m^0(\text{pure})} = -\frac{RV_1}{\Delta H_f^0 V_2}\chi_{12}\varphi_2^2 \qquad (2)$$

where $T_m^0(\text{pure})$ and $T_m^0(\text{blend})$ are the equilibrium melting points of the pure crystallizable polymer in the bulk and in the blend, respectively, ΔH_f^0 is the heat of fusion of the crystalline component, V and φ are the molar volume and the volume fraction of the components, respectively.
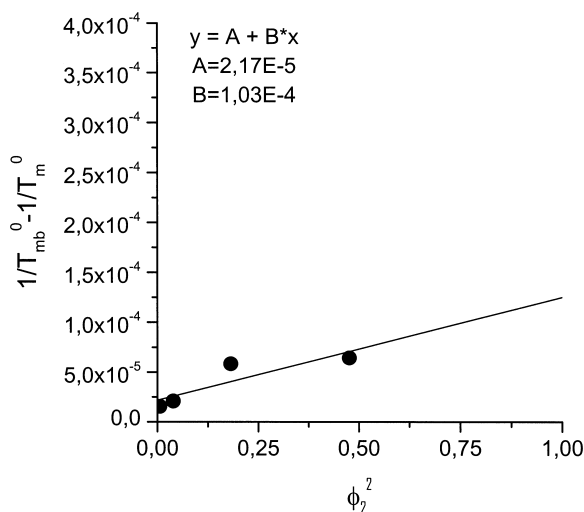

Fig. 2. Melting point depression of PA 11 as a function of blend composition, plotted according to the Nishi–Wang equation.

Subscripts 1 and 2 refer to the crystalline (PA 11) and noncrystalline (SPSFNa) polymers, respectively. If polymer–polymer interaction is independent of blend composition, a plot of the left-hand side of the above equation vs φ_2^2 should give a straight line [15], passing through the origin whose slope may yield the interaction parameter χ_{12}.

In order to calculate the left-hand side of the simplified Nishi–Wang equation from the experimental melting point data, the following constants have been used [16]: $\Delta H_f^0 = 9900$ cal/mol, $V_1 = 175.5$ cm^3/mol, and $V_2 = 364.61$ cm^3/mol (for SPSF(Na)$_{44}$ $V_2 = 378.01$ cm^3/mol and for SPSF(Na)$_{20}$ $V_2 = 389.47$ cm^3/mol). Weight fractions were converted to volume fractions using ρ(Nylon 11) = 1.044 g/cm^3 (calculated based on the crystallinity observed and on the densities of the pure amorphous and pure crystalline polymer—$\rho_{\text{aNylon 11}} = 1.01$ g/cm^3, $\rho_{\text{cNylon 11}} = 1.23$ g/cm^3) and ρ(SPSF(Na)$_{70}$) = 1.41 g/cm^3 (calculated based on the densities of the pure PSF and 100% sulfonated PSF—$\rho_{\text{PSF}} = 1.28$ g/cm^3, $\rho_{\text{SPSF(Na)100}} = 1.47$ g/cm^3) [17]. The plot of the Nishi–Wang equation using the experimental melting point data for PA 11 in its mixtures with SPSF(Na)$_{70}$ is shown in Fig. 2. It is seen that the straight line passing through the experimental points, intercepts the axis at 2.17×10^{-5} with a slope of 1.03×10^{-4}. The fact that this line does not pass through the origin is usually attributed to a residual entropic effect that is neglected in the derivation of the equation. Such results have been previously reported in the literature [18–21]. Considering the value of the intercept as very small, we can derive from the slope of the line obtained, the Flory–Higgins segmental interaction parameter χ_{12}. The obtained value χ_{12} −1.1, indicates strong interactions between the two polymers leading to stable single-phase mixtures at temperatures near the melting point of PA 11 [1,2]. Analogous Hoffman–Weeks analysis has been performed for the blends of PA 11 with SPSF(Na)$_{44}$ and SPSF(Na)$_{20}$, revealing also in these cases, the formation of almost stable crystals giving—according to Eq. (1)—T_m^0s equal to experimental T_ms. Subsequent treatment of pertinent data with Nishi–Wang equation allows us to estimate the values of the interaction parameters for these blends and the results in general are shown in Fig. 3. The χ_{12} of the blends became less negative by reducing the degree of sulfonation, which was consistent with the assumption that the observed miscibility is due to interactions involving the sodium sulfonate.

3.2. Glass transition temperature of the blends

Although PA 11 and SPSF(Na)$_x$ are compatible at elevated temperatures, as indicated by the negative values of the interaction parameters, compatibility should not be taken for granted at lower temperatures because an upper critical solution temperature may exist for the mixtures. The dynamic mechanical properties in terms of the temperature dependence of the storage E' and loss modulus E'' (Fig. 4)
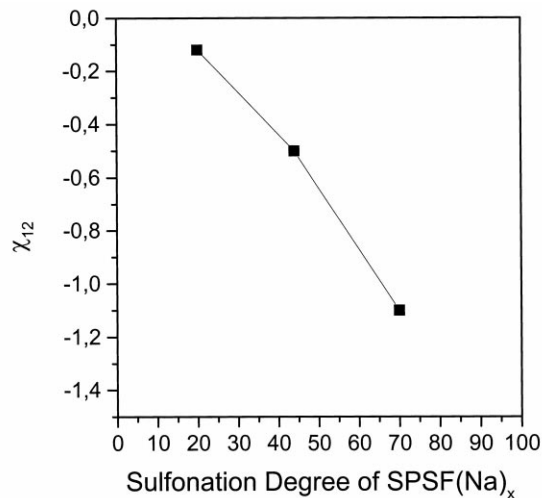
Fig. 3. Interaction parameter χ_{12} for the blends of PA 11 with SPSF(Na)$_x$ as a function of the sulfonation degree.

Table 3
Viscoelastic properties of the blends of PA 11 with SPSF(Na)$_x$ of different sulfonation degrees

Blend	T_g (°C)		
	PA 11/SPSF(Na)$_{20}$	PA 11/SPSF(Na)$_{44}$	PA 11/SPSF(Na)$_{70}$
100/0	54	54	54
90/10	55	57	60
75/25	64	65	87
50/50	70	72	87
0/100	217	229	–

indicated the existence of a PA 11 rich phase in the blends, giving a T_g close to that of the pure polyamide, shifting to higher temperatures as the amount of SPSF(Na)$_x$ is increasing. As we can see in Table 3, there is a systematic shift of the T_g of the blends with the composition, with a maximum of 16°C for PA 11/SPSF(Na)$_{20}$ 50/50 blend, 18°C for PA 11/SPSF(Na)$_{44}$ 50/50 blend and 33°C for PA 11/SPSF(Na)$_{70}$ 50/50 blend. Since PA 11 is melted at temperatures above 170°C (in the blends) and SPSF(Na)$_{70}$ is very brittle, we
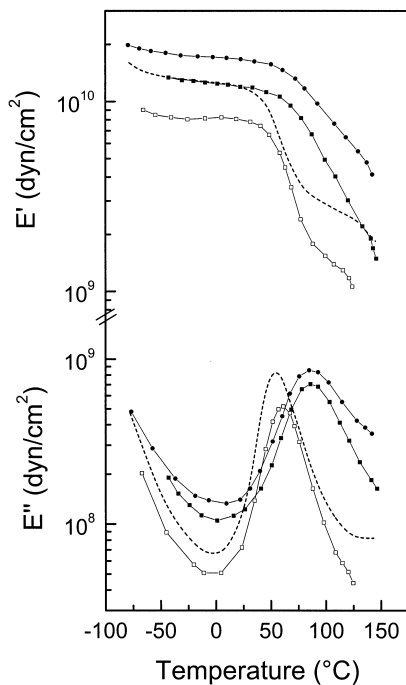
were not able to detect the T_g of the SPSF(Na)$_{70}$ rich phase. Judging from the second break of the $E' - T$ curve observed in some cases, there is evidence that the T_g of the SPSF(Na)$_x$ rich phase shifts to lower temperatures. This mutual shift of the T_gs gives an indication of possible partial miscibility at lower temperatures unlike the miscibility observed in the melt. Although the existence of specific interactions between the blend constituents does not allow the existence of an UCST (Upper Critical Solution Temperature), the situation is more complicated since dissociation phenomena of the clusters of the polysulfone ionomer take place and determine the final behavior of the blend. Another interesting observation is shown in Fig. 5 where the temperature dependence of the storage modulus E' for the blends of PA 11 with SPSF(Na)$_{20}$ and SPSF(Na)$_{44}$ is depicted. As seen there, the 25/75 blend seems to maintain its high modulus up to 150°C, for both cases, showing a behavior similar to pure polysulfone.
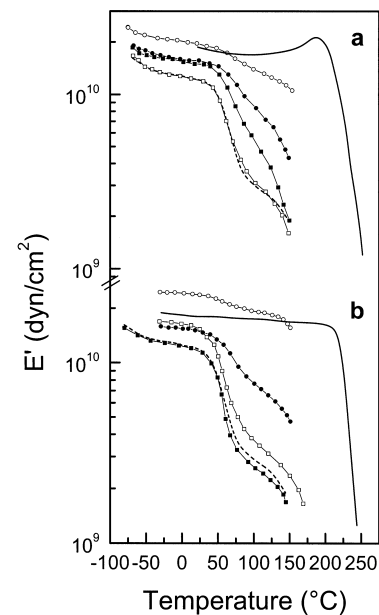

Fig. 4. Temperature dependence of the storage (E') and loss (E'') modulus of the blends of PA 11 with SPSF(Na)$_{70}$: (– – –) PA 11; (Δ) 90/10; (□) 75/25; (✕) 50/50.

Fig. 5. Temperature dependence of the storage modulus (E') of the blends of PA 11 with: (a) SPSF(Na)$_{20}$ and (b) SPSF(Na)$_{44}$: (– – –) PA 11; (Δ) 90/10; (□) 75/25; (✕) 50/50; (∇) 25/75; (—) SPSF(Na)$_x$.
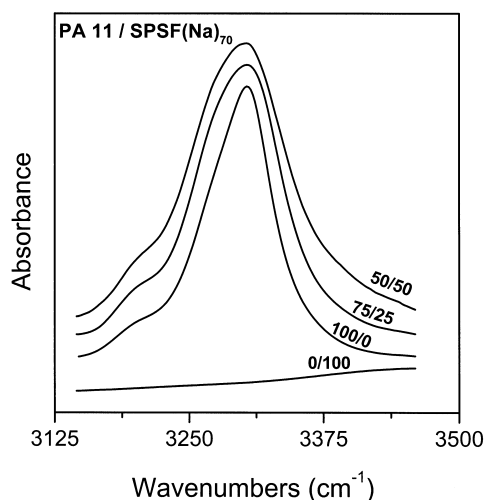
Fig. 6. FT-IR spectra of the blends PA 11/SPSF(Na)$_{70}$ in the N–H region (3400–3200 cm^{-1}).

3.3. Spectroscopic examination

3.3.1. FT-IR examination

In order to confirm the existence and understand the nature of the specific interactions that lead to thermodynamically miscible blends at elevated temperatures, spectroscopic examination was applied. In the region between 3400 and 3200 cm^{-1}, N–H groups of the PA 11 exhibit three characteristic bands. The N–H stretching bands appearing at 3300, 3310 and 3447 cm^{-1} correspond to stretching vibrations of hydrogen bonded N–H in the crystalline phase, hydrogen bonded N–H in the amorphous phase and free N–H groups, respectively [22,23].

The FT-IR spectra of the PA 11/SPSF(Na)$_{70}$ blends shown in Fig. 6 are characterized by an absorption band centered around 3310 cm^{-1} and a small shoulder around 3270 cm^{-1}. Although there is no change in peak maximum, a broadening of the absorption band at 3310 cm^{-1} is clearly
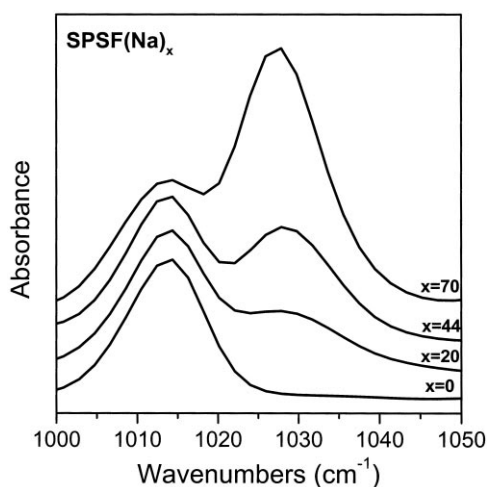

Fig. 7. FT-IR spectra of the SPSF(Na)$_x$ ($x = 0, 20, 44, 70$) in the sulfonate region (1050–1000 cm^{-1}).

observed upon blending. The width at half-height of the peak increases from 65 cm^{-1} in PA 11 to 85 cm^{-1} in the 75/25 blend. The broadening of the N–H stretching region with blending most probably indicates that specific interactions involving the amide and sulfonate groups occur. Analogous behavior has also been observed for other miscible systems such as PA6/sulfonated polystyrene blends [3,24].

Confirmation that the sulfonate group was involved in the interactions was obtained from the changes in the absorption bands characteristic for the stretching vibration of the sulfonate group, in the region 1050–1000 cm^{-1}. FT-IR spectra of polysulfone and SPSFs with different sulfonation degree are given in Fig. 7. The band located at 1014 cm^{-1} and assigned to the symmetric stretching vibration of diphenyl ether unit, should be more or less considered as insensitive to the sulfonation and could be used as an internal standard. So to facilitate comparison, all spectra have been normalized using this peak (the same intensity of the peak at 1014 cm^{-1}). It is clearly shown that the peak at 1028 cm^{-1} due to the symmetric stretching vibration of the sulfonate group is increased as the sulfonation degree is increased [11,25]. The position of this band is very sensitive to the local environment of the sulfonate anion [26], e.g. hydration by moisture or hydrogen bonding by a second component in a polymer blend, so that any interaction would shift the anion symmetric stretching vibration to lower frequencies. In Fig. 8, the FT-IR spectra of the PA 11/SPSF(Na)$_{70}$ blends are shown in the absorption region of 1050–1000 cm^{-1}. The peak at 1014 cm^{-1}, which is attributed to the aryl–ether–aryl stretching vibration, remains almost unaffected upon blending. The absorption band located at 1028 cm^{-1} in pure SPSF(Na)$_{70}$ and attributed to the symmetric stretching vibration of the S–O bond of the sulfonate group is shifted to lower wavenumbers in the blends. As mentioned above, the shift to lower wavenumbers is due to the weakening of the anion–cation interaction. This weakening of the anion–cation interaction observed in the blends is attributed to the specific interactions involving the SO$_3^-$ group, thus to the hydrogen bonding of the sulfonate group with the N–H group as well as to the complexation of the Na$^+$ cations with the carbonyl groups. It should also be noticed that this shift is composition dependent for the blends where the SPSF(Na)$_{70}$ is the minor component. In these cases, the large excess of the amide over the sulfonate groups leads to a situation where most of the existing sulfonate groups participate in interactions. In blends with high SPSF(Na)$_{70}$ content (above 50%), this shift is not present probably due to the fact that the non-interacting groups are predominant, making the differentiation from the interacting ones difficult.

3.3.2. FT-Raman examination

In Fig. 9, the spectral features observed in the region 1050–1000 cm^{-1} for the PSF and the SPSF with different sulfonation degrees have revealed that upon sulfonation a
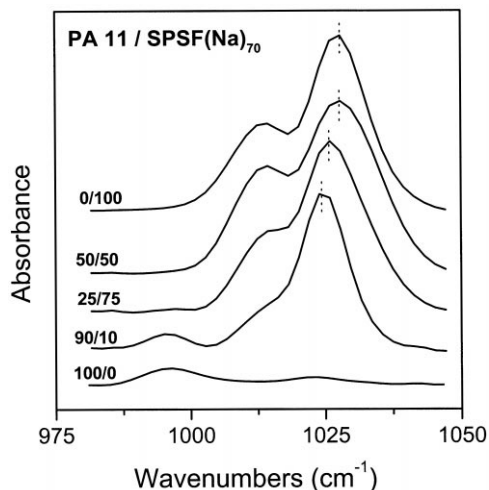
Fig. 8. FT-IR spectra of the blends PA 11/SPSF(Na)$_{70}$ in the sulfonate region (1050–1000 cm^{-1}).

Fig. 10. FT-Raman spectra of the blends PA 11/SPSF(Na)$_{70}$ in the sulfonate region (1050–1000 cm^{-1}).

new peak appears at around 1030 cm^{-1} which is attributed to the symmetric SO$_3^-$ stretching vibration. This vibrational peak as in the case of the FT-IR may be rationed against internal standards, such as either the 1010 cm^{-1} or/and the 793 cm^{-1} bands tentatively attributed to biphenyl ether group stretching along the main chain and to Ar–S–Ar stretching, respectively. FT-Raman spectra of the blends PA-11/SPSF(Na)$_{70}$ in the region 1000–1050 cm^{-1} are depicted in Fig. 10. Since Raman is a complementary technique to IR, the first information that should be obtained is related to the symmetric stretching vibration of the sulfonate group at 1030 cm^{-1}. So, as it is clearly shown in Fig. 10 the peak position at 1030 cm^{-1} in blends is red-shifted as the PA 11 content is increased. Again in blends with high SPSF(Na)$_{70}$ content this shift is hardly noticeable since the non-interacting groups are predominant. This shift to lower wavenumbers may be explained by the presence of specific interactions between the amide and the SO$_3^-$ groups. The
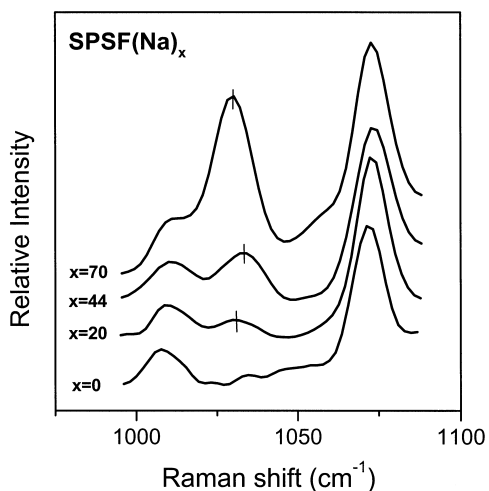
latter observation comes in agreement with the previous ones from the FT-IR study as far as the shift of the peak at 1028 cm^{-1} is concerned, which is directly related to the miscibility behavior of PA 11/SPSF(Na)$_{70}$. For the cases of the blends with SPSF(Na)$_x$ of a lesser degree of sulfonation, it is difficult to make an unambiguous judgement whether the peak at 1030 cm^{-1} shifts or not, since for these cases this peak is reduced in intensity. Also in these cases, the peak at 1010 cm^{-1} obscures interpretation of the spectrum since it is of comparable or even higher intensity than the peak of interest at 1030 cm^{-1} (see Fig. 9).

4. Conclusions

A sodium SPSF ionomer with different degrees of sulfonation and PA 11 formed miscible blends at temperatures close to the melting temperature of PA 11 as indicated by the negative values of the interaction parameter χ_{12} calculated from the melting point depression data. The higher the degree of sulfonation the less negative the interaction parameter, revealing the role of the sodium sulfonate group to the miscibility. FT-IR and FT-Raman spectroscopies were utilized to explore the possible molecular interactions that induced miscibility in these blends. These interactions are probably specific interpolymer interactions occurring between Na$^+$ and the oxygen of the carbonyl group and hydrogen bonding involving the sulfonate anion and the NH-group of the amide.

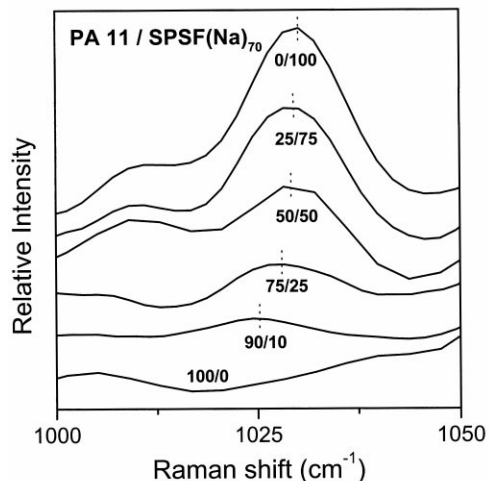Fig. 9. FT-Raman spectra of the SPSF(Na)$_x$ ($x = 0$, 20, 44, 70) in the sulfonate region (1050–1000 cm^{-1}).

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