

University of Massachusetts Amherst

From the Selected Works of William MacKnight

1994

Compatibility Enhancement of Blends of Nylon 4 with Lithium-Neutralized Sulfonated Polystyrene

William MacKnight, *University of Massachusetts Amherst*

C. -W. Alice Ng

Michelle A. Bellinger



Available at: https://works.bepress.com/william_macknight/274/

Compatibility Enhancement of Blends of Nylon 4 with Lithium-Neutralized Sulfonated Polystyrene

C.-W. Alice Ng, Michelle A. Bellinger,[†] and William J. MacKnight*

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

Received June 7, 1994*

ABSTRACT: A polymer/ionomer blend of nylon 4 (N4) with lithium-neutralized sulfonated polystyrene (SPS-Li) was investigated. Thermal analysis techniques (DSC and DMTA) were employed to examine the extent of compatibility of this multiphase polymer blend system. Particular efforts have been focused on the influence of the level of crystallinity of the N4 component and the water contents in the blends in relation to the phase behavior of the system. DSC and DMTA results show that blend compatibilization was achieved over the entire composition range by virtue of the presence of the specific intermolecular interactions between the amide groups and the lithium sulfonate groups. DSC and WAXD experiments revealed that "dry" samples with a higher level of crystallinity exhibit consistently higher T_g 's than those with lower crystallinity. Samples with different water contents were examined by DMTA. In comparison with the "wet" blends, it is found that the T_g 's are significantly higher for the "dry" blends. It is postulated that the increase in T_g upon drying/annealing is due to the combined effects of (a) suppression of the plasticization effect upon removal of water from the samples and/or (b) the increase in the crystallinity of the N4 component depending whether the compatible blends are in the semicrystalline/amorphous or amorphous/amorphous state.

Introduction

The development of polymer blend systems continues to be an important and versatile tool in designing new materials with tailored properties. The challenges of this method are to overcome the low entropy of mixing and the unfavorable enthalpy of mixing of most high molecular weight polymers due to the lack of specific interactions. One general approach to tackle this problem is to incorporate ionic moieties along either or both polymer chains to provide specific sites for intermolecular interactions between the otherwise immiscible polymer pair. These ion-containing polymers or ionomers constitute an interesting class of materials with a unique combination of covalent hydrocarbon polymer chains and ionic salt species in the same molecule. The ionic salt species are capable of interacting with other polymer chains through various types of interactions such as acid/base,^{1,2} hydrogen bonding,³ ion/dipole,⁴ or transition metal complexation⁵⁻⁸ to promote the compatibilization of otherwise immiscible polymers.

In recent years, polymer blends of nylon 6 (N6) with a lightly sulfonated polystyrene have been the focus of several studies.^{9,10} Results showed that enhanced compatibility was observed, the degree of which depends upon the choice of the counterions of the ionomer and the ion content or the distance between the ionic moieties along the polymer chains. In this study, another member of the nylon family, polyamide 4 or nylon 4 (N4), is explored. N4 has a higher amide group frequency than that of N6, namely 20 vs 14.3 amide groups per 100 chain atoms.¹¹ With the increase in the amide group frequency and thus the amount of hydrogen bonding, it is obvious that N4 will crystallize more readily to yield a higher melting transition and a higher level of crystallinity than N6. In blending N4 with lightly sulfonated polystyrene, it is interesting to examine how the extent of compatibility via the specific intermolecular interactions is influenced by the competing crystallization of the N4 component in the matrix and vice versa. Lithium was chosen as the

counterion of the ionomer partly because interactions between lithium cations and amide functional groups have been shown to be favorable based on a small-molecule study.¹² However, it is cautioned that when the same principle is applied to high molecular weight polymer systems, factors such as the proximity of the interacting groups, polymer chain conformations, and mobility should be taken into consideration. Despite the complexities involved with long-chain molecules, favorable mixing has been observed for blends of N6 with SPS-Li.⁹

The challenges inherent in the N4/SPS-Li blend system are the high water affinity, in particular that of N4, the extremely fast crystallization rate of the N4 component, and the thermal instability near its melting point.¹³ However, the extremely high moisture sensitivity of N4 (about 28% absorption at 99% relative humidity), which is similar to that of cotton in its absorbance over the whole range of relative humidities,¹³ renders it an interesting material for blend study, especially in textile applications. In this investigation, thermal analysis techniques, differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA), are employed to examine the degree of compatibility of this multiphase polymer blend system. The wide-angle X-ray diffraction (WAXD) technique is used to examine the crystalline structure of N4 in the blend matrix. The degree of crystallinity of N4 and any modification of the crystal structure within the matrix will be examined with respect to their impact on the compatibilization of the two otherwise immiscible polymers. Due to the high water affinity of the N4 component, additional studies are necessary to examine the role of water on the blend compatibilization.

Experimental Section

Materials Used. Nylon 4 (polypyrrolidone) was purchased from Barson Corp. It was purified by dissolving in formic acid and precipitating into distilled deionized water. Atactic polystyrene (PS) was purchased from Polymer Laboratories Ltd. The weight-average molecular weight of PS is 115 000 and the polydispersity index is less than 1.04. PS was sulfonated using the method of Makowski et al.¹⁴ The degree of sulfonation was

[†] Present address: Spalding Sports Worldwide, Chicopee, MA 01021.

* Abstract published in *Advance ACS Abstracts*, October 1, 1994.

found to be 9.7 mol % by titration and was confirmed by elemental analysis.¹⁵ The sulfonated PS in acid form was subsequently neutralized with lithium hydroxide to yield SPS-Li. All other chemicals and solvents were obtained from Fisher Scientific. They were used without further purification except *m*-cresol, which was purified by simple distillation.

Molecular Weight Determination of Nylon 4. Viscometric measurements were performed to determine the viscosity-average molecular weight (M_v) of N4. The intrinsic viscosity $[\eta]$ was determined in *m*-cresol at 25 °C using a Cannon-Ubbelohde viscometer. $[\eta]$ was found to be 4.39 dL/g. Using the Mark-Houwink equation, $[\eta] = K(M_v)^a$, where K and a are equal to 3.98×10^{-4} dL/g and 0.77, respectively,¹⁶ it was found that M_v is equal to 178 000.

Blend Preparation. N4/SPS-Li blends with compositions of 90/10, 70/30, 50/50, 30/70, and 10/90 (w/w) were prepared. Weighed amounts of N4 and SPS-Li were dissolved separately in a solvent mixture of 80/20 (v/v) *m*-cresol/methanol at room temperature to yield a 5% (w/v) solution. The polymer solutions were mixed in a nitrogen atmosphere at 60 °C to lower the solution viscosity for enhanced mixing. After 6 h of mixing, the blend was isolated by precipitating into hexane and was further Soxhlet extracted in hexane for 5 days to remove most of the *m*-cresol. The products were dried at 60 °C under vacuum for 1 week. They were then ground to a fine powder at cryogenic temperature. To remove the residual amount of *m*-cresol, the powdered samples were further heated to 130 °C for 20 h under vacuum. The homopolymers, N4 and SPS-Li, and an unmodified blend of N4/PS-50/50 were treated under identical conditions as the blends for purposes of comparison.

TGA Measurements. A Perkin-Elmer TGA-7 was used to obtain the thermal gravimetric measurements in a nitrogen atmosphere. Isothermal scans were performed at 130 °C to determine the water content of the samples. Thermal scans from 25 to 550 °C at a rate of 20 °C/min were also made to determine if there was residual solvent such as *m*-cresol remaining in the samples after drying.

DSC Measurements. A Perkin-Elmer DSC-7 was used to obtain the DSC thermograms and was calibrated with indium. Experiments were run with samples ranging from 10 to 15 mg under a dry nitrogen purge to prevent moisture and oxidative degradation. All samples were first heated to +275 °C for 1 min at a rate of 20 °C/min and quickly quenched to -20 °C to destroy the thermal history. They were then scanned from -20 °C to +275 °C at a rate of 20 °C/min. The glass transition temperatures (T_g) were taken as the midpoint of the change in heat capacity. The melting temperatures (T_m) were taken as the peaks of the endotherms. The heats of fusion (ΔH_m) were measured by calculating the area under the melting endotherms and were normalized per gram of N4 in the blends.

DMTA Measurements. The dynamic mechanical properties of the blends were measured using a Polymer Laboratories PL-DMTA instrument at a frequency of 1 Hz. The samples were prepared by compression molding under low pressure in a nitrogen atmosphere at 275 °C for 1 min to erase the thermal history and were quenched between two cold metal plates. The sample sizes were approximately $2.5 \times 1.2 \times 0.5$ mm³. Experiments were performed in a single-cantilever mode using a 2-mm free length from -110 to 200 °C at a rate of 2 °C/min. The glass transition temperatures were taken as the peaks in the $\tan \delta$ plots.

WAXD Measurements. A wide-angle X-ray diffractometer with Cu $K\alpha$ radiation was used to obtain diffractograms. The instrument was operated at an accelerating voltage of 39 kV and a current of 30 mA. The angular range scanned was between $2\theta = 2$ and 44°. The step size was 0.1° with a sampling time of 60 s per increment. All measurements were obtained with samples prepared in a similar manner to those of the DMTA samples.

Results and Discussion

TGA Study. As mentioned previously, the homopolymers, N4 and SPS-Li, are highly water-sensitive materials, the structures and the physical properties of which are likely to be affected to various extents by the amount of water present. Additionally, N4 is thermally unstable at elevated temperatures.¹³ Therefore, extreme caution was

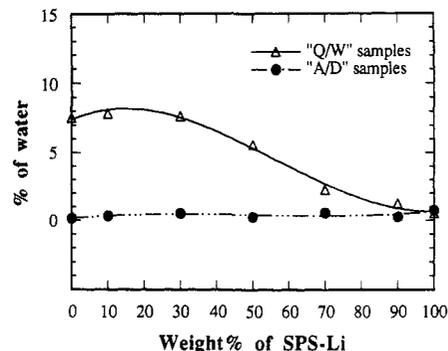


Figure 1. Determination of water content of Q/W and A/D samples by TGA measured at 130 °C in a dry nitrogen atmosphere.

necessary to monitor the water content of the samples and their integrity upon vigorous drying at a high temperature.

Two drying procedures were developed to prepare samples with different water contents. After samples were compression molded, they were dried either (a) at room temperature under vacuum in the presence of anhydrous phosphorus pentoxide (P_2O_5) or (b) at 130 °C for 10 h under vacuum. Samples that were treated with method a are designated as "quenched/wet" samples ("Q/W") while those with method b are designated as "annealed/dry" samples ("A/D"). All the treated samples were subjected to TGA measurements to determine the final water content, and the results are summarized in Figure 1. It is clear that high-temperature drying is capable of removing virtually all the water from the samples. However, it is cautioned that the drying treatment would cause the N4 component in the blend to further crystallize and thus lead to changes in the properties of the crystalline and amorphous phases. In view of the complications induced by the crystallinity effect of N4 and the water content effect, the phase behavior of the blend system will be addressed with respect to these two variables.

DSC Study. In this part of the study, the crystallinity effect of N4 is examined in relation to the phase behavior of the blend system. The samples examined here are considered to be in their driest state. Samples with two levels of crystallinity were prepared. The low-crystallinity samples, designated as "quenched" samples, were obtained by cooling rapidly from the molten state at 275 °C in the DSC chamber. The high-crystallinity samples, designated as "annealed" samples, were obtained by first cooling rapidly from the molten state at 275 °C to -20 °C and subsequently heating at 130 °C for 10 h.

DSC thermograms showing the glass transitions of the quenched and annealed samples are depicted in Figure 2, and the T_g values are summarized in Table 1. It is observed that both sets of the samples exhibit one broad T_g intermediate to those of their homopolymer constituents. One exception is the 70 wt % N4 blends which show two partially resolved T_g 's which become more prominent upon annealing. Unlike the N4/SPS-Li blends, the unmodified N4/PS-50/50 blend, not shown here, displays two distinct T_g 's characteristic of the two homopolymer constituents. This suggests that N4 is made compatible with SPS-Li in the amorphous phase by virtue of the specific intermolecular interactions between the amide groups and the lithium sulfonate groups over the entire composition range. However, the partial phase separation observed in the 70 wt % N4 blends is not well understood.

Further evidence regarding the enhanced compatibilization of the N4/SPS-Li blends can be discerned from the melting and crystallization behavior of the N4

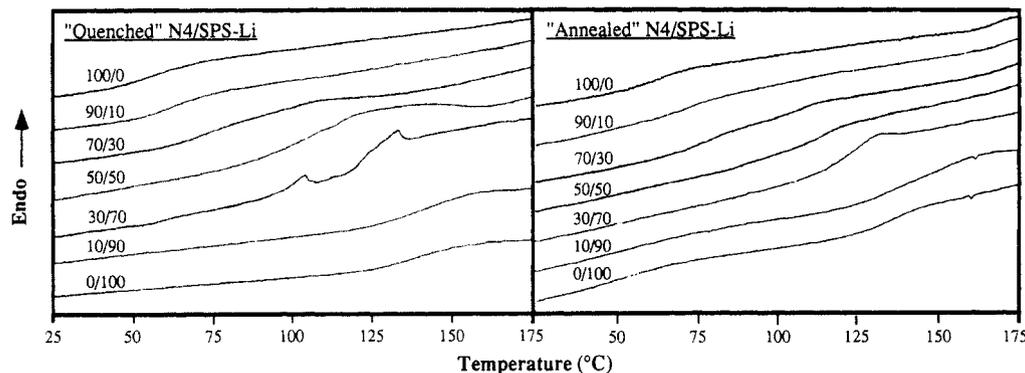


Figure 2. DSC thermograms showing the glass transition behavior of the quenched and annealed N4/SPS-Li blends.

Table 1. T_g 's, T_m 's, and ΔH_m 's for Quenched and Annealed Blends Determined by DSC

N4/SPS-Li	quenched samples			annealed samples		
	T_g (°C)	T_m (°C)	ΔH_m^a (J/g)	T_g (°C)	T_m (°C)	ΔH_m^a (J/g)
100/0	55	263	63	61	265	69
90/10	63	264	66	70	264	63
70/30	79	258	57	90	261	65
50/50	104	255	54	110	253	60
30/70	121			120	235	8
10/90	140			141		
0/100	139			135		
N4/PS-50/50	57	263	62	62	263	70
	100			104		

^a ΔH_m is normalized per gram of N4 in the blends.

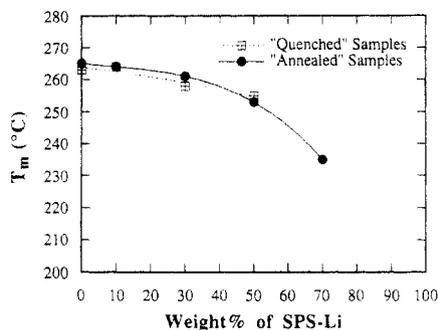


Figure 3. Melting depressions of the quenched and annealed N4/SPS-Li blends.

component in the blend matrix. It is worth noting that, owing to the extremely fast crystallization rate, completely amorphous N4 is practically impossible to obtain. However, as shown in Figure 3 and Table 1, both the quenched and annealed blends show a monotonic decrease of T_m with increasing SPS-Li content in the matrix. The blends are rendered completely amorphous when the N4 content reaches the critical limit of 50 wt % in the quenched blend matrices and 30 wt % in the annealed blend matrices. The difference in the critical limit between the quenched and annealed blends is probably due to the further crystallization of N4 upon annealing. The comparison between the N4/SPS-Li-50/50 and N4/PS-50/50 blends provides additional evidence for the suppression of the crystallization of N4 due to the enhanced mixing. From Table 1, melting behavior shows that the T_m of the modified blend is depressed by 10 °C while that of the unmodified blend indicates no changes as compared to the pure N4. This further supports that the enhanced compatibilization of the N4/SPS-Li blends via the specific interactions is achieved and manifested by a significant modification of the melting and crystallization behavior of the N4 component in the compatible blends.

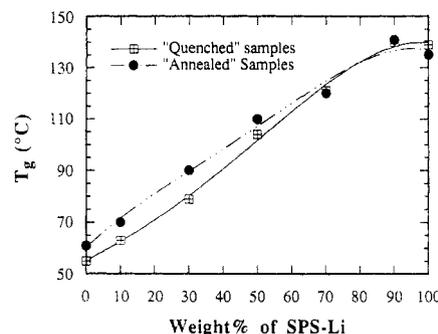


Figure 4. Comparison of the T_g 's as a function of blend compositions between the quenched and annealed N4/SPS-Li blends.

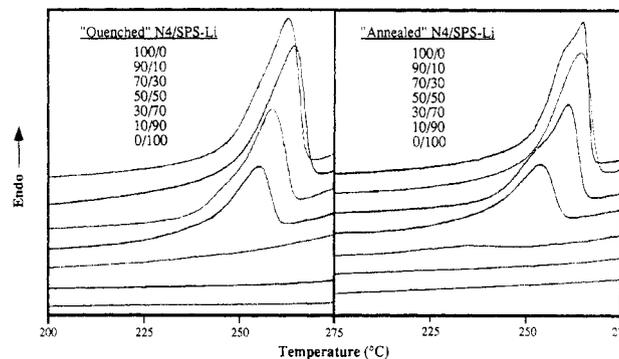


Figure 5. Melting behavior of the quenched and annealed N4/SPS-Li blends determined by DSC.

The T_g values of the annealed samples are consistently higher than those of the quenched samples when the blends are in the semicrystalline/amorphous state. However, no differences are observed when the blends are in the amorphous/amorphous state. These results are summarized in Figure 4 and Table 1. The differences found in the T_g values of the quenched and annealed samples may be attributed to the preferential enrichment of the SPS-Li component in the mixed amorphous phase when the N4 component in that phase undergoes crystallization as shown from the increase in the normalized ΔH_m upon annealing at a high temperature. However, the extent of the increase might be underestimated due to the melting/crystallization activity occurring at temperatures above T_g . A better estimate could possibly be obtained from the WAXD analysis and will be discussed later. DSC thermograms of the melting behavior of the quenched and annealed samples are shown in Figure 5, and the values of T_m and ΔH_m are summarized in Table 1. It is observed that there is an overall increase in the contribution of the lower melting endotherms in the annealed samples. This could possibly be associated with the growth of the less

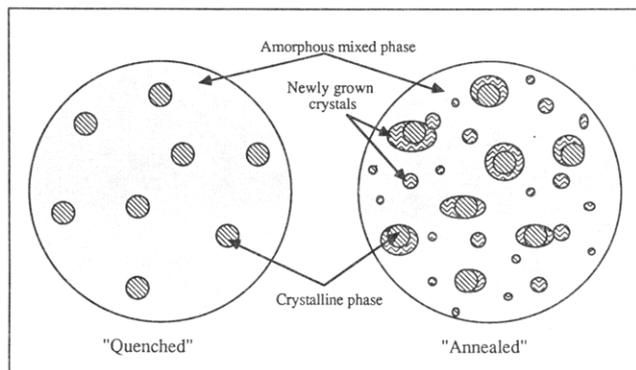


Figure 6. Schematic illustration of the morphological changes that might be encountered in the quenched and annealed N4/SPS-Li blends.

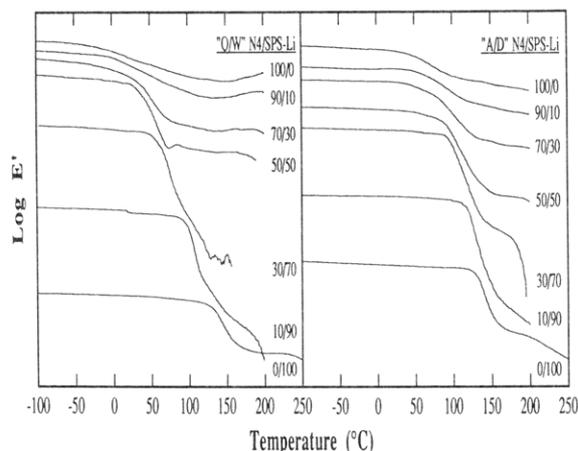


Figure 7. Temperature dependence of storage modulus ($\log E'$) for the Q/W and A/D N4/SPS-Li blends recorded at 1 Hz at a scan rate of 2 °C/min.

perfect crystals or crystals of different sizes within the blend matrix upon annealing. It is further speculated that these newly grown crystals could act, in part, as small cross-links to stiffen the amorphous mixed phase and contribute to the increase in T_g . A schematic diagram, shown in Figure 6, is proposed to illustrate the morphological changes occurring for the quenched and annealed N4/SPS-Li blends in the semicrystalline/amorphous state.

DMTA Study. In this part of the study, the storage modulus and the loss characteristics of the compatible blends are examined. It is anticipated that the analysis can provide further insight into the blend morphologies and the nature of the specific interactions which leads to the enhanced compatibilization. Due to the high water affinity of the N4 component in the blends, additional studies are necessary to examine the role of water on the blend compatibilization.

The moduli of the compatible blends are examined. Figure 7 shows the temperature dependence of the storage modulus of the Q/W and A/D N4/SPS-Li blends. Both homopolymers, N4 and SPS-Li, show an extended rubbery plateau above T_g , characteristic of a physically cross-linked network due to either the crystalline structure of N4 or the microphase separation of the ionic aggregates of SPS-Li. For the Q/W blends, with the addition of SPS-Li into the N4 matrix, the width of the rubbery plateau decreases, which indicates that the cross-linked networks of the two polymers are gradually disrupted by the intimate mixing. In particular, for the N4/SPS-Li-30/70 and -10/90 blends, their cross-linked networks are completely destroyed by the favorable mixing of the two polymers via the specific

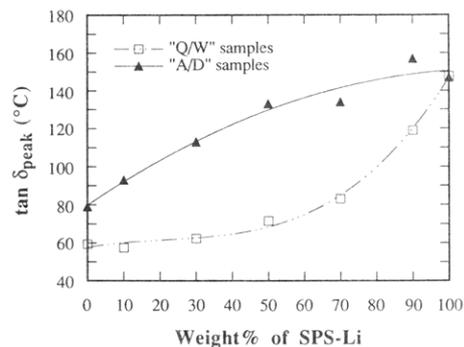


Figure 8. Comparison of the $\tan \delta$ peak values as a function of blend compositions between the Q/W and A/D N4/SPS-Li blends.

interactions as evidenced by the complete elimination of the rubbery plateau region. In addition, blends containing up to 50 wt % N4 show a slight increase in the plateau modulus above T_g . This could be due to some crystallization occurring at temperatures above T_g . In contrast, such an increase in modulus is not observed in the case of A/D blends as shown in Figure 7, probably because the A/D samples are previously treated at 130 °C, during which the N4 component has achieved its equilibrium crystallinity upon annealing. The A/D blends exhibit similar disruption of their rubbery plateaus upon blending, though a very small plateau can be found for the N4/SPS-Li-30/70 and -10/90 blends, probably as a result of annealing.

The $\tan \delta$ spectra of both the Q/W and A/D blends are examined. Figure 8 shows the composition dependence of the $\tan \delta$ peak values of the α -relaxation for the Q/W and A/D blends. It is found that the $\tan \delta$ peak values for the A/D samples are significantly higher than those of the Q/W samples, with the greatest differences being observed for samples containing 70, 50, and 30 wt % of N4 component. This strongly suggests that the water molecules act as a plasticizer within the Q/W blend matrices. More interestingly, it is observed that Q/W N4 and Q/W N4/SPS-Li-90/10 blend, which have the highest water contents, do not correspondingly exhibit the largest suppression of $\tan \delta$ peak values by virtue of the plasticization effect. It is thus speculated that plasticization might not be the only molecular mechanism that affects the relaxation behavior of the matrices. DSC studies indicate that in the absence of water T_g increases when the samples are subjected to high-temperature annealing. It is therefore believed that the changes in the phase compositions and hence the blend morphologies upon high-temperature annealing/drying are likely to influence the relaxation behavior to some extent. Evidence is to be found by examining the shape and broadness of the α -relaxation processes of the N4/SPS-Li blends.

Figure 9 shows the temperature dependence of the $\tan \delta$ for the Q/W and A/D samples. For the pure N4 and N4/SPS-Li-90/10 blend, the $\tan \delta$ peaks are much broader and less well-defined for the Q/W samples than those for the A/D samples. It is probable that the peak broadening, extending to the subzero temperatures, is a result of the relaxation of a broad range of microenvironments possibly created by the selective distribution of water molecules within the Q/W blend matrices. This supposition is substantiated by the following finding. Figure 10 shows the temperature dependence of the $\tan \delta$ spectra of pure N4 with different levels of water content. The sample with the highest water content of 13.6% exhibits a strong relaxation at around 0 °C with an extended shoulder near 60 °C. As the water content of the sample is reduced to 7.5%, the intensities of both the high-temperature and

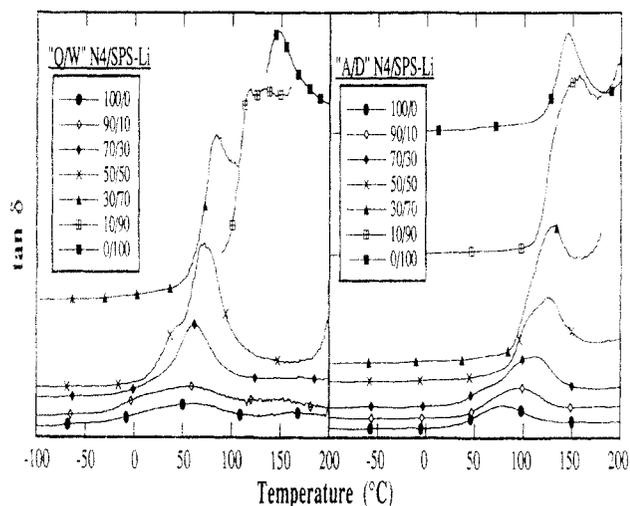


Figure 9. Dynamic mechanical spectra ($\tan \delta$) of the Q/W and A/D N4/SPS-Li blends recorded at 1 Hz at a scan rate of 2 °C/min.

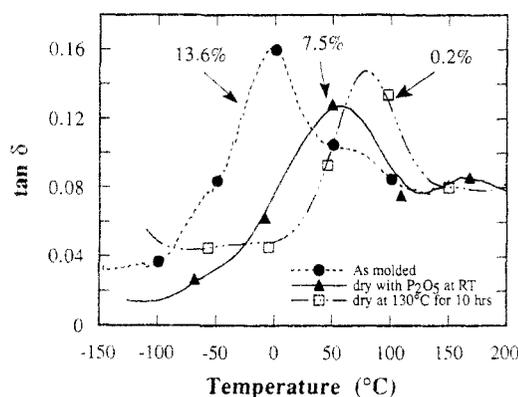


Figure 10. Dynamic mechanical spectra ($\tan \delta$) of pure N4 with different levels of water content recorded at 1 Hz at a scan rate of 2 °C/min.

low-temperature peaks become similar in magnitudes and hence they evolve into a broad peak. When the water content decreases to near 0%, the high-temperature peak becomes much narrower and distinct with a peak value at around 80 °C while the low-temperature peak disappears. The series of transitions observed due to the differences in water content are explained as follows. The low-temperature peak at around 0 °C is attributed to the relaxation process characteristic of the wet region of the polymer matrix. The accompanying shoulder at a higher temperature around 60 °C is probably associated with the relaxation behavior of the partially dried region of the matrix which results from the evaporation of water during the course of heating. When the water content decreases further, the high-temperature peak grows in intensity and shifts upward while the low-temperature peak gradually collapses. Finally, when the sample is close to its driest state, the high-temperature peak shifts further upward with the complete extinction of the low-temperature peak. Hence, it is believed that the suppression and the broadening of the α -relaxation processes of the Q/W N4 and N4/SPS-Li-90/10 blend to lower temperatures are mainly due to the plasticization by the water molecules. More quantitative studies on the effects of water on N4 are reported by this laboratory.¹⁷

Similar broad peaks are observed for the N4/SPS-Li-70/30 and -50/50 Q/W blends. Upon drying/annealing, the peaks are shifted to a higher temperature with a shoulder appearing at the low-temperature side. The overall upward shift of the peak temperature, on the one

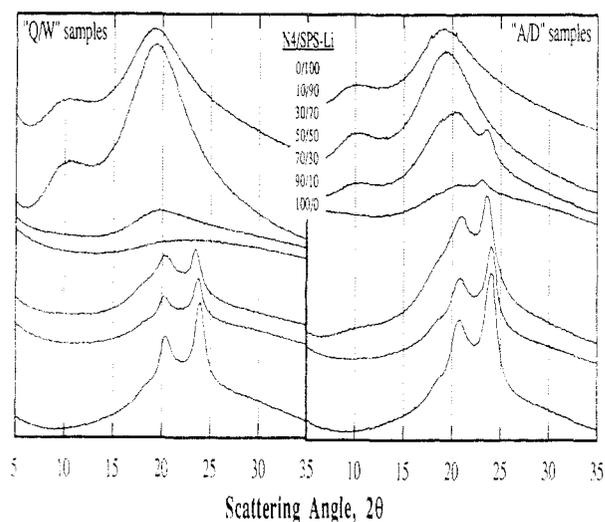


Figure 11. Wide-angle X-ray scattering profiles of Q/W and A/D N4/SPS-Li blends.

hand, is related to the suppression of the plasticization mechanism due to the absence of water molecules as discussed above. On the other hand, the change in the peak shape suggests that a partial phase separation might take place upon annealing/drying. This is possible due to a preferential enrichment of the SPS-Li component occurring in the mixed phase as the N4 component crystallizes during the annealing/drying process. Therefore, it is believed that such a change in the phase composition would further contribute to the shift of the T_g to higher temperatures.

For the SPS-Li-rich blends, the peaks are shifted to considerably higher temperatures and are slightly broadened for the A/D samples compared to those for the Q/W samples. Unlike the N4-rich blends as described above, this group of blends remains highly amorphous after the annealing/drying process as revealed by DSC studies. Hence it is unlikely that there is any crystallization affecting the relaxation to any significant extent. Instead, the peak broadening could be an indication of the morphological changes which contribute to the enormous change in the $\tan \delta$ peak value in addition to the major plasticization effect. However, it is noted that the pure SPS-Li exhibits no significant changes in the peak position and peak width between the Q/W and A/D samples. Therefore, it is interesting to find that with the incorporation of 30 wt % or less N4 into the SPS-Li matrix, the properties of the latter can be dramatically modified by only a few percentage of water present in the blends.

WAXD Study. WAXD analysis is used to probe the changes in the crystalline phase upon blending. The measurements are capable of providing more representative information about the phase behavior of the blends without the accompanying thermal effect imposed during the course of the experiments.

Figure 11 shows the WAXD patterns of both the Q/W and A/D N4/SPS-Li blends. Due to the overlap of the scattering from the crystalline component of N4 with that from the amorphous halos which consist of both the N4 and SPS-Li, it is very difficult to estimate the degree of crystallinity with reasonable precision. However, the WAXD patterns qualitatively show a significant increase in the degree of crystallinity of the N4 component upon drying/annealing at 130 °C. This confirms the results obtained from DSC studies that the depletion of the N4 component in the amorphous mixed phase is significant and leads to an increase in the T_g of the blends. For the

Table 2. WAXD Analysis of Q/W and A/D N4/SPS-Li Blends

N4/SPS-Li	Q/W samples		A/D samples	
	$d(200)^a$	$d(020)^a$	$d(200)^a$	$d(020)^a$
100/0	4.33	3.71	4.25	3.71
90/10	4.37	3.75	4.27	3.71
70/30	4.37	3.80	4.25	3.77
50/50			4.31	3.87
30/70			4.37	3.77
10/90				
0/100				
N4/PS-50/50	4.35	3.73	4.33	3.75

^a d represents the spacings of N4 crystal planes in angstroms.

Q/W samples, crystalline scattering can only be detected up to 70 wt % of N4, unlike the results obtained from DSC that crystallinity can be detected up to 50 wt % of N4, which is probably due to the further crystallization of N4 during the thermal heating above T_g in the DSC chamber. The WAXD pattern of the Q/W N4 shows two strong reflections from the (200) and (020) crystal planes at spacings 4.33 and 3.71 Å, respectively. The (200) and the (020) plane spacings are characteristic of the polyamides for their interchain distance within a hydrogen-bonded sheet and the intersheet distance, respectively.^{18,19} The addition of the SPS-Li component to N4 results in an increase in the d -spacings of the (200) and (020) crystal planes of N4 as shown in Table 2. With the observed small change in the d -spacings, it is highly unlikely that the sulfonate groups of the SPS-Li component can fit easily in the tight crystalline matrix. However, such change could be associated with the modification of the nature of the amorphous phase as a result of the enhanced mixing of the N4 and SPS-Li components. It is also noted that the scattering patterns become more diffuse upon annealing. This could be due to the growth of new N4 crystals of increased disorder because of the constraints imposed by the specific interactions with the SPS-Li components. As mentioned above, these new crystals residing in the amorphous phase could potentially act as small cross-links to stiffen the amorphous mixed phase and contribute to the increase in T_g .

Conclusion

N4 is made compatible with SPS-Li in the amorphous phase by virtue of the specific intermolecular interactions between the amide groups and the lithium sulfonate groups over the entire composition range as evidenced by the T_g measurements using DSC and DMTA. The presence of a small amount of water is found to profoundly affect the dynamic mechanical properties of the compatible blends as shown by the depression of T_g 's by DMTA. The subsequent removal of water from the blend matrices suppresses the plasticization effect exerted by the water molecules. However, the drying treatment leads to a further crystallization of the N4 component which in turn results in changes in the morphologies and properties of the crystalline and amorphous phases. As shown from the DSC and WAXD studies, an increase in the level of

crystallinity of the N4 component in the blends leads to an increase in the T_g 's by means of the preferential enrichment of the amorphous phase by the SPS-Li component and the stiffening effect due to the growth of the less ordered N4 crystals upon annealing. Therefore, it is believed that both the increase in the level of crystallinity and the suppression of the plasticization contribute to the increase in the T_g 's of the blends upon drying/annealing, the degree of which depends whether the blends are in the semicrystalline/amorphous state or amorphous/amorphous state. In addition to the T_g measurements, the blend compatibilization is manifest by the significant modification or suppression of the melting and crystallization of the N4 component in the blends as observed by DSC. Additionally, the moduli of the compatible blends decrease, indicating the disruption of the physically cross-linked network, characteristic of the homopolymers, due to the intimate mixing of both polymers.

Acknowledgment. The authors would like to acknowledge the financial support received from the Materials Research Laboratory at the University of Massachusetts, supported by the National Science Foundation through Grant NSF-DMR-9023848. Thanks are due Dr. A. J. Waddon for his technical assistance with the WAXD experiments.

References and Notes

- Zhou, A. L.; Eisenberg, A. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 223.
- Natansohn, A.; Murali, R.; Eisenberg, A. *Makromol. Chem., Macromol. Symp.* **1988**, *16*, 175.
- Otocka, E. P.; Eirich, F. R. *J. Polym. Sci., Part A-2* **1968**, *6*, 895, 913.
- Hara, M.; Eisenberg, A. *Macromolecules* **1984**, *17*, 1335.
- Peiffer, D. G.; Duvdevani, I.; Agarwal, P. K.; Lundberg, R. D. *J. Polym. Sci., Polym. Lett. Ed.* **1986**, *24*, 581.
- Agarwal, P. K.; Duvdevani, I.; Peiffer, D. G.; Lundberg, R. D. *J. Polym. Sci., Part B* **1987**, *25*, 839.
- Lundberg, R. D.; Phillips, R. R.; Peiffer, D. G. *J. Polym. Sci., Part B* **1989**, *27*, 245.
- Clark, J. N.; Higgins, J. S.; Peiffer, D. G. *Polym. Sci. Eng.* **1992**, *32*, 49.
- Molnar, A.; Eisenberg, A. *Macromolecules* **1992**, *25*, 5774.
- Lu, X.; Weiss, R. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (2), 616; *Macromolecules* **1992**, *25*, 3242.
- Mark, H. T.; Gaylord, N. G.; Bikales, N. M., Eds. *Encyclopedia of Polymer Science and Technology*; Interscience: New York, 1969; Vol. 10, p 400.
- Balasubramanian, D.; Misra, B. C. *Biopolymers* **1975**, *14*, 1019.
- Mark, H. T.; Gaylord, N. G.; Bikales, N. M., Eds. *Encyclopedia of Polymer Science and Technology*; Interscience: New York, 1969; Vol. 10, p 573.
- Makowski, H. S.; Lundberg, R. D.; Singhal, G. H. U.S. Patent 3870841, 1975.
- The elemental analysis was performed at the Microanalysis Laboratory at the University of Massachusetts, Amherst.
- Tuzar, Z.; Kleteckova, J.; Kralicek, J. *Collect. Czech. Chem. Commun.* **1974**, *39*, 2206.
- Bellinger, M. A.; Ng, C.-W. A.; MacKnight, W. J., in preparation.
- Fredericks, R. J.; Doyne, T. H.; Spragne, R. *J. Polym. Sci., Part A-2* **1966**, *4*, 913.
- Bellinger, M. A.; Waddon, A. J.; Atkins, E. D. T.; MacKnight, W. J. *Macromolecules* **1994**, *27*, 2130.