Near Infrared Analysis of Blends of Sulfonated Polystyrene Ionomers and Poly(ε-caprolactam)

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ABSTRACT: Near infrared spectroscopy (NIR) was used to characterize the nature of specific interactions in blends of lightly sulfonated polystyrene ionomers (M-SPS where M = Zn+2, Mn+2, or Li+) and poly(caprolactam) (PA6). The assignments of the NIR overtone bands that arise due to the interactions between the cation of the ionomer, and the amide groups were made using spectra of model compounds. The relative populations of the different environments of the N—H groups were qualitatively determined by deconvoluting the NIR spectra into five absorbances representing hydrogen-bonded N—H in crystalline and amorphous phases and an ion-amide complex. The ion-amide complex was specific for the blends. The interpolymer interactions were sensitive to composition and temperature, but qualitatively the behavior was the same for all three ionomer salts investigated. © 2008 Wiley Periodicals, Inc.

Keywords: blends; infrared spectroscopy; ionomers

INTRODUCTION

Polymer blends are generally immiscible because of a relatively small entropy of mixing and a positive enthalpy of mixing.1 Miscibility may be enhanced by introducing specific exothermic interactions between complementary functional groups on the two polymers. An example of this is a blend of a polyamide with a lightly sulfonated polystyrene ionomer (SPS) where an ion-dipole complex is formed between the metal sulfonate and amide groups.2–12 In this article, we report on the use of near-infrared spectroscopy to study the specific interactions in blends of SPS and poly(ε-caprolactam), PA6.

The near-infrared (NIR) spectral region covers the range between the visible and the mid-infrared (mid-IR) part of the electromagnetic spectrum, ~14,000–4000 cm⁻¹ (700–2500 nm). Mid-infrared spectroscopy, 4000–400 cm⁻¹ (2.5–25 mm) has been widely used to study interactions in polymer blends involving carbonyl groups.13,14 NIR, however, has not been widely used for analyzing mixing in blends because of the relatively weak overtone band intensities that occur in this absorption region. The overtone bands in this region generally arise from C—H, O—H, and N—H vibrations, and long pathlengths are required to produce reasonable absorbances. One advantage, however, of the relatively thick samples used for NIR is that the spectrum better represents the chemistry and structure of a bulk specimen as opposed to the spectra of thin films that are disproportionately influenced by surfaces. The low absorptivities of
the bands in this region also permit analysis in transmission,\textsuperscript{15,16} and commercially available, inexpensive fiber-optic probes allow \textit{in situ} NIR measurements. The latter attributes are particularly attractive for on-line monitoring of interactions during processing and application of blends.

NIR has found a niche in the analysis of pharmaceutical processes\textsuperscript{17} and food processing,\textsuperscript{18} and in on-line monitoring of polymerization, curing and polymer processing operations.\textsuperscript{19,20} Although its use for characterizing polymer blends has been known since the early 1990s, there is still relatively little literature concerning its use in studying polymer blends. NIR has been mostly used in polymer research to characterize blend composition\textsuperscript{21} or homogeneity.\textsuperscript{22} The use of NIR to characterize specific interactions in polymer blends is relatively small and focused primarily on hydrogen bonding.\textsuperscript{16,23–27} Chen and Hua\textsuperscript{28} used NIR to study electrostatic interactions between poly(sodium 2-(3'-thienylethanesulfonate) and poly(vinyl alcohol).

Blends of polyamides such as poly(\textit{l}-caprolactam), PA6, with lightly sulfonated polystyrene (SPS) ionomers are partially miscible due to hydrogen bonding, ion-dipole, or metal complexation between the sulfonate and the amide groups.\textsuperscript{2–12} Mid-frequency range infrared spectroscopy (MIR) has been previously used to characterize molecular interactions in blends of MSPS and PA6, where M denotes the metal sulfonate groups. Interpretation of the Mid-IR spectra is complicated by overlap of absorptions not associated with molecular interactions of the two polymers. The 6900–6400 cm\textsuperscript{-1} region of the N\textsuperscript{a}R spectrum can provide information about the interactions in polyamide blends, because of the relatively strong N–H stretching overtone vibrations that appear in that region. This article provides a detailed analysis of the effects of temperature and the ionomer cation on the sulfonate-amide interactions in blends of lightly sulfonated polystyrene ionomers and PA6 using NIR spectroscopy.

**EXPERIMENTAL**

Lightly sulfonated polystyrene ionomers were prepared according to the procedure described by Makowski et al.\textsuperscript{29} The starting polystyrene was a commercial polymer from Dow Chemical Co. (Styron\textsuperscript{8} 666) with \(M_n\) and \(M_w = 100,000\) and 280,000 g/mol, respectively. The sulfonation level was 9.1 mol % (i.e., the number of styrenes substituted per 100 styrene repeat units), which was determined by titration of the free acid derivative, HSPS, in a toluene/methanol (85/15 v/v) solution using a methanol solution of sodium hydroxide. The Zn\textsuperscript{2+}, Mn\textsuperscript{2+}, and Li\textsuperscript{+}-salts were prepared by neutralizing the free acid derivat-ives of SPS in a toluene/methanol solution with an excess of the appropriate metal acetate. The ionomers were precipitated in a large excess of ethanol and dried under vacuum for 5 days at 90 °C. The ionomer samples are designated as 9.1 MSPS, where M denotes the metal cation (M = Zn, Mn, or Li). PA6 with a \(M_w = 24,000\) g/mol was purchased from Polysciences.

Blends PA6 and 9.1M-SPS were prepared by mixing the polymers in a common mixed solvent of \(m\)- cresol and dimethylformamide, followed by evaporation of the solvent and drying at elevated temperature under vacuum. The blends were dried under vacuum for 5 days at 90 °C. Blends with ionomer mass fraction, \(x\), of 0.25, 0.4, 0.6, and 0.75 were prepared. Samples for thermal analysis were compression molded close to the melting point of the PA6, \(\sim 230 ^\circ C\), and cooled quickly to room temperature. A differential scanning calorimeter, Perkin–Elmer DSC-7, was used for measuring melting points, \(T_m\), and glass transition temperatures, \(T_g\), of the blends.

A dry nitrogen atmosphere and a heating rate of 20 °C/min were used. The melting point was defined as the temperature at the maximum in the melting endotherm and the \(T_g\) was taken as the mid-point in the change of the heat capacity at the glass transition.

Films, 2- to 10-mm thick, were prepared by compression molding the blends at 225 °C. NIR spectra were measured with a Mattson Galaxy Near-FTIR that uses a tungsten halogen source, a calcium fluoride beam-splitter, and an InSb detector. Temperatures were measured with an Omega thermocouple that was placed in the heating cell near the sample. The spectra were recorded from 100 scans with a resolution of 4 cm\textsuperscript{-1}.

**RESULTS AND DISCUSSION**

**NIR Model Compound Studies**

The effects of hydrogen bonding and crystallinity on the NIR spectrum of amides are shown in
Figures 1 and 2. Figure 1(a) shows the N–H stretching overtone region for a model compound, N-butylacetamide (BAA) in carbon tetrachloride (CCl4). The sharp peak centered at ~6770 cm$^{-1}$ is due to free, nonhydrogen bonded N–H.$^{15}$ Curves (b–d) in Figure 1 show what happens when varying amounts of tetrahydrofuran (THF) were added to the BAA/CCl$_4$ solution. The intensity of the 6770 cm$^{-1}$ band decreased as the concentration of THF increased, and a new, broad absorbance centered near 6600 cm$^{-1}$ became more prominent. The 6600 cm$^{-1}$ band arises from the formation of a hydrogen bond complex between the amide and the ether.

Another model compound, N-methylacetamide (MAA), with a relatively low melting point (26–28 °C) was used to determine the effect of crystallinity on the N–H stretch overtone bands. Figure 2 shows the NIR spectra of MAA as a function of temperature between 15 and 30 °C. The NIR spectrum of the as-crystallized MAA, curve (a) in Figure 2, shows an intense absorption at 6520 cm$^{-1}$ and a higher frequency shoulder, which are due to two different environments of associated NH. Our assignment, which is confirmed by the temperature studies described below, is that the peak at 6520 cm$^{-1}$ arises from NH in a crystalline phase and the shoulder at ~6600 cm$^{-1}$ is due to amorphous material. Considerable broadening of the NIR spectrum occurred as the temperature was raised and the MAA crystals melted, and the peak at 6520 cm$^{-1}$ shifted to higher frequency and the shoulder increased in intensity. Above the melting point, curve (d), the primary absorption was at 6600 cm$^{-1}$, which is consistent with the assignment of associated NH in an amorphous phase. In addition, a weak inflection at ~6770 cm$^{-1}$ is also seen in the partially and completely melted MAA, which based on the BAA solution studies described above was assigned to free NH groups in the amorphous phase.

Thermal Analysis of MSPS/PA6 Blends

Blends of PA6 and 9.1M-SPS, where M = Mn, Zn, or Li, are partially miscible and exhibit lower critical solution temperature (LCST) liquid–liquid phase behavior,$^{30,31}$ see Figure 3. Because PA6 is semicrystalline, a crystalline PA6 phase coexists with a single, miscible amorphous phase. The effect of blend composition on the thermal transitions and the amount of crystallinity in the blend for blends prepared from the three different ionomer salts is shown in Figure 4. The addition of M-SPS to PA6 depressed the melting point of the PA6 and suppressed its crystallization. Crystallinity of the PA6 was completely suppressed above an ionomer mass fraction of $x = 0.4$. All of the blends...
exhibited a single, composition-dependent glass transition temperature, $T_g$, which confirmed the miscibility of the two polymers in the amorphous phase. The $T_g$ and $T_m$ versus composition data were similar for all three salts, but, in general, the magnitude of the $T_g$ increased with cation in the order: $\text{Li}^+ < \text{Zn}^{2+} < \text{Mn}^{2+}$, which reflects the increasing strength of the ion-amide interaction. $T_m$ decreased with increasing ionomer concentration and the strongest ion-amide interaction ($\text{Mn}^{2+}$-PA6) produced the lowest melting point.

**NIR Spectrum of PA6**

Figure 5 shows the MIR and NIR spectra of the neat PA6 in the N–H stretch absorption region and the 2ν(N–H) overtone absorption region, respectively. Four bands are resolved in the NIR spectrum: 6475, 6525 (shoulder), 6620, and 6750 cm$^{-1}$. The distinct absorbances in the NIR spectrum are better resolved than in the 3200–3400 cm$^{-1}$ region of the MIR spectrum. Each absorption in the NIR spectrum corresponds to a different environment of the amide groups in PA6. Because the vibrational energy for the crystalline form of the polymer is expected to have lower translational energy than the amorphous or free forms, the band at 6475 cm$^{-1}$ is assigned to the crystalline phase of the polymer, and the shoulder at 6525 cm$^{-1}$ is attributed to the amor-
phous material within the crystallites (or, a mesomorphic phase) based on the model compound studies of crystalline MMA, Figure 2. Near the melting point, the peak arising from the crystalline material began to disappear and the band at 6525 cm\(^{-1}\) became the predominant absorption. Above the melting point, that band shifted to 6600 cm\(^{-1}\) as the amorphous material became the continuous phase. By analogy, the peak at 6620 cm\(^{-1}\) in the PA6 NIR spectrum is assigned to hydrogen bonded N–H in the bulk amorphous phase and the peak at 6750 cm\(^{-1}\) to unassociated N–H in the amorphous phase.

NIR of 9.1Zn-SPS/PA6 Blends

The room temperature NIR spectrum of an \(x = 0.25\) blend of 9.1 ZnSPS and PA6, which had an LCST at 245 °C,\(^{30,32}\) is shown in Figure 6. A curve fitting procedure was used to deconvolute the individual bands in the overlapped regions. The procedure used a least squares optimization analysis of the spectral data with the number of variables kept to a minimum to improve the uniqueness of the fit. Five bands, 6475, 6525, 6620, 6695, and 6750 cm\(^{-1}\), were chosen by visual inspection and a Fourier self-deconvolution routine was used to generate the five Gaussian peaks shown in Figure 6.\(^{31}\) The only variables in the curve fitting procedure were band heights and band widths. Except for the 6695 cm\(^{-1}\) band, these absorptions and their assignments correspond to the same absorptions observed in PA (see earlier section). The new band at 6695 cm\(^{-1}\) is specific to the blends, and by comparison to previous work on metal-cation/amide interactions studied by MIR\(^{2-4,32-35}\) is attributed to a complex of the ionomer cation with the amide group.

Figure 7 shows the NIR spectra for 9.1ZnSPS/PA6 blends with compositions ranging from \(x = 0.25–0.75\). The crystallinity of the blends decreased as the ionomer content increased, and as shown in Figure 3, no crystallinity was observed above \(x = 0.4\). As a consequence of the reduced crystallinity compared with the neat PA6, see Figure 5, intensities of the 6475 cm\(^{-1}\) crystalline and 6525 cm\(^{-1}\) mesophase bands reverse from their relative intensities for the PA6. The 6475 cm\(^{-1}\) shoulder weakens as \(x \rightarrow 0.4\), and, correspondingly, the 6525 cm\(^{-1}\) band becomes the predominant feature in the NIR spectrum. Above \(x = 0.4\), the blend is completely amorphous and the 6475 cm\(^{-1}\) absorption disappears, the mesophase 6525 cm\(^{-1}\) begins to decrease in intensity. The 6695 cm\(^{-1}\) corresponding to the ionomer-polyamide complex begins to grow and dominate the spectrum. The increase in the intensity of the complex with increasing ionomer concentration is not surprising, in that the ratios of Zn\(^{2+}\) to N–H in the blends with \(x = 0.25, 0.40, 0.60,\) and 0.75 were 0.03, 0.07, 0.15, and 0.30, respectively. The higher ratios of the cation and amide concentrations should favor more interactions.
The ionomer concentration had no noticeable effect on the relative areas of the other two higher frequency NIR absorbances that correspond to N–H stretching in the amorphous phase. The frequency of the 6695 cm\(^{-1}\) was independent of concentration of ZnSPS, which indicates that it arises from a specific complex structure and not a simple perturbation of vibrational energy levels associated with different concentrations of chemical species. This observation is consistent with the electron-redistribution model for a metal cation-amide complex in SPS ionomer/polyamide blends proposed by Feng et al.\(^8\) see Scheme 1. The complex involves a 1:1 interaction of the metal cation to amide, even for divalent cations.\(^6\)

The fractional areas of the deconvoluted Gaussian peaks, see Figure 6, were calculated by integration of the peaks and normalized by the total area of all the peaks. The values of the normalized fractional areas of each absorbance, which to a first approximation represent the relative concentrations of each chemical species (quantitative determination of the concentrations from these data would require knowledge of the extinction coefficients of each band) are plotted in Figure 8 for the blends with different polymer compositions. Below \(x = 0.4\), the concentrations of N–H in the crystalline phase and the mesophase were high and relatively constant. Above \(x = 0.4\), both concentrations decreased significantly, which is consistent with failure of these blends to crystallize. What was surprising, however, is that although the N–H concentration in the crystals (band 6475 cm\(^{-1}\)) goes to zero above \(x = 0.6\), the N–H concentration in the mesophase (band 6525 cm\(^{-1}\)) remained finite, even for \(x = 0.75\). Although those latter blends were judged to be amorphous from the DSC experiments and their optical clarity, the persistence of the 6525 cm\(^{-1}\) suggests that there still remained N–H groups that experienced restricted mobility, but were not the same as the hydrogen bonded N–H in the amorphous region (6620 cm\(^{-1}\)). That mesophase persisted in the blends with \(x > 0.4\) at 200 °C, but finally disappeared at 250 °C (data not shown). The fact that the mesophase disappeared above \(T_m\), further suggests that there may be remnants of a crystalline phase, or perhaps a micro-crystalline phase in the blends with higher ionomer concentrations. It is tempting to compare the morphology of these blends to that of micro-crystalline poly(vinyl chloride), but further speculation requires further study.

The effect of temperature on the NIR spectrum of the (\(x = 0.25\)) 9.1ZnSPS/PA6 blend is shown in Figure 9. \(T_m\) for this sample was 217 °C. The frequencies of the five deconvoluted peaks described above are marked for clarity in Figure 9. At room temperature, which is far below the melting point of the polyamide, all five peaks in the N–H overtone spectral region were observed, though the absorbance for the new ionamide complex was relatively weak. The values of the normalized fractional areas of each absorbance are plotted against blend composition in Figure 10. At 25 °C, the dominant chemical species are the hydrogen bonded N–H in the mesophase regions of the crystallites (band 6525 cm\(^{-1}\)) and in the amorphous phase (band 6620 cm\(^{-1}\)). When the temperature was increased to 200 °C, below \(T_m\), but high enough that small crystallites melted, the concentration of N–H

![Scheme 1](image_url)
associated with the crystalline phase (band 6475 cm\(^{-1}\)) and the mesophase within the crystallites (band 6525 cm\(^{-1}\)), decreased and the concentration of N–H related to the amorphous phase (bands 6620 and 6750 cm\(^{-1}\)), and the ion-amide complex (band 6695 cm\(^{-1}\)), increased. At 250 °C, which was above \(T_{m}\), the only environments of N–H that remained were the hydrogen bonded N–H and unassociated N–H in the amorphous phase (bands 6620 and 6750 cm\(^{-1}\), respectively) and the ion-amide complex (6695 cm\(^{-1}\)). At 250 °C, the dominant species was the complex. Similar behavior was exhibited by the blends with other compositions of 9.1ZnSPS and PA6.

**NIR of 9.1Mn-SPS/PA6 and 9.1Li-SPS/PA6 Blends**

Previous work demonstrated that SPS neutralized with Mn\(^{2+}\) interacted more strongly than Zn\(^{2+}\) with the amide group in PA6 and the Li\(^{+}\)-amide interaction was weaker.\(^{19}\) As for the 9.1Zn-SPS/PA6 blends, only materials with \(x < 0.4\) exhibited crystallinity, see Figure 4. The temperature dependence of the NIR spectra for the blends with 9.1MnSPS and 9.1LiSPS (not shown) were qualitatively the same as for the 9.1ZnSPS discussed in the previous section, and the conclusions were the same. Figure 11 compares the composition dependence of the normalized fractional areas for the 6475 cm\(^{-1}\) (N–H in crystallites) and 6695 cm\(^{-1}\) (N–H participating in the ion-amide complex) for blends involving all three salts of the ionomer. In each case, the concentration of N–H in the crystalline regions goes to zero and the concentration of the complex increases dramatically when the blends become completely amorphous. There is a large variation in the concentration of the complex for the three ionomer salts and it is tempting to compare them quantitatively. However, the relative concentrations of the complex showed by the data in Figure 11 suggest that it decreases as Mn\(^{2+}\) > Li\(^{+}\) > Zn\(^{2+}\). One might expect that

**Figure 9.** NIR spectrum of the 2\(\nu\)(N–H) stretching region for a \((x = 0.25)\) 9.1ZnSPS/PA6 blend at 25, 200, and 250 °C. The arrows correspond to the deconvoluted peaks that are described shown in Figure 5 and discussed in the text.

**Figure 10.** Fractional area of the deconvoluted peaks in the NIR spectrum of the 2\(\nu\)(N–H) stretching region for a \((x = 0.25)\) 9.1ZnSPS/PA6 blend as a function of temperature.

**Figure 11.** Fractional area of the deconvoluted peaks at 6475 and 6695 cm\(^{-1}\) for the Zn, Mn, and Li salts of \((x = 0.25)\) 9.1ZnSPS/PA6.

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the concentration of the complex would increase
as the strength of the complex increased, but
that order is Mn\(^{2+}\) > Zn\(^{2+}\) > Li\(^+\), which is not consistent with the results. We only bring this
point up, because we believe that a more careful
NIR study should be able to provide quantita-
tive results on the interactions in these systems.
In the present study, although the sample pre-
parations were very similar, small differences in
sample preparation may produce significant
enough changes in the microstructure to make
comparisons problematic. Similarly, not enough
replications of the experiments were made to
produce the statistics that would provide con-
vincing quantitative comparisons between the
different ionomer blends described herein.

CONCLUSIONS

NIR spectroscopy was able to resolve the local
environment of N–H groups in SPS ionomer/PA6 blends. Although similar results can be
accomplished using mid-IR spectroscopy, NIR
spectroscopy allows one to use thicker speci-
mens, employ remote, fiber-optic sensing, and
the separation of the absorbances from other
interfering absorbance is simpler. MSPS ionom-
ers interact strongly with PA6 through the for-
mation of a specific ion-amide complexation,
which produces miscibility in the amorphous
phase. NIR is able to characterize the develop-
ment of this complex as the composition and the
temperature of the blends is changed. The com-
plex develops in the amorphous phase. Increas-
ing the ionomer content of the blend decreases
the crystalline fraction and promotes complexation, and increasing the temperature of a
semicrystalline blend above the melting point
produces a reorganization of the amide groups
that produces more complexation. The technique
described in this article has potential application
for monitoring and controlling phase morphology
in these and similar blends involving complexes
of polymers with polyamides or other polymers
containing carbonyl and or N–H groups.

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