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Assessment of time–temperature superposition of linear viscoelastic behaviour of strongly interacting polymer blends: *N*-methylated nylon-2,10 and lightly sulfonated polystyrene ionomers

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The applicability of time–temperature superposition of dynamic mechanical data for miscible polymer blends that exhibit strong intermolecular interactions was investigated. Blends of the lithium salt of lightly sulfonated polystyrene ionomers (Li-SPS), 9–12 mol% sulfonation, and *N*-methylated nylon-2,10 (mPA) were miscible over the composition range studied, 30–70 wt% ionomer. Time–temperature superposition (TTS) of the storage and loss shear moduli measured at frequencies of 0.01–500 rad s^{-1} was applicable over the temperature range from 95 to 185°C. The molecular-weight distribution of the ionomer had no effect on the applicability of TTS. The success of TTS was attributed to the complexation of the metal sulfonate and amide groups, which couple the relaxation times of the two polymers in the blend. Na-SPS (9.5 mol%) and mPA were immiscible and TTS failed for these blends. TTS was obeyed for blends of Zn-SPS and mPA, though these blends appeared to be immiscible or partially miscible.

(Keywords: methylated nylon-2,10; miscible blends; time–temperature superposition)

INTRODUCTION

Dynamic rheological experiments are widely used for studying the viscoelastic properties of polymers. Experimental measurements are generally collected over a limited time or frequency scale, and the response of the material outside the experimentally accessible range is often estimated by constructing a master curve using the principle of time–temperature superposition[1]. Time–temperature superposition (TTS) has been found to be generally applicable to amorphous polymers, but it does not usually apply to multiphase or semicrystalline polymers[1,2]. For immiscible blends, TTS fails, because the relaxation times for the two phases are not affected equally by changes in temperature.

TTS has been reported both to be successful[3–5] and to fail[6–8] for miscible polymer blends, and there are some notable inconsistencies in the literature. For example, dynamic mechanical data of blends of poly(ethylene oxide) and poly(methyl methacrylate) (PEO/PMMA) were reported to obey TTS by Wu[5] but to fail to obey TTS by Colby[6]. Similarly, Breckner *et al.*[3] reported the successful construction of master curves for polystyrene/poly(vinyl methyl ether) blends (PS/PVME) where either oligomeric ($M_w = 800$) or polymeric ($M_w = 75\,000$) PS were used. The same miscible polymer pair, however, was reported by Han and Kim[7] to be microphase-separated, which resulted in a breakdown of TTS. Colby[6] proposed that the apparent applicability of TTS for miscible polymer blends may be a consequence of probing only a narrow experimental frequency range and/or using polydisperse component polymers that mask the inherent failure of TTS for single-phase mixtures of two polymers with different relaxation-time distributions. He also questioned whether the failure of TTS is a specific result for miscible blends with very small enthalpic interactions, where concentration fluctuations are expected to be quite large. One objective of the research discussed in this paper was to assess the validity of TTS for a blend that exhibits strong specific intermolecular interactions.

One widely used criterion for miscibility of polymer blends is the observation of a single, composition-dependent glass transition temperature T_g, which usually occurs between the T_g values of the pure components. This criterion may be complicated by crystallinity of one of the polymers, and its sensitivity depends on the experiment used for measuring T_g. Differential scanning calorimetry (d.s.c.) can resolve phases on the order of 50 nm (ref. 9) and thus may be insensitive to the presence of microheterogeneity[7,9]. Dynamic mechanical analysis (d.m.a.) can resolve phases of 5–10 nm (ref. 10). Optical clarity is also a sensitive indication of a single-phase

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system, as long as the refractive indices of the two polymers are suitably different.

Improved miscibility of two polymers may be accomplished by promoting specific intermolecular interactions, and, in this regard, ionomers offer a fairly rich chemistry for developing strong exothermic interactions with a variety of heteroatomic polymers. For example, miscibility has been reported for metal salts of lightly sulfonated polystyrene ionomers (SPS) and nylon-6[10–14], and the extent of miscibility depended on the particular metal cation that was used. Miscibility was not accomplished when the counterion was sodium (Na-SPS)[10], but partially miscible blends exhibiting lower critical solution temperature (*LCST*) behaviour were observed for magnesium, lithium, zinc or manganese salts[14]. The strength of the ionomer–polyamide interaction and the temperature of the *LCST* increased with cation in the order of $Na^+ < Mg^{2+} < Li^+ < Zn^{2+} < Mn^{2+}$. The degree of sulfonation of the polystyrene was also important, and, in general, miscibility increased with the sulfonation level. The zinc salt of SPS was also reported to be miscible with an amorphous polyamide when a relatively high sulfonate to amide ratio was used[15]. Use of an amorphous polyamide for studying ionomer/polyamide blends avoids many of the complications that result from crystallization of the polyamide.

For neat ionomers, TTS usually fails above a critical ion concentration[16–18] as a result of microphase separation of ion-rich aggregates. Differences in the rheological behaviour depend more on the ionization level than on the choice of the counterion[19]. For blends of nylon-6 and SPS ionomers, however, interaction between the sulfonate and amide groups inhibits microphase separation and only a single, homogenous phase is observed[10,11,13].

In this paper, the dynamic mechanical behaviour of blends of a methylated polyamide (nylon-2,10) and SPS ionomers is described. Methylated nylon-2,10 (mPA) was used to inhibit the self-hydrogen-bonding of the polyamide. As a result, the polymer crystallization rate was extremely slow and completely amorphous blends could easily be prepared below the melting point of the polyamide. The effects of sulfonation level of M-SPS, where M is the counterion (M = Li, Na and Zn), molecular-weight distribution (*MWD*) of the polystyrene starting material and blend composition on the applicability of TTS to blends with mPA are discussed.

EXPERIMENTAL

Materials

The synthesis of methylated nylon-2,10 (poly(*N*,*N*′-dimethylethylene sebacamide) (mPA)) is described elsewhere[20]. *N*,*N*′-Dimethylethylenediamine was dissolved in a mixture of 1,1,2,2-tetrachloroethane and pyridine (0.032/1 v/v) at −15°C and sebacoyl chloride was added with rapid stirring. Stirring was continued for 24 h while the solution gradually warmed to room temperature under a dry nitrogen atmosphere. The polymer was precipitated in hexane and dried at reduced pressure. mPA is a slowly crystallizing polyamide with a T_g of −3°C and a T_m of 60°C as determined by d.s.c. The mPA was used as polymerized and not further purified. Gel permeation chromatography (tetrahydrofuran (THF), 30°C) indicated that the material was composed of about 80 wt% of polymer ($M_w = 21\,000$, $M_w/M_n = 1.75$) and ca. 20 wt% of oligomers ($M \sim 2000$).

Two different polystyrenes, one with a relatively broad molecular-weight distribution ($M_w = 288\,000$, $M_w/M_n = 2.72$) from Dow Chemical Co. and one with a narrow molecular-weight distribution ($M_w = 280\,000$, $M_w/M_n = 1.09$) synthesized by anionic polymerization, were lightly sulfonated with acetyl sulfate using the method of Makowski *et al.*[21]. The sulfonation levels were 9.5 and 12 mol% for the PS and with the broad *MWD* and 9 mol% for the PS with the narrow *MWD*, as determined by titration of the SPS-free acid derivatives with methanolic NaOH to a phenolphthalein end-point. Salts (M-SPS, where M = Li, Na or Zn) were prepared by neutralizing the H-SPS in a toluene/methanol mixed solvent with a 20% excess of lithium hydroxide, sodium hydroxide or zinc acetate dihydrate in methanol to obtain the lithium, sodium or zinc salt, respectively. The nomenclature used for the ionomer salts is M-SPS*x*n or M-SPS*x*b, where *x* denotes the sulfonation level and n and b denote narrow and broad *MWD*s, respectively.

Blends of mPA and M-SPS were prepared by adding a solution of mPA in methanol dropwise to a stirred solution of M-SPS in methanol for the lithium and sodium salts of polystyrene. Because Zn-SPS was insoluble in methanol, dimethylsulfoxide (DMSO) was used to prepare the Zn-SPS/mPA blends. The compositions and T_g value(s) of the starting materials and the bends are summarized in *Table 1*.

The samples were compression moulded into ca. 1.5 mm thick specimens using a Carver Laboratory heat press by first heating to well above T_g for 10 min without any load, applying a 2 ton load (17.8 kN) for 2 min and finally a 4 ton load (35.6 kN) for another 2 min.

Table 1 List of materials

Sample	Composition	Description	T_g(°C)[a]
1	PS	$M_w/M_n = 2.71$	104
2	PS	$M_w/M_n = 1.09$	107
3	mPA	Amorphous polyamide	−3
4	Li-SPS9.5b	Sulf. level = 9.5 (mol%)[b]	133
5	Na-SPS9.5b	Sulf. level = 9.5[b]	132
6	Zn-SPS9.5b	Sulf. level = 9.5[b]	139
7	Li-SPS12b	Sulf. level = 12[b]	142
8	Zn-SPS12b	Sulf. level = 12[b]	148
9	Li-SPS9n	Sulf. level = 9[c]	153
10	Li-SPS9.5b/mPA	30/70 (w/w)	19
11	Li-SPS9.5b/mPA	50/50	46
12	Li-SPS9.5b/mPA	70/30	99
13	Na-SPS9.5b/mPA	30/70	2,109
14	Zn-SPS9.5b/mPA	30/70	−1, ?
15	Li-SPS12b/mPA	30/70	21
16	Zn-SPS12b/mPA	30/70	0, ?
17	Li-SPS9n/mPA	30/70	24
18	Li-SPS9n/mPA	50/50	46

[a] D.s.c., 20°C min^{-1}
[b] From polystyrene with broad molecular-weight distribution, $M_w/M_n = 2.71$
[c] From polystyrene with narrow molecular-weight distribution, $M_w/M_n = 1.09$

Analyses

Rheological measurements were performed with a Rheometrics System 4 mechanical spectrometer, using the dynamic shear mode and 25 mm parallel-plate fixtures. The gap height was ca. 1.5 mm. Measurements of the storage and loss shear moduli, G' and G'', were made at frequencies from 0.01 to 500 rad s^{-1} at temperatures from 95 to 185°C. At lower temperatures, frequencies from 0.1 to 500 rad s^{-1} were used, and at the higher temperatures, the frequency ranged from 0.01 to 100 rad s^{-1}. Strain sweeps were made at all temperatures to ensure that the experiments were within the linear viscoelastic region. Master curves of G' and G'' were constructed from isothermal data using the computer program SHIFTT developed by Gordon and Shaw[22].

Differential scanning calorimetry (d.s.c.) was performed with a Perkin Elmer DSC-7. Samples were annealed at 180°C for 15 min to remove any prior thermal history before running heating scans at 20°C min^{-1}. The glass transition temperature T_g was defined as the midpoint of the change in heat capacity at the transition, and miscibility of the blends was assessed by the criterion of a single composition-dependent T_g intermediate between those of the pure components.

RESULTS AND DISCUSSION

Thermal analysis

Films of the Li-SPS9.5b/mPA blends cast onto glass slides remained optically transparent below 190°C for all compositions studied. The optical clarity indicated that the polymers were miscible and no phase separation occurred in the temperature range studied.

Further evidence for miscibility is provided by the d.s.c. thermograms of blends of Li-SPS9.5b and mPA given in *Figure 1*. The samples were annealed at 180°C for 10 min before cooling to the starting temperature for the scan, which was below T_g. As a result, the thermograms in *Figure 1* represent the phase behaviour of the blend at 180°C. The blends exhibit a single, composition-dependent T_g intermediate between those of the starting materials, indicating miscibility of mPA and the ionomer at 180°C for the composition range studied, 30–70% mPA. Since SPS/polyamide blends exhibit *LCST* behaviour[14], the demonstration of miscibility at 180°C indicates that the blend was also miscible below that temperature.

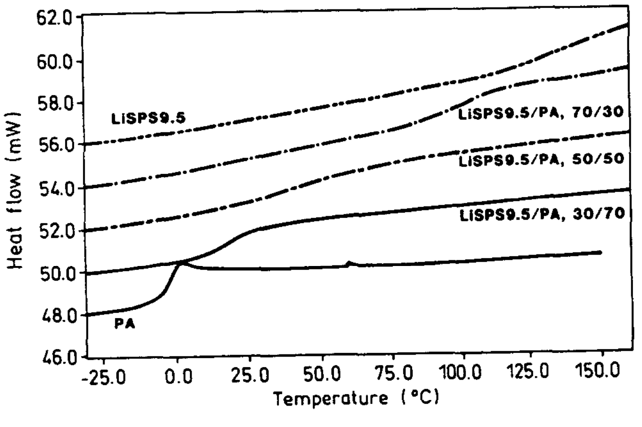

Figure 1 D.s.c. heating thermogram of Li-SPS9.5b, mPA and their blends

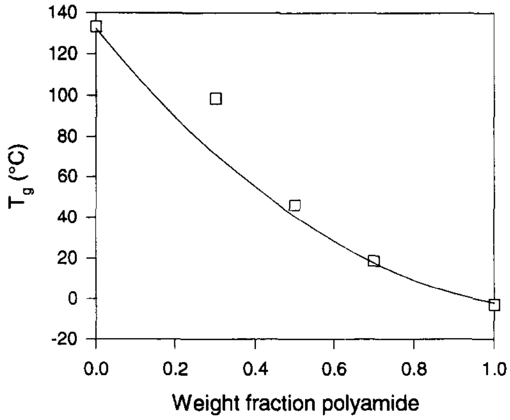

Figure 2 Comparison between experimental values (□) obtained by d.s.c. for T_g of Li-SPS9.5/mPA blends and predictions (—) of the Couchman equation[23]

The value of T_g increased with increasing ionomer concentration in the blend. The width of the transition broadened, especially for the 50/50 (w/w) blends, compared to the transition width of the neat component polymers. The widths of the transition regions, taken as the d.s.c. temperature interval over which the heat capacity changes, were ca. 90, 55 and 48°C for 50/50, 30/70 and 70/30 Li-SPS9.5b/mPA, respectively. The neat polymers exhibited a ΔT_g of 49°C for Li-SPS9.5b and 16°C for mPA. The rather broad ΔT_g for the ionomer is presumably a consequence of a distribution of ionic aggregates that give rise to a broad relaxation-time distribution. Similarly, the broad ΔT_g values for the ionomer/polyamide blends are probably due to a distribution of intermolecular complex structures. One cannot rule out microheterogeneity effects for the blends, which could arise from self-association of the ionomer, but a previous study of blends of nylon-6 and SPS ionomers indicated that the ionic aggregate structure, i.e. the so-called ionic clusters, were solvated by the stronger interactions between the amide and metal sulfonate groups[11] and those blends were homogeneous on a size scale of < 2 nm[10,14]. For the purposes of the present discussion, the single T_g observed for the blends in *Figure 1* is interpreted as evidence for a miscible system.

In *Figure 2*, the experimental T_g values for Li-SPS9.5b/mPA blends are compared with the values predicted from a weight-average calculation using the Couchman equation[23]:

$$\ln T_g = \frac{w_1 \Delta C_{p1} \ln T_{g1} + w_2 \Delta C_{p2} \ln T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \qquad (1)$$

where w_i represent the weight fractions, T_{gi} the glass transition temperatures and ΔC_{pi} the heat capacity change at T_{gi} for the two polymers. Values for ΔC_p were calculated from the d.s.c. thermograms. The experimental data exhibit a sigmoidal dependence on composition and deviate from the theoretical prediction for the ionomer-rich blends, which is presumably a consequence of strong, specific interactions as were previously reported for SPS/nylon-6 blends[24].

D.s.c. thermograms of SPS/mPA blends using ionomers with different metal cations are shown in *Figure 3*.

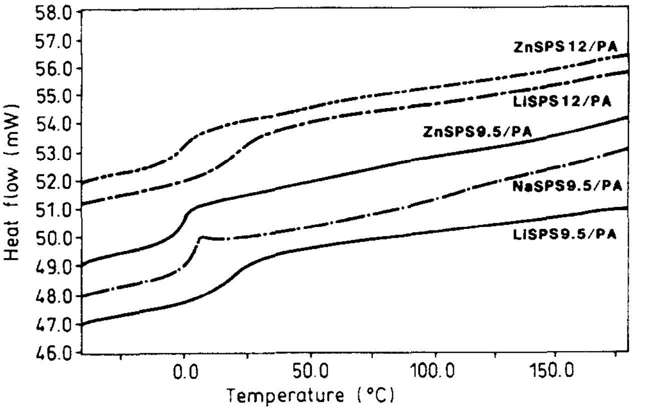

Figure 3 D.s.c. heating thermograms of 30/70 (w/w) blends of Na-SPS9.5/mPA, Li-SPS9.5b/mPA, Zn-SPS9.5b/mPA, Li-SPS12b/mPA

The Na-SPS9.5b/mPA blend (30/70 w/w) exhibited two separate T_g values, indicating a two-phase system. The lower T_g at 2°C corresponds to a mPA-rich phase and the higher T_g at 109°C represents an ionomer-rich phase. The increase in the lower T_g relative to that of neat mPA (−3°C) and the decrease in the higher T_g compared with the neat Na-SPS9.5b (132°C) indicate that there was some mixing of the two polymers in each phase.

For the Zn-SPS9.5b/mPA blend (30/70) only one distinct T_g was observed, at −1°C, which is fairly close to that of pure mPA. This result was surprising in that it suggests that the two polymers are immiscible, though a second T_g for the ionomer phase was not resolved. Previous studies of blends of SPS ionomers with nylon-6 showed that the Zn salt was more miscible with the polyamide than was the Li salt due to stronger intermolecular interactions[14]. In that case, however, n.m.r. studies indicated that the Zn–amide interaction involved the amide nitrogen[13], and it is possible that methylation of that nitrogen affects how it is able to complex with the zinc sulfonate groups. Recent i.r. and n.m.r. spectroscopy studies[25] of the M-SPS/mPA complexes indicate that the interaction involving the Zn^{2+} cation is much different from that involving the Li^+ cation, and the former probably involves both the nitrogen and the carbonyl oxygen. Nevertheless, in the current investigation, it appears that the Zn-SPS9.5b/mPA blends were immiscible at the annealing temperature used, 180°C. The failure to detect the ionomer T_g may be due to some mixing of the two polymers in the ionomer-rich phase which broadens the transition sufficiently to hinder resolution by d.s.c. Similar results were obtained for a blend containing Zn-SPS12b.

Viscoelastic behaviour

Neat polymers. Master curves of G' and G'' at $T = T_g + 70°C$ were constructed by superimposing isothermal viscoelastic data by shifting the data along the frequency axis. The shift factors are defined by the amount of horizontal shift required:

$$a_T = \frac{\omega_{T_g+70°C}}{\omega_T} \tag{2}$$

where ω is frequency. A vertical correction of the moduli by the factor T_g/T was also necessary to compensate for the temperature dependence of the modulus.

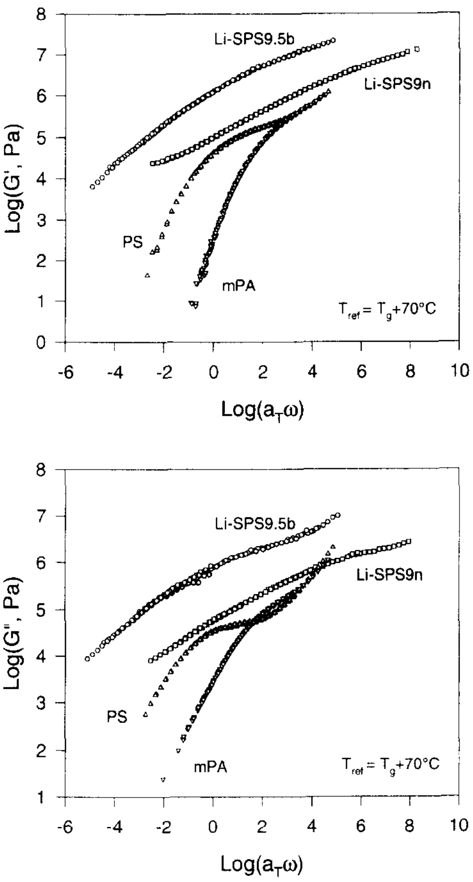

Figure 4 G' and G'' master curves of PS, mPA, Li-SPS9.5b and Li-SPS9n. The reference temperature was $T_g + 70°C$

Master curves of the starting materials, PS and mPA, and of Li-SPS prepared from two different polystyrenes with different *MWD*s (the per cent sulfonations of the two Li-SPS differed by 0.5) are shown in *Figure 4*. These curves were constructed from viscoelastic data measured at different temperatures; an example of the construction is shown in *Figure 5* for a blend sample. TTS was applicable for PS and mPA data, but was not completely successful for the G'' data of Li-SPS. The failure of TTS of G'' for the ionomers is consistent with previous viscoelasticity studies of SPS ionomers[26] and can be attributed to the presence of a microphase-separated, ion-rich phase. The G'' data are more sensitive to the slow relaxation of the ionic domains and, therefore, are more likely to show failure of TTS than the G' data, which are dominated by the elastic properties of the matrix[27]. Upon sulfonation, the rubbery region of the viscoelastic behaviour of PS is considerably broadened and the terminal region is not observed in *Figure 4*. That latter aspect is demonstrated by lower values for the slopes in *Figure 4* at low frequency for the ionomers than the theoretical terminal slopes of 2 for log G' vs. log ω and 1 for log G'' vs. log ω, which were observed for the starting PS. The broadening of the rubbery region and the shift of the terminal region to much lower frequency for SPS ionomers are consistent with previous studies of the rheology of ionomers[26,28] and may be attributed to an increase in relaxation times associated with association of the ionic species.

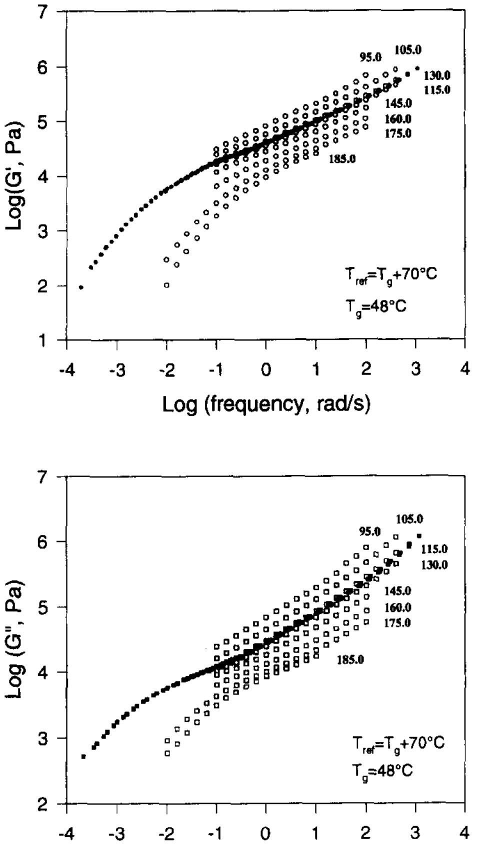

Figure 5 G' and G'' vs. frequency at various temperatures and the resulting master curves at $T_{ref} = T_g + 70°C$ for a 50/50 blend of Li-SPS9.5b/mPA

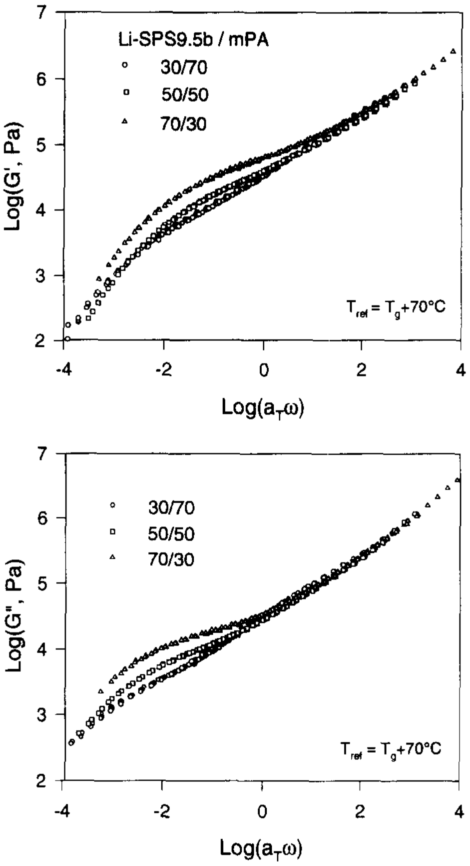

Figure 6 G' and G'' master curves for three compositions of Li-SPS9.5b/mPA blends. The reference temperature was $T_g + 70°C$

Blends using Li-SPSxb (*broad* MWD). Isothermal G' and G'' data for a 50/50 (w/w) blend of Li-SPS9.5b and mPA at eight different temperatures between 95 and 185°C are plotted *versus* frequency in *Figure 5*. The master curves referenced to a temperature of $T_g + 70°C$ are also shown. The master curves in *Figure 5* cover seven decades of frequency, while a single experiment covered at most only four decades. Unlike the data for the neat ionomer, the viscoelastic data for the blend obeyed TTS. The success of TTS in this case is probably due to solvation of the ionic aggregate structure by complexation of the polyamide with the metal sulfonate groups.

The frequency range covered in *Figure 5* is comparable to that studied by Colby[6] for PEO/PMMA blends for which TTS failed. One difference between the two systems is the strong exothermic interactions present in the ionomer/polyamide blend. A key reason for failure of TTS for miscible PEO/PMMA blends was the retention of the individual relaxation characteristics by each component polymer[6]. That fact is presumably a consequence of only weak interactions between PEO and PMMA. In contrast, Li-SPS9.5b and mPA form an intermolecular complex, and relaxation of either species must be coupled to that of the other. For example, Gao *et al.*[29] found that Li-SPS and nylon-6 blends exhibited only single n.m.r. relaxation times T_1 and $T_{1\rho}$. The perturbation of the ionomer relaxation times may also be inferred from a comparison of the low-frequency behaviour of the neat ionomer in *Figure 4* and that of the blend *Figure 5*. Clearly, the curves in *Figure 5* are closer to terminal behaviour. The low-frequency behaviour of the blend is expected to be dominated by the component with the longer terminal relaxation time, which in this case is the ionomer. Comparison of the data in *Figures 4* and *5* suggests that the addition of the polyamide decreases the terminal relaxation time for the ionomer, which is not unexpected since interactions of the sulfonate and amide groups also destroy the ionic aggregate microstructure that is responsible for the long relaxation times for the neat ionomer. One would also expect that the relaxation times for the polyamide would likewise be perturbed by complexation with the ionomer. As a result, the temperature dependences of the relaxation times for the two species in the blend are probably similar, or identical, in marked contrast to Colby's blend[6]. Thus, it appears that a preliminary response to Colby's question about the effect of weak *versus* strong interactions is that stronger intermolecular interactions are more favourable towards the applicability of TTS.

Master curves for three compositions of blends of Li-SPS9.5b and mPA are shown in *Figure 6*. Superposition of G' and G'' was successful for each composition. The values of G' and G'' increased with increasing ionomer concentration, and the slopes of the master curves at the lower frequencies studied were only about one-half the terminal values. The latter result indicates that the terminal zone of the blend occurs at lower frequency than was accessed in this study. In this case, however, the low frequency for terminal behaviour is thought to be a

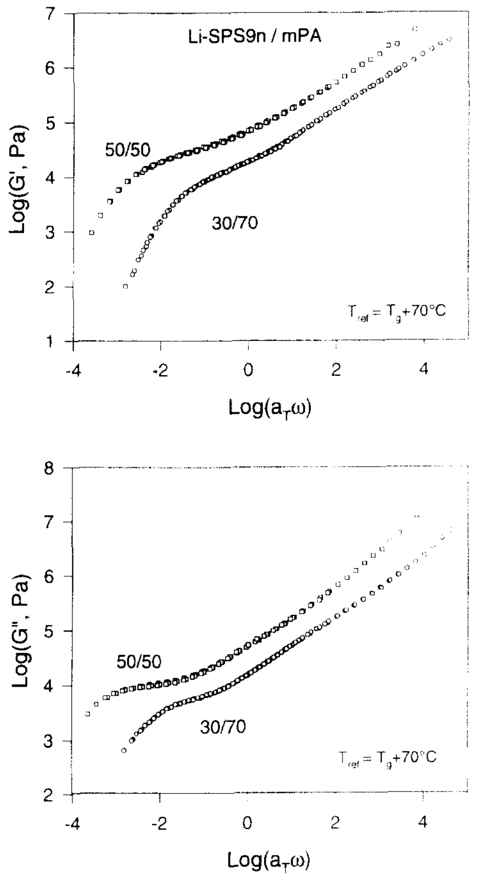

Figure 7 G' and G'' master curves for 50/50 and 30/70 Li-SPS9n/mPA blends ($T_{ref} = T_g + 70°C$)

consequence of intermolecular association of the two polymers, and not self-aggregation of the ionomer. Both mechanisms are expected to increase the effective size of the flow unit, which decreases segmental mobility and increases relaxation times.

Blends using Li-SPSxn (narrow MWD). Master curves of G' and G'' for miscible blends of the mPA and Li-SPS9n, which was prepared from the narrow *MWD* PS, are given in *Figure 7*. Two compositions are shown: 50/50 (w/w) and 30/70. TTS was successful for both blends, which together with the previously discussed results for blends made with the broad *MWD* ionomers (cf. *Figures 6* and *7*) indicates that the applicability of TTS for miscible blends of mPA and M-SPS is not affected by the *MWD* of the M-SPS. This result is in contrast to the prediction of Colby[6] that the use of polymers with narrow *MWD*s favours a breakdown of TTS for miscible blends, though in our case the success of TTS may be influenced by the broader *MWD* of the mPA and by the broad relaxation-time distribution of the ionomer. According to Colby[6], the breakdown of TTS for miscible blends is due to the retention of the individual characteristic relaxation times of the two components. This effect is masked when broad *MWD* polymers, with broader relaxation-time distributions, are used. The results of the present study suggest that, where the relaxation-time spectrum of the component polymers is perturbed by intermolecular complexation, any tendency for failure of TTS for a miscible blend may also be obscured.

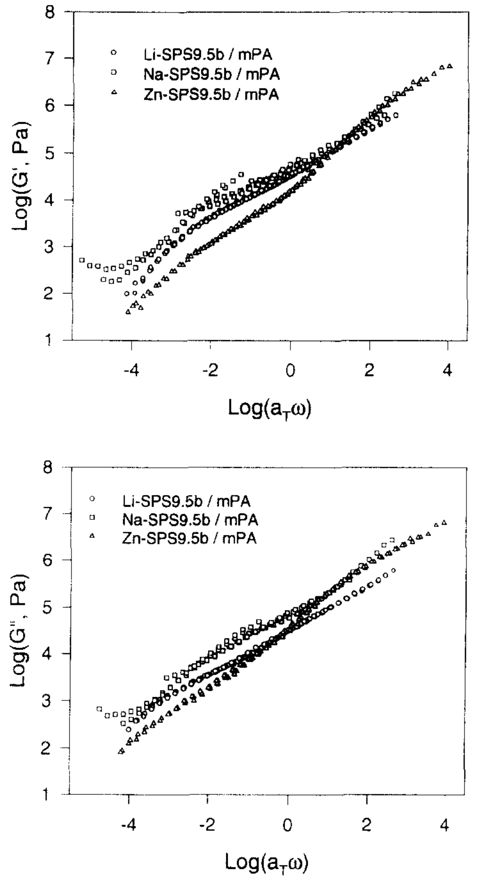

Figure 8 G' and G'' master curves of 30/70 (w/w) blends of Na-SPS9.5b/mPA, Li-SPS9.5b/mPA and Zn-SPS9.5b/mPA. The reference temperatures were taken as 135°C, $T_{ref} = T_g + 70°C$ and 91°C, respectively

The terminal zone is much better developed for the blends formed with the narrow *MWD* Li-SPS compared with those prepared from the broad *MWD* ionomer (cf. *Figures 6* and *7*). This result indicates that the *MWD* and the sulfonation are each partially responsible for broadening of the relaxation-time distribution in the blends. Note also that the terminal region for the blends of Li-SPS9n/mPA is much better developed than for the neat ionomer (cf. *Figures 4* and *7*). This result supports the hypothesis that the broadening of the low-frequency viscoelastic response in the two systems, i.e. the ionomer and the blends, results from two different mechanisms: self-association of the metal sulfonate groups in the neat ionomer, and intermolecular complexation of the amide and metal sulfonate groups in the blends.

Effect of using different ionomer cations. Master curves of 30/70 blends of different metal salts of SPS and mPA are compared in *Figure 8*. TTS fails for G' and G'' for the Na-SPS9.5b/mPA blend as a result of the immiscibility of the two polymers. Relatively good superposition, however, was attained for the Zn-SPS9.5b/mPA blend, which is surprising if it were truly immiscible. The G' and G'' data for this blend do show a little bit of mismatch at the lower frequencies, which correspond to the higher-temperature data. This may indicate that the blend was miscible at the lower experimental temperatures, but phase-separated at the higher temperatures used for the dynamic mechanical experi-

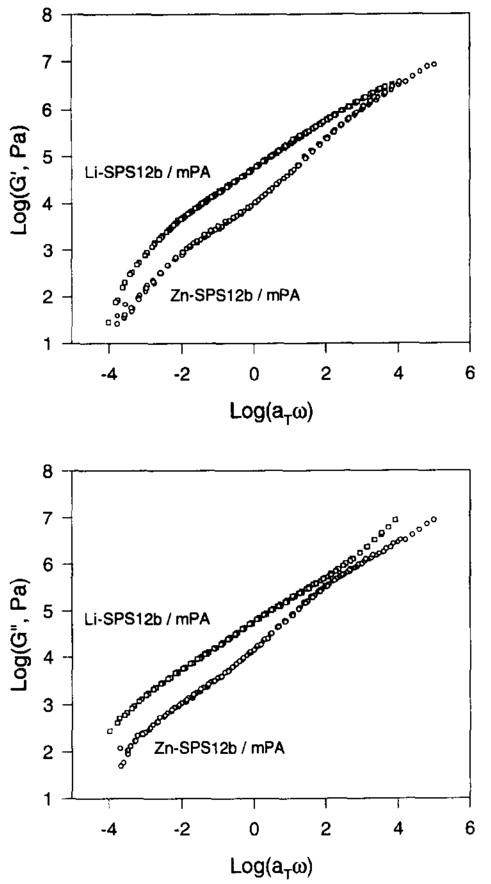

Figure 9 G' and G'' master curves of 30/70 (w/w) blends of Li-SPS12b/mPA and Zn-SPS12b/mPA. Reference temperatures were $T_{ref} = T_g + 70°C$ and 91°C, respectively

ments. The lower moduli values for this blend compared with the miscible blend of Li-SPS9.5b/mPA also suggest that they may have been more miscible than thought from the d.s.c. analysis, though the differences in the moduli may also be a consequence of using a low T_g for the reference temperature for the TTS (see 'Thermal analysis' in 'Results and Discussion').

Similar results (*Figure 9*) were obtained for blends containing ionomers with higher sulfonation levels, which were expected to enhance the interaction between M-SPS and mPA by increasing the concentration of interacting groups. The viscoelastic data for blends containing Li-SPS12b or Zn-SPS12b obeyed TTS, though the latter was thought to be immiscible (see 'Results and Discussion' above).

The temperature dependences of the shift factors a_T used to construct the master curves of 30/70 (w/w) blends of Li-SPS9.5b/mPA, Li-SPS9n/mPA and Li-SPS12b/mPA are shown in *Figure 10*. The data were fitted to the WLF equation[30]:

$$\log a_T = \frac{-c_1(T - T_{ref})}{c_2 + T - T_{ref}} \qquad (3)$$

where c_1 and c_2 are constants. The best fit of the WLF equation to the shift-factor data for each blend is shown by the full curves in *Figure 10* and the WLF constants for each are summarized in *Table 2*.

CONCLUSIONS

Linear viscoelastic data for miscible blends of methylated nylon-2,10 (mPA) and the lithium salt of lightly sulfonated polystyrene (Li-SPS) obeyed time–temperature superposition for compositions ranging from 30 to 70% ionomer. The molecular-weight distribution (*MWD*) of the ionomer did not influence the applicability of time–temperature superposition, though broadening the ionomer *MWD* for a fixed M_w also broadened the relaxation-time distribution and shifted the G' and G'' curves to lower frequency. In no case was terminal response for the blends observed, which is attributed to intermolecular complexation between the metal sulfonate and amide groups. The success of time–temperature superposition for the Li-SPS/mPA blends may be a consequence of strongly exothermic intermolecular interactions. Complexation is likely to perturb the characteristic relaxation times for the component polymers, and by doing so, couple their temperature dependences.

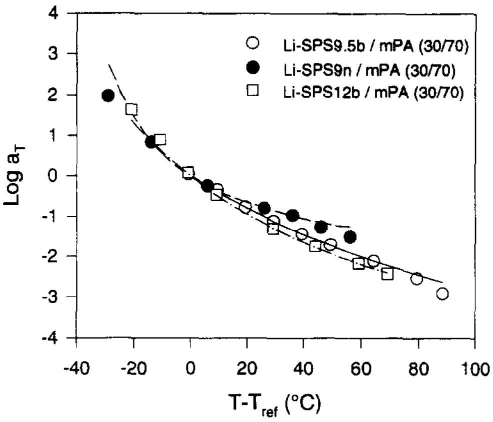

Figure 10 Shift factor, $\log a_T$, *versus* temperature difference, $T - T_{ref}$, for the 30/70 (w/w) blends of Li-SPS9.5b/mPA, Li-SPS9n/mPA. The full curves were calculated from equation (3) using the WLF constants in *Table 2*

Na-SPS9.5b/mPA blends were immiscible, and time–temperature superposition failed due to the different temperature dependences of the two separate phases. Blends of mPA with the zinc salts of SPS were judged to be only partially miscible, even though only a single T_g corresponding to a polyamide-rich phase was observed by calorimetry. Time–temperature superposition of G' and G'' worked fairly well for those blends, though there may have been some deviation from time–temperature superposition for the higher-temperature data for blends prepared from the ionomer containing 9.5 mol% sulfonation. At a higher sulfonation, i.e. 12 mol%, time–temperature superposition was applicable.

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Table 2 WLF constants for Li-SPS*x*/mPA blends

Sample	Composition (w/w)	c_1	c_2
Li-SPS9.5b/PA	30/70	7.9	177.9
Li-SPS12b/PA	30/70	6.7	122.9
Li-SPS9n/PA	30/70	2.5	55.2

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