

Miscibility and Mechanical Properties of Sulfonated Polystyrene–Polyurethane Blends

WEI YANG,¹ JIARUI SHEN,¹ SHUI-HAN ZHU,² CHI-MING CHAN²

¹ Institute of Materials Science & Engineering, South China University of Technology, Guangzhou, People's Republic of China

² Department of Chemical Engineering, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong

Received 31 October 1996; accepted 12 September 1997

ABSTRACT: A sulfonated polystyrene (SPS) and a polyurethane containing a tertiary amine group (NPU) were blended in solution. The effect of blend composition was studied in the blend of SPS with 9.83 mol % of sulfonation (SPS-9.83) and NPU with 33 mol % of MDEA (NPU-33). As the SPS concentration increases, a significant improvement of miscibility is observed. The tensile strength of the blends is greater than either pure NPU or SPS. A maximum strength and a maximum density occur at 50 wt % SPS. The stress–strain curve shows a well-defined yield when the SPS concentration in the blend is 30 or 50 wt %. The yield is more dramatic in the blend with 50 wt % SPS than that of 30 wt % SPS. At a lower SPS concentration, the blend behaves like a rubber, while a higher SPS concentration in the blend results in a brittle failure before yield. An increase in the sulfonation level of SPS in the SPS–NPU-33 (30/70) blends leads to an improved miscibility. A significant enhancement of tensile strength is observed as the sulfonation increases. A clear yield point on the stress–strain curves occurs when the sulfonation of SPS in the blend is 4.79 mol % or greater. Increasing the MDEA content of NPU up to 8.3 mol % can lead to an enhancement of tensile strength. A further increase in the MDEA content has little influence on the tensile strength, but a clear yield on the stress–strain curve occurs. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 2035–2045, 1998

Key words: SPS-NPU blends; miscibility; mechanical property; modulated d.s.c.

INTRODUCTION

It is well known that most polymer pairs are thermodynamically immiscible as a result of the small entropy of mixing and the endothermic enthalpy of mixing. Thus, compatibilization techniques are used to enhance the miscibility of polymer blends by using a compatibilizer or a specific interaction, which leads to an exothermic enthalpy of mixing. The compatibilization is important because it can

achieve the required improvement of mechanical properties in practical applications. One approach to acquire compatibilization is the addition of a block copolymer,^{1,2} which tends to locate at the interface of the blends, with the block in the enthalpically favored phases. The interfacial tension can be reduced and the interfacial thickness increased, leading to an enhanced interfacial adhesion. However, synthesis of these copolymers is usually carried out at a considerable cost. Therefore, much recent effort has been redirected to *in-situ* reactive compatibilization during blending. This reactive compatibilization technique can generate a strong interaction or a chemical cou-

Correspondence to: W. Yang.

Journal of Applied Polymer Science, Vol. 67, 2035–2045 (1998)
© 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/122035-11

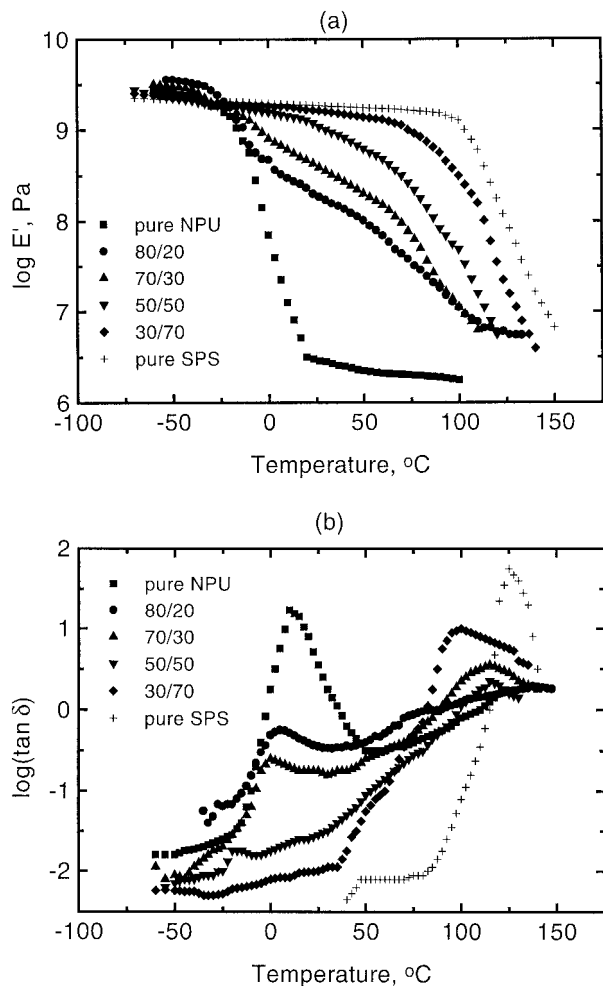


Figure 1 The storage modulus (a) and loss tangent (b) of SPS-9.83-NPU-33 blends as a function of temperature at different SPS-9.83 concentrations.

pling by tailoring specific functional groups into the blend components.³⁻⁶ Formation of covalent bonds, hydrogen bonds, and strong enthalpic and ionic interaction between the functional groups of the components has been demonstrated to be an effective method to improve the miscibility of the blends. Morphological control can be achieved by changing the extent of the interaction between the functional groups.

Sulfonated polystyrene (SPS) has been studied because the sulfonic acid can form very strong interactions with other moieties. The interaction between the sulfonic acid in sulfonated polystyrene and nitrogen-containing polymers like polyurethane,⁷⁻⁹ polyvinylpyridene,¹⁰ and polyamide^{11,12} has been shown to be particularly strong. In SPS-polyurethane blends, the proton in SPS is shown to be able to transfer to the nitrogen

atoms.¹³⁻¹⁴ A tertiary amine can be incorporated into polyurethane by using *N*-methyl diethanolamine (MDEA) as the chain extender in the synthesis. The amount of the tertiary amine group is easy to be changed in the synthesis without affecting the ratio of hard segment to soft segment. Thus, the amount of nitrogen atoms in the polyurethane, which is the interaction point with SPS, can be varied by controlling the amount of MDEA in polyurethane.

Stress-strain behavior of homopolymer has been studied and modeled.¹⁵⁻²² The yield point on the stress-strain curve is regarded as the onset of a strain softening or a plastic flow. A semicrystalline polymer, like polyethylene, usually has a well-defined yield, followed by a plastic flow, while an elastomer has only a strain softening region without a clear yield point. The yield behavior, which involves the disruption of a strong cohesion, is usually dependent on temperature, pressure, and strain rate of test. The morphology, molecular characteristics (molecular weight, branched and or linear), and crystallite structure have a profound effect on the yield.²⁰⁻²² However, the stress-strain behavior of polymer blends is less studied. Thermoplastic polyurethane is segmented linear copolymer, in which the hard-segment-rich phase functions as the physical crosslinks in the rubbery soft-segment-rich matrix. The hydrogen bond of the hard segment can be

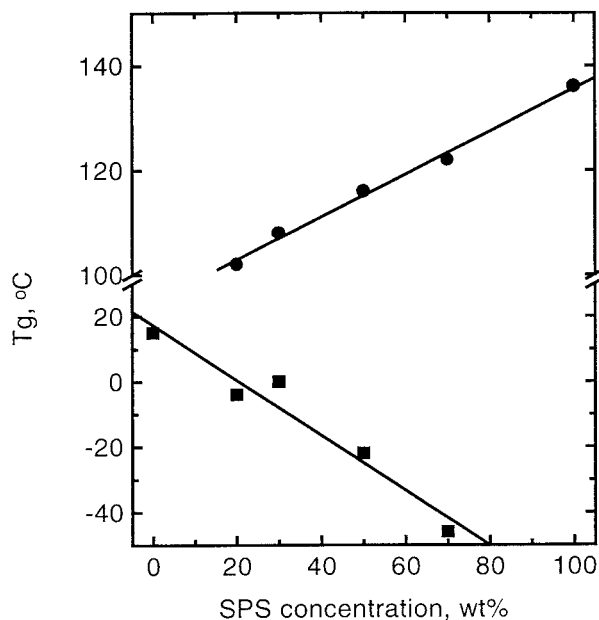


Figure 2 The glass transition temperature from DMA of SPS-9.83-NPU-33 blends as a function of SPS-9.83 concentration.

disrupted at high temperature, and thermoplastic processing techniques, such as injection molding, can be used for their processing. The excellent mechanical properties allow them to be used in many applications. Higher modulus and higher temperature resistance can be obtained, usually at the expense of elasticity loss. By blending with SPS, these properties are expected to be improved.

In the present study, polyurethane containing a tertiary amine group (NPU) with different amounts of tertiary amine group and SPS containing different sulfonation level were synthesized. Their blends were prepared in solution. The miscibility and the mechanical properties of SPS-NPU blends are presented.

EXPERIMENTS

The starting polystyrene in the preparation is a commercial resin (Gaofu Plastic Co., China). The

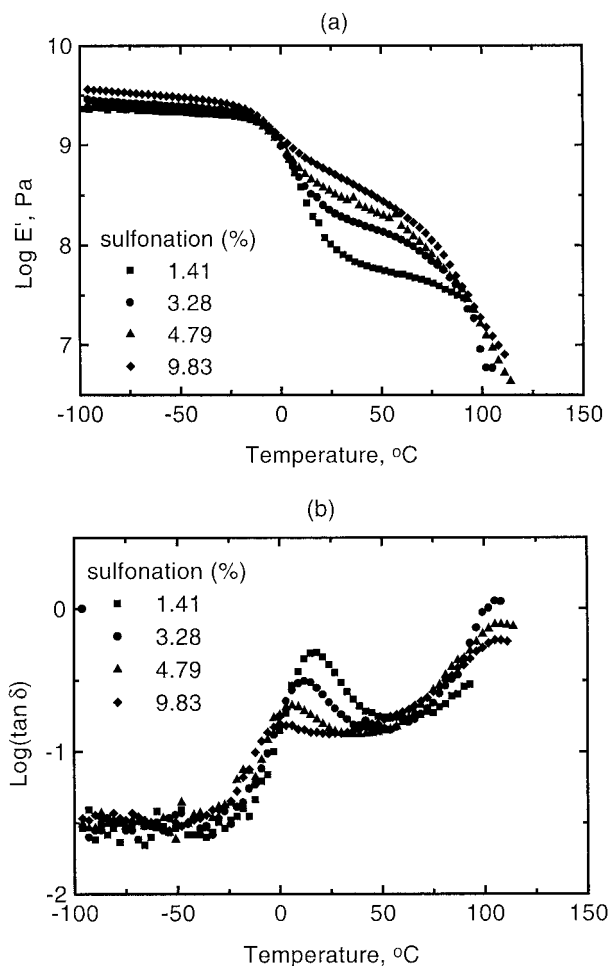


Figure 3 The storage modulus (a) and loss tangent (b) of SPS-NPU-33 (30/70) blends at different sulfonation levels in the SPS as function of temperature.

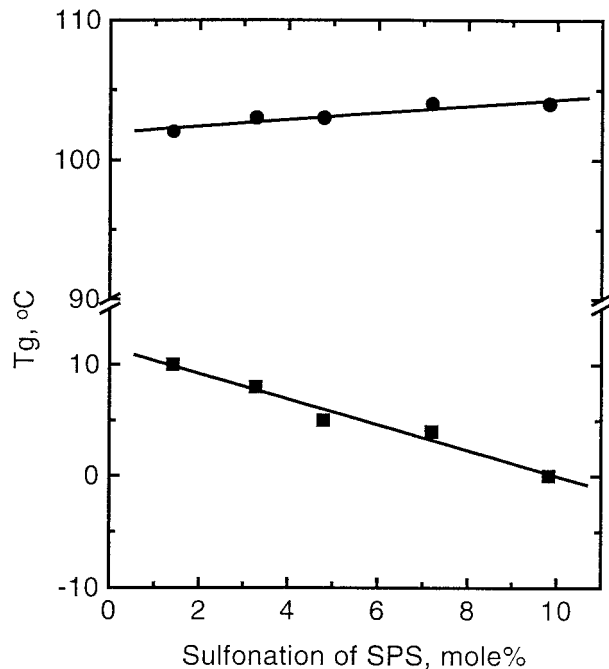


Figure 4 The glass transition temperature from DMA of SPS-NPU-33 (30/70) blends as a function of sulfonation level in the SPS.

number- and weight-averaged molecular weights were measured to be 7.85×10^5 and 2.60×10^6 , respectively, by gel permeation chromatography (GPC) (Waters 150C). The SPS was prepared by a mixed acetic anhydride and concentration sulfuric acid in 1,2-dichloroethane at 50°C, following the procedure of Makowski et al.²³ The sulfonation level in SPS was determined by titration with standard methanolic sodium hydroxide to the phenolphthalein end point in a 1% (w/v) toluene-methanol (90/10, v/v) mixture solution. The SPS containing 1.41, 3.28, 4.79, 7.20, and 9.83 mol % was designated SPS-1.41, SPS-3.28, SPS-4.79, SPS-7.20, and SPS-9.83, respectively.

A two-step condensation reaction was used to prepare the NPU. The first step was preparation of the prepolymer, as follows. 4,4'-diphenylmethane diisocyanate (MDI) was added to the vigorously stirred polypropylene glycol (PPG) (N210, Nanjing Plastic Co., China, $M_n = 1100$) with end-capped hydroxyl groups. The reaction between MDI and PPG was kept for 2 h under nitrogen atmosphere at 65°C. The amount of MDI and PPG was controlled at a NCO : OH molar ratio of 3 : 1. The second step is the chain extension of the prepolymer. The prepolymer was diluted in anhydride *N,N'*-dimethyl formamide (DMF). Two chain extenders, MDEA and butanediol (BD) in

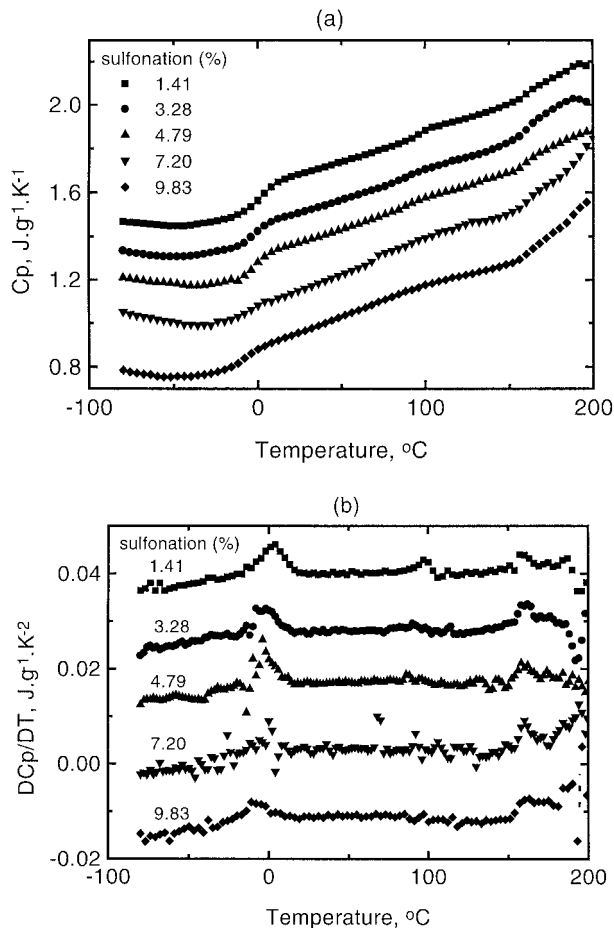


Figure 5 The heat capacity (a) and its derivative (b) of SPS–NPU-33 (30/70) blends with different sulfonation levels in the SPS as a function of temperature. The curves are offset for clarity.

desired ratio, were added into the diluted prepolymer solution in an appropriate quantity to maintain a NCO : OH ratio at 1 : 1. The molar percentage of MDEA segment in the NPU (MDI + MDEA + BD + PPG), in 2.08, 4.17, 8.33, 16.67, and 33 mol %, respectively, was obtained by adjusting the ratio of MDEA to BD. These NPUs were designated as NPU-2.08, NPU-4.17, NPU-8.33, NPU-16.67, and NPU-33, respectively. Stannous octoate at 0.03 wt % was used as the catalyst to carry the chain extension reaction to completion. The reaction lasted for 1 h, in which the amount of NCO group was measured to be less than the set value. The polymers were precipitated in water and dried under vacuum at 70°C for 1 week. The molecular weight and distribution of NPU was determined by GPC (Waters-150C) in the tetrahydrofuran (THF). Three columns (μ -Styragel: 50, 10^3 , and 10^4 nm, respectively) in the series

were used. Monodisperse polystyrene was used to as the standard for calibration. The number- and weight-averaged molecular weights were measured to be 3.18×10^4 and 1.76×10^5 , respectively.

The blends of NPU and SPS were prepared in solution. NPU was dissolved in a mixture solvent of THF and dimethyl sulfoxide (DMSO) in a ratio of 9 : 1 (v/v). The SPS was dissolved in THF and added dropwise to the vigorously stirred NPU solution. The solution mixture was stirred for 5 h, and the solvent was evaporated at ambient temperature. The blends were further dried at 70°C under vacuum for 1 week to remove the residual solvent. The blends containing 20, 30, 50, 70, and 80 wt % of SPS were prepared.

The samples used for the measurement were prepared by compression molding. The blends were heated in the mold to a temperature of approximately 20°C above T_g (depending on the sample) for approximately 20 min at 25 MPa, then removed to a cold press. After cooling down for 5 min, the samples were taken out and maintained in the desiccator.

The dynamic mechanical properties were measured using a dynamic viscoelastic analyzer (Rheovibron DDV II-EA). Thin slab samples ($40 \times 2 \times 0.2$ mm) were subjected to a sinusoidal tensile load with a frequency of 3.5 Hz. A pretension force was applied to assure a tensile load. The temperature ramped from -100 to 170°C at a heating rate of 2°C/min.

A modulated differential scanning calorimeter (MDSC, TA 2900) was used to study the heat flow at a ramp rate of 3°C/min from -120 to 210°C. A detailed description about MDSC is referred to in the literature.^{24–26} The linear temperature ramp was superposed by a sinusoidal temperature modulation (1.5°C amplitude and 60 period s), and the total heat flow was deconvoluted into the reversible and nonreversible components by a discrete fast Fourier transform program (a TA MDSC software). The heat capacity was calculated from the reversible heat flow. By setting the two points before and after the transition region on the reversible heat flow, the glass transition temperature was obtained from the position of the inflection point of the transition, which was computed by the computer software. The increment of heat capacity was calculated from the area under the derivative curve of heat capacity at the transition region. The temperature was calibrated using indium. No calibration for heat capacity was carried out.

Table I The Glass Transition Temperatures (T_g) and the Heat Capacity Increment (ΔC_p) at the Transition Obtained from MDSC for SPS–NPU-33 (30/70) Blends at Several Sulfonation Levels

Sulfonation of SPS (mol %)	T_{g1} (°C)	ΔC_{p1} (mJ·K ⁻¹ ·g ⁻¹)	T_{g2} (°C)	ΔC_{p2} (mJ·K ⁻¹ ·g ⁻¹)	T_{g3} (°C)	ΔC_{p3} (mJ·K ⁻¹ ·g ⁻¹)
1.41	3.6	36.12	97.9	14.25	158.8	29.24
3.28	-3.3	33.97	90.7	11.27	162.6	19.51
4.79	-3.6	27.24	86.8	2.41	157.5	17.20
7.20	-7.5	26.64	69.2	2.91	159.9	18.81
9.83	-9.6	18.73	—	—	159.1	19.61

The tensile stress–strain curves were obtained using a tensile tester (Monsanto 10) according to the ASTM method D638-90. The test was performed at ambient temperature at a crosshead speed of 100 mm/min.

The density of samples was determined by specific gravity bottle in water at 20°C. Five specimens were used for each sample test.

RESULTS AND DISCUSSION

Miscibility Enhancement

Effect of Blend Composition

Figure 1(a) and (b) shows the dynamic storage modulus and loss angle tangent as a function of temperature for NPU-33–SPS-9.83 blends at different blend compositions. Figure 1(a) shows the storage modulus of the blends. In the glass–rubber transition region, either pure NPU or SPS shows a sharp drop in moduli. In the case of the four blends, the transition regions lie between those of the neat polymers. There are two distinct transition regions in the blends containing 20 and 30 wt % of SPS. As SPS concentration increases, the transition step in modulus at the lower temperature decreases. Figure 1(b) shows the loss tangent ($\tan \delta$) for the pure components and their blends. The pure NPU-33 shows a high-intensity loss peak at 15°C, which is attributed to the glass transition of soft-segment-rich phase in the NPU. The SPS-9.83 has a loss peak around 130°C, corresponding to the glass transition of SPS matrix.²⁷ Two peaks are observed for the blends, the low-temperature peak related to the NPU component and the high-temperature to SPS component. Increasing the SPS concentration of the blends leads to a dramatic decrease in the intensity of the low-temperature peak and a change of the peak position. Since the peak intensity is proportional to

the volume fraction of the respective phases, the reduction in the intensity of the low-temperature peak indicates a decrease in the volume fraction of the soft-segment-rich phase of the NPU in the blends.

The position of the low-temperature or the high-temperature peak in the $\tan \delta$ curves is a measure of the glass transition temperature (T_g). The T_g thus obtained from $\tan \delta$ curves as a function of SPS concentration is shown in Figure 2. It is seen very clearly that the peak positions are strongly composition-dependent. As the SPS concentration increases, the low-temperature T_g shifts to a lower temperature while the high-temperature T_g moves to a higher temperature. This is a little surprising since strong interaction in a polymer blend usually draw the two T_g s closer.

These phenomena can be understood on the following basis. The glass transition temperature of soft segment for the polyurethane is about -5°C²⁸; however, the glass transition temperature of soft segment for NPU is found at about 15°C. It is suggested that the MDEA in hard segment of NPU cause more homogenous mixture of hard and soft segments.²⁹ Rutkowaska and Eisenberg,⁷ Estes et al.,³⁰ and Seymour and Cooper³¹ suggested that only the systems that contain more than 38 wt % MDI (like the present system) exhibit an interconnected hard domain morphology. As SPS is added, acidic proton transfer from SPS to the tertiary nitrogen in NPU can be expected. This would lead to strong Coulombic interaction between the sulfonate anion in SPS and the quaternary ammonium cation in the hard segment of NPU. It would result in very intimate mixing of SPS with the hard segment and the preferential exclusion of the soft segment from the blend of the hard segment and SPS. Such exclusion may result in a purer soft segment phase, thus, the decrease of the low-temperature T_g . The increase in the high-temperature T_g would be

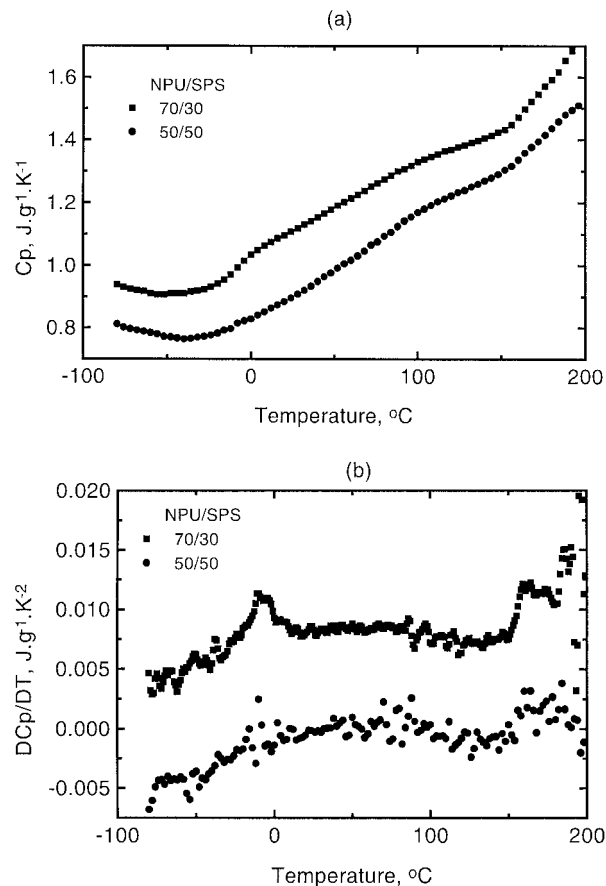


Figure 6 The heat capacity (a) and its derivative (b) of SPS-9.83–NPU-33 blends at two SPS concentrations as a function of temperature. The curves are offset for clarity.

attributed to the influence of the hard segment in NPU.

Around 50%, the SPS sample corresponds to a stoichiometric ratio of sulfonic acid to tertiary amine. We noticed that samples containing a higher concentration of SPS also seem to form excellent blends. This might suggest that the sulfonic acid can interact with other groups in NPU, with the most reasonable possibility being urethane group. It has been proven by Fourier transform infrared (FTIR)¹³ and nuclear magnetic resonance (NMR)¹⁴ spectra.

Effect of Sulfonation Level in SPS

Figure 3(a) and (b) shows the storage modulus and $\tan \delta$ for the SPS–NPU-33 (30/70) blends with a varying sulfonation level in the SPS. An increase in the sulfonation gives rise to an increase in the intermediate plateau modulus and a decrease in the peak intensity at the low tempera-

ture of $\tan \delta$, again suggesting the strong mixing between SPS and the hard segment of NPU. If this mixing had not occurred, the value of modulus at that point would be far less dependent on the sulfonation level in SPS.

The change in the T_g of the blends as a function of the sulfonation level is presented in Figure 4. As the sulfonation level increases, the low-temperature T_g decreases to a lower temperature. This phenomena supports the assumption that the interaction can result in the preferential exclusion of the soft segment from the blend of hard segment and SPS.

The increment of heat capacity in the transition region measured from differential scanning calorimetry (DSC) is proportional to the volume fractions of the respective phase in the blend.^{24–26,32,33} A MDSC can eliminate the disturbance for the samples, which are easy to absorb moisture by themselves, like polyurethane. A MDSC was used in the present study to determine the heat capacity (C_p), and the derivative (DC_p/DT) of the sample as a function of temperature. The C_p and DC_p/DT of the SPS–NPU-33 (30/70) blends at different sulfonation levels are shown in Figure 5(a) and (b). Figure 5(a) shows the C_p curves of the blends. There is a step at low temperature, corresponding to the glass transition of the soft segment in NPU. The high-temperature transition

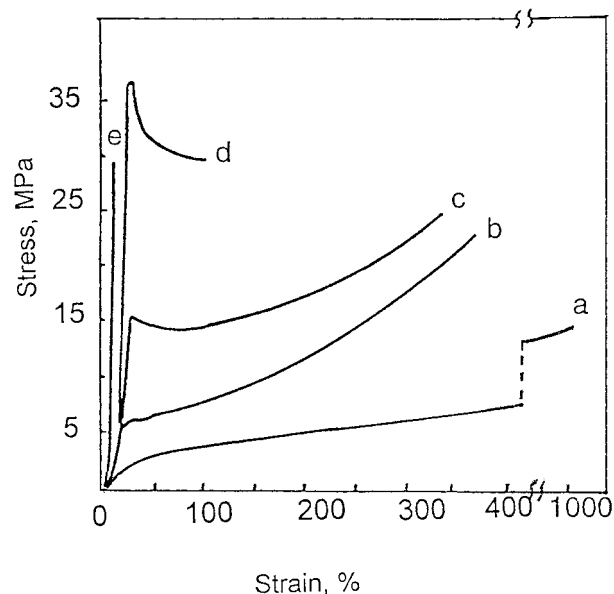


Figure 7 The stress–strain curves of SPS-9.83–NPU-33 blends at different SPS-9.83 concentrations: (a) pure NPU, (b) 20/80, (c) 30/70, (d) 50/50, and (e) 70/30.

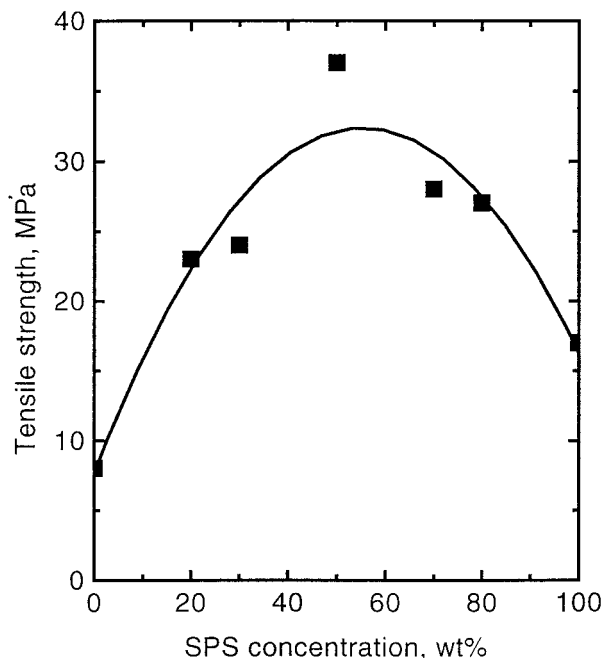


Figure 8 The tensile strength of SPS-9.83-NPU-33 blends as a function of SPS-9.83 concentration.

on the C_p curves is attributed to the hard segment phase of the NPU,²⁸ which may form hydrogen bonds. At the intermediate region, a very small step or a turn point on the C_p curves occurs.

The derivative curve gives a better presentation of the small changes. Figure 5(b) shows the derivative curves (DC_p/DT) of the data in Figure 5(a). A small step increment on the C_p curves becomes a peak on the derivative curves. With the increase of sulfonation in the SPS, the low-temperature peak shifts down to lower temperature, and the peak area becomes smaller [see Fig. 5(b)]. The intermediate peak can be observed on the curves. A clear peak around 90°C occurs for the blend with 1.41 mol % of sulfonation in SPS. This transition may be attributed to the glass transition of SPS matrix. The area under the peak obtained by integration is the heat capacity increment at the transition. The T_{gs} and ΔC_p s thus obtained from the MDSC data for the three transitions are summarized in Table I. The T_{g1} at the low-temperature transition region decreases with the increase of sulfonation in the SPS. This phenomenon is consistent with the DMA results.

The heat capacity increments show a decreased tendency with the increase of sulfonation level in SPS. This has been shown to be the indications of improved miscibility^{32,33} and increased degree of ionic crosslinking.^{34,35} The interdiffusion of two

miscible polymer has been studied using the decrease in the heat capacity increment at the transition as a function of the annealing time.²⁴

The C_p and DC_p/DT curves of two SPS-9.83-NPU-33 (30/70 and 50/50) blends are shown in Figure 6(a) and (b). In the case of the blend containing 30 wt % SPS, the transitions are visible from the step change on the C_p curve and the peak on the DC_p/DT curve. All the transitions become obscure for the blend with 50 wt % SPS. The obscure transitions of the SPS-9.83-NPU-33 (50/50) blend may be regarded as an indication of increased miscibility, which is a result of a higher degree of ionic interaction between the components.

Mechanical Properties

Effect of Blend Composition

Figure 7 shows the stress-strain behavior of the pure NPU-33 and the SPS-9.83-NPU-33 blends at several blend compositions. The pure NPU behaves like a typical elastomer with a very large elongation at break. The strain softening starts at a low strain, and the elongation at break exceeds 1000%. A strain hardening can be observed before break due to the molecular orientation. In the blend with 20 wt % SPS, the mechanical response is similar to that of an elastomer. However, when

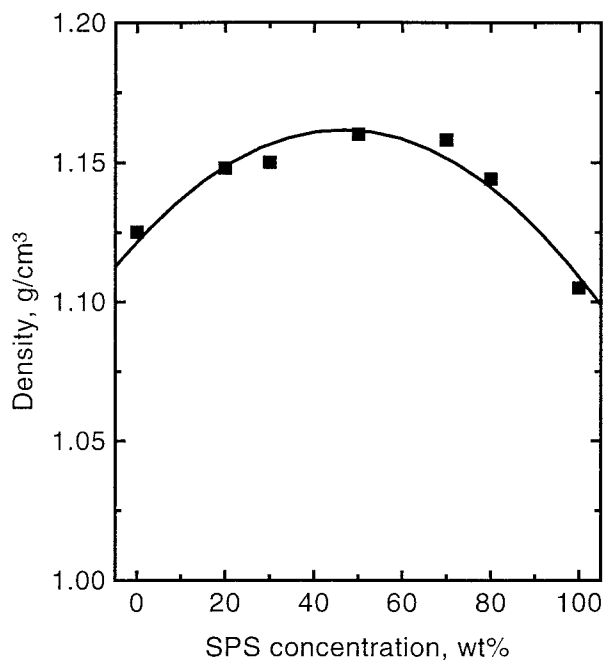


Figure 9 The density of SPS-9.83-NPU-33 blends as a function of SPS-9.83 concentration.

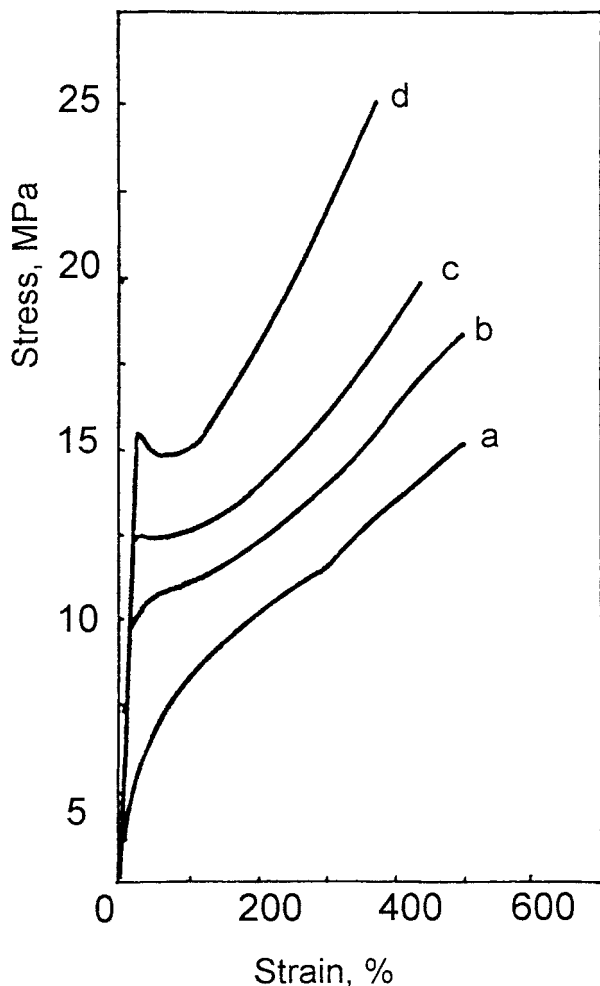


Figure 10 The stress-strain curves of SPS-NPU-33 (30/70) blends at different sulfonations in the SPS: (a) 1.41, (b) 3.28, (c) 4.79, and (d) 9.83 mol %.

SPS concentration increases up to 30 wt % in the blend, a distinct yield appears on the stress-strain curve. There is a small region of plastic flow after the yield and a long strain hardening region, resulting in a larger stress at break (tensile strength) than the yield stress. When the MDI content in polyurethane is greater than 38 wt %, the hard segment phase becomes interconnected, which is applicable to the NPU in this study. Addition of SPS decreases the volume fraction of soft-segment-rich phase, forming a morphology similar to those materials with a yield behavior. The semicrystalline polymers, such as polyethylene, and toughened plastics, such as high-impact polystyrene, are typical examples of those materials. A more profound yield can be observed for the blend containing 50 wt % SPS, in which the interaction is very strong. This result

suggests that the yield peak on the stress-strain curves is related to disruption of the ionic crosslinking. A higher degree of crosslinking in the blend means a higher barrier to the plastic flow. However, the strain-hardening region is absent in the case of the blend with 50 wt % SPS. A higher SPS concentration in the blend leads to a brittle failure.

The tensile strength of SPS-9.83-NPU-33 blends as a function of SPS concentration is shown in Figure 8. All the blends have higher tensile strength than either of the neat polymers. This synergism in strength is unusual and is a direct result of the strong ionic interaction between SPS and NPU molecules. At 50 wt % of SPS, maximum tensile strength is obtained. The higher tensile strength and the lower elongation at break of samples would be due to the network-like structure and ionic aggregation.³⁶⁻³⁷

The strong interaction between SPS and NPU may result in a decrease in the free volume and, thus, an increase in density. The density of the SPS-9.83-NPU-33 blends as a function of SPS concentration is shown in Figure 9. Similar to the

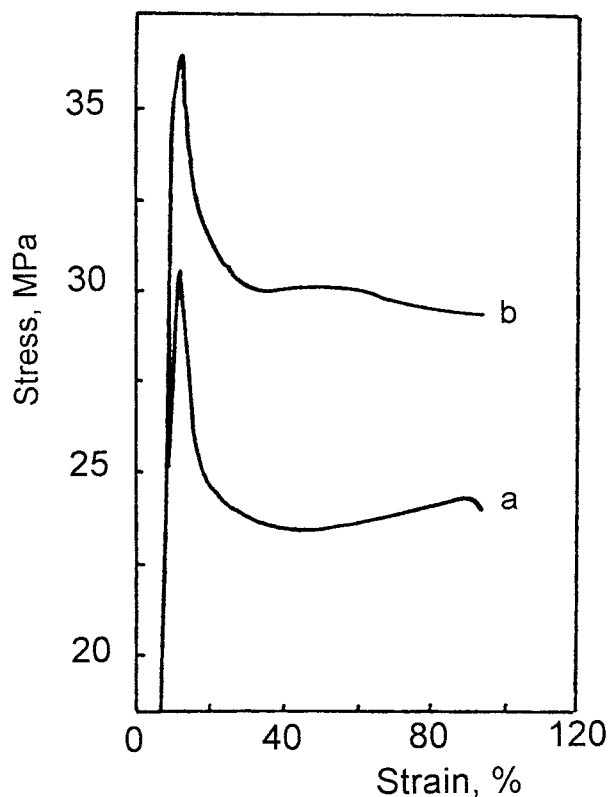


Figure 11 The stress-strain curves of SPS-NPU-33 (50/50) blends at two sulfonations in the SPS: (a) 4.79 and (b) 9.83 mol %.

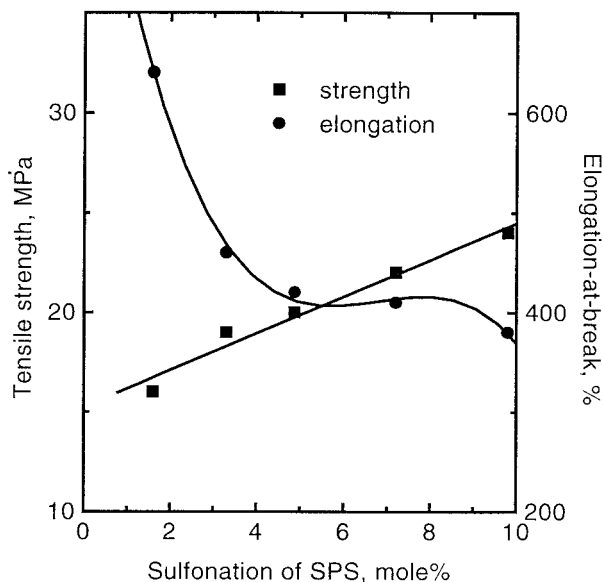


Figure 12 The tensile strength and elongation-at-break of SPS-NPU-33 (30/70) blends as a function of sulfonation level in the SPS.

tensile strength, all the blends have a higher density than either pure SPS or NPU. A maximum density is reached at 50 wt % SPS in the blend. The strongest interaction between the components results in a maximum contraction of the blends.

Effect of Sulfonation Level in SPS

Figure 10 shows the stress-strain curves for the SPS-NPU-33 (30/70) blends at several sulfonation levels. The blends containing SPS with a low sulfonations (1.41 or 3.28 mol %) behave like a filler-reinforced elastomer, with a large elongation at break and a strain hardening in the high-strain region ($>300\%$). A relatively higher sulfonation in the SPS enhances the tensile strength of the blends due to the higher degree of ionic crosslinking between the SPS and the NPU. At a high sulfonation (4.79 mol %), an unambiguous yield can be observed. It is well known that at a low ionic content, only an ionic multiplex exists in an ionomer. The ionic cluster is formed when the ionic content exceeds approximately 4 mol %.³⁸ In analogy, the occurrence of yield on the stress-strain curve of the blend containing SPS with a sulfonation of 4.79 mol % suggests that the yield behavior of the blend is related to the formation of ionic clusters. An increase in the sulfonation up to 9.83 mol % shows a sharp peak at

the yield, and the strain hardening is more abrupt due to the increase of ionic clusters content.

A more profound yield is found in the SPS-NPU-33 (50/50) blends, as is shown in Figure 11. In comparison with the SPS-NPU-33 (30/70) blends containing 30 wt % SPS (see Fig. 10), the SPS-NPU-33 (50/50) blend shows a more dramatic yield peak due to the higher degree of ionic crosslinking between SPS and NPU. With the increase of SPS concentration from 30 to 50 wt %, a drastic reduction in the elongation at break is observed, and the strain-hardening region disappears on the stress-strain curve. An increase in sulfonation of the SPS in the SPS-NPU-33 (50/50) blend leads not only to the enhanced tensile strength but also an increase in the yield stress (see Fig. 11). However, the elongation at break is unchanged as the sulfonation increases. This may be due to the formation of ionic clusters in

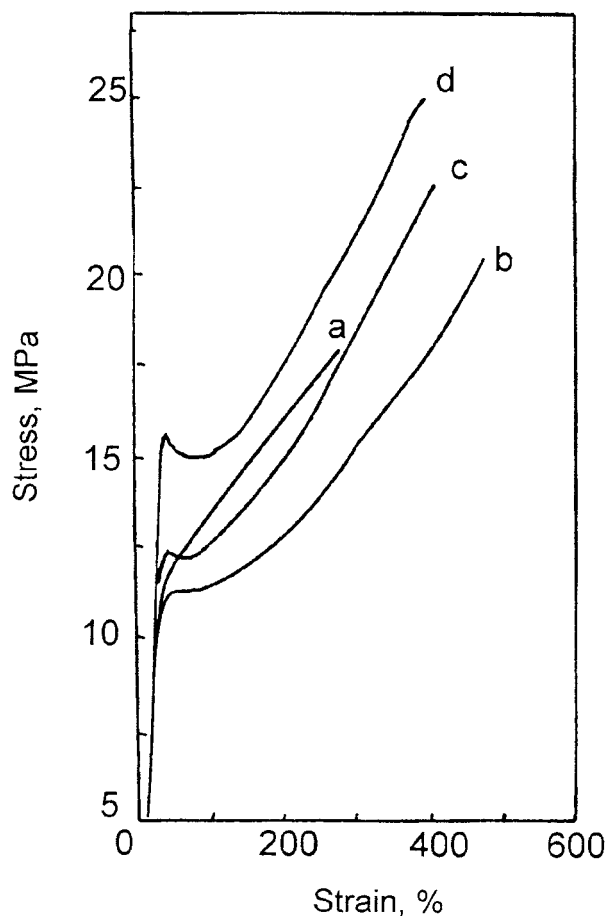


Figure 13 The stress-strain curves of SPS-9.83-NPU (30/70) blends at different MDEA contents in the NPU: (a) 2.08, (b) 8.33, (c) 16.67, and (d) 33.00 mol %.

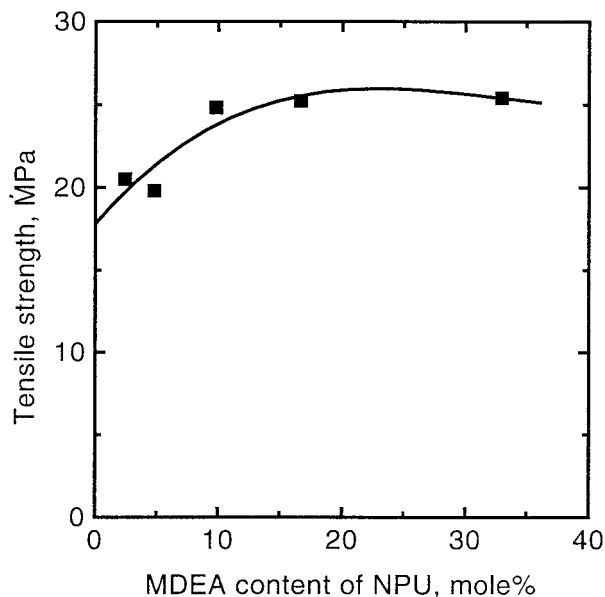


Figure 14 The tensile strength of SPS-9.83-NPU (30/70) blends as a function of MDEA content in the NPU.

both blends, which will be discussed in the subsequent paragraph.

Figure 12 shows the tensile strength and elongation at break of the blends. The tensile strength increases almost linearly with the increase of the sulfonation in the SPS up to 9.83 mol %. The elongation at break of the blends decreases with the increase of sulfonation in the SPS. The decrease in elongation at break is significant at a low sulfonation level, then levels off at 4.79 mol %, which corresponds to the threshold sulfonation to form ionic clusters. The elongation at break is almost the same for the SPS-NPU-33 (50/50) blend, where the sulfonation of SPS is above the critical sulfonation level for the formation of ionic clusters.

Effect of MDEA Content in NPU

Figure 13 shows the stress-strain curves for the SPS-9.83/NPU (30/70) blends with varying MDEA content in the NPU. At a low MDEA content (2.08 mol %), the blend material does not show a yield peak. With an increase of MDEA content from 8.33 to 33 mol %, the yield becomes increasingly significant. This indicates that the tertiary amine group in the MDEA segment of the NPU is a major contributor for the proton transfer between the labile protons of sulfonic acid in the SPS and the nitrogen in the NPU. The appearance

of the yield is related to the disruption of a sufficient number of ionic crosslinks in the blends. The more crosslinks, the more dramatic the yield behavior will be.

Figure 14 shows the tensile strength of the SPS-9.83-NPU (30/70) blends as a function of MDEA content in the NPU. The tensile strength of the blend increases at a low MDEA content. However, when the MDEA increases to 8.33 mol %, further increase in the MDEA content has little influence on the tensile strength of the blend, owing to the fact that the asymmetrical methyl group in MDEA cripples the aggregation of hard segment domain in NPU.²⁹

CONCLUSIONS

- It is shown that SPS-NPU blends are miscible. With the increase of the concentration of SPS in blends or the sulfonation level in SPS, the miscibility is improved. Strong interaction, resulting from proton transfer from sulfonic acid to tertiary amine, leads to miscibility enhancement, which leads, in turn, to the exclusion of the soft segment into a separated phase and to ionic crosslinking network formation.
- In the SPS-9.83-NPU-33 blends, the tensile strength exhibits a synergetic effect from linearly additivity of properties over a whole composition. The maxima of the strength and the density of blend exist around the stoichiometric ratio of sulfonic acid to tertiary amine. At a concentration of 30 to 50 wt %, there is a well-defined yield on the stress-strain curves. A SPS concentration greater than 50 wt % in the blend results in a brittle failure.
- For the SPS/NPU-33 (30/70) blend, there is a well-defined yield when the sulfonation is more than 4.79 mol %. Increasing the sulfonation level in the SPS enhances the strength of the blends and decreases the elongation at break. Increasing the MDEA content in the NPU leads to an increase in the tensile strength of the SPS-9.83-NPU (30/70) blends. A minimum of MDEA content (8.33 mol %) is necessary for the occurrence of a yield.

This research was supported by the Higher Education Bureau Foundation, Guangdong Province, P. R. China.

REFERENCES

1. L. A. Utracki, *Polymer Alloy and Blend Thermodynamics and Rheology*, Hanser, New York, 1989.
2. T. Li, V. A. Topolkaev, A. Hiltner, E. Baer, X. Z. Ji, and R. P. Quirk, *J. Polym. Sci., Part B*, **33**, 667 (1995).
3. I. Park, J. W. Barlow, and D. R. Paul, *J. Polym. Sci., Part B*, **30**, 1021 (1992).
4. R. E. Taylor-Smith and R. A. Register, *J. Polym. Sci., Part B*, **32**, 2105 (1994).
5. L. Mascia and A. Moggi, *J. Polym. Sci., Part B*, **31**, 1309 (1993).
6. A. Adedeji and A. M. Jamieson, *Polymer*, **34**, 5038 (1993).
7. M. Rutkowaska and A. Eisenberg, *Macromolecules*, **17**, 821 (1984).
8. M. Rutkowaska and A. Eisenberg, *J. Appl. Polym. Sci.*, **29**, 755 (1984).
9. M. Rutkowaska and A. Eisenberg, *J. Appl. Polym. Sci.*, **48**, 521 (1993).
10. A. Eisenberg, P. Smith, and Z. L. Zhou, *Polym. Eng. Sci.*, **22**, 1117 (1982).
11. A. Molnar and A. Eisenberg, *Polym. Eng. Sci.*, **33**, 1665 (1992).
12. A. Molnar and A. Eisenberg, *Polym. Commun.*, **32**, 370 (1992).
13. R. Tannenbaum, M. Rutkowska, and A. Eisenberg, *J. Polym. Sci., Part B, Polym. Phys.*, **25**, 663 (1987).
14. A. Natansohn, M. Rutkowaska, and A. Eisenberg, *Polymer*, **28**, 885 (1987).
15. L. Castellani and C. Maestrini, *Polymer*, **31**, 2278 (1990).
16. N. W. J. Brooks, R. A. Duckett, and I. M. Ward, *J. Rheol.*, **39**, 425 (1995).
17. N. W. J. Brooks, R. A. Duckett, and I. M. Ward, *Polymer*, **33**, 1872 (1992).
18. R. Seguela and F. Rietsch, *J. Mater. Sci. Lett.*, **9**, 46 (1990).
19. R. W. Truss, P. L. Clarke, R. A. Duckett, and I. M. Ward, *J. Polym. Sci., Polym. Phys. Ed.*, **22**, 191 (1984).
20. H. Andrews, *Pure Appl. Chem.*, **31**, 91 (1972).
21. Z. Bartzcak, R. E. Cohen, and A. S. Argon, *Macromolecules*, **25**, 4692 (1992).
22. R. N. Haward and G. Thackray, *Proc. R. Soc. London*, **A302**, 453 (1968).
23. H. S. Makowski, D. Robert, and G. H. Lundberg, U.S. Pat. 3,870,841 (1975).
24. M. Song, H. M. Pollock, A. Hammiche, D. J. Hourston, and M. Reading, *Polymer*, **38**, 503 (1997).
25. D. J. Hourston, M. Song, A. Hammiche, H. M. Pollock, and M. Reading, *Polymer*, **38**, 1 (1997).
26. M. Song, A. Hammiche, H. M. Pollock, D. J. Hourston, and M. Reading, *Polymer*, **37**, 5661 (1996).
27. W. Yang, J. Liu, and J. Shen, *Polym. Mater. Sci. Eng.*, **13** (Add. pub.), (1997), (in Chinese).
28. W. Yang, S. Zhu, C.-M. Chan, and J. Shen, *Polym. Mater. Sci. Eng.*, **13**, 63 (1997) (in Chinese).
29. T. A. Speckhand, K. K. S. Hwang, C. Z. Yang, and S. L. Cooper, *J. Macromol. Sci., Phys.*, **B23**, 175 (1984).
30. G. M. Estes, R. W. Seymour, and S. L. Cooper, *Macromolecules*, **4**, 152 (1971).
31. R. W. Seymour and S. L. Cooper, *J. Polym. Sci., Polym. Symp.*, **46**, 69 (1974).
32. T. A. Calldghan, K. Takakuwa, and D. R. Paul, *Polymer*, **34**, 3796 (1993).
33. M. Niwa and N. Higashi, *Macromolecules*, **21**, 1193 (1988).
34. K. K. S. Hwang, T. A. Speckhard, and S. L. Cooper, *J. Macromol. Sci., Phys.*, **B23**, 153 (1984).
35. M. Laleg and Y. Camberlin, *J. Macromol. Sci., Phys.*, **B23**, 233 (1984).
36. W. J. Macknight and T. R. Earnest, *J. Polym. Sci., Macromol. Rev.*, **16**, 41 (1981).
37. E. P. Otocka, *J. Macromol. Sci., Rev. Macromol. Chem.*, **5**, 275 (1971).
38. J. S. Kim and A. Eisenberg, in *Ionomers—Characterization, Theory, and Applications*, S. Schlick, Ed., CRC Press, New York, 1996, Chapt. 2.