

Rheological Properties of Polystyrene Blends with Rigid Ladderlike Polyphenylsilsesquioxane

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Received 25 April 2004; accepted 23 August 2004

DOI 10.1002/app.21503

Published online in Wiley InterScience (www.interscience.wiley.com).

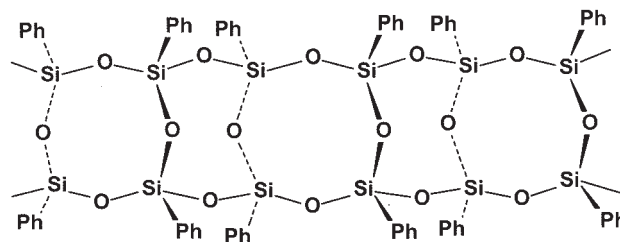
ABSTRACT: Polystyrene (PS) blends with rigid ladderlike polyphenylsilsesquioxane (PPSQ) were prepared by solution casting followed by hot pressing. The rheological properties of these blends were studied under dynamic shear and uniaxial elongation conditions. The loss modulus (G'') and dynamic shear viscosity (η^*) of the 95/5 PP/PPSQ blend were slightly lower than those of pure PS at low frequencies ($\leq 10^{-2}$ rad/s). However, the storage modulus (G'), G'' , and η^* of the other blends (90/10, 85/15, and 80/20) were higher than those of pure PS and increased with PPSQ content. The η_E data demonstrated that PS/PPSQ blends exhibited slightly weaker (5% PPSQ) or much weaker (10% PPSQ) strain hardening than PS. In contrast, the 85/15 and 80/20

PP/PPSQ blends showed strain softening, and the extent of strain softening increased with PPSQ content. PS entanglements might have been reduced by the specific interactions between PS and PPSQ, which locally ordered some PS molecules in the 95/5 blend sample, because most of the PPSQ might have been well dispersed in the PS continuous phase, and only a few small PPSQ particles ($\sim 1.3 \mu\text{m}$) were formed because of good miscibility. However, at high PPSQ contents ($\geq 10\%$), many larger hard PPSQ particles were formed, which acted as fillers during the rheological measurements. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 706–713, 2005

Key words: blends; polystyrene; rheology; viscosity

INTRODUCTION

Polyphenylsilsesquioxane (PPSQ) is a ladderlike polymer composed of two Si—O main chains bridged by oxygens. This polymer contains phenylsilsesquioxane (i.e., “phenyl-T” or $\text{C}_6\text{H}_5\text{SiO}_{1.5}$) units joined together to form syndiotactic chains and maintains tetrahedral bond angles on silicones and preferred bond angles of about 155° at oxygens.¹ X-ray diffraction studies¹ have indicated that the repeating distance in PPSQ is $5.0 \pm 0.5 \text{ \AA}$ and that its mean interchain spacing is about 12.5 \AA . Its special double-chain (ladder) structure makes PPSQ quite rigid and confers many outstanding properties. These include thermal and oxidative stability to temperatures of $400\text{--}500^\circ\text{C}$, electric insulating properties, and selective permeability to gases.²



PPSQ chemical structure

PPSQ blends with organic thermoplastics are of interest for their potential as flame-retardant plastics and for reduction of erosion due to atomic oxygen damage in space applications. During combustion, dispersed PPSQ should be converted to silica. Molecularly dispersed PPSQ should form nanosilica particles that can interlock to form a protective SiO_2 char-promoting nonflammable surface layer. However, rigid polymers are often noncompatible with other linear polymers. Blends phase separate. Thus, phase sizes will play an important role in the determination of properties. Our goal was to prepare polystyrene (PS)/PPSQ blends with varying amounts of PPSQ and to determine their rheological behavior and explore the processing conditions for PS/PPSQ blends.

The melting and flow behaviors of PPSQ has never been reported. PPSQ cannot be melted before some

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Contract grant sponsor: Air Force Office of Scientific Research; contract grant numbers: F49620-99-1-0191 and F49620-02-1-0260.

decomposition has occurred. However, PPSQ is easily dissolved in several common solvents, such as tetrahydrofuran (THF), toluene, benzene, and chloroform. Thus, a few binary blends of PPSQ with other linear polymers, including PS,^{3,4} polycarbonate,⁵ poly(ethylene terephthalate),⁶ and poly(vinyl chloride),⁷ have been prepared by solution casting or *in situ* polymerization. The mechanical and thermal properties of PS can be improved by blending with a small amount of PPSQ (≤ 10 wt %).⁴ PS and PPSQ are partially miscible. Their miscibility depends on the composition and molecular weight of the PPSQ being used.³ The miscibility between PS and low-molecular-weight PPSQ [weight-average molecular weight (M_w) = 1980] is much better than that of PS and a higher molecular weight PPSQ (M_w = 17200). At low PPSQ contents, the miscibility with PS is good, but phase separation has been observed when blends contained more than 10 wt % PPSQ.³ The rheological properties of PS/PPSQ blends have not been previously reported.

Rheological properties significantly determine processing behavior. Thus, the melt rheologies of miscible and immiscible polymer blends have been extensively studied in linear viscoelastic regions under shear deformation.⁸⁻¹² Wu⁸ reported that melt viscosity in miscible blends was affected by a reduction of entanglements, increases in the friction between dissimilar chains, and changes in free volume. In most cases, miscible polymer blends gave a reduction in melt viscosity. Linear rheological behavior in immiscible blends was interpreted with an emulsion model by Scholz et al.¹² However, it is very difficult to predict the nonlinear melt viscoelasticity of either miscible or immiscible blends from their linear viscoelastic properties because the polymer behavior and phase structure are dramatically changed by large elongational deformations. Nonlinear melt viscoelasticity has been frequently investigated under uniaxial elongational deformation.^{13,14} Elongational flow behavior is frequently observed in various polymer processing steps, such as fiber spinning, blow molding, and form extrusion. Our objective was to obtain and correlate the rheological properties of solution-cast, hot-pressed PS/PPSQ blends with their morphologies and compositions. The rheological properties were studied under dynamic shear and uniaxial elongation conditions.

EXPERIMENTAL

Sample preparation

PS [PS666, $M_w = 2.1 \times 10^5$, M_w /number-average molecular weight (M_n) = 2.2, linear], supplied by Asahi Chemical Industry Co., Ltd. (Tokyo, Japan) was used as received. PPSQ ($M_w = 1.7 \times 10^4$, $M_w/M_n = 2.4$), with a perfect ladderlike structure, was synthesized as previously reported.^{15,16} PS/PPSQ blends were pre-

pared for rheological measurements at weight ratios of 100/0, 95/5, 90/10, 85/15, and 80/20 by solution-casting and then hot pressing. PS and PPSQ were dissolved in a specific weight ratio (5 wt % PS and PPSQ) into THF at room temperature, which produced transparent solutions, which were magnetically stirred for 2 days. The solutions were then cast into stainless steel dishes, and the THF was evaporated at room temperature for 2 days to produce films of each blend. These films were placed in a vacuum oven (10 mmHg) at 130°C for 3 days to remove all residual THF. These blends were preprocessed by compression molding at 200°C (180°C for pure PS) into 25 mm diameter disks or plates. Disk samples were used for dynamic shear rheological measurements. Uniaxial elongational measurements were made on bars (3 × 4-mm cross-section, 150 mm long) cut from the plates. Pure PS was transparent, and the PS/PPSQ 95/5 sample was almost transparent. The other blends (PS/PPSQ 90/10, 85/15, and 80/20) were translucent or opaque. All of the samples were kept in a vacuum oven at 80°C until the dynamic shear and uniaxial elongational measurements were performed.

Measurements

Dynamic shear measurements were carried out under nitrogen with a dual strain-controlled and stress-controlled rheometer (ARES Rheometrics Scientific Co., Ltd., Piscataway, NJ). Both the existence and range of the linear viscoelastic region were determined by measurement of the storage modulus (G'), loss modulus (G''), and dynamic shear viscosity (η^*) as a function of strain at a temperature of 160°C and a frequency (ω) of 0.1 Hz. Then, a strain of 10% within the linear viscoelastic region was selected for the other measurements as a function of ω over the ω range 0.01 (or 0.03) to 100 Hz. These measurements were performed at 140, 160, 180, 200, and 220°C, respectively. The ω -dependence curves of G' , G'' , and η^* at this series of temperatures were superimposed onto the master curves at the reference temperature of 160°C according to the time-temperature superposition principle.

Uniaxial elongational viscosities (η_E 's) of the PS/PPSQ blends were measured at a constant strain rate at 160°C, with an elongational rheometer constructed at Yamagata University. A detailed description and discussion of the reliability of this elongational rheometer was published previously.¹⁷ Because the sample bars shrank slightly in the heated silicone oil used for temperature control in rheometer, these bars were equilibrated for 10 min. Strain rates of 0.25, 0.1, 0.05, and 0.01 s⁻¹ were used.

A BX50 optical microscope (Olympus Co., Ltd., Tokyo, Japan) was used to observe the morphology of the PS/PPSQ blends. The disklike blend samples were prepared by compression molding at 200°C. Then, the

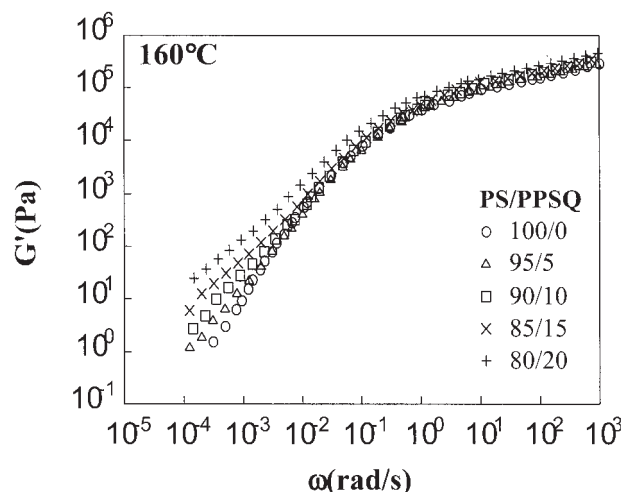


Figure 1 Master curves of G' versus ω at a reference temperature of 160°C for PS/PPSQ blends with composition ratios of 100/0, 95/5, 90/10, 85/15, and 80/20.

thin films (ca. 100 μm) for optical microscopy were cut from these disklike samples by a microcutter.

RESULTS AND DISCUSSION

Dynamic viscoelasticity

Figure 1 shows the master curves of G' versus angular ω at the reference temperature of 160°C for PS and the PS/PPSQ blends (95/5, 90/10, 85/15, and 80/20). The G' values of the PS/PPSQ blends increased with increasing PPSQ content at low frequencies ($<10^{-2}$ rad/s). At high frequencies, the values of G' increased only slightly with PPSQ content. Thus, PPSQ blending into PS can be used to raise G' at low frequencies. The master curves of G'' versus ω for all of the samples are shown in Figure 2. Similar to G' , the values of G'' increased slightly with PPSQ content at high frequencies. However, at low frequencies ($\leq 10^{-2}$ rad/s), the values of G'' for PS/PPSQ 95/5 were slightly lower than those of pure PS, but the PS/PPSQ blends with other compositions (90/10, 85/15, and 80/20) had higher G'' values. The magnitude of G'' also increased with PPSQ content at low frequencies.

The master curves of η^* versus ω at the reference temperature of 160°C are shown in Figure 3 for all of the PS/PPSQ blends. At low frequencies, PS/PPSQ 95/5 had slightly lower η^* values than pure PS, whereas the 90/10, 85/15, and 80/20 PS/PPSQ blends exhibited higher η^* values than PS. The η^* magnitude also increased gradually with the PPSQ content at low frequencies. At relatively high frequencies, all of the PS/PPSQ blends had higher η^* values than pure PS, but these viscosities increased only slightly with PPSQ content. This phenomenon was also observed in the master curves of G'' (Fig. 2). The inclusion of PPSQ into

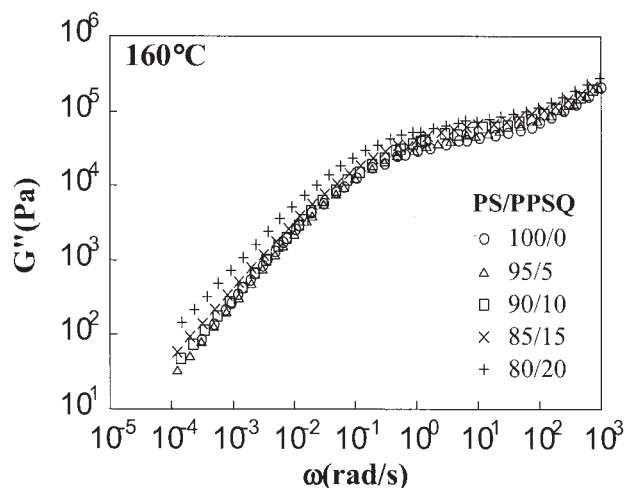


Figure 2 Master curves of G'' versus ω at a reference temperature of 160°C for PS/PPSQ blends with composition ratios of 100/0, 95/5, 90/10, 85/15, and 80/20.

PS reduced η^* and G'' at low frequencies only when the percentage of PPSQ was low (5 wt %). As the amount of PPSQ was increased to 10 wt % or greater in the blends, increases in G' , G'' , and η^* were achieved at both low and high frequencies, with more prominent increases occurring at low frequencies.

The miscibility level, the interaction between PS and PPSQ, and the states of dispersion (particle sizes and shapes) of PPSQ in PS contributed to the observed viscoelastic behavior. The interaction between PS and PPSQ could be justified by the fluorescence technique.³ It has been reported that strong interactions between PS and PPSQ in their 95/5 blend was demonstrated by a big blueshift on the absorption peak of an excited spectrum for a 95/5 PP/PPSQ blend.³ The absorption peak in the excited spectrum for the 95/5

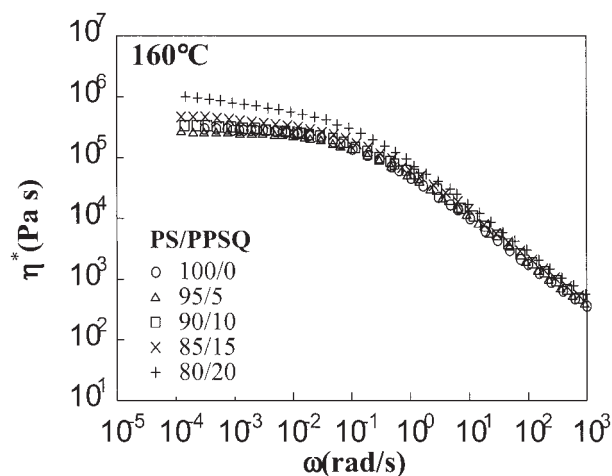


Figure 3 Master curves of η^* versus ω at a reference temperature of 160°C for PS/PPSQ blends with composition ratios of 100/0, 95/5, 90/10, 85/15, and 80/20.

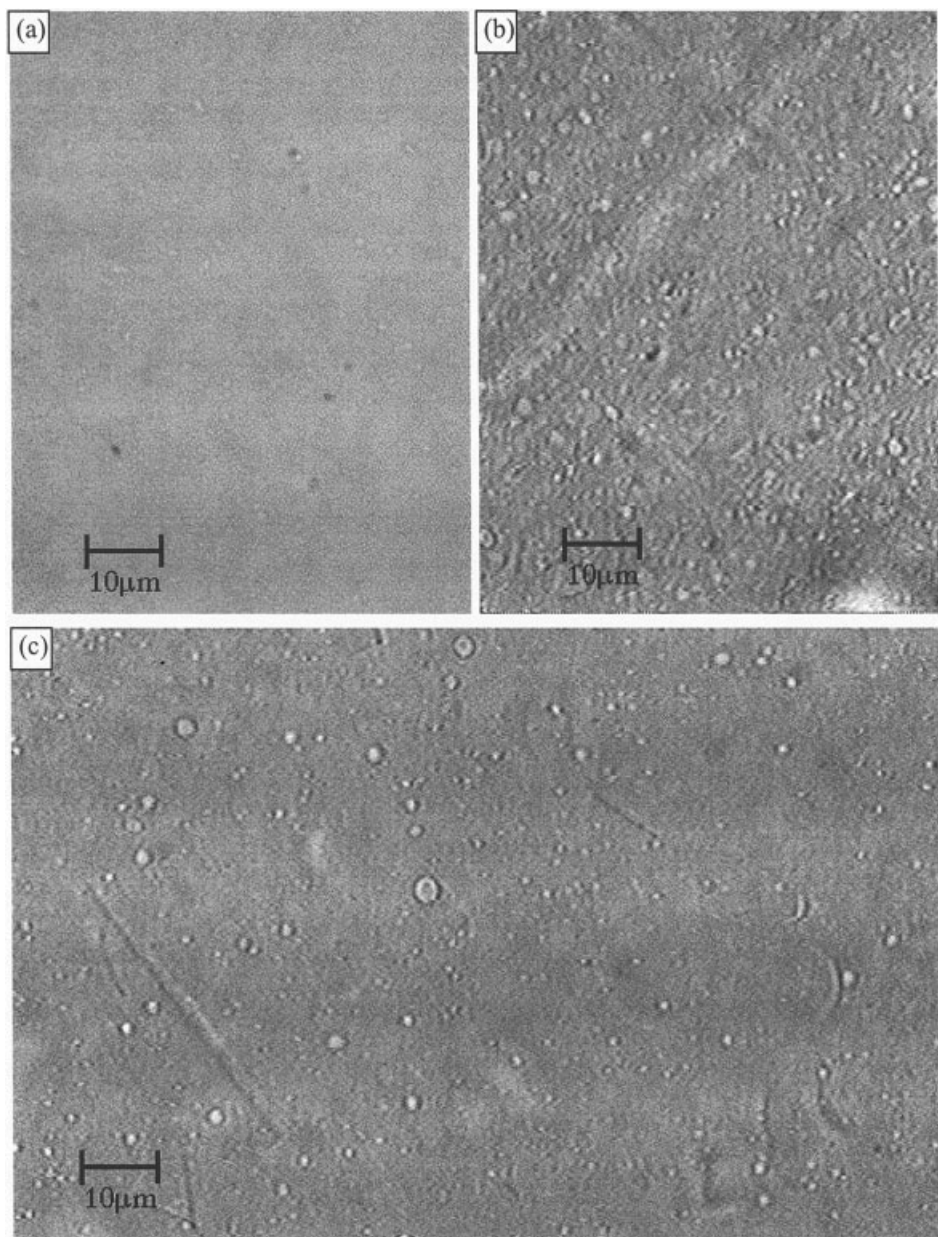


Figure 4 Optical micrographs for (a) 95/5, (b) 90/10, and (c) 80/20 PS/PPSQ blends.

PP/PPSQ blend (emission wavelength (λ_{em}) = 320 nm) was at about 270 nm, whereas the absorption peaks for PS and PPSQ were at 293 and 295 nm, respectively.³ However, at high PPSQ content (i.e. 20 wt %), there was almost no blueshift on the absorption peak (293 nm) for the 80/20 PPS/PPSQ blend. Phase separation in PS/PPSQ 80/20 occurred, and interaction between PS and PPSQ was reduced.³ The 95/5 PPS/PPSQ blend was almost transparent, whereas the 90/10, 85/15, and 80/20 blends were translucent or opaque. Thus, good miscibility between PS and PPSQ was only achieved at low weight fractions of PPSQ (e.g., 0% to about 5%). More serious phase separation occurred when the PPSQ weight percentage reached

10%. Many hard PPSQ particles were formed in the PS/PPSQ blends where the PPSQ content was ≥ 10 wt %. The optical micrographs of PS/PPSQ blends with compositions of 95/5, 90/10, and 80/15 are shown in Figure 4. Quite a few small white PPSQ particles were observed in the 95/5 PPS/PPSQ blend [Fig. 4(a)]. A dial caliper with a precision of 0.01 in. was used to measure the actual size of particles in the micrographs. This value was changed into micrometers by the scale shown in Figure 4. For an example, the biggest particle in the 95/5 PPS/PPSQ blend [Fig. 4(a)] was 0.055 in. in diameter, and the scale was $10 \mu\text{m} = 0.420$ in. ($1 \mu\text{m} = 0.042$ in.). Thus, the biggest particle in the 95/5 PPS/PPSQ blend was about 1.3

μm in diameter. However, at higher PPSQ loadings ($\geq 10\%$), many bigger PPSQ particles appeared [Fig. 4(b,c)]. The average size of these particles increased with PPSQ percentage. The biggest particle observed in the 90/10 blend [Fig. 4(b)] was about $2.5 \mu\text{m}$ in diameter, whereas the biggest particle in the 80/20 blend had a diameter of about $4.1 \mu\text{m}$.

Shear dynamic measurements were performed at a very small strain (oscillatory shear) where no particle deformation occurred. Because no change in particle shape occurred, microscopy measurements on the morphology of particles during the shear dynamic measurement were not performed. The properties of these PPSQ particles were quite similar to those of the PPSQ homopolymer. PPSQ did not exhibit a glass transition. Moreover, its G' was almost unchanged from room temperature to 380°C according to torsional braid analysis.⁷ Thus, PPSQ particles in the PS/PPSQ blends were very hard, even at the temperatures used in these viscoelastic studies (e.g. 140, 160, 180, 200, and 220°C). Therefore, PPSQ particles influenced the rheological properties of the PS/PPSQ blends (PPSQ $\geq 10\%$) by acting like hard-particle fillers.

X-ray diffraction data and Si-atom micrography distributions in the 95/5 PPS/PPSQ blend, prepared by the dissolution of PPSQ into styrene followed by polymerization, have been already published.³ Most of the PPSQ dispersed well into the PS continuous phase at low concentrations in the 95/5 PPS/PPSQ blend. However, a few PPSQ particles were formed. The difference between the fluorescence excitation spectra of the 95/5 PS/PPSQ blend and PS also demonstrated that there were specific interactions between PS and the dispersed PPSQ molecules in the 95/5 blend.³ This interaction might have enhanced the alignment of the PS molecules along the PPSQ molecular axes and inhibited or reduced the entanglement of PS molecules lying adjacent to PPSQ molecules. The molecular weight of PPSQ ($M_w = 1.7 \times 10^4$) was much lower than that of PS ($M_w = 2.1 \times 10^5$), and PPSQ had an extremely rigid ladder structure. Therefore, the PPSQ molecules were obviously not self-entangled. Entanglements in the 95/5 PPS/PPSQ blend were due to PS entanglements with other PS molecules and, perhaps, some more rare PS entanglements around PPSQ rigid rods. A decrease in entanglement density in the 95/5 PS/PPSQ blend would decrease its G' , G'' , and η^* values versus those of PS. Conversely, any PPSQ particles present in the 95/5 blend would act as hard fillers, which might increase the values of G' , G'' , and η^* . Therefore, these two factors would counteract each other, so the 95/5 PPS/PPSQ blend exhibited a slightly higher G' , lower G'' , and lower η^* values than those of pure PS at low frequencies.

PPSQ began to aggregate and phase-separate as the PPSQ concentration went up. At PPSQ contents of 10

wt % and greater, many PPSQ particles were formed in the PS continuous phase. Much larger PPSQ particles are observed with an increase in PPSQ content [shown in Fig. 4(b,c)]. Only a small fraction of the PPSQ molecules were present at the interface of PPSQ particles with the PS continuous phase. Thus, only this fraction was in contact with PS molecules together with a low concentration of molecularly dispersed PPSQ molecules. Therefore, the interaction between PS and PPSQ decreased dramatically per unit amount of PPSQ present. So, at higher PPSQ contents ($\geq 10\%$), the influence of PPSQ particles (phases) dominated PPSQ's overall contribution to the viscoelastic properties (G' , G'' , and η^*) of the blend.

PS melts, reinforced with inorganic fillers, such as calcium carbonate, titanium dioxides, and carbon black, showed much higher shear viscosities (η^*) than pure PS.¹⁸ Furthermore, the shear viscosities of these composites increased with the filler content. PPSQ particles in the 90/10, 85/15, and 80/20 blends maintained their high modulus and hardness values from 140 to 220°C (e.g., no glass-transition temperature was observed up to 380°C). In contrast, PS existed in its rubbery or viscous flow state. PS had a much lower modulus than PPSQ. Therefore, PPSQ particles acted as hard fillers during the rheological measurements. This caused an increase in G' , G'' , and η^* for the PS/PPSQ blends at PPSQ contents of 10% or greater versus those of pure PS. These values then continued to increase with increasing PPSQ content.

η_E

Rheological properties under uniaxial elongation were closely correlated with the processing behavior encountered in blow molding and extrusion. Thus, η_E of PS/PPSQ blends was also investigated. The η_E values of PS 666 are shown as a function of time (t) at 160°C under various strain rates in Figure 5. The solid line in Figure 5 is the threefold of η_0 , where $\eta_0(t)$ is the shear viscosity in the strain rate independent region and predicted from G' and G'' with the approximation proposed by Osaki et al.,¹⁹ as shown in eq. (1):

$$\eta_0(t) = t[G''(\omega) + 1.12G'(\omega/2) - 0.2G'(\omega)]_{\omega=1/t} \quad (1)$$

The η_E values for PS increased with time at low strain rate (0.01 s^{-1}), and there was a small upward deviation from its linear viscosity. However, at higher strain rates, 0.05, 0.10, and 0.25 s^{-1} , the η_E curves exhibited a progressively larger upward deviation from the linear viscosity as the strain rate increased. This property was defined as strain hardening. The strain hardening of PS increased as the strain rate increased. η_E of PS/PPSQ 95/5 at 160°C is shown in Figure 6. Unlike the behavior of pure PS, the low-strain-rate (0.01 s^{-1}) η_E values of the 95/5 PS/PPSQ

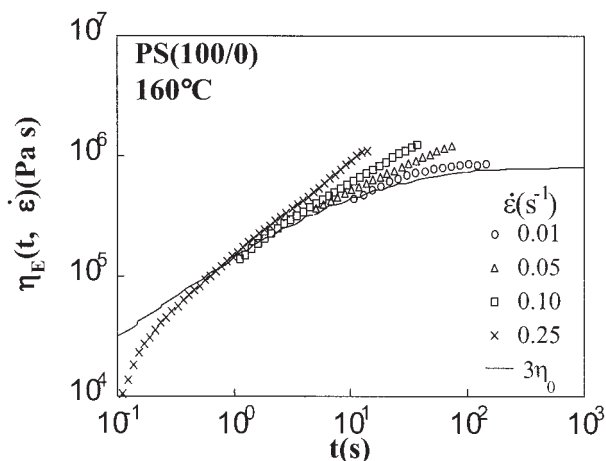


Figure 5 η_E curves as a function of time at various strain rates ($\dot{\epsilon}$) for PS at 160°C.

sample were quite similar to those of its linear viscosity. Strain hardening of the 95/5 PPS/PPSQ blend was observed only at a slightly higher strain rate (0.05 s^{-1}), and it was also more pronounced with increasing strain rate. As the PPSQ content reached 10%, a much weaker strain hardening (Fig. 7) occurred for this blend than for either pure PS (Fig. 5) or the 95/5 PPS/PPSQ blend (Fig. 6). The strain hardening of PS/PPSQ 90/10 started to appear at a higher strain rate, 0.10 s^{-1} , and the degree of strain hardening seemed to be independent of the strain rates. The strain rate at which the strain hardening began to appear was defined as the critical strain rate. The critical strain rate values of PS and 95/5 and 90/10 PS/PPSQ were 0.01 , 0.05 , and 0.10 s^{-1} , respectively. Thus, the strain hardening of the PS/PPSQ blends decreased with increasing PPSQ content.

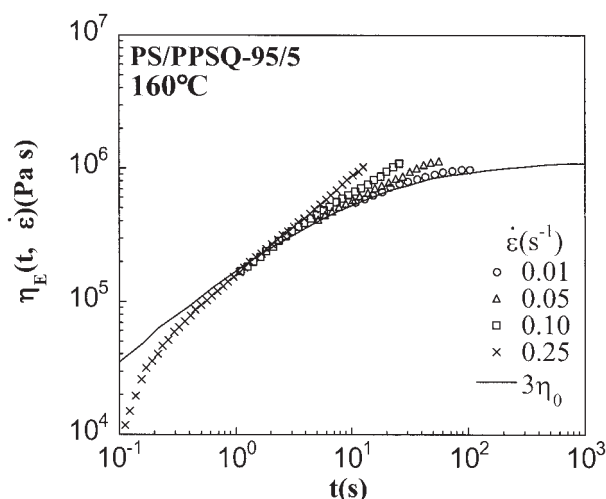


Figure 6 η_E curves as a function of time at various strain rates ($\dot{\epsilon}$) for PS/PPSQ 95/5 at 160°C (η_0 , the shear viscosity in the strain rate independent region).

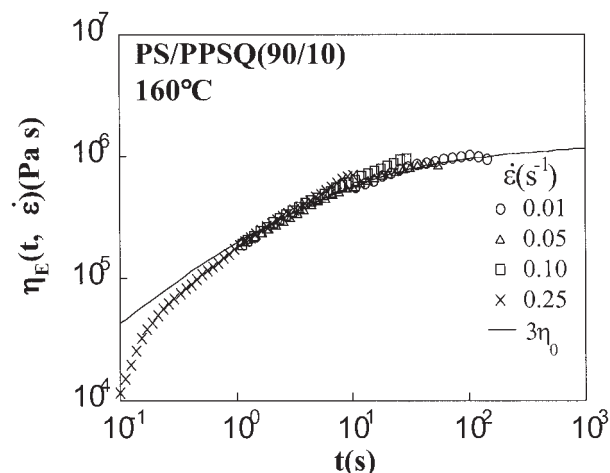


Figure 7 η_E curves as a function of time at various strain rates ($\dot{\epsilon}$) for PS/PPSQ 90/10 at 160°C (η_0 , the shear viscosity in the strain rate independent region).

The η_E curves of the 85/15 and 80/20 PPS/PPSQ blends are shown in Figures 8 and 9, respectively. In contrast to those of pure PS and 95/5 and 90/10 PS/PPSQ, the η_E curves of PS/PPSQ 85/15 and 80/20 displayed a downward deviation from the linear viscosity. This was strain softening. The strain softening of PS/PPSQ blends increased as the PPSQ content increased from 15 to 20 wt %. The 85/15 blend underwent strain softening only at the two lowest strain rates, 0.01 and 0.05 s^{-1} , whereas the 80/20 blend exhibited strain softening at strain rates of 0.01 , 0.05 , 0.10 , and 0.25 s^{-1} . Clearly, the strain hardening of the PS/PPSQ blends was weakened by PPSQ inclusion ($\leq 10\%$), and strain softening replaced strain hardening when the weight percentage of PPSQ reached 15%.

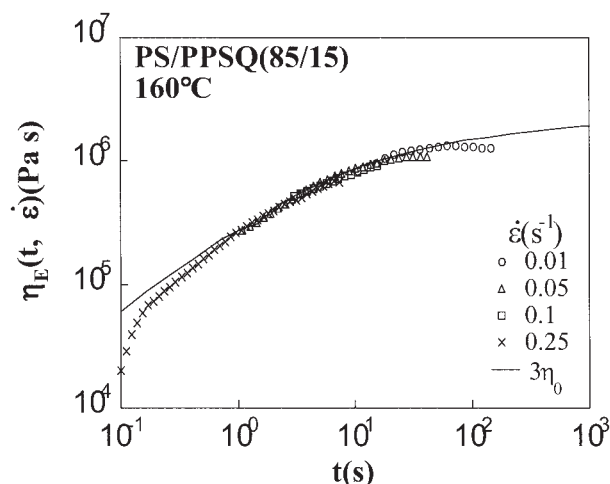


Figure 8 η_E curves as a function of time at various strain rates ($\dot{\epsilon}$) for PS/PPSQ 85/15 at 160°C (η_0 , the shear viscosity in the strain rate independent region).

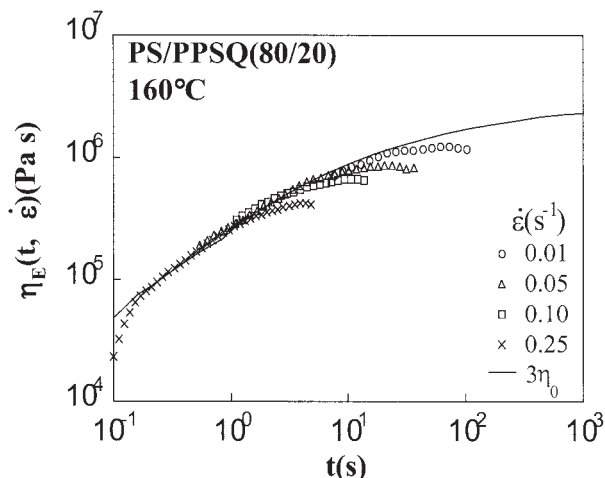


Figure 9 η_E curves as a function of time at various strain rates ($\dot{\epsilon}$) for PS/PPSQ 80/20 at 160°C (η_0 , the shear viscosity in the strain rate independent region).

Good miscibility between PS and PPSQ at a low PPSQ content (≤ 5 wt %) and the observed more serious phase separation at a high PPSQ content (≥ 10 wt %) was discussed earlier. The 95/5 and 90/10 PS/PPSQ blends showed less strain hardening than pure PS. The mechanisms for the decrease in strain hardening of the 95/5 and 90/10 PS/PPSQ samples may have been different. Most of the PPSQ was well dispersed in PS. These dispersed PPSQ molecules exhibited strong specific interactions with PS molecules. Quite a few small PPSQ particles up to about 1.3 μm in diameter were also present in the 95/5 PS/PPSQ blend. In this sample, the specific interactions between the molecularly dispersed PPSQ and PS molecules might have exerted a dominant effect on viscosity compared to the effect of a low concentration of PPSQ particles. Thus, some PS molecules may have aligned along the PPSQ molecules, inducing some PS local order. Specific PS/PPSQ interchain interactions in the blends would have aligned locally, in the chain segments. This reduced local chain coiling would have lowered the entanglement density between dissimilar PS chains.⁸ Therefore, entanglements among PS molecules in PS/PPSQ 95/5 may have, on average, been reduced because of the specific PS/PPSQ interactions. This decrease in entanglements in the 95/5 PS/PPSQ blend was a likely reason for its slightly weaker strain hardening versus that of PS because the strain hardening in the PS/PPSQ blends was determined by the long relaxation time component caused by PS molecular entanglements.

A more serious phase separation occurred at higher PPSQ contents (≥ 10 wt %). PPSQ molecules aggregated, phase separating into many particles [shown in Fig. 4(b,c)]. Only PPSQ molecules at the particles' surfaces could interact with PS molecules. This

sharply reduced the quantity of PS/PPSQ interactions, as a fraction of the total PPSQ present. As the number and size of PPSQ particles increased, these particles became the key factor by which PPSQ influenced the η_E behavior of the blend. The PPSQ particles in the blends containing 10% or more PPSQ were very hard at a temperature of 160°C during uniaxial elongation. Therefore, they acted as fillers within the PS, which was in its viscous flow state at 160°C. The existence of hard PPSQ particles in PS/PPSQ blends caused the great decrease in PS elasticity. This was in accord with the findings of Tanaka and White,¹⁸ who reported a decrease in strain hardening for various PS/inorganic filler composite melts.

As the PPSQ content in the blends continued to increase to 15 and 20 wt %, the PPSQ particle sizes increased. The 80/20 blend contained PPSQ particles as large as 4.1 μm . Previous studies have shown that hard particles affect the uniaxial elongational rheological properties of thermoplastic polymer melts. Takahashi et al.²⁰ found that glass-fiber-filled low-density polyethylene exhibited strain-softening properties. Takahashi et al.²¹ also reported that the strain softening was observed in acrylonitrile-butadiene-styrene (ABS), which contained hard crosslinked butadiene particles. The presence of hard particles was the key factor responsible for these strain-softening properties. Because of the high PPSQ modulus at 160°C, the PPSQ particles in the 85/15 and 80/20 blends did not deform. During the large PS deformations occurring in uniaxial elongation studies, the hard PPSQ particles did not deform. This generated a shear flow of PS around the PPSQ particles. We believe this may have caused the decrease in η_E at the large deformations and induced strain softening in the 85/15 and 80/20 blends.

PS/PPSQ 95/5 exhibited a slightly weaker strain hardening than PS. This was most likely due to the decrease in entanglement density among PS molecules. The 90/10 PS/PPSQ blend showed much weaker strain hardening, and at PPSQ levels of 15% or greater, strain softening occurred due to the presence of undeformed hard PPSQ particles.

CONCLUSIONS

The rheological properties of PS/PPSQ blends under dynamic shear and uniaxial elongation depended on their compositions and morphologies. At low PPSQ contents (≤ 5 wt %), G' and η^* of PS-PPSQ 95/5 were lower than those of pure PS at low frequencies. The 95/5 PS/PPSQ blend exhibited a slightly weaker strain hardening than PS because of a decrease in the entanglement density among PS molecules. Some decrease in entanglements occurred because some fraction of PS molecules specifically interacted with the dispersed PPSQ molecules. A large fraction of the

PPSQ molecules present in the 95/5 blend were very well dispersed in the PS continuous phase. These rod-like PPSQ molecules induced some local order in PS molecules that were in close contact with PPSQ. At higher PPSQ contents ($\geq 10\%$), G' , G'' , and η^* of the PS/PPSQ blends were higher than those of pure PS. These values increased with increasing PPSQ content at both low and high frequencies. The strain hardening in these blends was greatly weakened by the inclusion of 10% PPSQ. In fact, the blends containing 15% or more PPSQ were influenced strongly enough to exhibit strain softening. Strain softening became more pronounced when the PPSQ content was raised to 20%. These rheological changes, summarized previously, resulted from phase separation induced many hard PPSQ particles with sizes as large as about 2.5 μm (the 90/10 blend) to 4.1 μm (the 80/20 blend) in blends containing more than 10 wt % PPSQ. These hard PPSQ particles acted as fillers under the conditions used in the rheological measurements. They caused a decrease in η_E due to the shear flow of PS around hard PPSQ particles at large PS deformations.

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