

Rheological Properties of Poly(methyl methacrylate)/Rigid Ladderlike Polyphenylsilsesquioxane Blends

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ABSTRACT: A series of poly(methyl methacrylate) (PMMA) blends with rigid ladderlike polyphenylsilsesquioxane (PPSQ) were prepared at weight ratios of 100/0, 95/5, 90/10, 85/15, and 80/20 by solution casting and then hot-pressing. Their rheological properties have been studied under both dynamic shear and uniaxial elongation conditions. Their rheological properties depend on the compositions. The storage modulus, G' , loss modulus, G'' , and dynamic shear viscosity, η^* , of the PMMA/PPSQ 95/5 blend were slightly lower than those of pure PMMA. However, the values of G' , G'' , and η^* for the other PMMA/PPSQ blends are higher than those of PMMA. The G' values increase with an increase in PPSQ content from 5% through 15% PPSQ at low frequencies and then drop as the PPSQ content increases to 20%. Uniaxial elongational viscosity (η_E) data demonstrate that

PMMA/PPSQ blends exhibit slightly weaker (5% PPSQ) and much weaker (10% PPSQ) strain-hardening than PMMA. In contrast, the PMMA/PPSQ 85/15 blend shows strain-softening. Neither strain-hardening nor strain-softening was observed in the 80/20 blend. The special rheological properties for the 95/5 blend is probably due to a decrease in PMMA entanglements brought by the specific PMMA–PPSQ interactions. Rheological properties of PMMA/PPSQ blends with higher PPSQ content ($\geq 10\%$) are mainly affected by formation of hard PPSQ particles. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 352–359, 2007

Key words: poly(methyl methacrylate) (PMMA)/polyphenylsilsesquioxane (PPSQ) blend; rheology; dynamic shear viscosity; uniaxial elongational viscosity

INTRODUCTION

Polyphenylsilsesquioxane (PPSQ) is a ladderlike polymer composed of two Si–O main chains bridged by oxygens (Scheme 1). This polymer contains phenylsilsesquioxane (i.e., “phenyl-T” or $C_6H_5SiO_{1.5}$) units joined together to form syndiotactic chains while maintaining tetrahedral bond angles at silicone and preferred bond angles of $\sim 155^\circ$ at oxygen.¹ The double chain (ladder) contributions to the structure make PPSQ quite rigid and lead to many outstanding properties, including thermal and oxidative stability (withstands temperature of 400–500°C), electric insulating properties, and selective permeability to gases.²

The melting and flow behavior of PPSQ has never been reported because PPSQ could not be melted before

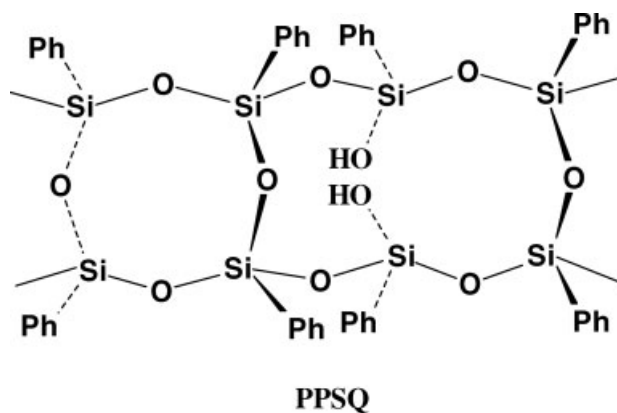
some decomposition occurred.² However, PPSQ is easily dissolved in several common solvents, including tetrahydrofuran (THF), toluene, benzene, and chloroform, etc. Thus, several binary blends of PPSQ with linear polymers, including poly(methyl methacrylate) (PMMA),³ poly(methyl methacrylate-*co*-methyl acrylic acid) (P(MMA-*co*-MAA)) (1 wt % MAA),⁴ polystyrene (PS),^{5,6} polycarbonate (PC),⁷ poly(ethylene terephthalate) (PET),⁸ and poly(vinyl chloride) (PVC),⁹ have been prepared by solution casting or *in situ* polymerization. PMMA and PPSQ are partially miscible in their casting film. The extent of their miscibility depends on the composition and the molecular weight of PPSQ being used.³ The miscibility of PMMA with low molecular weight PPSQ ($M_w = 2180$) is much better than that of PMMA with high molecular weight PPSQ ($M_w = 40,900$). P(MMA-*co*-MAA)/PPSQ *in situ* blends, prepared by dissolving PPSQ in 99/1 wt/wt MMA/MAA followed by copolymerization, were compatible (highly miscible) at low PPSQ content (≤ 5 wt %).⁴ However, rheological properties of PMMA/PPSQ blends have never been reported previously.

The processing behaviors of polymers are significantly determined by their rheological properties.

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Scheme 1

Thus, the melt rheologies of miscible and immiscible polymer blends have been extensively studied in the linear viscoelastic region under shear deformation.^{10–14} Wu reported that the melt viscosity of miscible blends was affected by a reduction of entanglements, increases in the friction between dissimilar chains, and changes in free volume.¹⁰ In most cases, miscible polymer blends gave a reduction in melt viscosity. Linear rheological behavior exhibited by immiscible blends was interpreted with an emulsion model by Scholz et al.¹⁴ However, it is very difficult to predict nonlinear melt viscoelasticity of either miscible or immiscible blends from their linear viscoelastic properties because the polymer's behavior and phase structure are dramatically changed by large elongational deformations. Nonlinear melt viscoelasticity has frequently been investigated successfully under uniaxial elongational deformation.^{15,16} Therefore, the rheological properties of PMMA/PPSQ blends, prepared by solution casting and then hot pressing, have been studied in this article under both dynamic shear and uniaxial elongation.

EXPERIMENTAL

Sample preparation

Poly(methyl methacrylate) (PMMA, $M_w = 9.66 \times 10^4$, $M_w/M_n = 1.67$, linear), supplied by Asahi Chemical Industry, Japan, was used as received. Polyphenylsilsesquioxane (PPSQ, $M_w = 1.65 \times 10^4$, $M_w/M_n = 3.6$) with 88.7 mol % ladderlike structure (shown in Scheme 1) was synthesized, purified, and characterized as previously reported.^{17,18} The presence of some Si—OH groups in PPSQ can improve the miscibility between PMMA and PPSQ. This most likely results from hydrogen-bonding between these Si—OH groups and PMMA carbonyl oxygen atoms.

PMMA/PPSQ blends were prepared for rheological measurements in weight ratios of 100/0, 95/5, 90/10, 85/15, and 80/20, by solution casting and then hot-pressing. PMMA and PPSQ at each specific weight

ratio were dissolved (5 wt %) in tetrahydrofuran (THF) at room temperature, giving transparent solutions that were magnetically stirred for 2 days. The solutions were then cast into stainless steel dishes. THF was evaporated at room temperature for 2 days to produce films of each blend. These films were kept under vacuum (about 10 mmHg) at 130°C for 3 days to remove all residual THF. These blends were processed by compression molding at 200°C (190°C for pure PMMA) into the 25 mm diameter disks or plates. Disk samples were employed for dynamic shear rheological measurements. Uniaxial elongational measurements were carried out on bars ($3 \times 4 \text{ mm}^2$ cross section, 150 mm long) cut from the plates. Pure PMMA and PMMA/PPSQ 95/5 samples are transparent and the other blends (90/10, 85/15, and 80/20) are translucent or opaque. All samples were stored in the vacuum oven at 80°C until the dynamic shear and uniaxial elongational measurements were made.

Measurements

Dynamic shear measurements were carried out under nitrogen using a dual strain-controlled and stress-controlled rheometer (ARES Rheometrics Scientific). Both the existence and range of the linear viscoelastic region were determined by measuring the storage modulus G' , loss modulus G'' , and dynamic viscosity η^* as a function of strain at 160°C and a frequency of 0.1 Hz. Then, a strain of 10% within the linear viscoelastic region was selected for the other measurements as a function of frequency over the frequency range from 0.03 to 100 Hz. These measurements were performed at 140, 160, 180, 200, and 220°C, respectively. The frequency-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.^{19,20}

Uniaxial elongational viscosities, η_E , of PMMA/PPSQ 100/0, 95/5, 90/10, 85/15, and 80/20 blends were measured at a set of predetermined constant strain rates at 160°C, using an elongational rheometer constructed at Yamagata University. A detailed description and discussion of the reliability of this elongational rheometer has been published.²¹ Since the sample bars shrank slightly in the heated silicone oil, these bars were first pre-equilibrated for 10 min. The strain rates employed were 0.25, 0.1, 0.05, and 0.01 s⁻¹, respectively.

RESULTS AND DISCUSSION

Dynamic rheological properties

Figure 1 shows the master curves of storage modulus, G' , versus angular frequency at a reference tem-

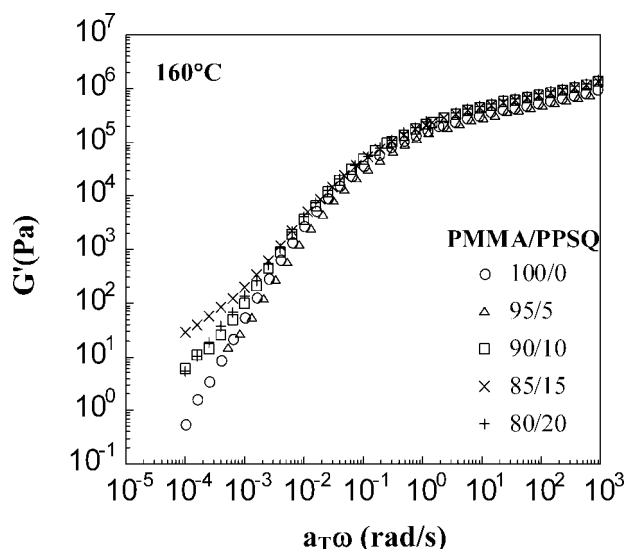


Figure 1 Master curves of the storage modulus G' versus frequency at a reference temperature of 160°C for PMMA/PPSQ blends with compositions of 100/0, 95/5, 90/10, 85/15, and 80/20.

perature of 160°C for PMMA/PPSQ blends (100/0, 95/5, 90/10, 85/15, and 80/20). The G' values of the 95/5 blend are slightly lower than those of pure PMMA over the entire frequency range. The G' values of the PMMA/PPSQ blends increase with an increase in PPSQ content at low frequencies ($<10^{-2}$ rad/s) except for the 80/20 blend. At low frequency, the 80/20 blend exhibited smaller G' values than the 85/15 blend. Its G' values are quite similar with those of the 90/10 blend. At high frequencies, the G' values of PMMA/PPSQ 90/10, 85/15, and 80/20 blends are quite similar and are slightly higher than those of pure PMMA. Thus, PPSQ blending into PMMA (≤ 15 wt % PPSQ) can be used to raise the storage modulus at low frequencies.

Master curves of the loss modulus, G'' , versus frequency for all samples are shown in Figure 2. As is the case for G' , the G'' values of the 95/5 blend are slightly smaller than those of pure PMMA over the entire frequency range. However, the 90/10, 85/15, and 80/20 blends display slightly higher G'' values than that of pure PMMA. The three blends with compositions of 90/10, 85/15, and 80/20 have almost the same G'' values at high frequencies. The G'' values obtained at low frequencies of the 85/15 and 80/20 blends are quite similar and slightly higher than those of the 90/10 blend. It is clearly noted that the G'' values of the 80/20 blend are almost the same as those of the 85/15 blend across the entire frequency range.

The master curves for the dynamic shear viscosity, η^* , versus frequency, at a 160°C reference temperature for all PMMA/PPSQ blend samples appear in Figure 3. Like G'' , the 95/5 blend has slightly lower

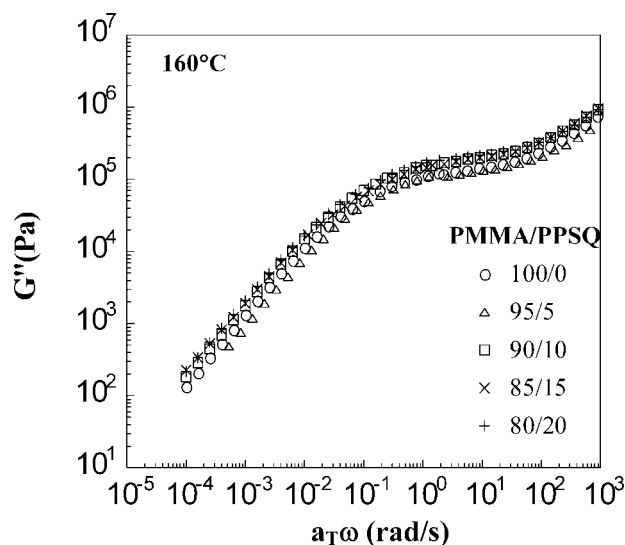


Figure 2 Master curves of the loss modulus G'' versus frequency at a reference temperature of 160°C for PMMA/PPSQ blends with compositions of 100/0, 95/5, 90/10, 85/15, and 80/20.

η^* values than those of pure PMMA throughout the entire frequency range. In contrast, the 90/10, 85/15, and 80/20 blends exhibit higher η^* values than those of PMMA. The η^* magnitude also increases gradually as the PPSQ content is raised from 5 to 15% at low frequencies and then η^* decreases slightly for the 80/20 blend. In fact, the η^* values of the 80/20 blend are almost the same as those of the 85/15 blend over the entire frequency range. At relatively high frequencies, the 90/10, 85/15, and 80/20 blends all exhibit quite similar η^* values. This phenomenon

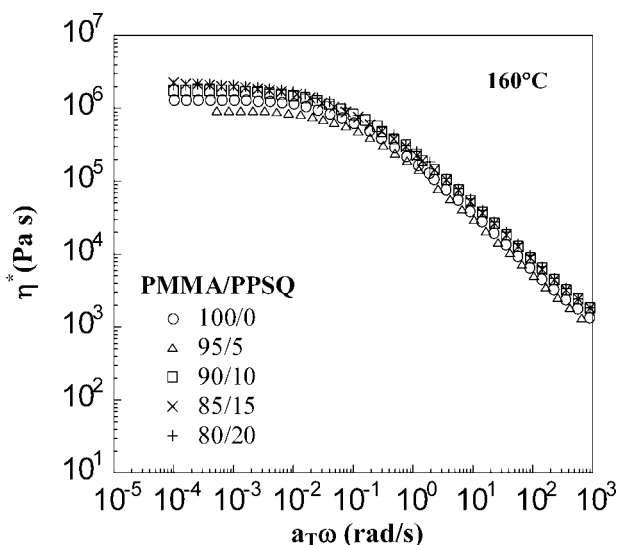


Figure 3 Master curves of the dynamic shear viscosity η^* versus frequency at a reference temperature of 160°C for PMMA/PPSQ blends with compositions of 100/0, 95/5, 90/10, 85/15, and 80/20.

is also observed in the master curves of G'' . The addition of PPSQ lowers G' , G'' , and η^* across the entire frequency range, only when the PPSQ is compatible and present in low weight percent (5%). As the amount of PPSQ is increased to ≥ 10 wt %, phase-separation occurs. Improvements in the G' , G'' , and η^* are achieved at both low and high frequencies, with more prominent improvement occurring at low frequencies. However, the 90/10, 85/15, and 80/20 blends exhibit the similar G' , G'' , and η^* values at high frequencies. The G'' and η^* values of the 85/15 and 80/20 blends are almost the same (just slightly higher than) as those of the 90/10 blend at low frequencies. The G' values of PMMA/PPSQ 80/20 are lower than those of the 85/15 blend and are quite similar with those of the 90/10 blend at low frequencies ($\leq 10^{-2}$ rad/s).

The miscibility and intermolecular interactions between PMMA and PPSQ and the states of dispersion of PPSQ molecules or solid PPSQ particles in PMMA cause the observed viscoelastic behavior differences in this series of blends. The PMMA/PPSQ 95/5 blend is transparent, while the 90/10, 85/15, and 80/20 blends are translucent or opaque. Thus, good PMMA/PPSQ miscibility is only achieved at low weight fractions of PPSQ (e.g., 0 to at least 5 wt %). However, micro phase-separation occurred when the PPSQ weight percentage reached 10%. PPSQ-rich particles are formed in PMMA/PPSQ blends where the PPSQ content ≥ 10 wt %. Optical micrographs for PMMA/PPSQ blends with compositions of 90/10 and 80/20 are shown in Figure 4. Many small white particles with sizes of 1–2 μm are observed in PMMA/PPSQ 90/10 blend [Fig. 4(a)]. Because there is only 10 wt % PPSQ, there are so many white particles formed. It is deduced that the white particles are PPSQ-rich particles and there are some PMMA molecules incorporated in these particles. As the percentage of PPSQ in this blend increases to 20 wt %, some big PPSQ-rich particles with sizes of 4–5 μm formed [Fig. 4(b)]. The average size of these particles increases with PPSQ percentage. The biggest particle observed in the 90/10 blend [Fig. 4(a)] is about 2 μm in diameter, while the biggest particle in the 80/20 blend [Fig. 4(b)] has a diameter of about 5 μm .

PPSQ molecules are dispersed well in the PMMA continuous phase at low concentrations (≤ 5 wt %). Intermolecular hydrogen bonding between PMMA and PPSQ containing some Si—OH groups has been demonstrated by IR.³ This interaction might induce some net alignment of the PMMA molecules along the PPSQ molecules and inhibit or reduce the entanglement of PMMA molecules in the region adjacent to PPSQ. The molecular weight of the PPSQ ($M_w = 1.65 \times 10^4$) is much lower than that of PMMA ($M_w = 9.66 \times 10^4$) and PPSQ has an extremely rigid

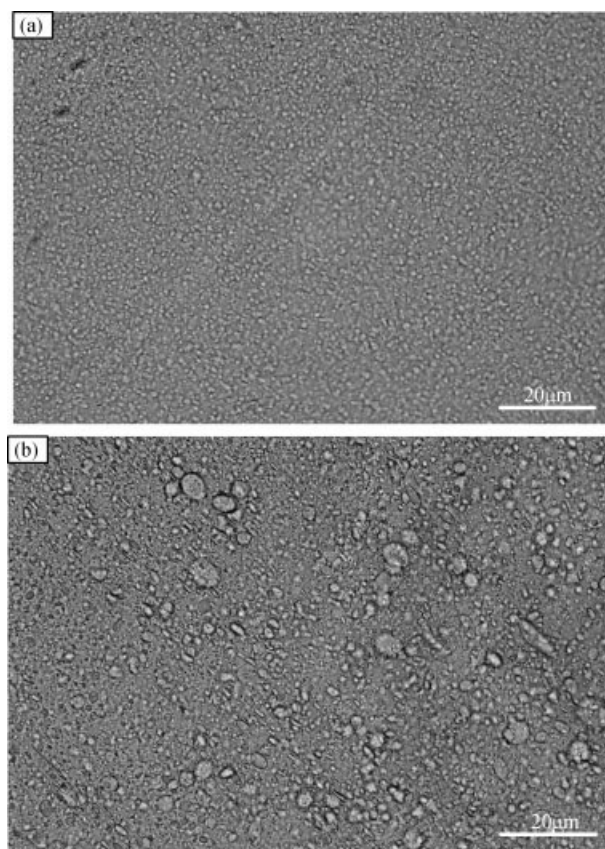


Figure 4 Optical micrographs for PMMA/PPSQ (a) 90/10 and (b) 80/20 blends.

ladder structure. Therefore, PPSQ molecules are not entangled. Entanglements in the PMMA/PPSQ blends are almost entirely due to PMMA entanglements with other PMMA molecules and, perhaps, some rare PMMA entanglements around PPSQ rigid rods. Therefore, the compatible PMMA/PPSQ 95/5 blend exhibited values G' , G'' , and η^* , which were lower than those of pure PMMA due to this reduction in entanglement density.

PPSQ molecules begin to aggregate and phase-separate as the PPSQ concentration goes up. At ≥ 10 wt %, PPSQ particles are formed in the PMMA continuous phase, causing the 90/10, 85/15, and 80/20 blends to be translucent and opaque. As shown in reference,³ PMMA/PPSQ blends (PPSQ; $M_w = 4.09 \times 10^4$; 88.7 mol % ladderlike structure) with weight ratios of 80/20, 60/40, 50/50, 40/60, and 20/80, prepared by solution casting, exhibited only one T_g . These T_g values were higher than that of pure PMMA and increased with an increase in PPSQ content.³ PPSQ has no T_g up to its decomposition temperature. Thus, the glass transitions observed for PMMA/PPSQ blends must be ascribed to the PMMA-rich phase. The increase of T_g with the PPSQ content indicated that the PMMA-rich phase contained PPSQ and the PPSQ fraction in PMMA-rich

phase increased with PPSQ content. This demonstrates that a fraction of PPSQ molecules can be dispersed well in PMMA-rich phase even if some phase-separation occurs and some PPSQ-rich particles form. Therefore, a fraction of PPSQ molecules are well dispersed in the PMMA-rich continuous phase after PPSQ particles form when the PPSQ content is ≥ 10 wt %.

The PPSQ fraction dispersed in PMMA-rich continuous phase increases with PPSQ content as it rises from 10 to 20 wt %. Thus, two factors can affect the G' , G'' , and η^* of the PMMA/PPSQ blends at PPSQ ≥ 10 wt %. The first factor is the specific interaction between PMMA and the PPSQ molecules, which are distributed throughout the PMMA-rich continuous phase. This interaction can align the PMMA molecules and lead to a lower entanglement density in PMMA molecules, thereby causing the decrease in G' , G'' , and η^* . The second factor is the formation of PPSQ particles. The PPSQ particle properties must be quite similar to those of the PPSQ homopolymer. PPSQ does not exhibit a glass transition. Moreover, its storage modulus is almost unchanged going from room temperature to 380°C according to torsional braid analysis (TBA).⁹ Thus, PPSQ particles in the blends are very hard even at the 140–220°C temperatures employed in these viscoelastic studies. Therefore, PPSQ particles influence the rheological properties by acting like small hard particle fillers.

Molten polystyrene (PS), reinforced with such inorganic fillers as calcium carbonate, titanium dioxide, and carbon black, showed much higher shear viscosities (η^*) than pure PS.²² Furthermore, the shear viscosities of these composites increased with the filler content. PPSQ particles in the 90/10, 85/15, and 80/20 blends maintain their high modulus and hardness from 140 to 220°C, where PMMA exists in either its rubbery or viscous flow state. PMMA has a much lower modulus than PPSQ in this temperature range. Therefore, PPSQ particles act as hard fillers during the rheological measurements. This causes an increase in G' , G'' , and η^* for these blends when the PPSQ contents are ≥ 10 wt %.

Overall, the influence of PPSQ content on the G' , G'' , and η^* of the blends are determined by two counteracting factors: (1) specific intermolecular interactions between PMMA and compatible PPSQ molecules in the PMMA-rich phase and (2) phase-separated PPSQ particles acting as hard fillers. The higher G' , G'' , and η^* values of the 90/10, 85/15, and 80/20 blends versus those of pure PMMA are dominated by the role of the PPSQ hard particles. However, more PPSQ molecules are compatibly dispersed in PMMA-rich continuous phase and more PPSQ hard particles are formed as PPSQ content increases. The counteraction of the two factors (1) and (2) (above) might result in the G' , G'' , and

η^* quantities of the 90/10, 85/15, and 80/20 blends exhibiting quite similar values at high frequencies. These counteracting factors also rationalize why the G'' and η^* values of PMMA/PPSQ 80/20 are almost the same as those of the 85/15 blend and why these values are slightly higher than those of the 90/10 blend at low frequencies. Why does PMMA/PPSQ 80/20 exhibit lower G' values than those of the 85/15 blend? One possible explanation is that the specific PMMA/PPSQ interaction in the 80/20 blend is stronger than that in the 85/15 blend if more PPSQ molecules are dispersed in the PMMA-rich continuous phase of the 80/20 blend. Since phase separation may be kinetically controlled, this is possible.

Uniaxial elongational viscosity

Rheological properties under uniaxial elongation are closely correlated with processing behavior encountered in blow molding and extrusion. Thus, the uniaxial elongational viscosity of PMMA/PPSQ blends was also investigated. Figure 5 shows uniaxial elongational viscosities, η_E , of PMMA as a function of time at 160°C under various strain rates. The solid line in Figure 5 is the three-fold linear elongational viscosity (η_0), where $\eta_0(t)$ is the shear viscosity in the strain rate independent region and predicted from G' and G'' , using the approximation equation proposed by Osaki et al.²³ 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 PMMA increase with time at low strain rate (0.01 s⁻¹) and there is a small upward deviation from the linear viscosity. At higher strain

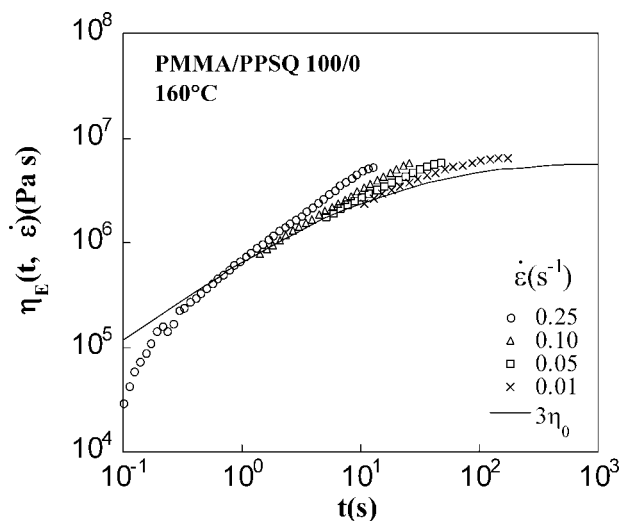


Figure 5 Uniaxial elongational viscosity, η_E , curves as a function of time at various strain rates for PMMA at 160°C.

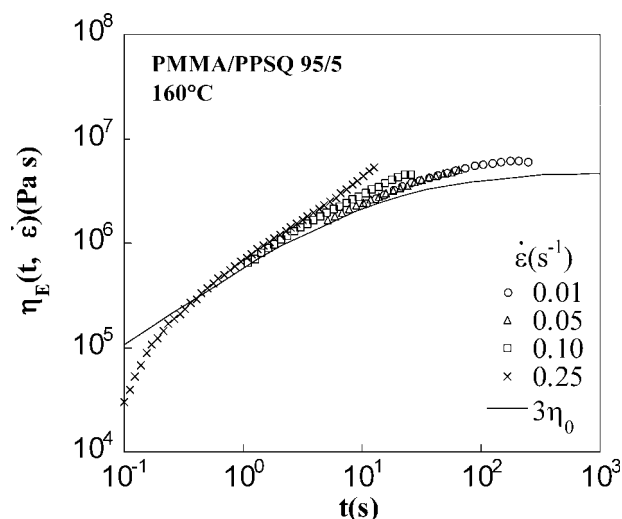


Figure 6 Uniaxial elongational viscosity, η_E , curves as a function of time at various strain rates for PMMA/PPSQ 95/5 at 160°C.

rates, i.e., 0.05, 0.10, and 0.25 s^{-1} , the η_E curves exhibit a progressively larger upward deviation from the linear viscosity as the strain rate increases. This property is defined as strain-hardening. The strain-hardening of PMMA increases as strain rate increases.

The uniaxial elongational viscosity, η_E , of PMMA/PPSQ 95/5 at 160°C is shown in Figure 6. Like the behavior of PMMA, strain-hardening of the PMMA/PPSQ 95/5 blend is also observed at the lowest strain rate (0.01 s^{-1}) and it becomes more pronounced with increasing strain rate. Unlike PMMA, the η_E values of the 95/5 blend at 0.05 s^{-1} are almost the same as those at 0.01 s^{-1} . As the PPSQ content reaches 10%, much weaker strain-hardening (Fig. 7) occurs than those observed in either pure PMMA (Fig. 5) or the 95/5 blend (Fig. 6). The strain-hardening of PMMA/PPSQ 90/10 starts to appear at the highest strain rate, 0.25 s^{-1} . The strain rate at which the strain-hardening begins to appear is defined as the critical strain rate, $\dot{\epsilon}_c$. The $\dot{\epsilon}_c$ of PMMA, PMMA/PPSQ 95/5 and 90/10 are 0.01, 0.01 and 0.25 s^{-1} , respectively. Thus, strain-hardening of the blends decreases as the amount of PPSQ goes up.

The uniaxial elongational viscosity, η_E , curves of PMMA/PPSQ 85/15 and 80/20 blends are given in Figures 8 and 9, respectively. In contrast to pure PMMA and the 95/5 and 90/10 blends, the η_E curves for the 85/15 blend display a downward deviation from the linear viscosity. This deviation is defined as strain-softening. The 85/15 blend undergoes strain-softening only at the two lowest strain rates, 0.01 and 0.05 s^{-1} . However, the 80/20 blend exhibits neither strain-softening nor strain-hardening at all strain rates from 0.01 to 0.25 s^{-1} . Clearly,

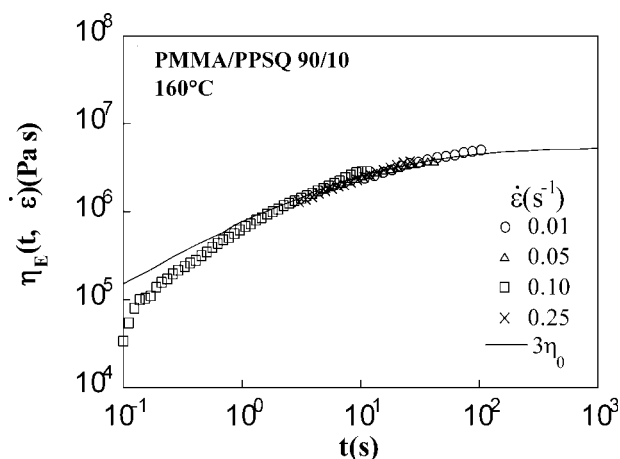


Figure 7 Uniaxial elongational viscosity, η_E , curves as a function of time at various strain rates for PMMA/PPSQ 90/10 at 160°C.

strain-hardening of PMMA/PPSQ blends has been reduced by PPSQ inclusion ($\leq 10\%$) and strain-softening replaces strain-hardening when the weight percentage of PPSQ reaches 15%. Neither strain-hardening nor strain-softening is observed in PMMA/PPSQ 80/20 blend.

The miscibility between PMMA and PPSQ was discussed earlier. PMMA/PPSQ 95/5 and 90/10 show less strain-hardening than pure PMMA. Good miscibility of PMMA with PPSQ occurs in the 95/5 blend, while the 90/10 blend exhibited micro phase-separation. Therefore, the mechanisms for the decrease in strain-hardening of PMMA/PPSQ 95/5 and 90/10 may be different. PPSQ is well dispersed in PMMA and exhibits strong specific molecular interactions with PMMA in the 95/5 blend. PMMA alignment along the PPSQ molecules is caused by specific PPSQ/PMMA interchain interactions and this leads to local chain segment alignment.¹⁰ This alignment reduces local

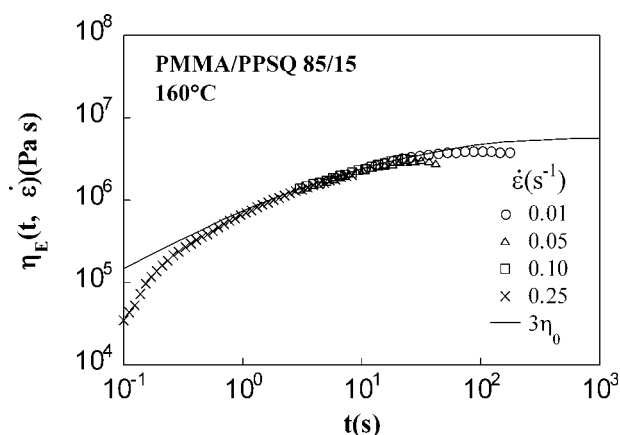


Figure 8 Uniaxial elongational viscosity, η_E , curves as a function of time at various strain rates for PMMA/PPSQ 85/15 at 160°C.

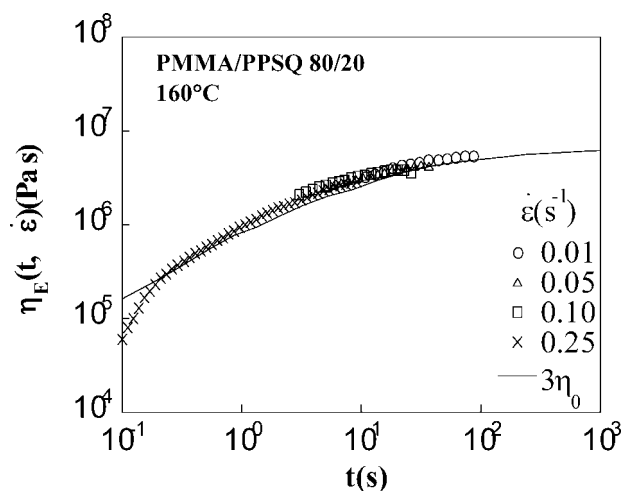


Figure 9 Uniaxial elongational viscosity, η_E , curves as a function of time at various strain rates for PMMA/PPSQ 80/20 at 160°C.

chain convolution, thereby reducing the entanglement between different chains.¹⁰ Strain-hardening in the blends is determined by the long relaxation time caused by PMMA entanglements. Therefore, the decrease in entanglements in the 95/5 blend, relative to in PMMA, leads to slightly weaker strain-hardening versus that of PMMA.

The miscibility between PMMA and PPSQ appears poorer and the phase-separation occurs at higher PPSQ contents (≥ 10 wt %). PPSQ molecules, which are initially cosoluble with PMMA in THF, begin to aggregate and phase separate into particles as the cast solutions become films and THF is lost. A fraction of the PPSQ remains dispersed well in PMMA-rich continuous phase at all PPSQ contents (≥ 10 wt %). One might initially suspect the PPSQ concentration in the PMMA-rich phase would remain constant once its solubility limit was reached and the remainder would separate as particles. However, kinetic control of this phase separation could result in different amounts of PPSQ being present in the PMMA-rich phase for samples where the blend ratios were varied from 90/10 to 80/20. So, the amount of PPSQ in PMMA-rich phase and the reduction in entanglement density that this PPSQ causes are not easily predicted. However, this compatible PPSQ does give a reduction in strain-hardening. The PPSQ particles that are formed in all blends with PPSQ $\geq 10\%$ appear to be very hard, based on their effect under uniaxial elongation at a temperature of 160°C. The particles act as fillers within the viscous flow state of PMMA at 160°C. The existence of hard PPSQ particles in the blends causes a substantial reduction in PMMA's elasticity. Thus, the 90/10 blend exhibits much less strain-hardening than PMMA. This is in accord with the findings of Tanaka and White,²² who reported a decrease of

strain-hardening properties in various PS/inorganic filler composite melts.²²

As the PPSQ content continues to increase to 15 wt %, more PPSQ particles form in the blend. These particles should decrease strain-hardening or cause strain-softening under uniaxial elongation. Takahashi et al. found that glass-fiber-filled LDPE exhibited strain-softening properties.²⁴ Takahashi et al. also reported that the strain-softening was observed in ABS copolymers containing hard crosslinked butadiene particles.²⁵ The presence of hard particles seemed to be the key factor in both these cases, which was responsible for strain-softening properties. Because the PPSQ particles have a high modulus at 160°C, they are very difficult to deform in the 85/15 blend. At the large deformations occurring during uniaxial elongation, these hard PPSQ particles do not deform with the PMMA, thereby generating a shear flow of PMMA around the PPSQ particles. We suggest that this causes the decrease in η_E at large deformations and induces the strain-softening in the 85/15 blend.

A relatively high fraction of PPSQ molecules remained dispersed well in the PMMA-rich continuous phase of the 80/20 blend. Thus, the resulting enhanced alignment of PMMA around the PPSQ molecules further reduces the net PMMA entanglement density. This, in turn, should decrease strain-hardening. However, this PMMA-rich phase (with greater PPSQ loading versus that in the 85/15 blend) will not readily deform. Therefore, the difference between the deformation ability of PPSQ particles and the PMMA-rich continuous phase for the 80/20 blend is lower than this difference in the 85/15 blend. Perhaps, the PPSQ hard particles in the 80/20 blend may deform somewhat with the PMMA-rich continuous phase at large elongational deformations. This may be why the 80/20 blend exhibits neither strain-hardening nor strain-softening.

In summary, PMMA/PPSQ 95/5 exhibits a slightly weaker strain-hardening than PMMA due to the decrease in entanglement density among PMMA molecules. PMMA/PPSQ blends show much weaker strain-hardening (at PPSQ = 10%) and even strain-softening (at PPSQ $\geq 15\%$) because of the formation of undeformed hard PPSQ particles and a further decrease in the entanglement density. We suggest that the PPSQ particles in the 80/20 blend may deform somewhat with the PMMA-rich continuous phase, so neither strain-hardening nor strain-softening is observed in this blend.

CONCLUSIONS

The rheological properties of PMMA/PPSQ blends under dynamic shear and uniaxial elongation depend on the weight fractions of the mixed components. At

the low PPSQ content (≤ 5 wt %), the storage modulus G' , loss modulus G'' , and dynamic shear viscosity η^* of the 95/5 blend are slightly lower than those for pure PMMA throughout the entire frequency range. The 95/5 blend also shows slightly weaker strain-hardening than pure PMMA due to the decrease in PMMA entanglement density that occurs when the PPSQ dispersed in the continuous PMMA-rich phase induces some local order in adjacent PMMA molecules. At PPSQ contents $\geq 10\%$, the storage modulus G' , loss modulus G'' , and dynamic viscosity η^* of the blends are higher than those of pure PMMA. These values for the 90/10, 85/15, and 80/20 blends are quite similar at high frequencies. At low frequencies, the G'' and η^* values of the 85/15 and 80/20 are quite similar and are slightly higher than those of the 90/10 blend. The 80/20 blend exhibits lower G' values than the 85/15 blend at low frequencies. The strain-hardening in these blends was clearly weakened by inclusion of 10% PPSQ, while the 85/15 blend exhibits strain-softening. Neither strain-hardening nor strain-softening is observed in PMMA/PPSQ 80/20 blend. All of the rheological changes for PMMA/PPSQ 90/10, 85/15, and 80/20 summarized above could result from just two factors: (1) the formation of PPSQ hard particles by phase-separation and (2) specific PMMA-PPSQ interactions among PMMA and the PPSQ molecules, which are well dispersed in the PMMA-rich continuous phase. These hard PPSQ particles act as fillers under the conditions employed in the rheological measurements. They cause a decrease in η_E due to shear flow of PMMA around hard PPSQ particles at a large deformation in the 85/15 blend. The PPSQ hard particles in PMMA/PPSQ 80/20 blend may deform with the PMMA-rich continuous phase (containing a relative high fraction of PPSQ molecules) in the 80/20 blend.

Neither strain-hardening nor strain-softening was observed in the 80/20 blend.

References

1. Brown, J. F., Jr.; Vogt, L. H., Jr.; Katchman, A.; Eustance, J. W.; Kiser, K. M.; Krantz, K. M. *J Am Chem Soc* 1960, 82, 6194.
2. Baney, R. H.; Itoh, M.; Sakaibara, A.; Suzukii, T. *Chem Rev* 1995, 95, 1409.
3. Li, G. Z.; Zhou, C. G.; Qiao, G. L.; Li, X. *Gaofenzi Cailiao Kexue Yu Gongcheng* 1998, 14, 75.
4. Li, G. Z.; Shi, L. H.; Ye, M. L. *Gaofenzi Xuebao* 1998, 2, 160.
5. Li, G. Z.; Jin, Y.; Shi, L. H.; Ye, M. L. *J Polym Sci Part B: Polym Phys* 1996, 34, 1079.
6. Li, G. Z.; Ye, M. L.; Shi, L. H. *J Appl Polym Sci* 1996, 60, 1163.
7. Li, G. Z.; Shi, L. H. *Chin J Polym Sci* 1999, 17, 37.
8. Li, G. Z.; Shi, L. H.; Ye, M. L. *Chin J Polym Sci* 1995, 13, 366.
9. Li, G. Z.; Zhou, C. G. *Youjigui Cailiao Ji Yingyong* 1997, 3, 1.
10. Wu, S. *J Polym Sci Part B: Polym Phys* 1987, 25, 2511.
11. Saito, H.; Matsuura, M.; Inoue, T. *J Polym Sci Part B: Polym Phys* 1991, 29, 1541.
12. Saito, H.; Takahashi, M.; Inoue, T. *Macromolecules* 1991, 24, 6536.
13. Aoki, Y. *Macromolecules* 1990, 23, 2309.
14. Scholz, P.; Froelich, D.; Muller, R. *J Rheol* 1989, 33, 481.
15. Takahashi, T.; Takimoto, J.; Koyama, K. *J Appl Polym Sci* 1999, 73, 757.
16. Takahashi, T.; Takimoto, J.; Koyama, K. *J Appl Polym Sci* 1999, 72, 961.
17. Li, G. Z.; Ye, M. L.; Shi, L. H. *Chin J Polym Sci* 1994, 12, 331.
18. Li, G. Z.; Shi, L. H.; Ye, M. L. *Chin J Polym Sci* 1996, 14, 41.
19. Carreau, P. J.; DeKee, D. C. R.; Chhabra, R. P. *Rheology of Polymeric Systems: Principles and Applications*; Gardner: New York, 1997.
20. Macaubas, P. H. P.; Demarquette, N. R. *Polym Eng Sci* 2004, 42, 1509.
21. Ishizuka, O.; Koyama, K. *Polymer* 1980, 21, 164.
22. Tanaka, H.; White, J. L. *Polym Eng Sci* 1980, 20, 949.
23. Osaki, K.; Murai, A.; Bessho, N.; Kim, B. S. *J Soc Rheol Jpn* 1976, 4, 166.
24. Takahashi, T.; Nakejima, H.; Masubuchi, Y.; Takimoto, J.; Koyama, K. *Sen-I Gakkaishi* 1998, 54, 538.
25. Takahashi, T.; Wu, W.; Toda, H.; Takimoto, J.; Akatsuka, T.; Koyama, K. *J Non-Newtonian Fluid Mech* 1997, 68, 259.