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Description			



Effect of morphology on shear viscosity for
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binary biends of polycarbonate and polystyrene
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30 Abstract

The structure and rheological properties of binary blends of polycarbonate (PC) and 31 polystyrene (PS) were investigated using various PS samples with different molecular 32 weights, namely PS1k ($M_w = 1000$), PS53k ($M_w = 53000$), and PS240k ($M_w = 240000$). 33 34 The blends with PS53k and PS240k show phase-separated structures, whereas the blend with PS1k is miscible. The shear viscosity decreases greatly on addition of PS53k and 35 PS240k, especially at high shear rates, which would be a great advantage at processing 36 operations. Because the non-linear response occurs in the small strain region for 37 multilayered films of PC and PS240k, the origin of the significant viscosity drop for the 38 phase-separated system is interfacial slippage at the phase boundary. 39

40

41 Keywords: Polymer blend; Rheological properties; Polycarbonate; Shear viscosity

43 **1. Introduction**

The field of polymer blends is developing in terms of both scientific understanding and industrial utility. It is well understood that a major purpose of synthesizing polymer blends is to decrease the shear viscosity to improve the processability. The addition of rubbery materials to enhance the mechanical toughness is another major target for polymer blends.¹⁻⁴ Although various blend techniques have been proposed recently to improve the processability,⁵⁻¹¹ there is still a strong need to reduce the shear viscosity, especially for injection molding of engineering plastics.

The miscibility between components is a key factor that determines the structure and 51 rheological properties of polymer blends. When two polymers are thermodynamically 52 53 immiscible, phase separation occurs. In the case of blends with a sea-island structure, the continuous phase greatly affects the rheological properties in the molten state, although 54 the interfacial tension provides melt elasticity to some degree, as described by the 55 emulsion model¹²⁻¹⁴ and the Doi-Ohta theory.^{15,16} Therefore, the addition of a low-56 molecular-weight compound that shows miscibility with a matrix polymer is known to be 57 an effective method for decreasing the viscosity. In the plastic and rubber industries, 58 therefore, plasticizers, waxes, process oils, and oligomers are usually employed to 59 decrease the viscosity to improve the flowability. 60

For bisphenol-A polycarbonate (PC), which is one of the most important engineering plastics, there is a strong need to decrease the shear viscosity. Because PC has a high glass-transition temperature T_g , solidification occurs immediately in the mold in injection molding. Moreover, a recent trend to reduce product thicknesses makes it difficult to fill

the molten material into a mold, especially for a large product. Meanwhile, we reported that the addition of polystyrene (PS) of low molecular weight decreases the shear viscosity of PC. Moreover, the spiral flow length at injection molding was greatly enhanced by the addition of only 5% of PS (148 mm for pure PC and 208 mm for PC/PS (95/5)).¹⁷ Although this is a novel result to the best of our knowledge, the mechanism of the viscosity drop was not clarified.

In this study, therefore, we investigated the effect of the molecular weight of PS on the rheological properties and morphology of PC/PS blends. Although conventional PC and PS are known to be immiscible,¹⁷⁻²⁰ the PS sample with a low molecular weight used in this study is miscible with PC. Furthermore, it should be noted that PS samples showing phase separation from PC can decrease the shear viscosity greatly, especially at high shear rates. The decrease is more obvious than that for the PS sample that is miscible with PC. We investigated the mechanism from the viewpoint of interfacial slippage between phases.

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79 2. Experimental

80 2.1. Materials

A commercially available bisphenol-A polycarbonate (PC, Iupilon S-2000, Mitsubishi Chemical Engineering-Plastics, Japan) was used in this study. Three types of atactic polystyrene (PS) samples of different molecular weights were employed. The number- (M_n) and weight-average (M_w) molecular weights, measured by gel permeation chromatography (HLC-8020, Tosoh, Japan) using chloroform as the solvent and with polystyrene standard samples, are shown in Table 1. The number in the PS sample code represents its $M_{\rm w}$. The $T_{\rm g}$ was evaluated by differential scanning calorimetry (DSC8500,

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88 Perkin-Elmer, MA) at a heating rate of 10 °C/min.
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Code	M_n	M_w	M_w/M_n	T_g (°C)
PC	2.1×10 ⁴	4.2×10^{4}	2.0	158
PS1k	8.7×10 ²	1.0×10 ³	1.2	17
PS53k	3.4×10 ⁴	5.3×10 ⁴	1.6	106
PS240k	9.9×10 ⁴	2.4×10 ⁵	2.4	112

90 Table 1. Characteristics of polymers

91

92 **2.2. Sample preparation**

After being dried in a vacuum oven at 80 °C for 4 h, the materials were melt-mixed 93 using an internal mixer (Labo Plastomill, 10M100, Toyo Seiki Seisakusho, Japan) at 94 250 °C for 6 min. The blade rotation speed was 30 rpm. The blend ratio of PC to PS was 95 96 95 to 5 by weight. The obtained blends were cut into small pieces and used for capillary 97 extrusion measurements. Furthermore, the blends were compression-molded into flat films. After application of a pressure of 10 MPa for 4 min at 250 °C, the sample was 98 cooled at 25 °C by a cooling unit. For reference, pure PC was subjected to the same 99 process. 100

Multilayered films consisting of 20 alternating laminated films of PC and PS240k were prepared by compression-molding under the same conditions. The total thickness of the multilayered film was ca. 1 mm. Pure PC and PS films of thickness 1 mm were also prepared separately in a similar manner.

106 **2.3. Measurements**

107 The light transmittance of the films was evaluated by using a UV-vis 108 spectrophotometer (Lambda25, Perkin-Elmer). The refractive indices were measured by 109 using a multiwavelength Abbe refractometer (DR-M2, Atago, Japan) at 23 °C with α -110 bromonaphthalene as the contact liquid.

111 The frequency dependences of the shear storage modulus *G*' and loss modulus *G*'' in 112 the molten state were determined using a cone-and-plate rheometer (AR2000ex, TA 113 Instruments, DE) in the angular frequency range from 0.1 to 628.3 s⁻¹. The angle of the 114 cone was 4° and the diameter was 25 mm. The linearity of the rheological response was 115 examined by measuring the strain dependence of the oscillatory shear modulus at 250 °C. 116 The shear stress σ caused by an applied strain (amplitude γ_0) at an angular frequency 117 ω was expressed by a Fourier expansion, as follows:^{21,22}

118
$$\sigma = G'_{1}\gamma_{0}\sin\omega t + G''_{1}\gamma_{0}\cos\omega t - G'_{3}\gamma_{0}^{3}\sin 3\omega t - G''_{3}\gamma_{0}^{3}\cos 3\omega t + G''_{5}\gamma_{0}^{5}\sin 5\omega t + G''_{5}\gamma_{0}^{5}\cos 5\omega t - \cdots$$
(1)

The pressure-driven shear flow behavior was evaluated using a capillary rheometer (140SAS, Yasuda Seiki Seisakusyo, Japan). Two circular dies with diameter D to length L ratios (L/D) of 10/1 and 20/2 (mm/mm) were employed. The entrance angle of both dies was 180°. The temperature in the barrel and die was maintained at 250 °C. The measurements were performed in the shear rate range from 28 to 1000 s⁻¹.

The temperature dependences of the tensile storage modulus E' and loss modulus E''were determined using a dynamic mechanical analyzer (Rheogel E4000, UBM, Japan) at temperatures from 30 to 180 °C. The frequency and the heating rate were 10 Hz and

127 2 °C/min, respectively. A rectangular specimen of dimensions $20 \times 5 \times 0.3 \text{ mm}^3$ cut from 128 the film was employed for the measurements.

Morphological observations were performed using a scanning electron microscope 129 130 (SEM; S-4100, Hitachi, Japan) at an accelerating voltage of 20 kV. Both compressionmolded films and extruded strands of PC/PS (95/5) were used. After cryofracturing in 131 liquid nitrogen, the samples were immersed in cyclohexane at room temperature to 132 133 dissolve the PS. Then the fractured surface was sputtered with Pt/Pd after drying. Strands were obtained from the capillary rheometer and quenched with ice water. These strands 134 were sliced using a microtome (RX-860, Yamato Kohki, Japan) along the flow direction. 135 Mechanical properties in the solid state were evaluated by a uniaxial tensile machine 136 137 (LSC-50/300, Tokyo Testing Machine, Japan) at 25 °C. Dumbbell-shaped specimens, cut from the compression-molded films with 300 mm thickness, were used for the 138 measurements. One of the cross-heads of the tensile machine moved at a stretching speed 139 of 10 mm/min. The initial gage length was 30 mm. The average value of 5 measurements 140 was calculated for each sample. 141

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143 **3. Results and Discussion**

The angular frequency dependences of shear storage modulus G', loss modulus G'', and complex viscosity η^* for PC, PS, and their blends are shown in Figure 1. Because of the low moduli due to their low molecular weight, G' and G'' for PS1k and G' for PS53k were not evaluated at this temperature. It was found that individual pure polymers display a typical rheological behavior in the terminal region, i.e., $G' \propto \omega^2$ and $G'' \propto \omega$.

Furthermore, the G' values of the blends with PS53k and PS240k were almost twice as 149 high as that of pure PC at 1 rad/s, even though these PS samples show lower G' values. 150 This behavior is explained by the emulsion model, in which the contribution of interfacial 151 tension is considered.^{12,13} In contrast, both the G' and G'' values for PC/PS1k were lower 152 than those for pure PC across a wide range of angular frequencies, which is completely 153 different from the other blends. The result suggests that PS1k with low viscosity is 154 155 miscible with PC due to the contribution of mixing entropy and acts as a plasticizer. According to Berry and Fox, the viscosity of a polymer melt with a diluent decreases with 156 the volume fraction of the polymer, which is provided by the following relation,²³ 157

158
$$\eta_0 = \zeta_0 \phi^{3.6}$$
 (2)

159 where is ζ_0 the monomeric frictional coefficient and ϕ is the volume fraction of a 160 polymer. A similar behavior was reported for blends of PC and poly(methyl methacrylate) 161 of low molecular weight.^{24,25}



Figure 1. Frequency dependences of (closed symbols) shear storage modulus G', (open symbols) loss modulus G'', and (lines) absolute values of complex shear viscosity η^* for (circles and thin solid line) PC, (diamonds and bold dotted line) PS, and (triangles and thin dotted line) PC/PS (95/5) at 250 °C: (a) PS240k, (b) PS53k, and (c) PS1k.

These rheological properties correspond well to the blend morphologies shown in Figure 2. The blends showed higher *G'* values in the low-frequency range (1 - 10 rad/s); i.e., PC/PS240k (95/5) and PC/PS53k (95/5) clearly exhibited a phase-separated structure. In contrast, phase separation was not observed in PC/PS1k (95/5) even at a high magnification. Furthermore, the droplet size of PC/PS53k seems to be smaller than that of PC/PS240k. The huge difference in the viscosity would be responsible for the coarse morphology for PC/PS53k, as discussed by previous researchers.²⁶⁻²⁸

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Figure 2. SEM images of PC/PS (95/5) blends: (left) PS240k, (center) PS53k, and (right)
PS1k.

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Figure 3 shows the temperature dependences of dynamic tensile moduli such as the storage modulus E' and loss modulus E'' for compression-molded films of PC and PC/PS (95/5) blends. The E'' curves for the PC/PS240k and PC/PS53k blends exhibited distinct double peaks, which were ascribed to the glass-to-rubber transitions of individual pure polymers. The corresponding E' values showed step-wise decreases at 100 and 150 °C, i.e., the T_{gs} of PS and PC, respectively. This is reasonable because PS is known to be immiscible with PC.¹⁷⁻²⁰ In contrast, the blend with PS1k was found to be miscible, owing to the large contribution of the mixing entropy.

The molecular weight of PS necessary for it to be miscible with PC can be estimated 189 from the Flory–Huggins interaction parameter χ . Kim and Burns calculated the χ value 190 between PC and PS to be 0.038 \pm 0.004 at 250 °C.²⁹ This value of the interaction 191 parameter suggests that PS of molecular weight approximately 10000 is miscible with PC 192 at this blend ratio (PC/PS = 95/5), which corresponds well with results in the present 193 194 study (miscible with PS1k and immiscible with PS53k). Furthermore, the E' values at 195 around room temperature for PC/PS1k were slightly higher than those for pure PC, indicating that PS1k acts as an antiplasticizer.^{30,31} 196

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Figure 3. Temperature dependences of (closed symbols) tensile storage modulus E' and (open symbols) loss modulus E'' at 10 Hz for (circles) PC, (diamonds) PC/PS240k (95/5),

201 (triangles) PC/PS53k (95/5), and (squares) PC/PS1k (95/5).

The light transmittances of the films are shown in Figure 4. Considering that the surface reflection R_e of both surfaces, predicted by eq. (3), was ca. 10%, the blends exhibited good transparency, irrespective of the miscibility, which is one of the reasons to employ PS as a processing modifier. Because PC and PS have almost the same reflective index across a wide range of wavelengths, as shown in Figure 5, the blend was transparent, similarly to pure PC, even when phase separation occurs as reported previously.^{32,33}



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Figure 4. Light transmittances in the visible wavelength for PC, PC/PS240k (95/5), and

214 PC/PS1k (95/5) films of thickness 300 μm.



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Figure 5. Refractive indices of PC and PS240k.

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Although the linear viscoelastic properties suggested that PS240k and PS53k do not have any plasticization effect on the linear viscoelasticity of PC, we observed a significant viscosity decrease by performing capillary extrusion measurements. The flow curves for PC, PS240k, PC/PS240k (95/5), PC/PS53k (95/5), and PC/PS1k (95/5), which were constructed with data obtained by using a capillary rheometer with a circular die (L = 10mm, D = 1 mm) at 250 °C, are shown in Figure 6, in which the apparent values on the wall are plotted for both the shear rate $\dot{\gamma}$ and steady-state shear viscosity η .

The shear viscosity of PC/PS1k (95/5) at a low shear rate was lower than those of the other blends. This is a typical flow curve for plasticized polymer systems.^{34,35} In contrast, pronounced viscosity drops were observed at a high shear rate on addition of PS240k and PS53k, and the drops were much more prominent than that caused by PS1k. In general, the shear viscosity of an immiscible blend is dominated by that of the continuous phase. Therefore, a great decrease in the shear viscosity is not expected on addition of an immiscible polymer. Therefore, the experimental result is noteworthy. Of 233 course, the Cox-Merz empirical rule is not applicable for the immiscible blend systems.

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Figure 6. Shear rate dependences of shear viscosities for PC, PS240k, PC/PS240k (95/5),
PC/PS53k (95/5), and PC/PS1k (95/5).

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239 In capillary extrusion measurements, wall slippage can be the origin of an apparent viscosity decrease. The slippage can be evaluated by Mooney's method, by using various 240 dies with different diameters and the same L/D ratios.^{36,37} Figure 7 shows the flow curves 241 obtained using two dies with the same L/D ratio (10/1 and 20/2). When slippage takes 242 place, the apparent shear stress measured by the die with the smaller diameter is lower 243 than that obtained by the die with the larger diameter. However, in the case of our 244 245 measurements, the flow curves obtained by the different dies are identical, demonstrating that the viscosity decrease is not attributable to slippage on the wall. Furthermore, the 246 extruded strands have a smooth surface without any distortion; i.e., flow instabilities, such 247 as shark-skin failure and gross melt fracture, do not take place. 248



Figure 7. Apparent shear viscosity η on wall at 250 °C for (left) PC, (middle) PC/PS240k, and (right) PC/PS53k, obtained by two capillary dies with the same *L/D* ratio: (closed symbols) *L/D* = 10/1 and (open symbol) *L/D* = 20/2.

255 Figure 8 shows SEM images of the core region in cross-sections of PC/PS strands along the flow direction, extruded from a circular die with an L/D ratio of 10/1 at 250 °C. 256 The apparent shear rates on the wall were 73 s⁻¹ and 1000 s⁻¹. At both shear rates, no 257 258 phase-separated structure was detected in strands of PC/PS1k. In contrast, spherical droplets of PS were observed for PC/PS240k and PC/PS53k at 73 s⁻¹. Furthermore, 259 deformed small particles aligned with the flow direction, which must be generated by the 260 disintegration of deformed droplets arising from the Rayleigh disturbance,^{38,39} appear at 261 1000 s⁻¹. Since the Rayleigh disturbance occurs after the cessation of flow, PS droplets 262 are greatly deformed in the flow direction, leading to a pronounced interfacial area. 263



Figure 8. SEM images of extruded strands for blends of (a) PC/PS240k (95/5), (b) PC/PS53k (95/5), and (c) PC/PS1k (95/5) at (top) 73 s⁻¹ and (bottom) 1000 s⁻¹.

The strain dependence of the oscillatory shear modulus was evaluated to clarify the mechanism of the huge viscosity drop for the immiscible blends. The oscillatory moduli in the non-linear region were obtained by using a Fourier expansion. The samples were prepared by laminating 20 films, even for pure PC. In the case of the laminated sample PC–PS240k, 20 films of both PC and PS240k were alternately piled and compressed at 250 °C. Figure 9 shows the strain dependences of G_1' and G_1'' normalized by the G' and G'' values, respectively, in the linear viscoelastic region.

It was apparent that the maximum strain needed to show linearity is smaller for the layered sample, i.e., PC–PS240k, than those for PC and PS at any frequency. The origin of the non-linearity for the layered sample is interfacial slippage. This is reasonable because the interfacial thickness between immiscible polymers is significantly thin, leading to interfacial slippage, as demonstrated by multilayered extrusion.⁴⁰⁻⁴² Such slippage should occur even in blend systems during capillary extrusion and must be pronounced at high shear rates because of the high shear stress. The results suggested that the significant viscosity drop in the high shear rates of the phase-separation system is attributable to polymer–polymer interfacial slippage.

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Figure 9. Strain dependences of (top) G_1'/G' and (bottom) G_1''/G'' for PC, PS240k, and their multilayered film, i.e., PC–PS240k, at (left) 0.628, (center) 6.28, and (right) 62.8 s⁻¹.

290

291 The adhesive strength between phases must be determined by the interfacial 292 thickness λ , which has a close relationship with the interaction parameter χ as follows,⁴³⁻ 293 ⁴⁵

$$\lambda = \frac{2l_K}{\left(6\chi\right)^{1/2}} \tag{4}$$

295 where l_K is the segment length.

Since the segment length of PS is 1.67 nm (ref.46) and the interaction parameter between PC and PS is 0.038 at 250 °C,²⁹ the interfacial thickness is calculated to be 7.0 nm. Considering that the entanglement spacing, i.e., tube diameter, of PS is around 8.5 nm,⁴⁷ the interfacial thickness is too thin to show the adhesive strength. Although it is still unknown that such phenomenon can be detected for other blend systems, the weak boundary and greatly deformed dispersions with large interface would play an important role on this viscosity drop.

Considering the industrial application, the stress-strain curves in the solid state were evaluated as shown in Figure 10. Both stress and strain in the figure are the engineering values. Furthermore, the average values of yield stress and strain at break are summarized in Figure 11.

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308

309 Figure 10. Stress-strain curves for PC, PC/PS240k (95/5), PC/PS53k (95/5), and PC/PS1k

310 (95/5).



Figure 11. Yield stress and strain at break for PC, PC/PS240k (95/5), PC/PS53k (95/5),
and PC/PS1k (95/5).

Although PC is known to exhibit a good mechanical toughness, the addition of PS1k decreased the strain at break. This is attributed to the antiplasticized effect.^{30,31} In fact, the modulus (see Figure 3) and yield stress were obviously enhanced by the PS1k addition. In contrast, the addition of PS53k and PS240k barely affect the tensile properties greatly at this blend ratio. In future, we should evaluate the impact strength for industrial applications, because it is one of the most attractive properties for PC.

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323 4. Conclusions

The effect of PS addition on the rheological properties of PC was studied using PS samples with various molecular weights. It was found from the dynamic mechanical properties and SEM observations that PS1k is miscible with PC, whereas PS53k and

PS240k are immiscible. It should be noted that addition of PS53k and PS240k resulted in a marked viscosity drop, especially at high shear rates. Moreover, the mechanical properties are hardly affected. Therefore, the rheology modification only by 5% of PS must be recognized as a novel method, which could be applicable for actual processing operations.

It was found from the strain dependences of the oscillatory shear moduli that a multilayered film composed of PC and PS240k shows non-linearity in the small strain region, unlike pure PC and PS240k. The non-linear response detected for the multilayered film must be attributed to interfacial slippage between PC and PS. This interfacial slippage should occur in the immiscible blends under capillary flow, and is responsible for the anomalous viscosity drop at high shear rates.

338

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