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Description	

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5 **Effect of morphology on shear viscosity for**
6 **binary blends of polycarbonate and polystyrene**
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30 **Abstract**

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

40

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

42

43 1. Introduction

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

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

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

65 the molten material into a mold, especially for a large product. Meanwhile, we reported
66 that the addition of polystyrene (PS) of low molecular weight decreases the shear
67 viscosity of PC. Moreover, the spiral flow length at injection molding was greatly
68 enhanced by the addition of only 5% of PS (148 mm for pure PC and 208 mm for PC/PS
69 (95/5)).¹⁷ Although this is a novel result to the best of our knowledge, the mechanism of
70 the viscosity drop was not clarified.

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

78

79 **2. Experimental**

80 **2.1. Materials**

81 A commercially available bisphenol-A polycarbonate (PC, Iupilon S-2000,
82 Mitsubishi Chemical Engineering-Plastics, Japan) was used in this study. Three types of
83 atactic polystyrene (PS) samples of different molecular weights were employed. The
84 number- (M_n) and weight-average (M_w) molecular weights, measured by gel permeation
85 chromatography (HLC-8020, Tosoh, Japan) using chloroform as the solvent and with
86 polystyrene standard samples, are shown in Table 1. The number in the PS sample code

87 represents its M_w . The T_g was evaluated by differential scanning calorimetry (DSC8500,
88 Perkin-Elmer, MA) at a heating rate of 10 °C/min.

89

90 Table 1. Characteristics of polymers

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

91

92 2.2. Sample preparation

93 After being dried in a vacuum oven at 80 °C for 4 h, the materials were melt-mixed
94 using an internal mixer (Labo Plastomill, 10M100, Toyo Seiki Seisakusho, Japan) at
95 250 °C for 6 min. The blade rotation speed was 30 rpm. The blend ratio of PC to PS was
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
98 films. After application of a pressure of 10 MPa for 4 min at 250 °C, the sample was
99 cooled at 25 °C by a cooling unit. For reference, pure PC was subjected to the same
100 process.

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

105

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}

$$118 \quad \sigma = G_1' \gamma_0 \sin \omega t + G_1'' \gamma_0 \cos \omega t - G_3' \gamma_0^3 \sin 3\omega t - G_3'' \gamma_0^3 \cos 3\omega t \quad (1)$$

$$+ G_5' \gamma_0^5 \sin 5\omega t + G_5'' \gamma_0^5 \cos 5\omega t - \dots$$

119 The pressure-driven shear flow behavior was evaluated using a capillary rheometer
 120 (140SAS, Yasuda Seiki Seisakusyo, Japan). Two circular dies with diameter D to length
 121 L ratios (L/D) of 10/1 and 20/2 (mm/mm) were employed. The entrance angle of both
 122 dies was 180°. The temperature in the barrel and die was maintained at 250 °C. The
 123 measurements were performed in the shear rate range from 28 to 1000 s⁻¹.

124 The temperature dependences of the tensile storage modulus E' and loss modulus E''
 125 were determined using a dynamic mechanical analyzer (Rheogel E4000, UBM, Japan) at
 126 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.

129 Morphological observations were performed using a scanning electron microscope
130 (SEM; S-4100, Hitachi, Japan) at an accelerating voltage of 20 kV. Both compression-
131 molded films and extruded strands of PC/PS (95/5) were used. After cryofracturing in
132 liquid nitrogen, the samples were immersed in cyclohexane at room temperature to
133 dissolve the PS. Then the fractured surface was sputtered with Pt/Pd after drying. Strands
134 were obtained from the capillary rheometer and quenched with ice water. These strands
135 were sliced using a microtome (RX-860, Yamato Kohki, Japan) along the flow direction.

136 Mechanical properties in the solid state were evaluated by a uniaxial tensile machine
137 (LSC-50/300, Tokyo Testing Machine, Japan) at 25 °C. Dumbbell-shaped specimens, cut
138 from the compression-molded films with 300 μm thickness, were used for the
139 measurements. One of the cross-heads of the tensile machine moved at a stretching speed
140 of 10 mm/min. The initial gage length was 30 mm. The average value of 5 measurements
141 was calculated for each sample.

142

143 **3. Results and Discussion**

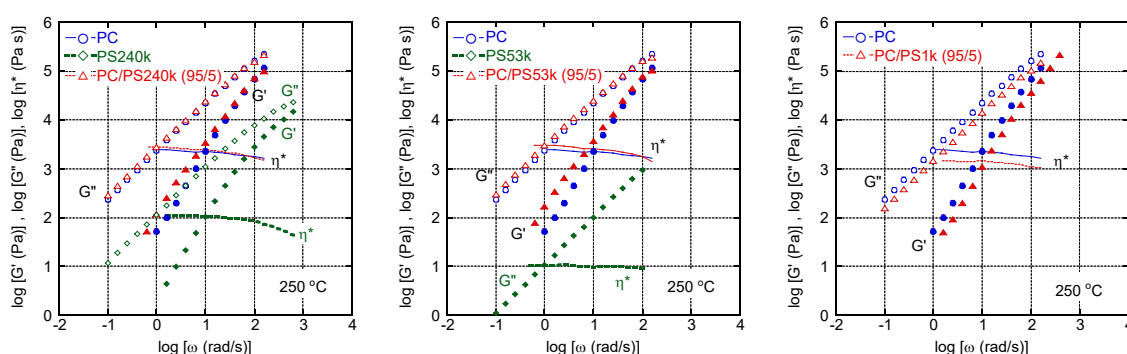
144 The angular frequency dependences of shear storage modulus G' , loss modulus G'' ,
145 and complex viscosity η^* for PC, PS, and their blends are shown in Figure 1. Because of
146 the low moduli due to their low molecular weight, G' and G'' for PS1k and G' for PS53k
147 were not evaluated at this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

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

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

159 where ζ_0 is 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}

162



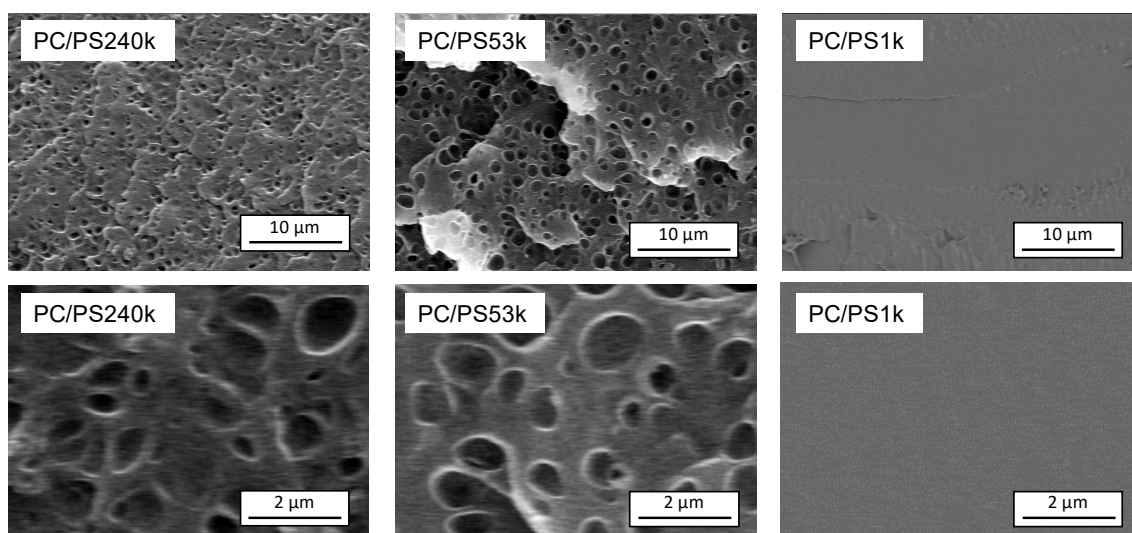
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164 Figure 1. Frequency dependences of (closed symbols) shear storage modulus G' , (open
 165 symbols) loss modulus G'' , and (lines) absolute values of complex shear viscosity η^* for
 166 (circles and thin solid line) PC, (diamonds and bold dotted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

168

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

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

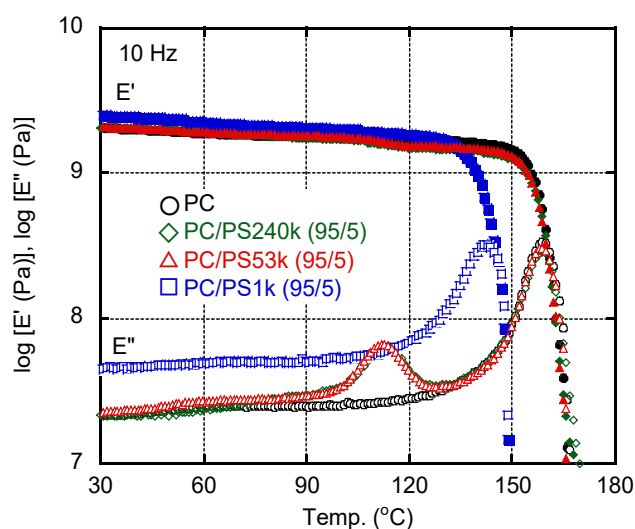
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181 Figure 3 shows the temperature dependences of dynamic tensile moduli such as the
182 storage modulus E' and loss modulus E'' for compression-molded films of PC and PC/PS
183 (95/5) blends. The E'' curves for the PC/PS240k and PC/PS53k blends exhibited distinct
184 double peaks, which were ascribed to the glass-to-rubber transitions of individual pure

185 polymers. The corresponding E' values showed step-wise decreases at 100 and 150 °C,
 186 i.e., the T_{gs} of PS and PC, respectively. This is reasonable because PS is known to be
 187 immiscible with PC.¹⁷⁻²⁰ In contrast, the blend with PS1k was found to be miscible, owing
 188 to the large contribution of the mixing entropy.

189 The molecular weight of PS necessary for it to be miscible with PC can be estimated
 190 from the Flory–Huggins interaction parameter χ . Kim and Burns calculated the χ value
 191 between PC and PS to be 0.038 ± 0.004 at 250 °C.²⁹ This value of the interaction
 192 parameter suggests that PS of molecular weight approximately 10000 is miscible with PC
 193 at this blend ratio (PC/PS = 95/5), which corresponds well with results in the present
 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,
 196 indicating that PS1k acts as an antiplasticizer.^{30,31}

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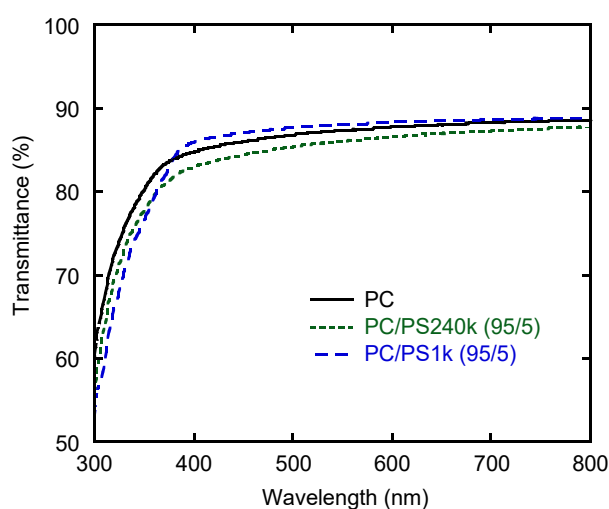
199 Figure 3. Temperature dependences of (closed symbols) tensile storage modulus E' and
 200 (open symbols) loss modulus E'' at 10 Hz for (circles) PC, (diamonds) PC/PS240k (95/5),
 201 (triangles) PC/PS53k (95/5), and (squares) PC/PS1k (95/5).

202

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

$$210 \quad R_e = \left(\frac{n-1}{n+1} \right)^2 \quad (3)$$

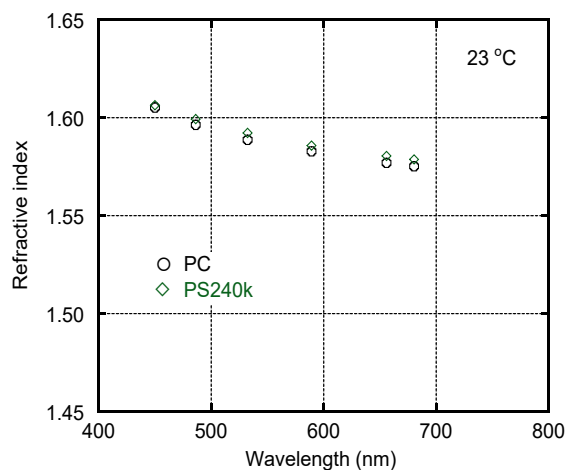
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213 Figure 4. Light transmittances in the visible wavelength for PC, PC/PS240k (95/5), and
 214 PC/PS1k (95/5) films of thickness 300 μm .

215



216

217

Figure 5. Refractive indices of PC and PS240k.

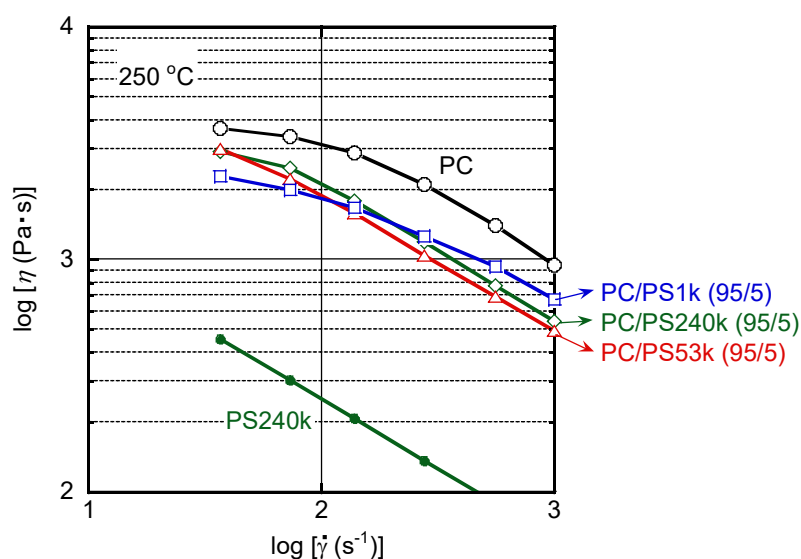
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219 Although the linear viscoelastic properties suggested that PS240k and PS53k do not
 220 have any plasticization effect on the linear viscoelasticity of PC, we observed a significant
 221 viscosity decrease by performing capillary extrusion measurements.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

226 The shear viscosity of PC/PS1k (95/5) at a low shear rate was lower than those of
 227 the other blends. This is a typical flow curve for plasticized polymer systems.^{34,35} In
 228 contrast, pronounced viscosity drops were observed at a high shear rate on addition of
 229 PS240k and PS53k, and the drops were much more prominent than that caused by PS1k.
 230 In general, the shear viscosity of an immiscible blend is dominated by that of the
 231 continuous phase. Therefore, a great decrease in the shear viscosity is not expected on
 232 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.

234



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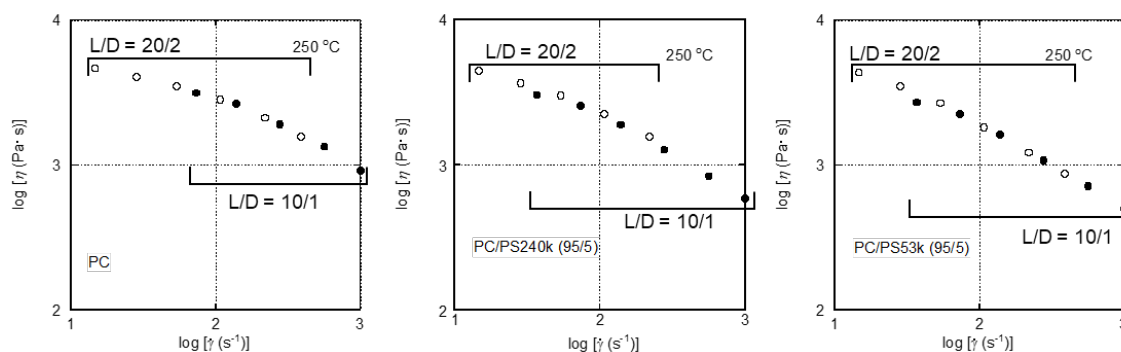
236 Figure 6. Shear rate dependences of shear viscosities for PC, PS240k, PC/PS240k (95/5),

237 PC/PS53k (95/5), and PC/PS1k (95/5).

238

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

249



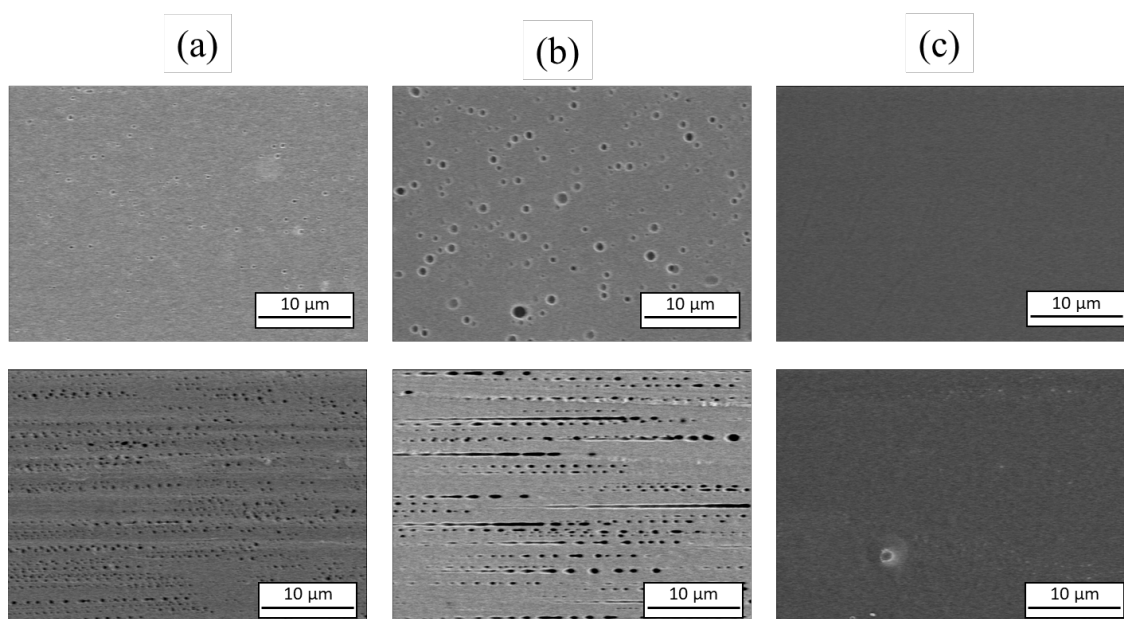
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251 Figure 7. Apparent shear viscosity η on wall at 250 °C for (left) PC, (middle) PC/PS240k,
 252 and (right) PC/PS53k, obtained by two capillary dies with the same L/D ratio: (closed
 253 symbols) $L/D = 10/1$ and (open symbol) $L/D = 20/2$.

254

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

264



265

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

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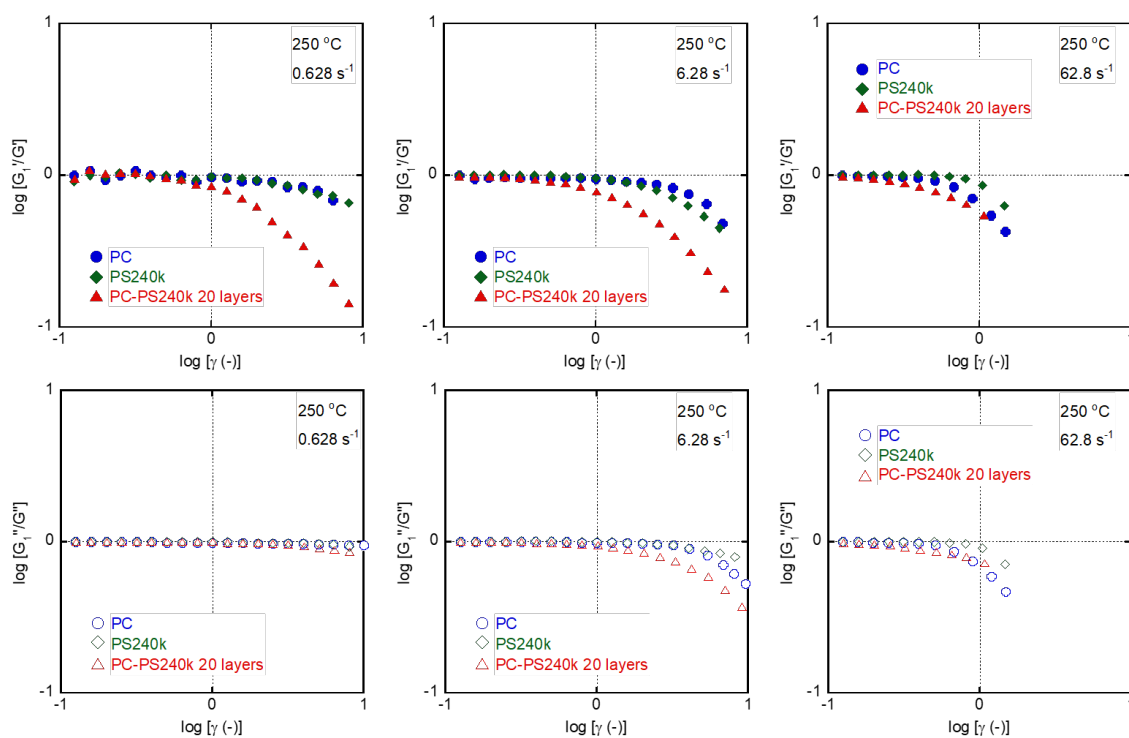
269 The strain dependence of the oscillatory shear modulus was evaluated to clarify the
 270 mechanism of the huge viscosity drop for the immiscible blends. The oscillatory moduli
 271 in the non-linear region were obtained by using a Fourier expansion. The samples were
 272 prepared by laminating 20 films, even for pure PC. In the case of the laminated sample
 273 PC–PS240k, 20 films of both PC and PS240k were alternately piled and compressed at
 274 $250 \text{ }^\circ\text{C}$. Figure 9 shows the strain dependences of G_1' and G_1'' normalized by the G' and
 275 G'' values, respectively, in the linear viscoelastic region.

276

277 It was apparent that the maximum strain needed to show linearity is smaller for the
 278 layered sample, i.e., PC–PS240k, than those for PC and PS at any frequency. The origin
 279 of the non-linearity for the layered sample is interfacial slippage. This is reasonable
 280 because the interfacial thickness between immiscible polymers is significantly thin,
 leading to interfacial slippage, as demonstrated by multilayered extrusion.⁴⁰⁻⁴² Such

281 slippage should occur even in blend systems during capillary extrusion and must be
 282 pronounced at high shear rates because of the high shear stress. The results suggested that
 283 the significant viscosity drop in the high shear rates of the phase-separation system is
 284 attributable to polymer–polymer interfacial slippage.

285



286

287 Figure 9. Strain dependences of (top) G_1'/G' and (bottom) G_1''/G'' for PC, PS240k, and
 288 their multilayered film, i.e., PC–PS240k, at (left) 0.628, (center) 6.28, and (right)
 289 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

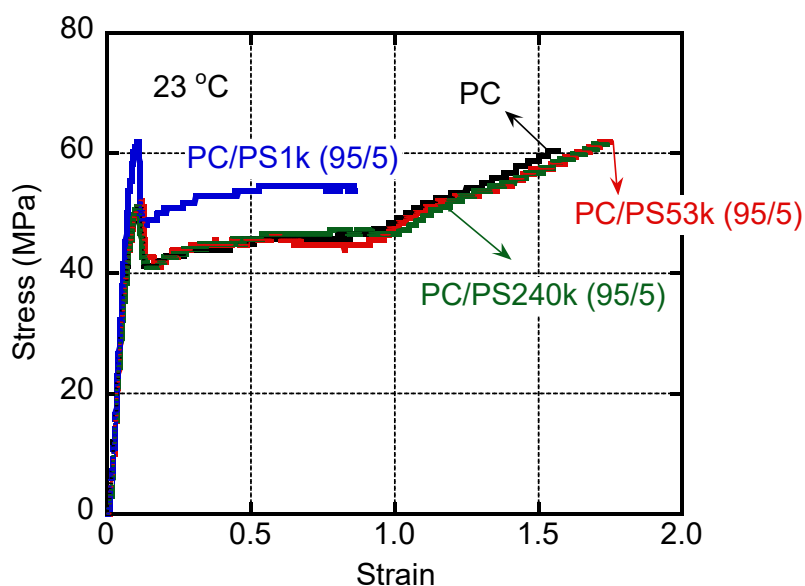
$$294 \quad \lambda = \frac{2l_K}{(6\chi)^{1/2}} \quad (4)$$

295 where l_K is the segment length.

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

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

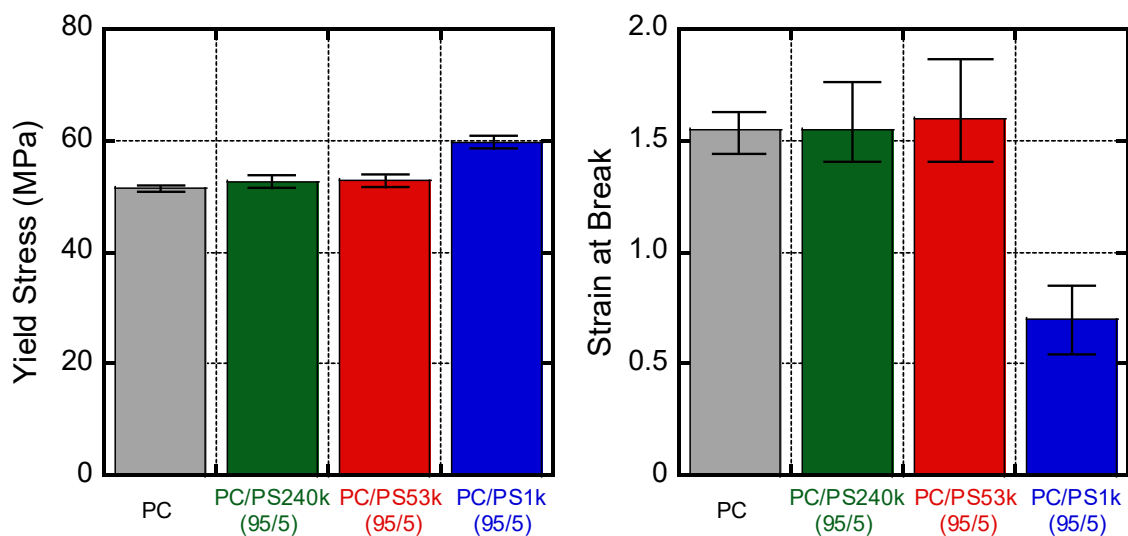
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309 Figure 10. Stress-strain curves for PC, PC/PS240k (95/5), PC/PS53k (95/5), and PC/PS1k
 310 (95/5).

311



312

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

315

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

322

323 4. Conclusions

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

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

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

338

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