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**Autonomic healing of thermoplastic elastomer  
composed of triblock copolymer**

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26 **Abstract**

27 In this paper, we demonstrated that commercially available triblock copolymers such as  
28 polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) and  
29 polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS), used as thermoplastic elastomers,  
30 exhibit autonomic self-healing behavior at room temperature without any chemical  
31 reaction even after cutting into two separate pieces. The healing efficiency is improved  
32 by immediate recombination after cutting, and is attributed to the destruction of the  
33 microstructure, i.e., polystyrene domains, leading to marked molecular mobility.  
34 Furthermore, quenched samples with obscure phase-separation exhibit good healing  
35 behavior. Finally, SBS has better healing efficiency than SIS because the solubility  
36 parameter of polybutadiene is closer to that of polystyrene than that of polyisoprene; to  
37 some extent, the solubility parameter is responsible for enhanced molecular motion  
38 owing to the mutual dissolution of both components.

39

40 **Keywords:** thermoplastic elastomer; triblock copolymer; self-healing; viscoelastic  
41 properties

## 42 INTRODUCTION

43 It is well known that triblock copolymers have microstructures, such as spheres,  
44 cylinders, gyroids, and lamellae, which are basically determined by the compatibility,  
45 volume fraction, and molecular weight of the components [1–6]. Ambient temperature,  
46 flow field, and the addition of another component such as a plasticizer also affect the  
47 structure [4–13]. Although detailed academic studies on the microdomain structure of  
48 triblock copolymers have been carried out, the use of such copolymers in industrial  
49 applications such as thermoplastic elastomer, adhesive, and impact modifier for  
50 thermoplastic resins have reemphasized the importance of a basic understanding of their  
51 structure [5, 14]. Of the triblock copolymers,  
52 polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS),  
53 polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS), and  
54 polystyrene-*b*-(ethylene-*co*-1-butene)-*b*-polystyrene (SEBS) are the most readily  
55 available materials in industry. When the Shell Oil Company began to commercially  
56 manufacture SBS in 1964, one of their objectives was to provide an alternative for  
57 vulcanized rubber, because SBS acts as a thermoplastic elastomer [5].

58 In this paper, we demonstrate that commercially available SBS and SIS can exhibit  
59 self-healing behavior without any manual intervention. Although they have been used

60 as a substitute for vulcanized rubber for a long time, to the best of our knowledge their  
61 self-healing behavior has not been reported.

62 There have been several approaches to the material design of self-healing polymers  
63 [15-19]. In this study, the interdiffusion of polymer chains through the boundary of the  
64 cut surface is used to repair triblock copolymers such as SBS and SIS. Such a  
65 mechanism was originally proposed by Wool [15]. He found that rubber autohesion can  
66 be attributed to the interdiffusion of molecular chains, and explained this phenomenon  
67 using the tube model [20]. Self-healing is detected even for plastics when the ambient  
68 temperature is above the glass transition temperature ( $T_g$ ); this is known as crack  
69 healing or thermal healing. However, because a material can flow macroscopically at  
70 temperature above the  $T_g$ , the phenomenon has not been exploited for the design of  
71 self-healing polymers. Yamaguchi et al. proposed a new design for a self-healing  
72 polymer in which the interdiffusion of dangling chains in a weak gel would be  
73 responsible for healing [21-23]. Above the  $T_g$ , dangling chains show marked diffusion  
74 through the boundary, leading to self-healing behavior. Moreover, the material would  
75 never flow macroscopically because of the permanent network. Yamaguchi's team also  
76 found that poly(ethylene-*co*-vinyl acetate), which has a low degree of crystallinity,  
77 exhibits self-healing behavior [24]. Because crystallites act as crosslink points, the

78 material shows a similar mechanical behavior to a weak gel above the  $T_g$ . This material  
79 has the disadvantage of poor heat resistance because it has a low melting point and a  
80 sticky surface due to low crystallinity. In this study, we demonstrate the self-healing  
81 property of SBS and SIS. Because commercially available SBS and SIS do not have  
82 sticky surfaces, this interesting property could be beneficial to certain applications.

83

## 84 **MATERIALS AND METHODS**

### 85 **Materials and sample preparation**

86 We used commercially available SBS with a styrene content of 24 wt.% (TR2827, JSR,  
87 Japan), kindly provided by the JSR Corporation, and SIS with a styrene content of 18  
88 wt.% (SEPTON2004, Kuraray, Japan), kindly provided by Kuraray Co., Ltd. The  
89 number- and weight-average molecular weights ( $M_n$  and  $M_w$ , respectively), evaluated  
90 by size exclusion chromatography (HLC-8020, Tosoh, Japan) with TSK-GEL GMHXL  
91 using chloroform as a solvent and as a polystyrene standard, were  $M_n = 9.5 \times 10^4$  and  
92  $M_w = 1.1 \times 10^5$  for SBS, and  $M_n = 8.7 \times 10^4$  and  $M_w = 9.0 \times 10^4$  for SIS.

93 The sample was compressed into a flat sheet using a compression-molding machine as  
94 follows. After pre-heating in the machine at 160°C for 5 min, the sample was  
95 compressed under 20 MPa for 2 min. The sheet was subsequently cooled to 25°C for 3

96 min using another compression-molding machine. Another compressed sheet was  
97 prepared at 200°C and cooled to 5°C to investigate the effect of the processing  
98 conditions on the microstructure and healing properties. In this paper, the samples  
99 heated at 160°C are referred to as “slow-cooling”, and the samples heated at 200°C are  
100 called “rapid-cooling”. Once the sheets had been prepared they were immediately used  
101 for the measurements.

102

### 103 **Measurements**

104 We measured the oscillatory shear modulus as a function of angular frequency using a  
105 strain-controlled rheometer with a parallel-plate geometry (MR-500, UBM, Japan) at  
106 160°C and 200°C. The circular plates (25 mm in diameter) were separated by a  
107 distance of approximately 0.9 mm.

108 The small-angle X-ray scattering pattern was measured using an X-ray diffractometer  
109 (SmartLab, Rigaku, Japan). The thickness of the specimen was 3 mm. The  
110 measurements were performed using CuK $\alpha$  radiation operating at 40 kV and 30 mA at a  
111 scanning speed of 0.50 degree·min<sup>-1</sup>.

112 The temperature dependence of the oscillatory tensile modulus of the samples was  
113 evaluated with a rectangular specimen (5 mm × 20 mm × 1 mm) using a dynamic

114 mechanical analyzer (E4000-DVE, UBM, Japan) in the temperature range from  $-120$  to  
115  $150^{\circ}\text{C}$ . The frequency and heating rate used were  $10\text{ Hz}$  and  $2^{\circ}\text{C}\cdot\text{min}^{-1}$ , respectively.  
116 The self-healing property of each sample was evaluated using a uniaxial tensile machine  
117 (LSC-50/300, Tokyo Testing Machine, Japan) at  $25^{\circ}\text{C}$ . The crosshead speed was  $10$   
118  $\text{mm}\cdot\text{min}^{-1}$  and the initial gauge length was  $10\text{ mm}$ . The sample preparation method is  
119 shown in Fig. 1.

120 [Fig. 1]

121 After the rectangular virgin samples ( $10\text{ mm} \times 30\text{ mm} \times 3\text{ mm}$ ) had been  
122 prepared by cutting the compressed sheet, they were further cut into two pieces using a  
123 razor blade at room temperature. The cut surfaces of the pieces were immediately  
124 jointed together by manual operation. A slight pressure, that was removed after  
125 recombination, was applied initially to promote perfect attachment of the surfaces, i.e.,  
126 wetting. According to Wool, the level of an applied pressure has no/little impact on the  
127 healing, i.e., mutual diffusion, as long as surfaces are jointed perfectly [15]. The  
128 recombined pieces were stored in a temperature- and humidity-controlled chamber  
129 (IG420, Yamato, Japan) at  $25^{\circ}\text{C}$  and  $50\%$  relative humidity for various times, i.e.,  
130 healing periods. Moreover, some of the cut pieces were kept in the temperature- and



131 humidity-controlled chamber before the recombination. All tensile tests were performed  
132 at least 10 times and the average value was calculated.

133 The surface free energies of the compressed sheet and cut surface were evaluated by  
134 measurements of the contact angle (Drop Master DM-301, Kyowa, Japan). The surface  
135 free energy was calculated according to the acid-base theory. To determine the surface  
136 free energy components and parameters of a solid, the contact angles of three liquids,  
137 such as water, ethylene glycol, and diiodomethane, were measured.

138

## 139 **Results and discussion**

### 140 **Effect of processing condition on morphology**

141 Figure 2 shows the angular frequency dependence of the shear storage modulus  $G'$  and  
142 the loss modulus  $G''$  measured at 160°C and 200°C of SBS. The sample prepared by the  
143 slow-cooling was employed. A plateau modulus in the low frequency region, i.e., the  
144 network structure, is clearly discernable at 160°C, suggesting that polystyrene (PS)  
145 microdomains still existed at that temperature even beyond the  $T_g$  of PS. In contrast,  
146 both moduli decreased rapidly with decreasing angular frequency at 200°C, indicating  
147 that mutual dissolution of PS and polybutadiene (PB) blocks occurred, at least to some

148 degree. The results demonstrate that the system shows thermorheological complexity, as  
149 reported [25]. The order–disorder transition occurred between 160 and 200°C.

150 [Fig. 2]

151 The microstructure of the sample in the solid state was evaluated by small-angle X-ray  
152 scattering, as shown in Fig. 3. The slow-cooling sample produced a sharp peak, whereas  
153 the rapid-cooling sample produced a small peak. The long periods were calculated to be  
154 25.6 nm for the slow-cooling sample and 27.2 nm for the rapid-cooling sample. The  
155 results suggest that the slow-cooling sample had a well-developed phase-separated  
156 structure and the rapid-cooling sample exhibited the rheological properties of the molten  
157 state.

158 [Fig. 3]

159 The temperature dependence of the dynamic tensile moduli is shown in Fig. 4. As seen  
160 in the figure, double peaks were detected in the  $E''$  and  $\tan \delta$  curves; one is located at  
161 approximately  $-90^\circ\text{C}$ , which can be attributed to the glass transition temperature ( $T_g$ ) of  
162 the PB block, whereas the other is at approximately  $90^\circ\text{C}$ , i.e., the  $T_g$  of the PS block.  
163 Furthermore, the slow-cooling sample shows high-level  $E'$  in the rubbery region due to  
164 well-developed phase separation. In contrast, there is no obvious peak in the  $\tan \delta$  curve  
165 ascribed to the  $T_g$  of PS for the rapid-cooling sample. The results indicate that PS

166 domains are not distinctly formed by rapid cooling because phase separation cannot  
167 occur during the cooling process.

168 [Fig. 4]

169

### 170 **Self-healing behavior**

171 Figure 5 shows the stress–strain curves with the photographs of the recombined samples  
172 jointed immediately after cutting. The samples were prepared by the slow-cooling. The  
173 numerals in the figure represent the healing periods at 25°C in the temperature- and  
174 humidity-controlled chamber. The given stresses and strains are the engineering values.  
175 It should be noted that the sample with a prolonged healing period had a large strain at  
176 break, revealing that SBS exhibited self-healing behavior even at room temperature  
177 without any chemical reaction. This result indicates mutual diffusion through the jointed  
178 boundary. The phenomenon is interesting because such compressed samples do not  
179 have sticky surfaces and therefore never exhibit autohesion. In contrast, the cut surface  
180 showed autohesion, i.e., healing. Furthermore, the stress–strain curves for the repaired  
181 samples were the same as that of the original compressed sample without cutting,  
182 although the strain at break was smaller.

183 [Fig.5]

184 Figure 6 shows the stress–strain curves for the samples recombined after leaving the cut  
185 surface for 1 week at 25°C. As shown in the figure, the samples showed poor healing,  
186 although the strain at break increased slightly with the length of the healing period. This  
187 result suggests that the characteristics of the cut surface change with duration of  
188 exposure to the atmosphere.

189 [Fig.6]

190 We measured the increase in surface tension of the cut surface to evaluate the  
191 compositional change after cutting, and found that the surface tension of the cut surface  
192 was approximately  $32.0 \text{ mJ}\cdot\text{m}^{-2}$ , which is between that of polystyrene ( $34.3 \text{ mJ}\cdot\text{m}^{-2}$ )  
193 and polybutadiene ( $23.5 \text{ mJ}\cdot\text{m}^{-2}$ ) [26]. Furthermore, the value did not change with time,  
194 suggesting that the composition of the segments remained constant. Favorable healing  
195 behavior was detected in samples recombined immediately after cutting, and many free  
196 molecules whose chain ends were not trapped in the PS domains appeared at the cut  
197 surface, presumably owing to the extremely large deformation at/near the cutting area.  
198 After leaving the cut surface for a while, chain mobility is eventually reduced by the  
199 reorganization of the microstructure, i.e., well-developed PS domains on the surface,  
200 which leads to poor healing.

201 The microstructure prior to cutting also affects healing efficiency. As shown in Fig. 7,  
202 the rapid-cooling sample exhibited better healing behavior than the slow-cooling sample.  
203 The mutual dissolution of both segments in the rapid-cooling sample was responsible  
204 for the pronounced molecular mobility.

205 [Fig.7]

206 To gain a better understanding of the self-healing behavior of the triblock copolymer,  
207 we performed the same experiments using the SIS samples prepared by rapid cooling,  
208 i.e., heating to 160°C and cooling to 5°C. Figure 8 shows the dynamic mechanical  
209 properties of the SIS samples obtained by the slow-cooling (open symbols) and the  
210 rapid cooling (closed symbols). Furthermore, the SBS sample with the rapid cooling  
211 was shown by the lines for comparison. The glass-to-rubber transition of PS was clearly  
212 detected for SIS, indicating that SIS had well-developed phase-separation compared  
213 with SBS (rapid-cooling) obtained under the same cooling conditions. Considering that  
214 the PS content in SIS is lower than in SBS, this can be explained by the difference in PS  
215 compatibility between PB and polyisoprene (PI). Because the solubility parameter of PI  
216 is  $16.7 \text{ mJ}\cdot\text{m}^{-2}$  [26], its compatibility with PS is poor compared with PB.

217 [Fig.8]

218 The stress–strain curves of the recombined samples, i.e., the healed samples, are shown  
219 in Fig. 9. Both SBS and SIS samples were prepared by the rapid-cooling. It was found  
220 that healing efficiency is not as good in the SIS sample as in the SBS samples  
221 irrespective of the annealing period. This is as expected because the well-developed PS  
222 domains trap the PS segments in SIS and reduce molecular motion, which is responsible  
223 for healing.

224 [Fig. 9]

225

## 226 **Conclusion**

227 We investigated the microstructure and self-healing behavior of two commercially  
228 available thermoplastic elastomer: polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS)  
229 and polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS). First, we found that the triblock  
230 copolymers exhibited self-healing behavior at room temperature, whereas the  
231 compressed sample pieces did not show autohesion without sticky surfaces. The healing  
232 behavior was pronounced in the surfaces of the separate pieces immediately after  
233 cutting, although the surface tension of the cut surfaces did not change with time after  
234 cutting. Moreover, the sample with well-developed phase-separation showed poor  
235 healing behavior. These experimental results indicate that the destruction of the

236 microstructure leads to free molecules in the PS domains, which are responsible for  
237 healing. After the reconstruction of the microstructure, therefore, the cut surface loses  
238 its healing ability.

239

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245

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306 **Figure Captions**

307 **Figure 1** Schematic illustration of the sample preparation methods for the self-healing  
308 test. All procedures were carried out at 25°C. The dimensions of the initial  
309 sample shape before cutting were 10 mm width, 30 mm length, and 3 mm  
310 thickness. The samples were cut into two pieces with a razor blade at room  
311 temperature. The cut pieces were attached together with a slight pressure  
312 immediately after cutting or after leaving the pieces for a week. The  
313 recombined samples were then kept in the temperature-humidity controlled  
314 chamber at 25 °C for various waiting times (10 min - 72 hr).

315 **Figure 2** Angular frequency dependence of (closed circles) shear storage modulus  $G'$   
316 and (open circles) loss modulus  $G''$  at 160°C and 200°C for SBS.

317 **Figure 3** Small-angle X-ray scattering patterns for SBS; (open symbols) slow-cooling  
318 and (closed symbols) rapid-cooling.

319 **Figure 4** Temperature dependence of (circles) tensile storage modulus  $E'$  and  
320 (diamonds) loss tangent  $\tan \delta$  for SBS; (open symbols) slow-cooling and  
321 (closed symbols) rapid-cooling.

322 **Figure 5** Stress-strain curves of the healed samples recombined immediately after  
323 cutting for SBS. The samples were obtained by the slow-cooling. The

324 numerals represent the annealing periods after recombination of the cut  
325 pieces. In the figure, photographs at the tensile testing are shown; (blue  
326 frame) strain at 0.19 of the sample annealed for 10 min. and (red frame)  
327 strain at 0.8 of the sample annealed for 72 hr.

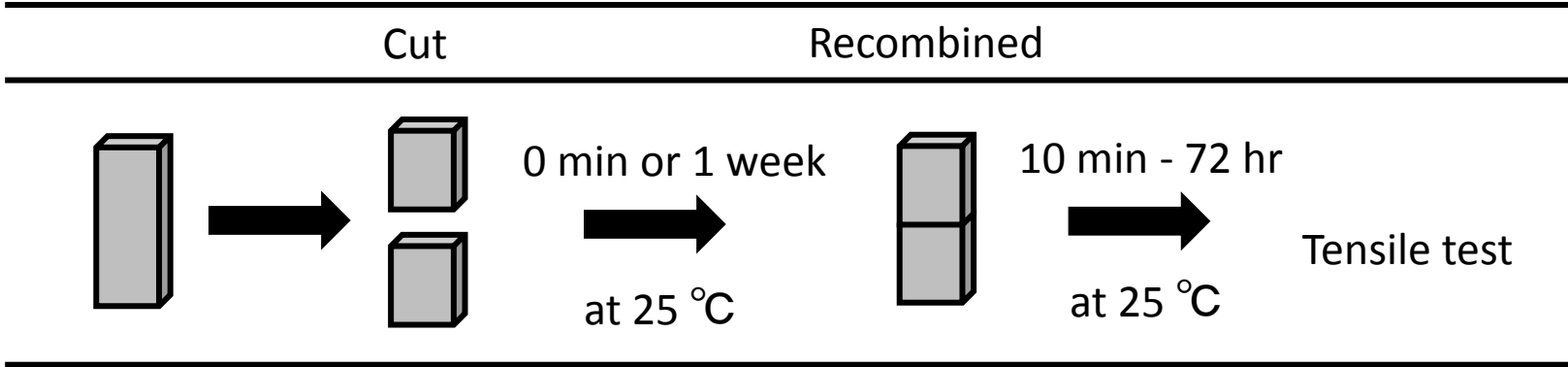
328 **Figure 6** Stress-strain curves of samples with waiting for 1 week after cutting for SBS.  
329 The numerals represent the annealing periods after the recombination of the  
330 cut pieces.

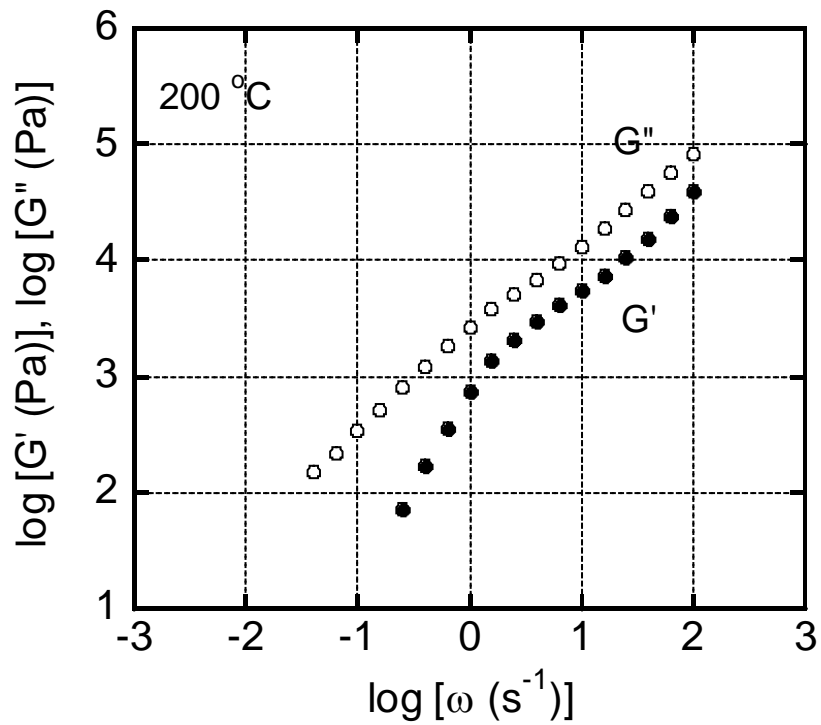
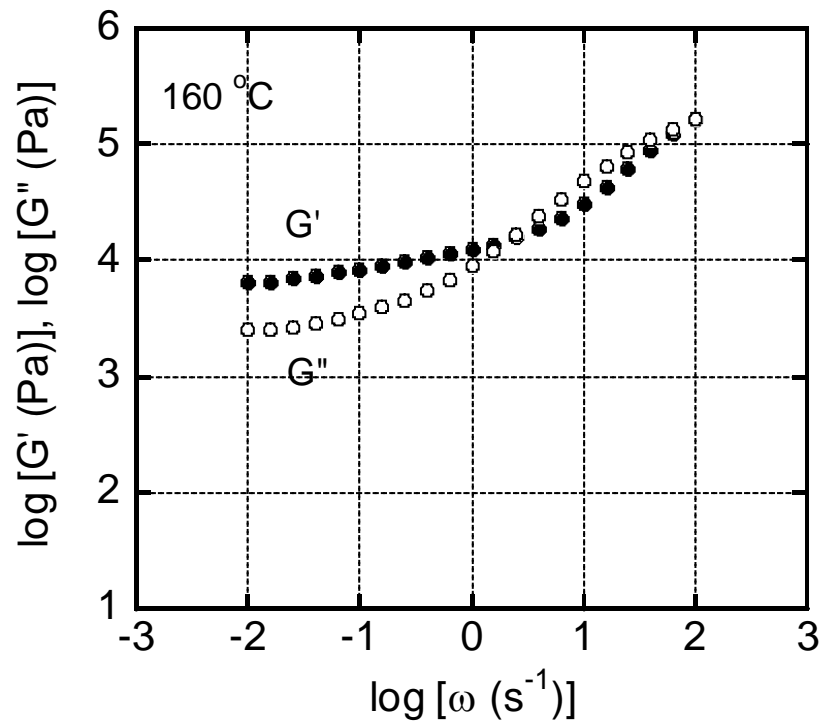
331 **Figure 7** Strain at break evaluated by tensile tests; (left) the separated pieces were  
332 recombined immediately after cutting and (right) the separated pieces were  
333 kept at room temperature for 1 week before the recombination. The  
334 annealing periods at room temperature after the recombination were 10 min  
335 and 72 hr.

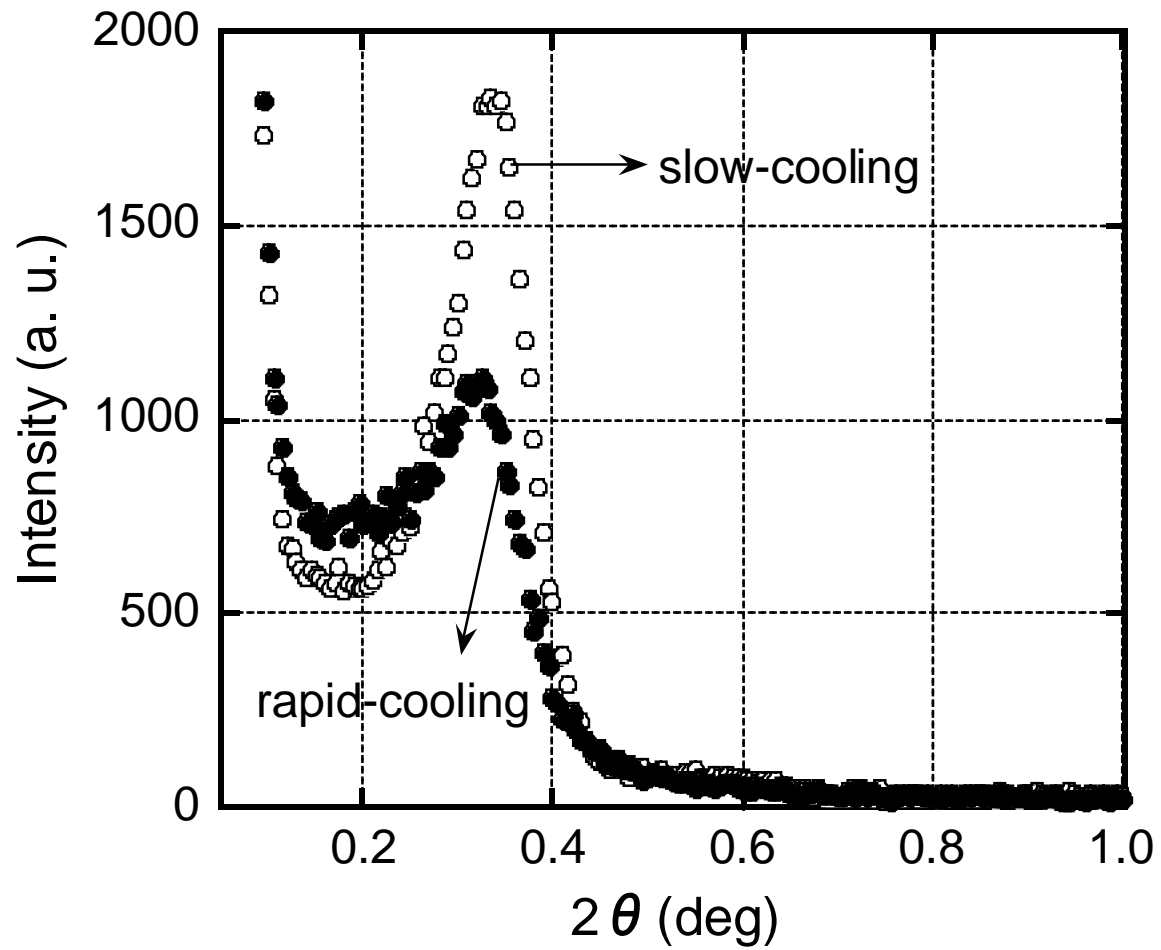
336 **Figure 8** Temperature dependence of (circles and solid line) tensile storage modulus  $E'$   
337 and (diamonds and dotted line) loss tangent  $\tan \delta$ ; (lines) SBS, rapid-cooling,  
338 (open symbols) SIS, slow-cooling, and (closed symbols) SIS, rapid-cooling.

339 **Figure 9** Stress-strain curves of the healed samples recombined immediately after  
340 cutting; (open symbols) SIS and (closed symbols) SBS, obtained by the

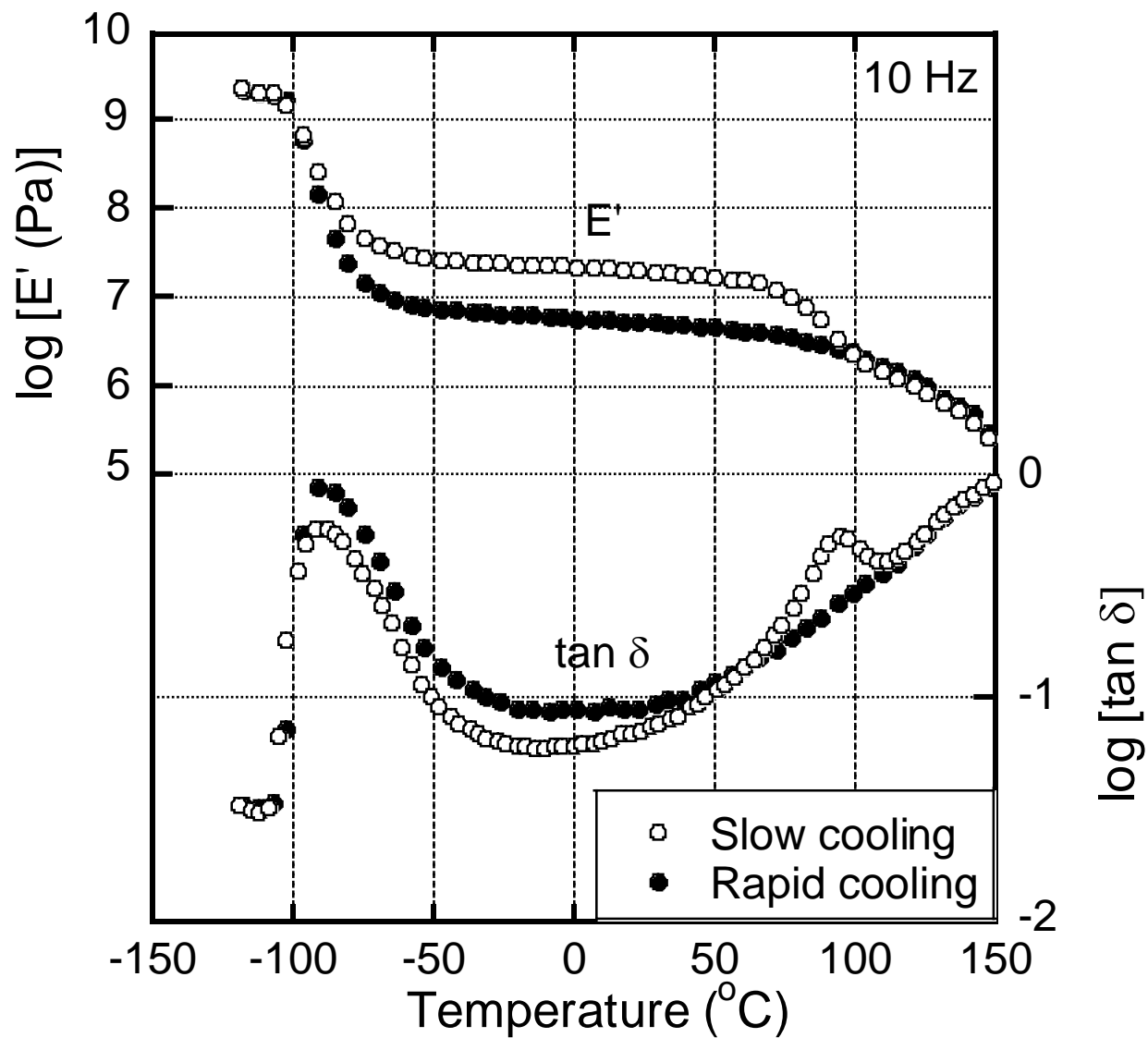
341 rapid-cooling. The annealing periods at room temperature after the  
342 recombination were (dotted lines) 10 min and (solid lines) 72 hr.

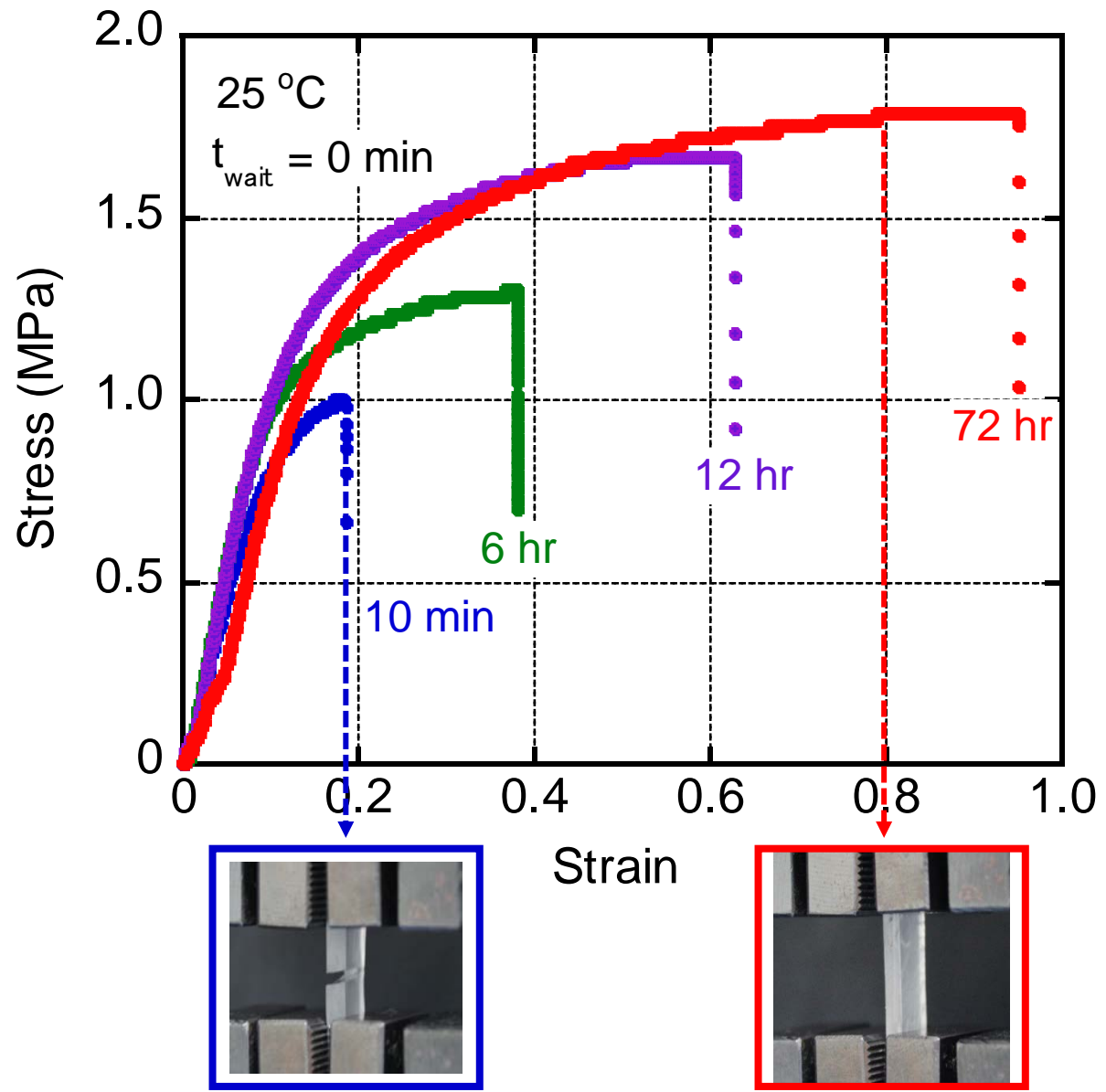




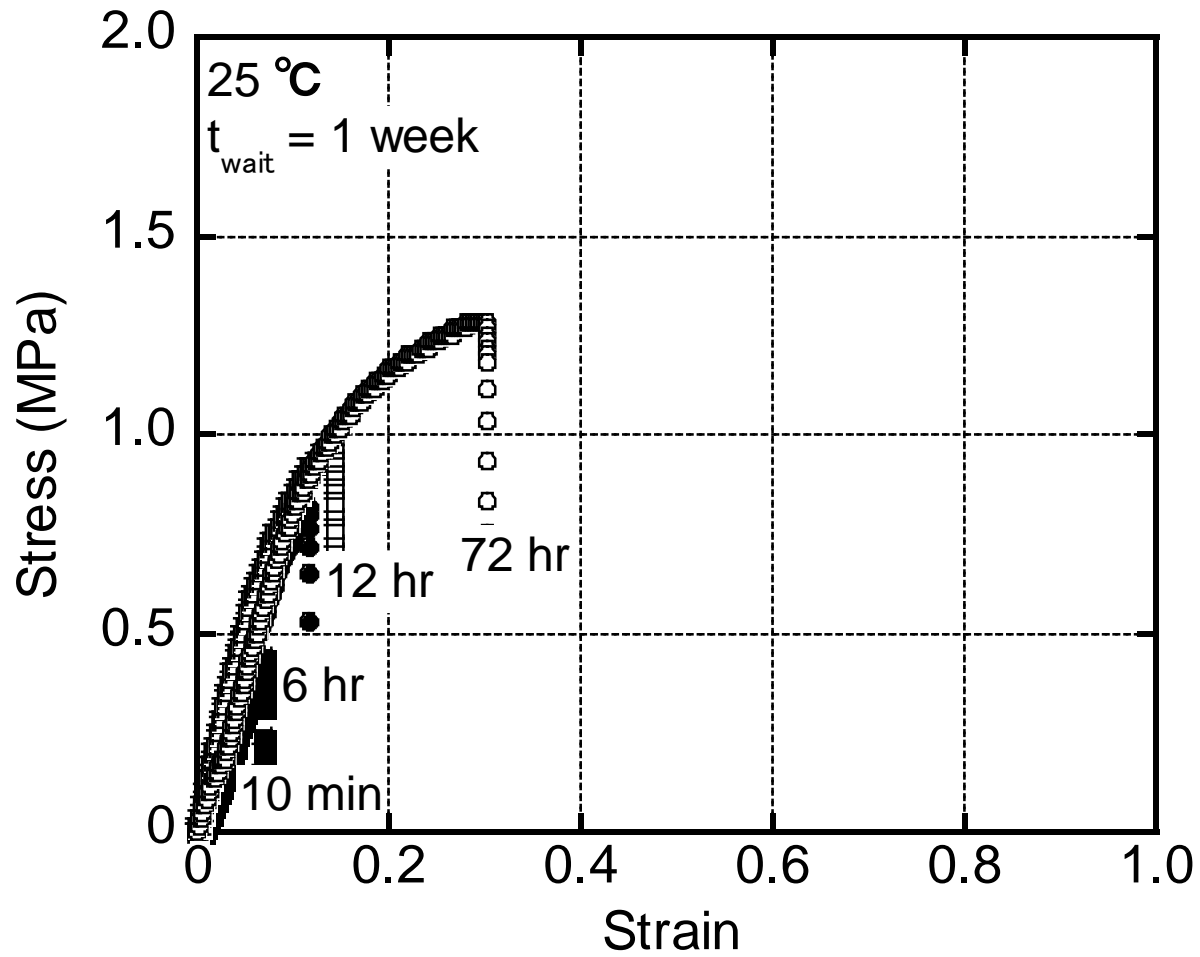


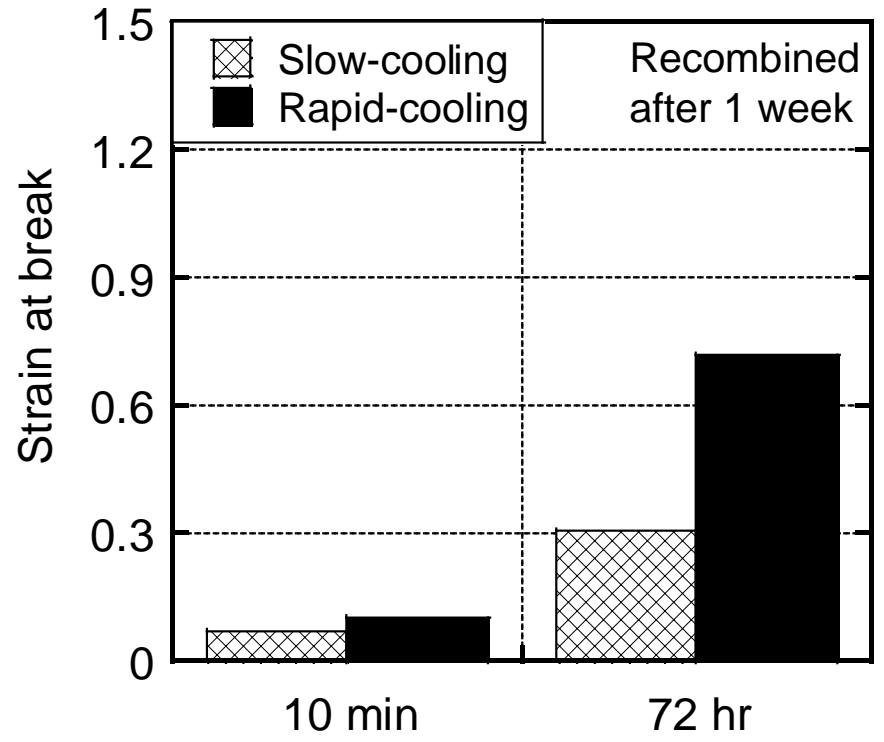
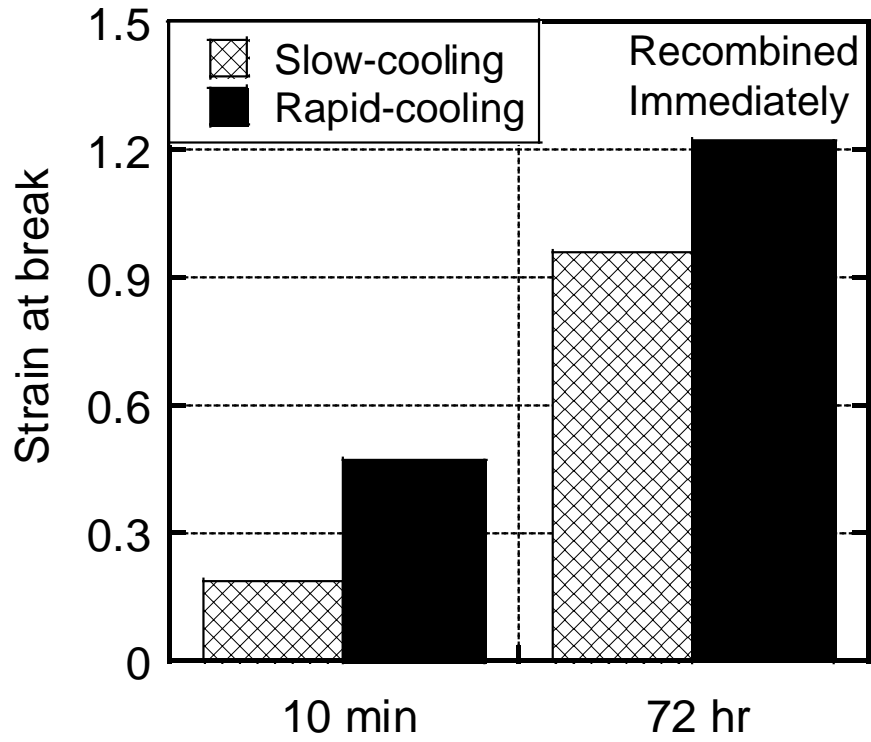


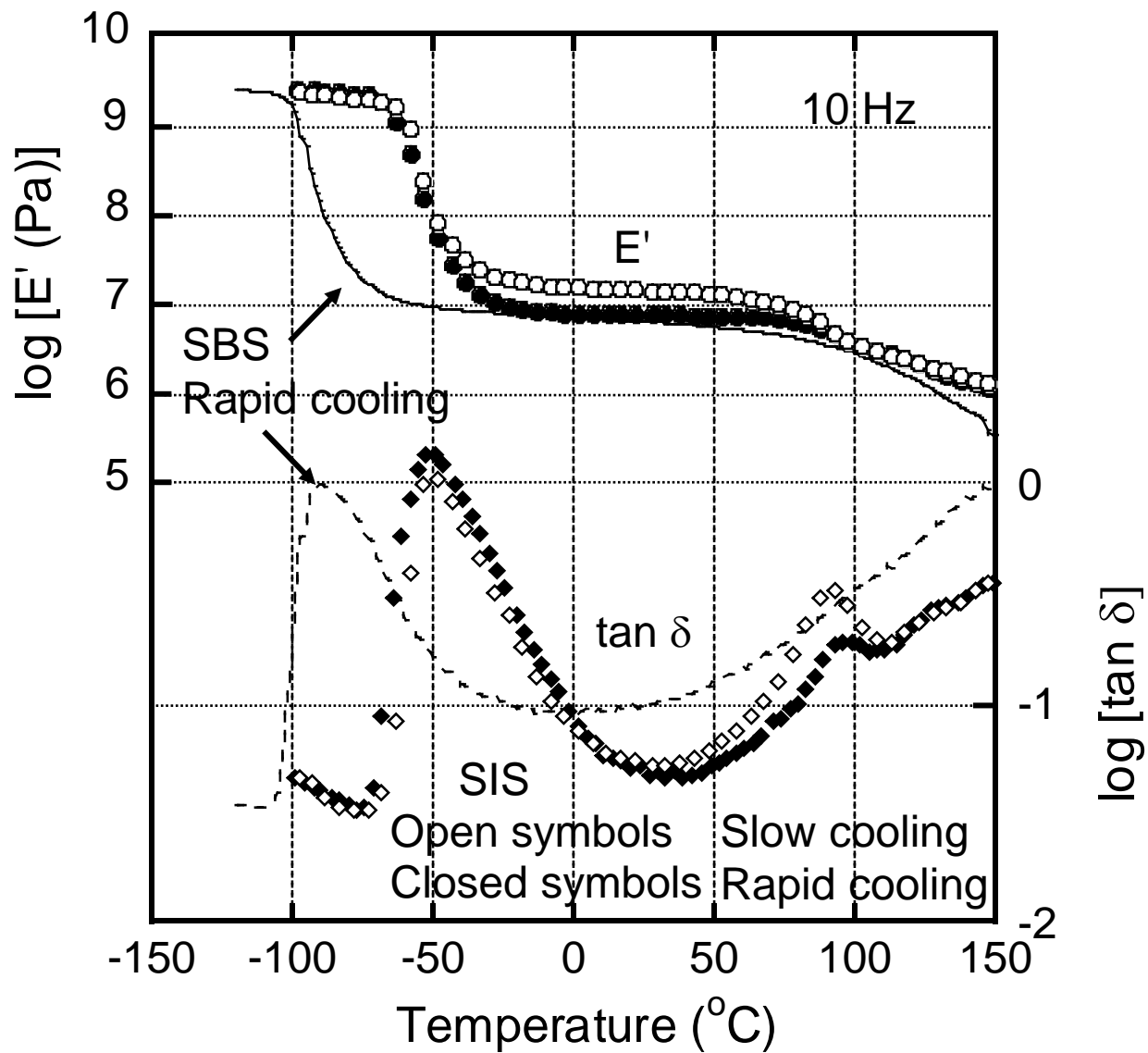




Watanabe et al., Figure 5







Watanabe et al., Figure 8

