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Description	



Japan Advanced Institute of Science and Technology

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5	Autonomic healing of thermoplastic elastomer
6	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 polystyrene-b-polyisoprene-b-polystyrene (SIS), used as thermoplastic elastomers, 29 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 behavior. Finally, SBS has better healing efficiency than SIS because the solubility 35 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, volume fraction, and molecular weight of the components [1–6]. Ambient temperature, 45 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 applications such as thermoplastic elastomer, adhesive, and impact modifier for 49 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 available materials in industry. When the Shell Oil Company began to commercially 55 56 manufacture SBS in 1964, one of their objectives was to provide an alternative for vulcanized rubber, because SBS acts as a thermoplastic elastomer [5]. 57 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

61

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

There have been several approaches to the material design of self-healing polymers 62 [15-19]. In this study, the interdiffusion of polymer chains through the boundary of the 63 cut surface is used to repair triblock copolymers such as SBS and SIS. Such a 64 mechanism was originally proposed by Wool [15]. He found that rubber autohesion can 65 be attributed to the interdiffusion of molecular chains, and explained this phenomenon 66 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 healing or thermal healing. However, because a material can flow macroscopically at 69 temperature above the  $T_g$ , the phenomenon has not been exploited for the design of 70 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 responsible for healing [21-23]. Above the  $T_g$ , dangling chains show marked diffusion 73 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, exhibits self-healing behavior [24]. Because crystallites act as crosslink points, the 77

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.

## 84 MATERIALS AND METHODS

### 85 Materials and sample preparation

We used commercially available SBS with a styrene content of 24 wt.% (TR2827, JSR, 86 Japan), kindly provided by the JSR Corporation, and SIS with a styrene content of 18 87 88 wt.% (SEPTON2004, Kuraray, Japan), kindly provided by Kuraray Co., Ltd. The number- and weight-average molecular weights ( $M_n$  and  $M_w$ , respectively), evaluated 89 by size exclusion chromatography (HLC-8020, Tosoh, Japan) with TSK-GEL GMHXL 90 using chloroform as a solvent and as a polystyrene standard, were  $M_n = 9.5 \times 10^4$  and 91  $M_w = 1.1 \times 10^5$  for SBS, and  $M_n = 8.7 \times 10^4$  and  $M_w = 9.0 \times 10^4$  for SIS. 92 93 The sample was compressed into a flat sheet using a compression-molding machine as follows. After pre-heating in the machine at 160°C for 5 min, the sample was 94

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		

strain-controlled rheometer with a parallel-plate geometry (MR-500, UBM, Japan) at
160°C and 200°C. The circular plates (25 mm in diameter) were separated by a
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  $\times$  20 mm  $\times$  1 mm) using a dynamic

114	mechanical analyzer (E4000-DVE, UBM, Japan) in the temperature range from -120 to
115	150°C. The frequency and heating rate used were 10 Hz and $2^{\circ}C \cdot \min^{-1}$ , 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°C. The crosshead speed was 10
118	$\text{mm}\cdot\text{min}^{-1}$ and the initial gauge length was 10 mm. The sample preparation method is
119	shown in Fig. 1.
120	[Fig. 1]
121	After the rectangular virgin samples (10 mm $\times$ 30 mm $\times$ 3 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°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) microdomains still existed at that temperature even beyond the  $T_g$  of PS. In contrast, 145 146 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]
- The microstructure of the sample in the solid state was evaluated by small-angle X-ray scattering, as shown in Fig. 3. The slow-cooling sample produced a sharp peak, whereas the rapid-cooling sample produced a small peak. The long periods were calculated to be 25.6 nm for the slow-cooling sample and 27.2 nm for the rapid-cooling sample. The results suggest that the slow-cooling sample had a well-developed phase-separated structure and the rapid-cooling sample exhibited the rheological properties of the molten state.
- 158

# [Fig. 3]

The temperature dependence of the dynamic tensile moduli is shown in Fig. 4. As seen in the figure, double peaks were detected in the E'' and tan  $\delta$  curves; one is located at approximately -90°C, which can be attributed to the glass transition temperature  $(T_g)$  of the PB block, whereas the other is at approximately 90°C, i.e., the  $T_g$  of the PS block. Furthermore, the slow-cooling sample shows high-level E' in the rubbery region due to well-developed phase separation. In contrast, there is no obvious peak in the tan  $\delta$  curve 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 result suggests that the characteristics of the cut surface change with duration of 187 188 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 mJ·m<sup>-2</sup>, which is between that of polystyrene (34.3 mJ·m<sup>-2</sup>) 193 and polybutadiene (23.5 mJ·m<sup>-2</sup>) [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.

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

The microstructure prior to cutting also affects healing efficiency. As shown in Fig. 7,

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

201

[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-polysoprene-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 lose		
238	its healing ability.		
239			
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243	society that can coexist with the Earth for centuries - Supported by Japan Science and		
244	Technology Agency (JST).		
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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 3



Watanabe et al., Figure 4









