Supporting Information

Stress-Strain and Stress-Relaxation Behaviors of Solution Coated Layers Composed of Block Copolymers Mixed with Tackifiers

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1. Reduction of stress in the stress-strain behavior for the specimen of the SIS/SI with the tackifier.

Figures 1(a-c) in the main text show the true stress-stretching ratio (S-S) curves ($\sigma$ vs. $\lambda$ curves) for the SIS/SI-tackifier specimens with various types of tackifiers, including the result for the neat SIS/SI specimen at room temperature. The tackifier contents are (a) 23, (b) 33, and (c) 50 wt%. It was found that the S-S curves of all the SIS/SI-tackifier specimens had lower overall stress and higher elongation at break than that of the SIS/SI neat specimen. The stress-reduction is considered to be a decrease in the fraction of the bridge conformation of the mid-PI block chains in the SIS triblock copolymer in the matrix (PI-mat) because the loop conformation of the mid-PI chains cannot impart the stress in the slightly stretched specimen. In order to confirm this conjecture, the stress is normalized by the fraction of the PI-mat ($w_{PI\cdot mat}$) because the stress is proportional to the number of the stretched PI-chains, which is especially correct in the initial stage of stretching. Figure S1 shows the S-S curves normalized by $w_{PI\cdot mat}$ ($\sigma'w_{PI\cdot mat}$ - $\lambda$ curves) for the SIS/SI-tackifier specimens with various types of tackifiers, including the result for the neat SIS/SI specimen. Nevertheless, the normalized S-S curves did not merge together. Rather, they were more decreased with an increase in the tackifier content and also decreased in the order of $RE < C5-C9 < C5$. The reduction of the normalized stress ($\sigma'w_{PI\cdot mat}$) of the SIS/SI-tackifier specimens compared to that of SIS/SI neat specimen implies the decrease in the fraction of the bridge conformation.
Based on the idea that the reduction in the normalized stress ($\sigma/w_{PI\cdot mat}$) is ascribed to the decrease in the fraction of the bridge conformation, we tried to evaluate the reduction factor ($f_\sigma$) from the normalized S-S curve. Figures 1(d-f) in the main text show the master curves of $\sigma/w_{PI\cdot mat}$ with the shift factor ($f_\sigma^{-1}$) to attain almost complete overlaps of the S-S curves in the range of $1 \leq \lambda \leq 12$. Note that these overlap operations were conducted by the vertical shift with the factor ($f_\sigma^{-1}$) for the plot of the log ($\sigma/w_{PI\cdot mat}$) vs. strain, shown in Figure S2.

![Figure S1](image)

**Figure S1** S-S curves normalized by $w_{PI\cdot mat}$ ($\sigma/w_{PI\cdot mat}$ - $\lambda$ curves) for the SIS/SI-tackifier specimens with various types of tackifiers, including the result for the neat SIS/SI specimen. The tackifier contents are (a) 23, (b) 33, and (c) 50 wt%. Note that the $w_{PI\cdot mat}$ indicates the weight fraction of mid-PI block chains of the SIS triblock copolymer in the matrix of the SIS/SI-tackifier specimen.
Figure S2  Log-normalized S-S curves for the SIS/SI-tackifier blend specimens with various types of tackifiers, including the result for the neat SIS/SI specimen. The tackifier contents are (a) 23, (b) 33, and (c) 50 wt%.
2. **Structural changes upon uniaxial stretching of the SIS/SI neat specimen.**

We conducted the 2-dimentional small-angle X-ray scattering (2D-SAXS) measurements in order to analyze the structural changes upon uniaxial stretching. Figure S3 shows the through-view 2D-SAXS patterns for the SIS/SI neat specimen stretched at $\lambda = 2$ (a-1 and a-2) and $\lambda = 13$ (b-1 and b-2). The panels (a-1) and (b-1) show the results obtained just after reaching the stretched state, while the panels (a-2) and (b-2) are results obtained at 10 min elapsed. Note that the definition of the azimuthal angle ($\mu$) is shown in the panel (a-1), and that $n$ denotes the normal vector of the film specimen.

**Figure S3** Through-view 2D-SAXS patterns for the SIS/SI neat specimen stretched at $\lambda = 2$ (a-1 and a-2) and $\lambda = 13$ (b-1 and b-2). The panels (a-1) and (b-1) show the results obtained just after reaching the stretched state, while the panels (a-2) and (b-2) are results obtained at 10 min elapsed. Note that the definition of the azimuthal angle ($\mu$) is shown in the panel (a-1), and that $n$ denotes the normal vector of the film specimen.
3. Calculation of the model particle scattering profile by assuming Gaussian distribution for the sphere radius $R$.

The model particle scattering profile were calculated by using the following equation;

$$f(q) = 3A_e \Delta \rho \frac{\sin(qR) - qR \cos(qR)}{(qR)^3} \exp\left(-\frac{\sigma_s^2 q^2}{2}\right) \tag{S1}$$

where $f(q)$ denotes the scattering amplitude due to the intraparticle interference, $A_e$ is the scattering amplitude of Thomson scattering, $\Delta \rho$ is the difference in the electron density between sphere and matrix, $V$ is the volume of the spheres, and $\sigma_s$ is a parameter characterizing the variation of the (electron) density in the interfacial region ($\sigma_s$ determines the characteristic interfacial thickness $t_I$ through the relationship $t_I = (2\pi)^{1/2} \cdot \sigma_s$). For a spherical particle with its radius, $R$, equation (S1) is obtained by the Fourier transform of the variation of the electron density in the real space. Then, the scattering intensity due to the intraparticle interference ($I_p(q)$) is formulated as;

$$I_p(q) = \int [f(q)]^2 \ G(R) \ dR / \int G(R) \ dR \tag{S2}$$

with the Gaussian distribution function $G(R)$ for the radius of sphere ($R$), as;

$$G(R) = \frac{1}{\sqrt{2\pi} \ \sigma_R^{-1}} \exp\left[-(R - \bar{R})^2/(2\sigma_R^2)\right] \tag{S3}$$

with $\bar{R}$ and $\sigma_R$ being the average of the sphere radius $R$ and the standard deviation for $R$, respectively.
4. Structural changes upon uniaxial stretching of the SIS/SI-tackifier specimens (tackifier content: 33 wt%).

Figure S4 shows the through-view 2D-SAXS patterns for the SIS/SI-tackifier specimens (tackifier content: 33 wt%) stretched at $\lambda = 2$. The panels (a-1), (b-1) and (c-1) show the results obtained just after reaching the stretched state, while the panels (a-2), (b-2) and (c-2) are the results obtained at 10 min elapsed. Table S1 shows the summary of SAXS results to reveal the temporal changes in the nanostructures at the stretched state ($\lambda = 2$). Figure S5 shows the azimuthal angle ($\mu$) dependence of peak position of the first-order peak for the SIS/SI-tackifier specimens (tackifier content: 33 wt%), obtained from the 2D-SAXS patterns shown in Figure S4. The tackifiers are (a) C5 resin, (b) C5-C9 resin, and (c) RE resin. (d) $\mu$ dependence of the peak position ratio ($q_{10\text{min}}/q_{0\text{min}}$) estimated from the results of the panels (a-c). The definition of $\mu$ is shown in Figure S3(a-1).
Figure S4  Through-view 2D-SAXS patterns for the SIS/SI-tackifier specimens (tackifier content: 33 wt%) stretched at $\lambda = 2$. The panels (a-1), (b-1) and (c-1) show the results obtained just after reaching the stretched state, while the panels (a-2), (b-2) and (c-2) are the results obtained at 10 min elapsed.

Table S1  Summary of SAXS results to reveal the temporal changes in the nanostructures at the stretched state ($\lambda = 2$).

| $d_{\text{10 min}} / d_{\text{0 min}}$ at $\lambda = 2$ | direction to SD | reflection plane | SIS/Sl neat specimen  | SIS/Sl-tackifier specimen (TF content: 33 wt%) |
|------------------------------------------------|----------------|------------------|-----------------------|-----------------------------------------------|
| $d_{\text{0 min}}$: $d$ spacing of the reflection planes just after reaching the stretched state ($\lambda = 2$). | parallel       | {110}            | 1.00                  | + C5  | 1.10 | 1.07 | 1.14 |
|                                                | perpendicular  | {211}            | 1.00                  | + C5-C9 | 1.08 | 1.04 | 1.09 |
| $I_{\text{10 min}} / I_{\text{0 min}}$ at $\lambda = 2$ | parallel       | {110}            | 1.00                  | + RE   | 0.97 | 0.98 | 0.97 |
|                                                | perpendicular  | {211}            | 1.00                  |        | 0.97 | 0.98 | 0.97 |

Note here that $I_{\text{0 min}}$ and $I_{\text{10 min}}$ for the (211) reflection peak are the scattering intensities at $q = \sqrt{3} q_{110}$ where $q_{110}$ denotes the $q$ value of the peak for the (110) reflection.
Figure S5  Azimuthal angle (\( \mu \)) dependence of peak position of the \{110\} reflection (the first-order peak) for the SIS/SI-tackifier specimens (tackifier content: 33 wt\%), obtained from the 2D-SAXS patterns shown in Figure S4. The tackifiers are (a) C5 resin, (b) C5-C9 resin, and (c) RE resin. (d) \( \mu \) dependence of the peak position ratio (\( q_{10\min}/q_{0\min} \)) estimated from the results of the panels (a-c). The definition of \( \mu \) is shown in Figure S3(a-1).
5. Structural changes upon uniaxial stretching of the SIS/SI-tackifier specimens (tackifier content: 50 wt%).

Figure S6 shows the through-view 2D-SAXS patterns for the SIS/SI-tackifier specimens (tackifier content: 50 wt%) stretched at \( \lambda = 2 \). The panels (a-1), (b-1) and (c-1) show the results obtained just after reaching the stretched state, while the panels (a-2), (b-2) and (c-2) are the results obtained at 10 min elapsed.

**Figure S6**  Through-view 2D-SAXS patterns for the SIS/SI-tackifier specimens (tackifier content: 50 wt%) stretched at \( \lambda = 2 \). The panels (a-1), (b-1) and (c-1) show the results obtained just after reaching the stretched state, while the panels (a-2), (b-2) and (c-2) are the results obtained at 10 min elapsed.
6. Stress relaxation curves of normalized stress ($\sigma/\sigma_0$) for the SIS/SI-tackifier specimens.

The corresponding plots of the relaxation of the normalized stress ($\sigma/\sigma_0$) were shown in Figure S7. Roughly speaking, the remained stress was in the order of RE $<$ C5-C9 $<$ C5. Such tendency correlates with the cohesive force in the PS phase. For instance, the high amount of the RE resin was solubilized in the PS phase so that easiness of the pulling-out of the PS chains and in turn the easiness of the stress relaxation were resulted for the SIS/SI-RE resin specimens.

![Figure S7](image-url)  
Figure S7 Relaxation of the normalized stress ($\sigma/\sigma_0$) for the SIS/SI-tackifier specimens stretched at $\lambda = 2$, 10 and 15 where $\sigma_0$ denotes the initial value of the stress at $t = 0$. Note that the broken curves in the panels (g-i) show the results of the SIS/SI neat specimen stretched at $\lambda = 13$, instead of $\lambda = 15$. The panels (a, d, g) are the results of the tackifier content of 23 wt%, the panels (b, e, h) are for the case of 33 wt%, and the panels (c, f, i) are for the case of 50 wt%.
7. Relationship of relaxation times ($\tau_b/\tau_a$ and $\tau_c/\tau_a$) for the stress relaxation.

In our current study, we were able to explain the stress relaxation behavior by fitting with the following three component exponential functions in the main text.

$$\sigma(t) = \sigma_a \cdot \exp(t/\tau_a) + \sigma_b \cdot \exp(t/\tau_b) + \sigma_c \cdot \exp(t/\tau_c) + \sigma_{\text{const}} \quad (1) \quad \text{(in the main text)}$$

Here, $\sigma_K$ and $\tau_K$ are the prefactor and relaxation time for $K = a$, $b$, or $c \quad (\tau_a < \tau_b < \tau_c)$. $\sigma_{\text{const}}$ is the remained stress. Since it is expected that there would be strong correlation among $\tau_a$, $\tau_b$, and $\tau_c$, the ratios of $\tau_b/\tau_a$ and $\tau_c/\tau_a$ were examined in Figure S8 where (a-c) $\tau_b/\tau_a$ and (d-f) $\tau_c/\tau_a$ are plotted as a function of $\lambda$ for the SIS/SI neat specimen and the SIS/SI-tackifier specimens (tackifier content: 23 and 33 wt%). Note that the results of the SIS/SI-tackifier specimens (tackifier content: 50 wt%) are shown in Figure 13 in the main text. Note also that the thick broken lines indicate the approximate lines for all of the plots in each panel.
Figure S8  Plots of the ratios of the relaxation times; $\tau_b/\tau_a$ (panels (a-c)) and $\tau_c/\tau_a$ (panels (d-f)) as a function of $\lambda$ for the SIS/SI-tackifier specimens (tackifier contents: 23 and 33 wt%), including the results for the SIS/SI neat specimen. Here, $\tau_a$, $\tau_b$ and $\tau_c$ are the relaxation times ($\tau_a < \tau_b < \tau_c$) which were evaluated by the fitting to the stress-relaxation curves using eq. (1) in the main text. Note that the thick broken lines indicate the approximate lines for all of the plots in each panel.
8. Results of the linear viscoelastic measurements for the SIS/SI-C5 resin specimens.

The shear viscoelastic behaviors of the SIS/SI-tackifier blend specimens were measured using “Physica MCR301” (Anton Paar Japan K. K., Tokyo, Japan), using a parallel-plate fixture. The stacked specimens (thickness, 1 mm) were punched into a disk shape with a diameter of 20 mm. The frequency sweep (0.1 ~ 628 rad/s) of the viscoelasticity measurement was conducted with a strain amplitude of 0.001 in the temperature range of -30 to 130 °C (-30, -10, 10, 20, 30, 50, 70, 90, 110 and 130 °C). Figure S9 shows the frequency (ω) dependence of storage modulus (G’) with various temperatures for the SIS/SI-C5 resin specimens. Tackifier contents are (a) 23 wt%, (b) 33 wt%, and (c) 50 wt%. Figure 13 in the main text shows the master curves derived after time-temperature superposition referenced at 20 °C obtained from the results shown in Figure S9. Figure S10 shows the smoothing of master curves of G’ in the range of 20 °C to 70 °C (for the specimens with 23 and 33 wt% tackifier) or in the range of -30 °C to 70 °C (for the specimens with 50 wt% tackifier), which are shown in Figure 13 in the main text to calculate the relaxation spectrum H (τ) (Figure 15 in the main text). The black curves in Figure S10 are the smoothed results.
Figure S9  Frequency \( (\omega) \) dependence of the storage modulus \( (G') \) with various temperatures for the SIS/SI-C5 resin specimens. Tackifier contents are (a) 23 wt%, (b) 33 wt%, and (c) 50 wt%.

Figure S10  Smoothing of master curves of \( G' \) in the range of 20 °C to 70 °C (for the specimens with 23 and 33 wt% tackifier) or in the range of - 30 °C to 70 °C (for the specimens with 50 wt% tackifier), which are shown in Figure 13 in the main text to calculate the relaxation spectrum \( H (\tau) \) (Figure 15 in the main text). The black curves are the smoothed results.