

Effects of Compatibility Between Tackifier and Polymer on Adhesion Property and Phase Structure: Tackifier-Added Polystyrene-Based Triblock/Diblock Copolymer Blend System

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ABSTRACT: The effects of compatibility of tackifier with polymer matrix and mixing weight ratio of triblock/diblock copolymers as the matrix on the adhesion property and phase structure of tackifier-added polystyrene triblock/diblock copolymer blends were investigated. For this purpose, polystyrene-*block*-polyisoprene-*block*-polystyrene triblock and polystyrene-*block*-polyisoprene diblock copolymers were used and the diblock weight ratio in the blend was varied from 0 to 1. Spherical polystyrene domains with a mean size of about 20 nm were dispersed in the polyisoprene (PI) continuous phase. In the case of the hydrogenated cycloaliphatic resin as tackifier having a good compatibility with PI and a poor compatibility with polystyrene, the peel strength increased with an increase of the tackifier content, and the degree of increase became significant above 40 wt % of tackifier. It was found that the nanometer-sized agglomerates of tackifier in the PI matrix were

formed and the distance between the nearest neighbors of agglomerates was about 15 nm from SAXS measurement. The peel strength increased with an increase of the nanometer-sized agglomerates of tackifier from TEM observation. On the other hand, in the case of the rosin phenolic resin as tackifier having a good compatibility with both polystyrene and PI, the peel strength increased effectively at the lower tackifier content, while no significant increase at higher tackifier content was observed. The agglomerates of tackifier were never confirmed in this system. The higher peel strength was obtained at the diblock weight ratio in the blend of 0.5–0.7 for both tackifier-added systems. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2251–2260, 2011

Key words: adhesion; adhesives; block copolymers; morphology; SAXS

INTRODUCTION

In many cases, pressure-sensitive adhesive tapes are consisting of a tackifier and a base polymer, such as natural rubber, synthetic rubber, or block copolymer. The tackifier improves not only the flowability of base polymer as a diluent but also the peel strength. The amount of tackifier in the commercially available pressure-sensitive adhesive tapes is usually several tens wt %. Many researchers investigated the relationship between the phase separation and tackiness development by the tackifier, and observed μm -sized phase separation in the polymer/tackifier mixture.^{1–9}

In a series of our investigations,^{10–15} we investigated the effects of tackifier content on the peel strength and the phase separation using a model pressure-sensitive adhesive consisting of polystyrene-*block*-polyisoprene-*block*-polystyrene triblock copolymer (SIS) as a base polymer and an aliphatic petroleum resin (C5 series) as a tackifier. The mixture of SIS and the tackifier formed a phase separated structure consisting of polystyrene (PS) domains with a mean size of about 20 nm and polyisoprene (PI) as continuous phase. C5 series tackifier showed a good compatibility with PI, whereas a poor compatibility with PS. The phase structure was studied using transmission electron microscopy (TEM) and pulse ¹H nuclear magnetic resonance (pulse NMR). As a result, it was estimated that the nanometer-sized agglomerates of the tackifier seemed to form in the PI continuous phase, and they improved the peel strength.

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TABLE I
Weight-Average Molecular Weights of SIS and SI Block Copolymers. SI Contents and PS Contents for SIS/SI Blends Used in this Study

Sample	M_w of SIS	M_w of SI	SI content/wt %	PS content/wt %
SI-0	220,000	—	0	15
SI-17	220,000	110,000	17	15
SI-50	250,000	125,000	50	16
SI-70	230,000	115,000	70	15
SI-100	—	110,000	100	15

In general, so called "SIS" for the base polymer of pressure-sensitive adhesive is a blend of SIS and polystyrene-*block*-polyisoprene diblock copolymer (SI). It is said that the pure SIS is hard and show lower interfacial adhesion, because the molecular mobility of PI unit in SIS is strongly restricted by the PS unit. The PI unit in SI has higher degree of freedom than that in SIS. We previously used a commercially available SIS/SI blend (1/1, w/w) as a base polymer of model pressure-sensitive adhesive in the studies above-mentioned.^{10,11} Gibert et al.¹⁶ and Roos and Creton¹⁷ already investigated some properties of SIS/SI blend. We also investigated the influences of SI amount in the SIS/SI blend on the molecular mobility and the adhesion properties of SIS/SI blend at a constant PS content at 15 wt %.¹⁴ Tack increased with an increase of SI content below 70 wt %, then decreased over 70 wt %. We succeeded in characterization of the molecular mobility by measuring the spin-spin relaxation time (T_2) using a pulse NMR and found that there was a relationship between the molecular mobility and the interfacial adhesion.

In this study, the effects of both compatibility of tackifier with SIS/SI blend and SIS/SI blend ratio on adhesion properties and phase structure were investigated. For this purpose, two kinds of tackifiers were used. One is the hydrogenated cycloaliphatic resin having a good compatibility with PI and a poor compatibility with PS, and the other is the rosin phenolic resin having a good compatibility with both PI and PS. The formation of the nanometer-sized agglomerates of the tackifier was confirmed by a small-angle X-ray scattering (SAXS).

EXPERIMENTAL

Materials

Table I shows chemical structures and weight-average molecular weights (M_w) of SIS and SI block copolymers and SI contents and PS contents of the SIS/SI blends used in this study. The SI content was varied keeping a constant PS content of ~ 15 wt %. The SIS/SI blends were kindly donated from Kraton JSR Elastomers K. K., Tokyo, Japan. Commercially available PI with a M_w of 84,000 (IR-10, Kuraray, Tokyo, Japan) was used.

Two tackifiers, namely hydrogenated cycloaliphatic resin with a softening point of 125°C and a M_w of 750 (tackifier HC, Arkon P-125, Arakawa Chemical Industries, Tokyo, Japan) and rosin phenolic resin with a softening point of 130°C and a M_w of 550 (tackifier RP, Tamanol 901, Arakawa Chemical Industries, Tokyo, Japan) were used as received (Fig. 1).¹⁸ Reagent grade toluene was used as a solvent as received.

Qualitative compatibility test

The approximate compatibility between the tackifier and PI or PS component in SIS was estimated by conducting the following simple test.^{11,12} First, the compatibility between PS and the tackifier was examined. The PS and tackifier 40 wt % toluene solutions were prepared separately. Two solutions were mixed in a test tube and stirred using an agitator for 1 h. The test tube was let stood for 1 week after mixing, and then the phase separation was observed visually. Secondly, the compatibility of the tackifier to PS and PI components was examined as follows. The PS, PI, and tackifier 40 wt % toluene solutions were prepared separately. The PS and PI solutions were mixed in the test tube and stirred for 0.5 h, and then the tackifier solution was added to the test tube and stirred for another 0.5 h. After 1 week passed, the uneven distribution of tackifier to PS and PI phase was determined by measuring the lengths of both phases in the test tube. The weight ratio of PS/PI was 1/1 and their total solid content in the tube was 40 wt %. The tackifier contents were set at 10, 30, and 50 wt % in the total solid.

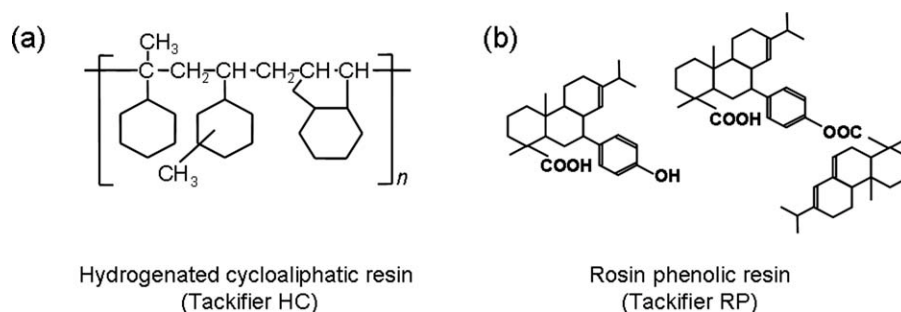


Figure 1 Chemical structure of the tackifiers used in this study.

Sample preparation

About 40 wt % toluene solutions of SIS/tackifier were prepared. The tackifier concentration was varied from 10 to 60 wt % based on the total solid. The solutions were casted on a poly(ethylene terephthalate) (PET, thickness: 38 μm) sheet. After evaporation of the toluene at room temperature, the cast film was heated at 100°C for 10 min *in vacuo*. The thickness of the pressure-sensitive adhesive layer was about 50 μm , which was measured using a thickness indicator (Dial thickness gauge H-MT, Ozaki Mfg., Tokyo, Japan). Next, the PET sheet with the cast pressure-sensitive adhesive film was cut into strips of 25 mm in width and adhered onto the stainless steel plate (SUS304BA, Nippon Tact, Tokyo, Japan) as the adherend. The prepared specimen was pressed using a 2 kg iron roller for sufficient interfacial adhesion. The iron roller was moved backward and forward (one press) and the press was repeated five times. To achieve the sufficient interfacial adhesion, the test specimen was heated at 80°C for 2 h after five times press. The prepared specimens were let stood for 20–40 min before peel adhesion test.

Peel strength

The 180° peel strength was measured at a peel rate of 300 mm/min at room temperature using a tensile testing machine (AG-5KNIS, Shimadzu, Kyoto, Japan) in accordance with JIS Z 0237 (Japanese Industrial Standards).^{10–12}

Tack

Tack of the SIS/SI blend was measured using a probe tack tester (TE-6002, Tester Sangyo, Saitama, Japan) using a stainless-steel (SUS 304) probe with 5 mm diameter at 23–25°C as described in our previous study.¹⁴ The sample adhesive tape was attached on the weight, and the weight was set on the supporting board. When the supporting board declined and the probe lifted up the weight, the contact of probe and the sample adhesive tape started. In this apparatus, the probe is fixed. After a constant contact time, the peeling occurred when the supporting board elevated. The stress–displacement curve of the peeling process was recorded, and the tack was calculated from the maximum stress of the curve. The displacement rate of probe is 10 mm/s, the compressive force by the weight is 0.10N, and the contact time is 1 s.

Phase structure

The following methods were employed to investigate the phase structure of tackifier-added SIS/SI blends.

The dynamic viscoelastic properties were studied using a dynamic mechanical analyzer (DVA-200, ITRK, Osaka, Japan) in a shear mode at 10 Hz frequency with 0.25% applied strain as shown in our previous studies.^{10–12} The measurements were conducted at temperatures ranging from –80 to 180°C (heating rate, 6°C/min).

TEM images were obtained using a TEM (JEM-1210, JEOL, Tokyo, Japan) with 120 kV acceleration voltage in the same way as our previous studies.^{10–12} A drop of 0.1 wt % SIS/tackifier toluene solution was cast onto a collodion-coated cupreous mesh and then dried at room temperature. The sample on the mesh was stained with OsO₄ vapor before observation.

For SAXS measurement, the SIS/SI (50/50, w/w) blend film was cast from 5 wt % toluene solution on a PET film at room temperature, and the as-cast sample was annealed at 180°C for 6 h in nitrogen atmosphere. The SAXS measurements were conducted using a beamline (BL-9C) at the Photon Factory in the Research Organization for High Energy Accelerator, Tsukuba, Japan in the same way as our previous study.¹⁴ The wavelength of incident X-rays, λ , was tuned at 0.154 nm. The details of the SAXS apparatus are available in literature.^{19,20} The imaging plate (250 \times 200 mm²), of which actual pixel size is 100 \times 100 μm^2 , was used as a two-dimensional detector, where the sample film was placed perpendicular to the incident beam (through-view geometry). The typical exposure time was \sim 30 s. BAS2500 (Fuji Photo Film) was used for development of exposed 2d-SAXS images. The 2d-SAXS patterns were further converted to one-dimensional profile by conducting so-called circular average. No further correction such as a background subtraction was made on the 1d- and 2d-SAXS results.

RESULTS AND DISCUSSION

Figure 2 shows the PS toluene solution (a), the mixtures of PS and tackifier HC toluene solutions (b) and the mixtures of PS and tackifier RP toluene solutions (c) in the test tube. The test tubes were let stood for 1 week after mixing. The planar interface was clearly observed in the test tubes with the mixtures of PS and tackifier HC (b) as indicated with a dotted line. This result indicates that the tackifier HC have a poor compatibility with PS. The upper and lower parts in the test tube are the tackifier-rich and the PS-rich solutions, respectively, which was confirmed by the fact that the upper solution in the test tube was well mixed with the PI toluene solution, whereas, never mixed with the PS solution. On the other hand, the mixture of PS, tackifier RP, and toluene formed homogeneous solution (c), which indicates that the tackifier RP have a good compatibility with PS. The compatibility of tackifier HC/PI

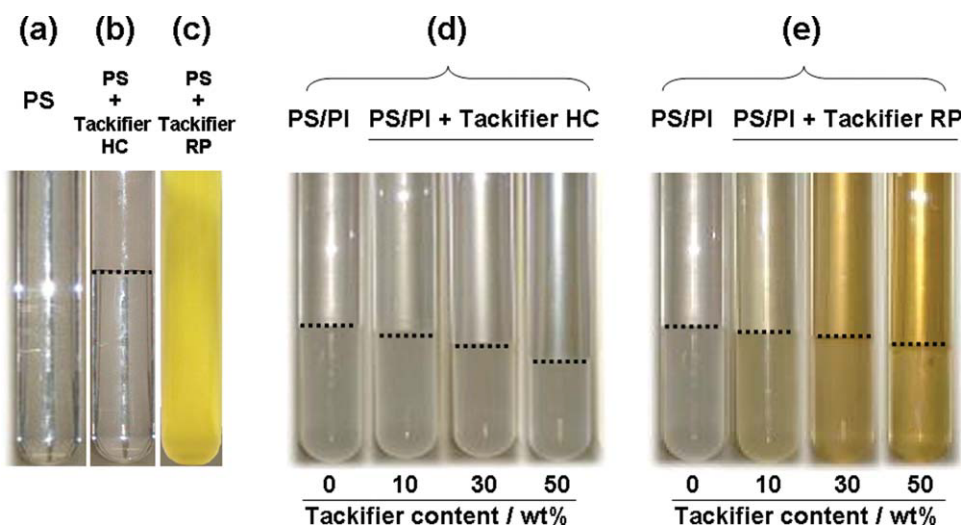


Figure 2 Mixing test of polymer/toluene and tackifier/toluene solutions: (a) PS/toluene solution, mixed toluene solutions of (b) PS and tackifier HC, (c) PS and tackifier RP, (d) PS/PI and tackifier HC, and (e) PS/PI and tackifier RP. PS/tackifier ratio is 1/1 (w/w) (a–c). Polymer and tackifier content in the solution is 40 wt %. The test tubes were let stood for 1 week after mixing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and tackifier RP/PI was also tested in the same way. The good compatibility of these systems was confirmed.

Figure 2(d,e) show PS, PI, and tackifier toluene solutions. The planar interface was clearly observed for all test tubes. The upper and lower parts are the PI-rich and the PS-rich solutions, respectively. The PI-rich phase volume increased with an increase of the tackifier content for both tackifiers. However, the degree of increase of PI phase was larger for tackifier HC (d) than for tackifier RP (e). From these results, the tackifier HC should distribute preferentially in the PI phase in the SIS/SI blends, whereas the tackifier RP should distribute in both the PI and the PS phases.

Next, the peel strength was measured and the results were shown in Figures 3–6. In these Figures, three failure modes were observed: cohesive failure (*), adhesive transfer when peeling (+), and interfacial failure (no symbol). In the case of stick-slip peeling, largest and smallest strength values during peeling were plotted and the dotted line was drawn between these values. Adhesion strength increases by the development of cohesive strength of adhesive and interfacial adhesion. The effect of tackifier addition or SIS/SI ratio on these two factors was discussed.

Figure 3 shows the peel strength of tackifier HC-added SIS/SI blend as a function of the tackifier content. All SIS/SI blends without tackifier HC showed the low peel strength. The peel strength increased with an increase of the tackifier content, which indicates that the interfacial adhesion was developed by the addition of tackifier. Furthermore, the degree of increase of the peel strength became more remarkable above the tackifier content of 40 wt %. The

stick-slip peeling occurred at the higher tackifier content, especially at 60 wt %. The pure SI (■) showed low peel strength below the tackifier content of 30 wt %, and it increased drastically above 30 wt %. The peel strength for pure SI closed to those for the SIS/SI blends above the tackifier content of 40 wt %. These results mean the tackifier increases the cohesive strength of adhesive at higher content.

Figure 4 shows the peel strength of tackifier HC-added SIS/SI blend after heating at 80°C for 2 h to obtain the sufficient interfacial adhesion of adherend interface. The heating temperature was set slightly below the glass transition temperature (T_g) of PS. The peel strength was approximately constant independent of the tackifier content below the content of

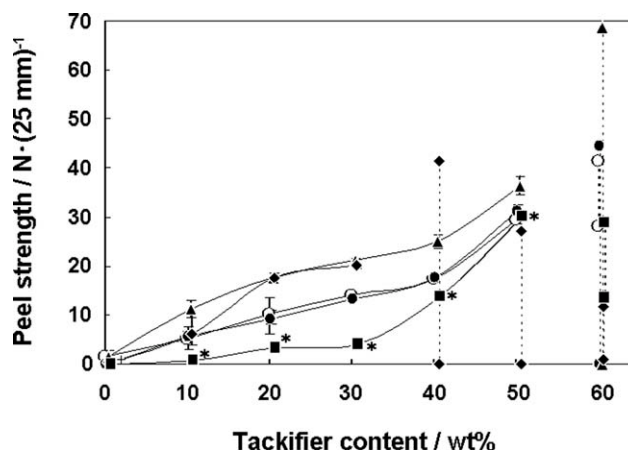


Figure 3 Effect of tackifier content on the peel strength of tackifier HC-added SIS/SI blends of SI-0 (○), SI-17 (●), SI-50 (▲), SI-70 (◆), and SI-100 (■). The test specimen was five times pressed with 2 kg roller. The failure modes were cohesive failure (*), adhesive transfer when peeling (+), and interfacial failure (no symbol).

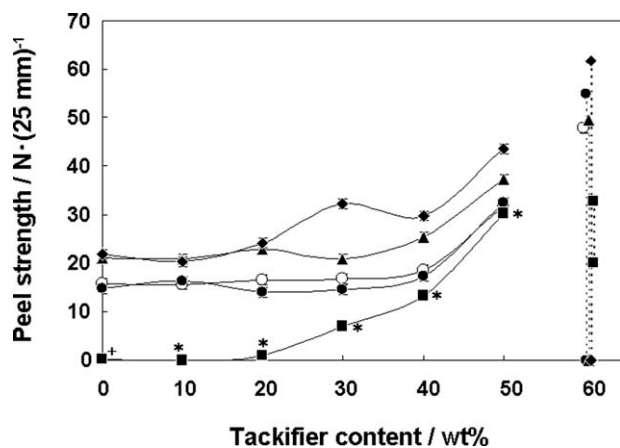


Figure 4 Effect of tackifier content on the peel strength of tackifier HC-added SIS/SI blends of SI-0 (○), SI-17 (●), SI-50 (▲), SI-70 (◆), and SI-100 (■). The test specimen was heated (80°C, 2 h) after five times pressed before peel test. The failure modes were cohesive failure (*), adhesive transfer when peeling (+), and interfacial failure (no symbol).

40 wt % except the SI-100 (pure SI). The tackifier improves interfacial adhesion below the content of 40 wt % as shown in Figure 3, however the sufficient interfacial adhesion was obtained by the heating in Figure 4. The peel strength hardly increased by the heating above the tackifier content of 40 wt %. The effect of heating on the peel strength was smaller in the tackifier content range above 40 wt % than in that below 40 wt %. This result indicates that the tackifier addition improves cohesive strength more effectively than interfacial adhesion at higher content. The SI-50 and SI-70 showed the higher peel strength in Figures 3 and 4.

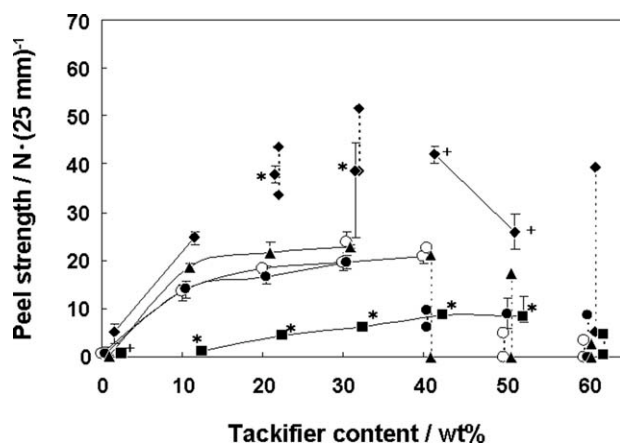


Figure 5 Effect of tackifier content on the peel strength of tackifier RP-added SIS/SI blends of SI-0 (○), SI-17 (●), SI-50 (▲), SI-70 (◆), and SI-100 (■). The test specimen was five times pressed with 2 kg roller. The failure modes were cohesive failure (*), adhesive transfer when peeling (+), and interfacial failure (no symbol).

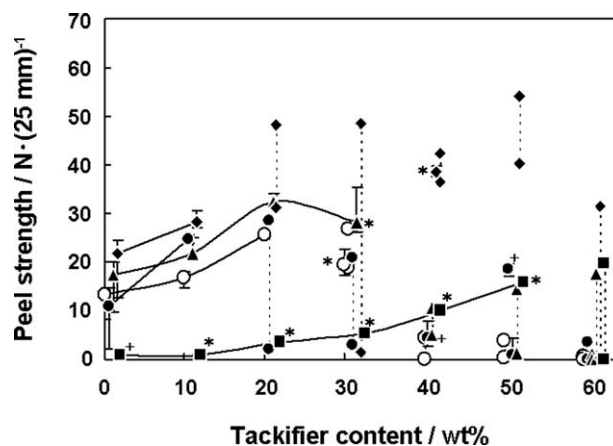


Figure 6 Effect of tackifier content on the peel strength of tackifier RP-added SIS/SI blends of SI-0 (○), SI-17 (●), SI-50 (▲), SI-70 (◆), and SI-100 (■). The test specimen was heated (80°C, 2 h) after five times pressed before peel test. The failure modes were cohesive failure (*), adhesive transfer when peeling (+) and interfacial failure (no symbol).

Figure 5 shows the peel strength of tackifier RP-added SIS/SI blend. The peel strength increased drastically at the tackifier content of 10 wt %, and then increased gradually above 10 wt % (except the SI-100). The peel strength of SI-100 (■) increased gradually with an increase of the tackifier content above 20 wt %. The significant increase of peel strength at higher tackifier content as observed in the tackifier HC-added system (Fig. 3) was never observed in this system. These results indicate that the tackifier RP improved interfacial adhesion more effectively than cohesive strength.

Figure 6 shows the peel strength of tackifier RP-added SIS/SI blend after heating at 80°C for 2 h. The peel strengths of without tackifier systems increased significantly and those with tackifier systems increased slightly by the heat treatment. The significant development of peel strength at the low tackifier content by the heat treatment observed in the tackifier HC-added system (Figs. 3 and 4) was never observed. These results also indicate that the tackifier RP improved interfacial adhesion more effectively than cohesive strength. The highest peel strength was observed for the SI-70, but the failure mode was stick-slip peeling in Figures 5 and 6. The influence of SIS/SI ratio on the peel strength was smaller in the tackifier RP-added system (except the SI-100) than in the tackifier HC-added system shown in Figures 3 and 4.

From the results shown above, the influence of tackifier on the peel strength was completely different between the tackifier HC-added and the tackifier RP-added systems. The SI-50 and SI-70 showed the highest peel strength for the tackifier HC-added system. The highest peel strength was observed for the

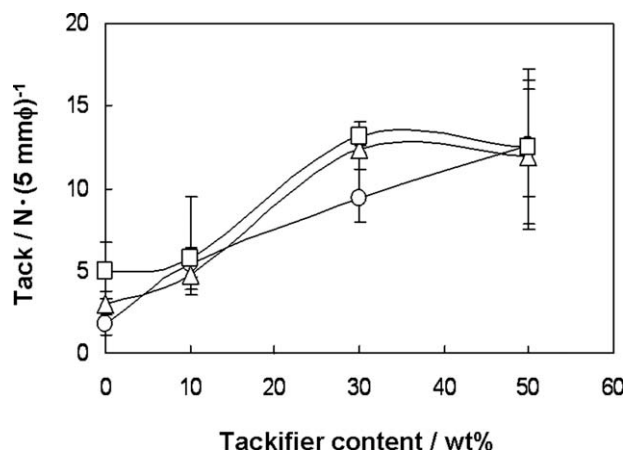


Figure 7 Effect of tackifier content on the tack of tackifier HC-added SIS/SI blends of SI-0 (○), SI-50 (△), and SI-70 (□). Tack was measured by a probe tack test with the contact time of 1 s.

SI-70 in the tackifier RP-added system, but the influence of SIS/SI ratio on the peel strength was smaller in the tackifier RP-added system than in the tackifier HC-added system.

Next, the tack was measured by a probe tack test. The peel strength was measured after sufficient interfacial contact, whereas the tack is measured after contact with lower load and shorter time. Therefore, the influence of interfacial adhesion seems to appear more significantly in the tack than in the peel strength.

Figure 7 shows the effect of tackifier content on the tack of tackifier HC-added SIS/SI blends for the SI-0, SI-50, and SI-70. The tack increased gradually with an increase of tackifier content for the pure SIS. The SI-50 and SI-70 showed slightly higher tack than that of the SI-0 (pure SIS) only at the tackifier content of 30 wt %. The influence of SI addition on the tack was smaller than that of tackifier addition. It was found that the tackifier HC improves interfacial adhesion of SIS more effectively than the SI addition.

In the peel test for tackifier HC-added system (Fig. 3), the peel strength increased with tackifier content, however the peak showed at 30 wt % of tackifier content for tack for the SI-50 and SI-70. The reason is as follows. The peel test is measured with sufficient interfacial adhesion, whereas the tack is measured after instant contact. The tackifier addition improves both the molecular mobility (namely the interfacial adhesion) and the cohesive strength of adhesive. Higher cohesive strength made insufficient interfacial adhesion and the tack decreased at 50 wt % of tackifier content for the SI-50 and SI-70.

Figure 8 shows the effect of tackifier content on the tack of tackifier RP-added SIS/SI blends. The tack increased gradually with an increase of tackifier

content below the tackifier content of 30 wt %. The tack was developed more effectively at the tackifier content of 10 wt % than that of the tackifier HC-added system. However, the tack decreased at the tackifier content of 50 wt %. It was caused by the insufficient interfacial adhesion. The influence of SI addition on the tack was smaller than that of tackifier addition as the same as the tackifier HC-added system. The influence of tackifier on the tack was completely different in the tackifier HC-added and the tackifier RP-added systems as the same as the peel strength shown in Figures 3–6.

In our previous study,¹⁴ tack of SIS/SI blends without tackifier was investigated and it was highest for the SI-70. The tack increases by the development of cohesive strength and interfacial adhesion. Therefore, we discussed that the tack showed the maximum at the optimum contribution balance between cohesive strength and interfacial adhesion. The SI-50 and SI-70 were also optimum in the tackifier-added system for both peel strength (Figs. 3–6) and Tack (Figs. 7 and 8).

Figure 9 shows the temperature dependence of the storage shear modulus (G') for SIS (SI-0, —) and tackifier HC-added SIS with tackifier contents of 10 (○), 30 (△), and 50 wt % (□). The G' decreased drastically at about -50°C for SIS. This temperature is based on the T_g of the PI matrix. The T_g increased with an increase of the tackifier content. The G' of tackifier-added SIS was lower than that of SIS above the G' plateau region. The tackifier hardens the PI (increases the modulus and T_g) in the low temperature range, whereas it softens (decreases the modulus) in the high temperature range. That is, the tackifier plays the roles both as filler in the low temperature range and as well as plasticizer in the high temperature range. Usually, the G' plateau

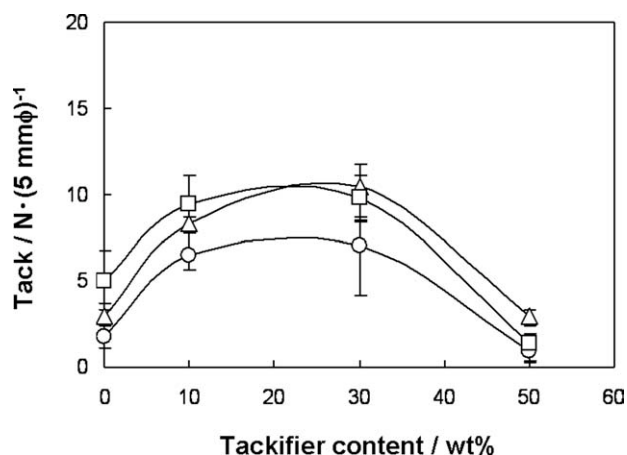


Figure 8 Effect of tackifier content on the tack of tackifier RP-added SIS/SI blends of SI-0 (○), SI-50 (△), and SI-70 (□). Tack was measured by a probe tack test with the contact time of 1 s.

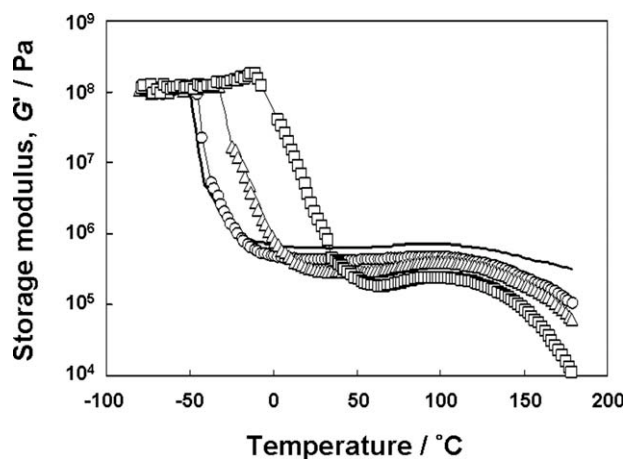


Figure 9 Storage modulus (G') of tackifier HC-added SIS (SI-0) with tackifier contents of 0 (—), 10 (○), 30 (△), and 50 wt % (□). G' was measured by a dynamic mechanical analysis at a frequency of 10 Hz.

region appears in the polymer which possesses rubber elasticity because the PS domains in SIS act as pseudo-crosslinked point.

Figure 10 shows the temperature dependence of the loss tangent ($\tan \delta$) for SIS (SI-0) and tackifier HC-added SIS. The sharp peaks that are based on the T_g of PI moved to the higher temperature with an increase of the tackifier. The shoulder peak adjacent to the $\tan \delta$ peak appeared and it was more significant in the tackifier content of 50 wt % (↓ mark). This shoulder peak should be based on the PI molecules in which mobility was restricted by the tackifier distributed in the PI matrix. That is, this seemed to be caused by the formation of nanometer-sized agglomerates of tackifier as described in our previous studies.^{10–12}

Figure 11 shows the temperature dependence of the G' for SIS (SI-0) and tackifier RP-added SIS. The

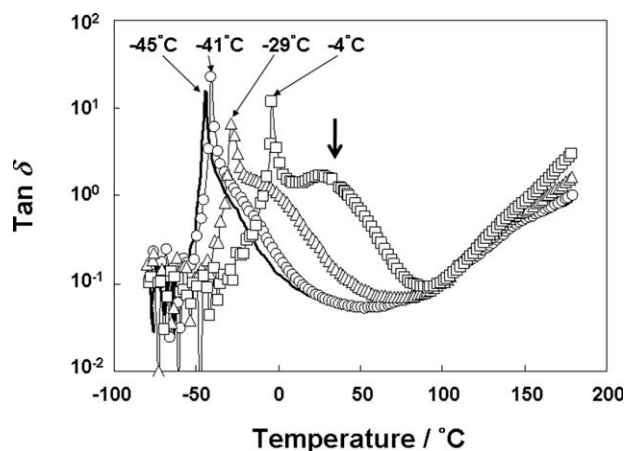


Figure 10 Loss tangent ($\tan \delta$) of tackifier HC-added SIS (SI-0) with tackifier contents of 0 (—), 10 (○), 30 (△), and 50 wt % (□). $\tan \delta$ was measured by a dynamic mechanical analysis at a frequency of 10 Hz.

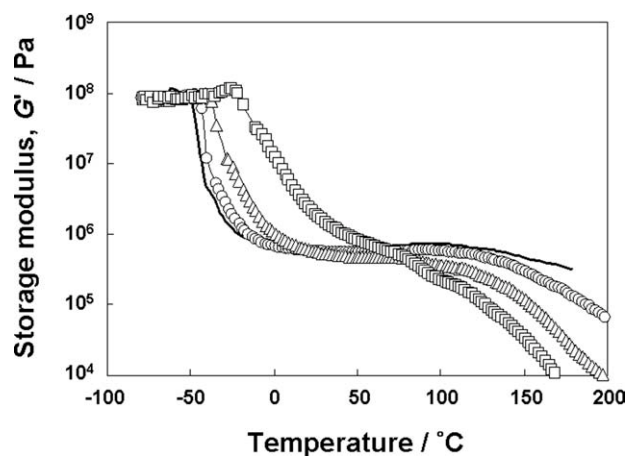


Figure 11 Storage modulus (G') of tackifier RP-added SIS (SI-0) with tackifier contents of 0 (—), 10 (○), 30 (△), and 50 wt % (□). G' was measured by a dynamic mechanical analysis at a frequency of 10 Hz.

G' decreased drastically at about -50°C for SIS. This temperature is based on the T_g of the PI matrix. The drastically decrease of G' , namely T_g increased with an increase in the tackifier content, but the degree of increase was smaller than that observed the tackifier HC-added system shown in Figure 9. The G' of the tackifier-added SIS was lower than that for pure SIS, however the clear G' plateau region disappeared with an increase in the tackifier content.

Figure 12 shows the temperature dependence of the $\tan \delta$ for SIS (SI-0) and tackifier RP-added SIS. The sharp peaks that are based on the T_g of PI moved to the higher temperature with an increase of the tackifier, however the degree of increase was smaller than that for the tackifier HC-added SIS as shown in Figure 10. The shoulder peak adjacent to the $\tan \delta$ peak as observed in tackifier HC-added SIS was far smaller. This result indicates that the

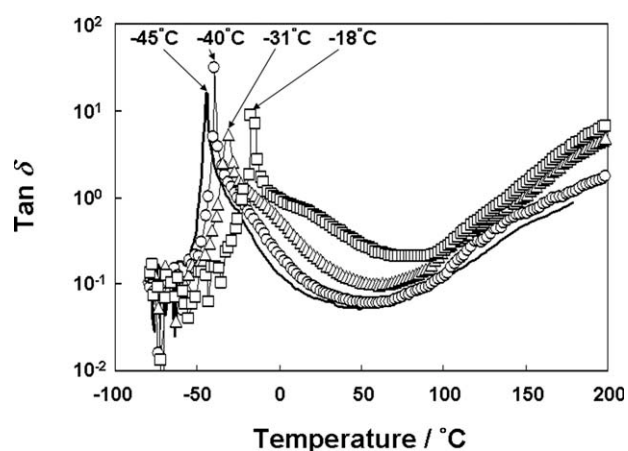


Figure 12 Loss tangent ($\tan \delta$) of tackifier RP-added SIS (SI-0) with tackifier contents of 0 (—), 10 (○), 30 (△), and 50 wt % (□). $\tan \delta$ was measured by a dynamic mechanical analysis at a frequency of 10 Hz.

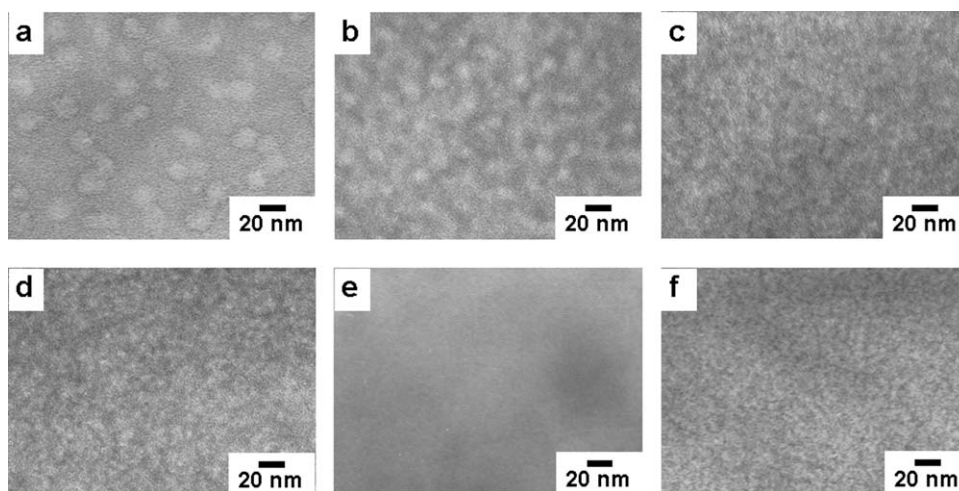


Figure 13 TEM images of tackifier HC-added SIS (SI-0, a–d) and tackifier HC-added PI (e,f) with tackifier contents of 0 (a,e), 10 (b), 30 (c), and 50 wt % (d,f).

agglomerates of tackifier were hardly formed in the tackifier RP-added SIS.

In a dynamic mechanical analysis, to prevent the slipping between sample and plate of shear mode test, the shallow slits were introduced on the plate. It was preliminarily confirmed that the introduced slits never affects on the measured value. Sufficient adhesion between sample and plate before and after measurement was confirmed. However, only slight degree of slipping was observed as shown in Figure 10.

Next, the phase structure was observed by TEM. In our previous study,¹⁴ the phase structure of SIS/SI blend was observed using an atomic force microscopy and a SAXS. All blends formed the sea-island structure in which spherical polystyrene domains were dispersed in PI matrix and mean domain size was ~ 20 nm. The influence of the SI content on the domain size was small degree.

Figure 13 shows the TEM micrographs of the tackifier HC-added SIS (SI-0) and PI. The tackifier contents were 10, 30, and 50 wt %. In this study, the TEM sample was stained by OsO_4 vapor, so the dark part is the PI matrix. The spherical PS domains whose mean size was about 20 nm were clearly observed in the PI matrix in the no-tackifier (a) and the tackifier HC-added SIS (b–d). Homogeneous phase was observed in the PI without tackifier (e), whereas it became heterogeneous in the tackifier HC-added PI (f). The PI matrix in the tackifier HC-added SIS (b–d) also became heterogeneous and it became more significant with an increase of tackifier content. We estimated these heterogeneous PI phase is caused by the formation of the agglomerates of tackifier previously.^{10–12}

Figure 14 shows the TEM micrographs of the tackifier RP-added SIS (SI-0) and PI. The tackifier contents were 10, 30, and 50 wt %. The PS domain became unclear with an increase in the tackifier con-

tent (a–c). The PI with tackifier was also homogeneous (d) and the heterogeneous PI phase as observed in the tackifier HC-added SIS [Fig. 13(f)] was never observed. This result indicates that the agglomerates of tackifier observed in the tackifier HC-added SIS never formed in the tackifier RP-added SIS.

To confirm the nanometer-scale agglomerates in the PI/tackifier blend, we conducted SAXS measurements. The SAXS profiles of the tackifier HC-added and the tackifier RP-added PI is shown in Figure 15. The first order peak was clearly observed (\downarrow mark) in the tackifier HC-added PI. This indicates that comparatively regular structure of the agglomerates of tackifier was formed. From the peak position, the distance between the nearest neighbors of domains (agglomerates) is about 15 nm. On the other hand, no peak was observed in the tackifier RP-added PI. This indicates that there was no regular structure of

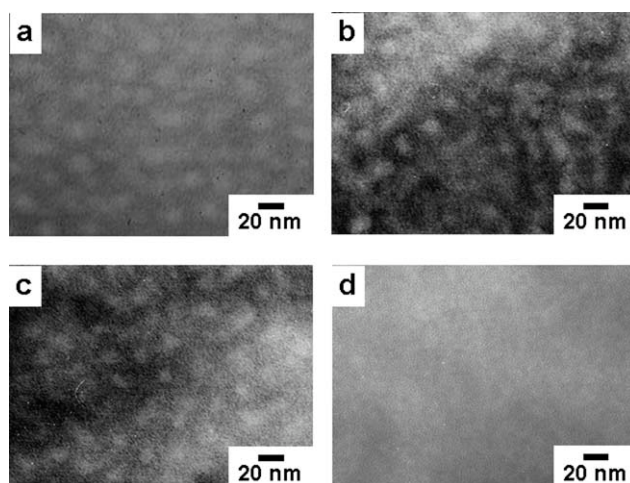


Figure 14 TEM images of tackifier RP-added SIS (SI-0, a–c) and tackifier RP-added PI (d) with tackifier contents of 10 (a), 30 (b), and 50 wt % (c,d).

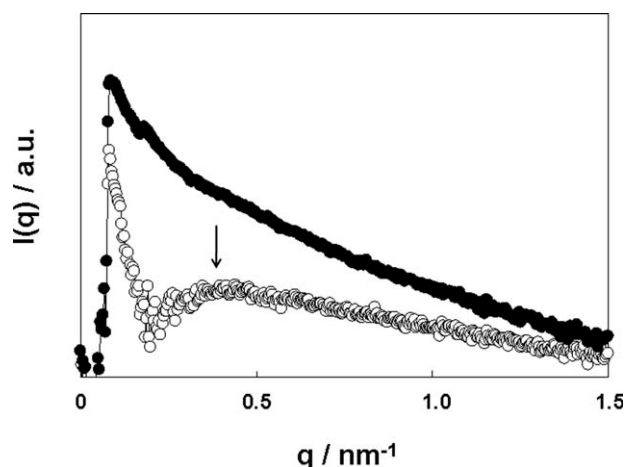


Figure 15 Small angle X-ray scattering profile of tackifier HC-added PI (○) and tackifier RP-added PI (●).

the agglomerates of tackifier. For the SAXS profile of the tackifier RP-added PI sample, it was possible to apply the Debye-Bueche analysis²¹ and found that the average chord length of the phase-separated structure was only several nanometers, suggesting quite fine structures which can be never detected by the dynamic viscoelastic properties or TEM observation as described above in this article. Namely, the tackifier RP-added PI sample shows better compatibility when compared with the case of the tackifier HC-added PI sample, showing the formation of nanometer-sized agglomerates of tackifier.

In our previous study,¹² the μm -sized spherical silica particles-added polyacrylic block copolymer was prepared and compared with the tackifier-added one. The silica particles increased G' above T_g , however the increase of T_g at lower temperature and the decrease of G' at higher temperature were never observed. The influences of agglomerates size of tackifier and silica particle size on the increase of T_g will be discussed in our future study.

From the results of dynamic mechanical analysis (Figs. 9–12) and the TEM observation (Figs. 13 and 14), it was indicated that the agglomerates of tackifier increase T_g of PI phase more effectively than the dissolved tackifier. To confirm this point, the relation between the peak temperature of $\tan \delta$ shown in Figures 10 and 12 and the tackifier content was plotted in Figure 16. The measured values were compared with those predicted by the Fox equation.²² The T_g values of tackifiers HC and RP measured by a thermo-mechanical analysis were reported to be about 75 and 80°C, respectively.¹⁸ The tackifier-HC added system showed higher T_g and closed to the predicted value at the higher tackifier content.

From the results above, it was found that the tackifier acts as follows to develop adhesion strength. In the tackifier HC-added SIS, the tackifier molecules are

well dissolved in the PI matrix and then the amount of dissolved tackifier increased with the content. The dissolved tackifier in the PI matrix develops the molecular mobility of PI, i.e., the interfacial adhesion, whereas decreases the cohesive strength. The agglomerates of tackifier began to form in the PI matrix, and the amount increased with the content as reported previously.^{10–12} The peel strength developed significantly above 40 wt % of the tackifier content (Fig. 3). The development effect of cohesive strength by the formation of agglomerates became significant above 40 wt % of tackifier content.

In the tackifier RP-added SIS, the tackifier distributed in the PS domains swelled the PS domains and increased the molecular mobility of PI. And then the adhesion of adherend interface increased although at lower tackifier content. On the other hand, the tackifier distributed in the PI phase is smaller than that in the tackifier HC-added system. Therefore, they never form the agglomerates and never improve the cohesive strength although at higher tackifier content.

As mentioned above, it was found that the compatibility of tackifier with the base polymer affects strongly both on the morphology and the adhesion properties.

CONCLUSION

The effects of both SIS/SI blend ratio and compatibility of tackifier with SIS/SI blend on adhesion properties were investigated. The following results were obtained.

- i. In the case of tackifier HC (PI compatible and PS incompatible), the peel strength increased gradually with the tackifier content, and the degree of increase became more significant

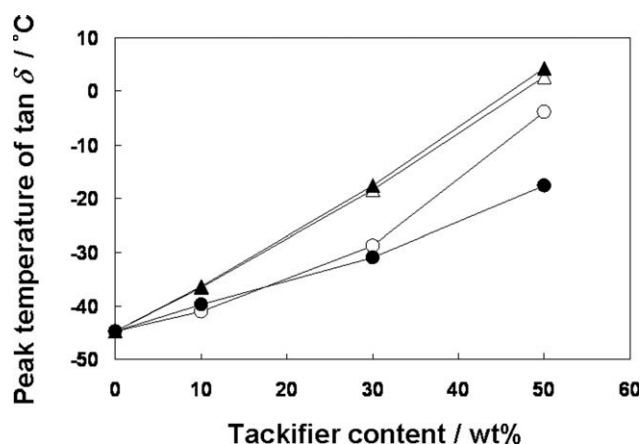


Figure 16 Peak temperature of $\tan \delta$ measured for tackifier HC-(○) and RP-added (●) SIS (SI-0) by a dynamic mechanical analysis and that calculated by the rule of mixture (Fox equation) for tackifier HC-(△) and RP-added (▲) SIS.

above 40 wt %. In the case of tackifier RP (both PI and PS compatible), the peel strength increased drastically at the lower tackifier content, however, the significant increase at the higher tackifier content was never observed.

- ii. In the both tackifier-added systems, the higher peel strength was obtained for the SI-50 and SI-70.
- iii. In the case of tackifier HC, it was found that the nanometer-sized agglomerates of tackifier in the PI phase were formed and the distance between the nearest neighbors of agglomerates was about 15 nm from SAXS measurement.
- iv. The agglomerates of tackifier were never confirmed in the case of tackifier RP.

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