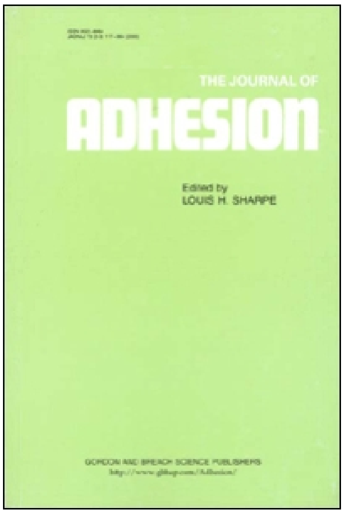

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Surface Property and Compatibility of Poly(styrene-isoprene-styrene) Triblock Copolymer/Tackifier Blend System

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The frictional forces between pressure sensitive adhesives (PSAs) and a probe tip were measured with a scanning probe microscopy (SPM). A peak appeared in the scanning rate-frictional force curve shifted to a lower scanning rate with decreasing temperature. In the case of the miscible system of isoprene matrix of SIS base polymer, the tendency of a peak to shift to a lower scanning rate was observed with increasing tackifier content; however, in the case of the immiscible system of styrene domain of SIS base polymer, no remarkable shift was observed. The frictional force is influenced by viscoelastic properties of the PSA which systematically changed with miscibility.

In this study, it is aimed to clarify the correlation between the observation of phase structure and the behavior of surface rheology by using two kinds of tackifiers that have different miscibility with the polyisoprene phase or the polystyrene phase of SIS triblock copolymer.

Keywords: Atomic force microscopy; Frictional force; Interfaces; Master curve; Pressure sensitive adhesive; Rheology

1. INTRODUCTION

We have been studying pressure sensitive adhesives (PSAs) from the standpoint of viscoelastic properties and phase structures of polymers [1–7]. It was found that the PSA's performance, such as peel strength, tack, and shear creep resistance were greatly dependent on the viscoelastic properties of the bulk of PSAs. For example, Kim *et al.*

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investigated the relation between the phase structure and the probe tack in the acrylic copolymer/tackifier resin blend system [4]. They made master curves of probe tack in terms of pull-off rate. The master curve of the miscible blends shifted to a lower rate when there was an increase in tackifier content. In the case of the immiscible blends, no shift was observed in the master curve when there was a change in tackifier content; however, the probe tack decreased with increased tackifier content.

On the other hand, on the polymer surface, it was found that the surface Tg of the monodisperse polystyrene is different from the bulk Tg [8]. Furthermore, it was reported that the surface structure of the PSAs, including tackifier resin, was different from that of the bulk; that is, the tackifier migrated in the PSA film in order to minimize the magnitude of interfacial free energy between the PSA and the adherend [9,10]. Thus, the fundamental understanding of the surface properties of PSAs is also considered important for performance of PSAs.

Recently, scanning probe microscopy (SPM) has been used to analyze adhesive surfaces in nano-scale [11–13]. Frictional force microscopy (FFM), a part of the SPM, enables us to measure the frictional force between a sample surface and a probe tip by detecting the changing angle of the twisting of the cantilever as it moved from left to right and from right to left.

Sasaki *et al.* investigated the relationship between the 180° peel strength and the phase structure of the tackifier where the SIS/tackifier system was used as a model pressure sensitive adhesive. In this study, it refers to the "phase structure model" used with this paper [14].

The objective of this study is to elucidate the relationship between the frictional behavior and the rheological properties on the surface of the poly(styrene-isoprene-styrene) triblock copolymer (SIS) including a copolymerized petroleum tackifier resin or aromatic tackifier resin. The frictional forces between the PSAs and the probe tip are measured with the FFM at various scanning rates and temperatures in nano-scale. Further, it is discussed whether the time-temperature superposition principle is established in the frictional force on the surface of PSAs. Then, the relationship between the scanning rate dependence of frictional force and the miscibility between the SIS base polymer and the tackifier resins is discussed.

2. EXPERIMENTAL

2.1. Materials

Commercially available SIS (PS segment content: 18 wt%, Vector 4111, ExxonMobil, Yokohama, Japan) was used as a base polymer for the model pressure sensitive adhesive. This SIS consists of 100% triblock component. The Tackifier A used was are copolymerized petroleum resin ($C_5 + C_9$ series, melting point: 86°C, M_W: 2940, petrotack-90HM, TOSOH, Yamaguchi, Japan), which has a good miscibility with polyisoprene (PI). The Tackifier B used was an aromatic resin (C9 series, melting point: 118°C, MW: 1560, petcal-120, TOSOH), which has a good compatibility with polystyrene.

2.2. Preparation of Pressure Sensitive Adhesives (PSAs) Films

The SIS base polymer and Tackifiers A and B were blended in a variety of blend ratios: 70/30, 50/50, and 30/70, respectively, in 10% toluene solution. The thin films were prepared by a spin coating technique onto a PET substrate. The PSA films were kept at 110°C for 24 h in vacuum to remove the solvent from the sample. The adhesive layer was about 30 μm in thickness. The mixture ratio of the PSA films is shown in Table 1.

2.3. DSC Measurements

The Tgs of the PSAs were determined by a Perkin Elmer DSC-7 differential scanning calorimeter equipped with a thermal analysis data station and a helium purge (Perkin-Elmer, Yokohama, Japan). The samples were heated from −200 to 180°C at a heating rate of 40°C/min. Tgs were determined with a second scan.

2.4. Phase Diagrams

PSA blends were coated onto glass in 30 μm thickness with a glass rod. After drying at room temperature for 24 h, they were further dried

TABLE 1 Mixture Ratios of PSA Films

	SIS base polymer	Tackifier resin	
Sample code	SIS	A	B
1	70	30	
2	50	50	
3	30	70	
4	70		30
5	50		50
6	30		70

at 80°C for 24 h, followed by drying in a vacuum oven at 110°C for another 24 h. Then they were kept at 25°C for 48 h, and visually observed to see whether they became transparent or opaque at this temperature. The same procedures were repeated by changing the temperature in a stepwise manner from 25 to 180°C in an air circulation oven.

2.5. SPM Measurements

Frictional forces of the PSA's surface were determined by the SPM (SII3800N, SPA300-HV, Seiko Instruments Inc., Tokyo, Japan) equipped with a liquid nitrogen cooling system. Frictional force measurements were performed in frictional curve measurement mode under a normal force of 0.1 nN, using a Si_3N_4 tip mounted on a cantilever with a bending spring constant of 0.93 nN. The scanning rate was calculated by following equation;

$$v = 2df,$$

where v is the scanning rate, d is the scanning distance, and f is the frequency.

Frictional force measurements using the AFM were carried out on spin coated films. The normal applied force was calculated from force-distance curves by the product of normal deflection of the cantilever (d) and spring constant (k) of the cantilever. Deflection of the cantilever is due to intermolecular force between the tip and surface, which may be attractive and/or repulsive in nature. The cantilever experiences a torque imposed by the tip, which is recorded as a voltage (mV) signal. Figure 1 shows trace and retrace images obtained in FFM. The frictional force for a given normal load is calculated as the mean value of separation distance between the trace and retrace signals.

2.6. The Scanning Rate-Frictional Force Curve

In this study, the scanning rate-friction force curve was obtained by scanning the surface of the adhesive from −60 to −100°C using the AFM system. This temperature range is low enough compared with the Tg of samples shown in Figs. 2 and 3. The surface of the adhesive at a temperature of higher than Tg cannot be scanned, because the AFM cantilevers stick to the surface of the adhesive. Therefore, the scanning was made after the surface of the adhesive was cooled enough. A horizontal axis of the scanning rate-frictional force curve was decided from the expression explained in 2.5.

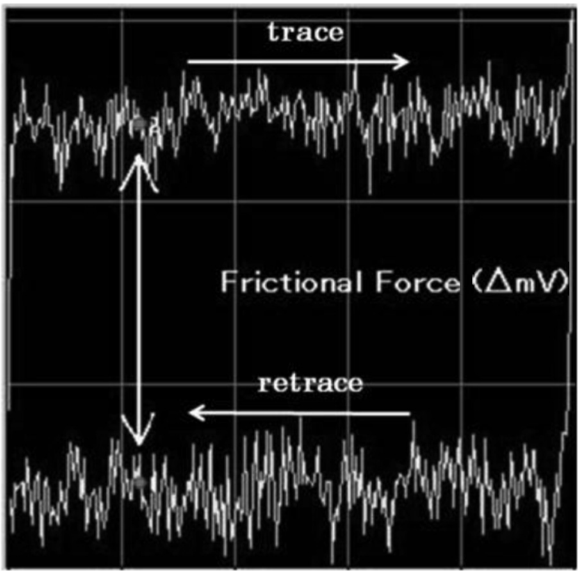


FIGURE 1 The trace and retrace image obtained in FFM.

The scanning distance was fixed to 1000 nm and the scanning rates were changed from 0.1 to 10 Hz for Samples 1–3. Also, the scanning distance was fixed at 100 nm for Samples 4–6, because a long distance could not be scanned as the polystyrene exists in the surface when

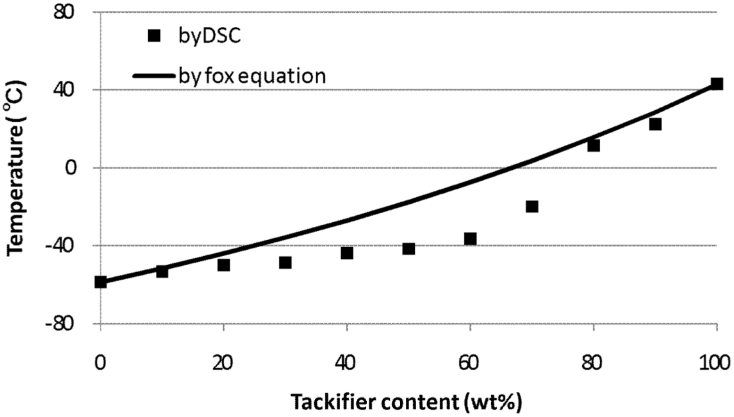


FIGURE 2 Tg-composition curve of the polyisoprene domain of the SIS base polymer and Tackifier A which is compatible with the polyisoprene phase.

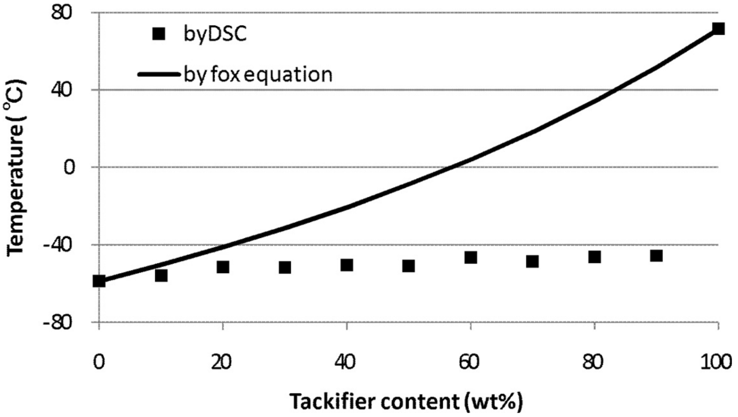


FIGURE 3 Tg-composition curve of the polyisoprene domain of the SIS base polymer and Tackifier B which is compatible with the polystyrene phase.

scanning the PI phase. The magnitude of the frictional force of the vertical axis is expressed by the signal (ΔV) obtained from AFM.

2.7. Master Curve

The Arrhenius equation can be used for many thermally induced processes/reactions. The master curve is made by using the Arrhenius equation and the time-temperature superposition principle.

The Arrhenius equation given in the form:

$$\mathrm{k} = \mathrm{A}\exp\left(-\frac{\mathrm{Ea}}{\mathrm{RT}}\right) \tag{1}$$

can be written equivalently as:

$$\ln(k) = \ln(A) - \frac{Ea}{R}\left(\frac{1}{T}\right), \tag{2}$$

where k is the rate constant, A is the pre-exponential factor Ea is the activation energy (J/mol), R is the gas constant (8.314 J/Kmol), and T is the absolute temperature (k).

When plotted in the manner described above, the value of the y-intercept will correspond to ln(A), and the gradient of the line will be equal to −Ea/R.

The expression −Ea/R represents the fraction of the molecules present in a gas which have energies equal to or in excess of the activation energy at a particular temperature.

So, if a plot of the ln(k) of the rate constant *vs.* the inverse absolute temperature is a straight line, the Arrhenius equation is said to be valid and activation energy is then determined from the slope of the plot using Eq. (1).

According to the principles of the time-temperature superposition method, both time and temperature are equivalent, *i.e.*, the material parameter values obtained for short times at a given temperature are identical with those measured for longer times at a lower temperature, except that the curves are shifted on a logarithmic time axis.

The curves of the measured material parameter *vs.* logarithmic loading time at different temperatures can be superimposed by proper scale changes on the time axis. The shift distance along the logarithmic time axis is called the time-temperature shift factor, a_T, and is given by

$$a_T = t_{ref}/t_T, \tag{3}$$

where t_{ref} is the test time at a reference temperature, and t_T is the time required to give the same response at the test temperature T. The value of the shift factor, a_T, depends not only on the reference temperature but also on the material properties.

For every reference temperature chosen, a fully superimposed curve can be formed, which is called the master curve. If a smooth master curve can be produced, extrapolations to temperatures lower than the experimental temperatures become possible.

The shift factors of a master curve have some relationship with the temperature. Generally, the Arrhenius equation is acknowledged with a reasonably good accuracy to determine the shift factor.

Combining Eqs. (2) and (3) gives

$$\log a_T = \frac{Ea}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right), \tag{4}$$

where both T and T_{ref} are absolute temperatures.

If Eq. (4) can be shown to be valid, *i.e.*, a plot of the logarithm of the empirically determined shift factor values *vs.* the reciprocal absolute temperature produces a straight line, this then will allow us to calculate a shift factor for any desired temperature [15].

3. RESULTS AND DISCUSSION

3.1. Miscibility of PSAs

Miscibility between the SIS base polymer and tackifier resins was determined by DSC measurements. In the DSC measurement, the phase structures of the blends were assessed by the number of Tgs observed in the thermograms and by comparisons of the Tgs obtained by DSC and those calculated based on the Fox equation [16].

Figure 2 shows the Tg-composition curve of the polyisoprene domain of the SIS base polymer/Tackifier A. Figure 3 shows the Tg-composition curve of the polystyrene domain of SIS base polymer/Tackifier B.

In the case of the polyisoprene domain, single Tgs are detected for each blend and they locate near the Tgs calculated based on the Fox equation. Existence of the single Tgs near the Tgs calculated based on the Fox equation are evidence that the polyisoprene of the SIS base polymer is miscible with Tackifier A. On the other hand, the Tg of the polyisoprene phase of the SIS base polymer is independent of the content of Tackifier B which is compatible with polystyrene. This result indirectly proves that Tackifier B is incompatible with polyisoprene.

Phase diagrams of the polyisoprene of SIS base polymer/Tackifier A are shown in Fig. 4. The blend system shows a phase diagram of a typical lower critical solution temperature (LCST) type, and the blends are miscible at any blend ratio between 40 and 100°C.

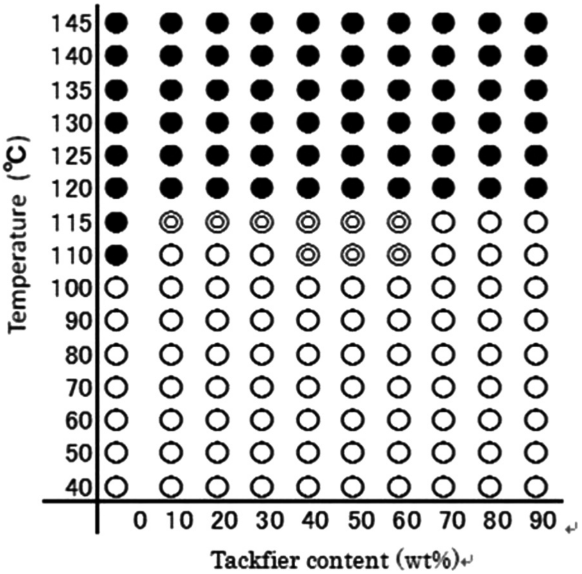


FIGURE 4 Phase diagram of SIS base polymer/tackifier resin. ○: miscible, ◎: intermediate, ●: immiscible.

3.2. Scanning Rate Dependence of Frictional Force

The frictional forces of the blends were measured as the changing angle of the twisting of the cantilever as it moved from left to right and from right to left, at various scanning rates, at each temperature. The frictional forces were expressed as a scanning rate-frictional force curve. In this study, we used a new cantilever for every experiment at each testing temperature to avoid contamination of the polymer. However, the value of the frictional force may vary using different cantilevers, which is a problem. In this study, the value of the frictional force between samples is arranged by using the cantilever that specializes in the frictional force.

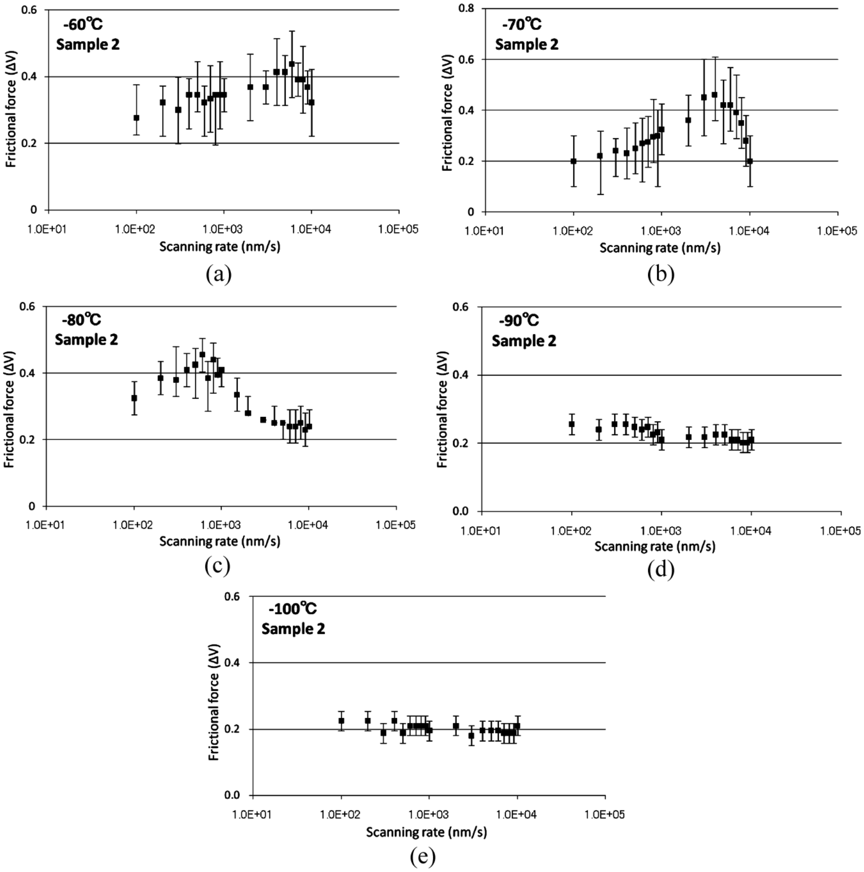
Figure 5 shows the scanning rate-frictional force at various temperatures for Sample 2. A peak appears in the scanning rate-frictional force curve at −60°C. The frictional force decreases with increasing scanning rate at −70°C. From the comparison of these curves, we have found that the frictional behavior at the high-scanning rate region at −60°C corresponds to the behavior at −70°C. This suggests that the curve at −70°C is the curve at −60°C shifted to the lower scanning rate. Even other temperatures are similar. The peak shifts to that of a lower scanning rate with decreasing temperature in all the samples used in this study.

These tendencies indicate that master curves for the scanning rate-frictional force could be obtained. It seems reasonable to consider that the time-temperature superposition, which is established at dynamic mechanical property of amorphous polymer, is also applied to the frictional behavior at the surface of the adhesive. This similarity shows that the frictional force changes in response to the changing rheological behavior of the polymer. In addition, frictional behavior on the surface of the adhesive has a tendency similar to the performance of the bulk of PSAs [4].

On the other hand, with the polystyrene domain of the SIS base polymer/Tackifier B system, no remarkable shift was observed by a change in tackifier contents. Figure 6 shows the scanning rate-frictional force curve of Samples 4–6 at −70°C. This scanning rate-frictional force curve was obtained from the polyisoprene domain. The peak that appeared at each tackifier content hardly shifted, and we concluded that the Tackifier B and the polyisoprene of SIS were immiscible.

3.3. Master Curve

Figure 7 shows the master curve of Sample 2. The scanning rate-frictional force curves from −60 to −100°C have been utilized, and the master curve can be drawn reduced to −80°C.



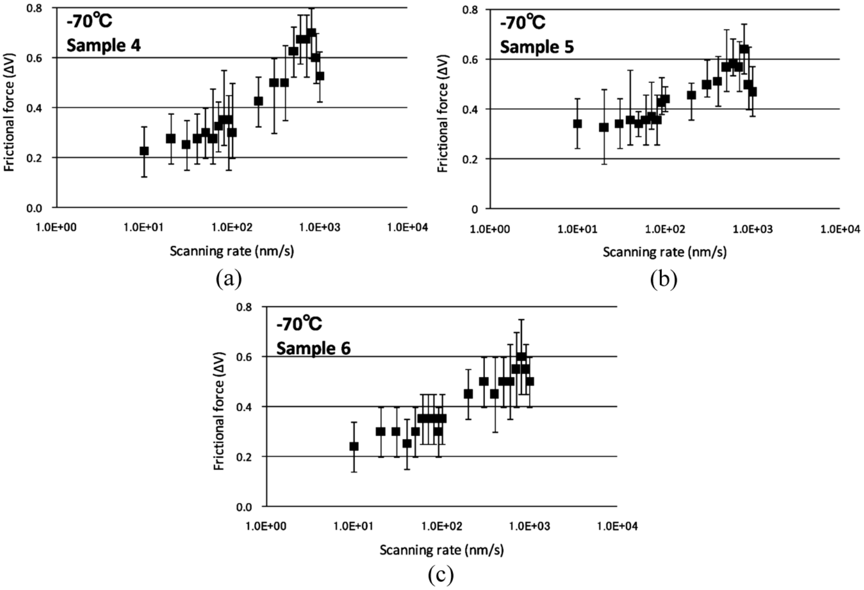
(a) (b) (c) (d) (e)

FIGURE 5 Scanning rate-frictional force at various temperatures for Sample 2.

For this plot it was assumed that the shift factor took the Arrhenius form.

Figure 8 shows the scanning rate of the peak at −60, −70, and −80°C of Fig. 5 *vs.* the reciprocal of each temperature. Because the value was unchanged by the change in the cantilever, the master curve could be drawn. The activation energy can be calculated from the indication of the straight line from Fig. 8 and Eq. (3). The apparent activation energy of Sample 2 was 39.55 KJ/mol.

In the same way, when the activation energies of Samples 1 and 3 were calculated, they were 39.68 and 25.01 KJ/mol, respectively.



(a) (b) (c)

FIGURE 6 The scanning rate-frictional force curve of Samples 4–6 at −70°C.

To evaluate the validity of the master curve, Fig. 9 shows the plot of the shift factor of Fig. 7. The plot of log a_T *vs.* reciprocal temperature showed a straight line.

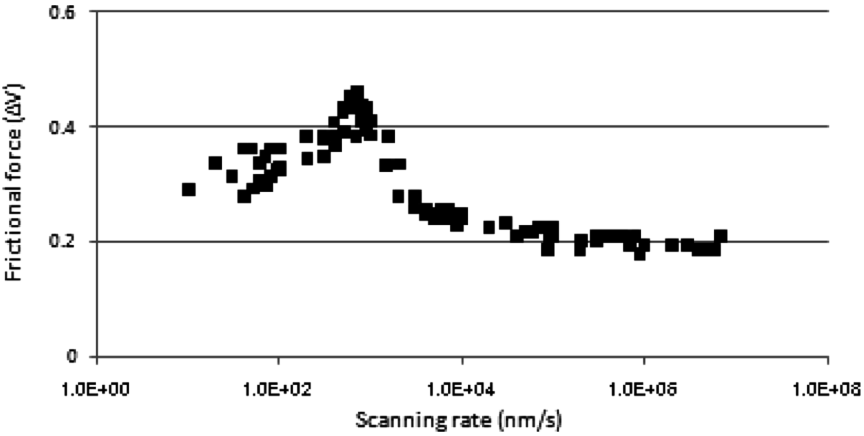


FIGURE 7 Master curve of Sample 2 from −60 to −100°C.

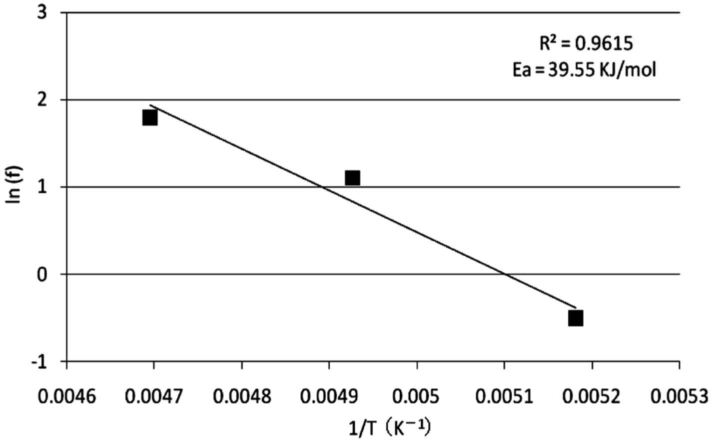


FIGURE 8 Arrhenius plot of Sample 2.

3.4. Relationship Between the Frictional Behavior with Changing Scanning Rates and Tackifier Contents

The best way to see the relationship between the frictional behavior with changing scanning rates and tackifier contents is to compare master curves of the scanning rate-frictional force curves for each tackifier content.

Figure 10 shows the master curve from −60 to −100°C of Samples 1–3. However, the value of frictional force was arbitrarily moved in the

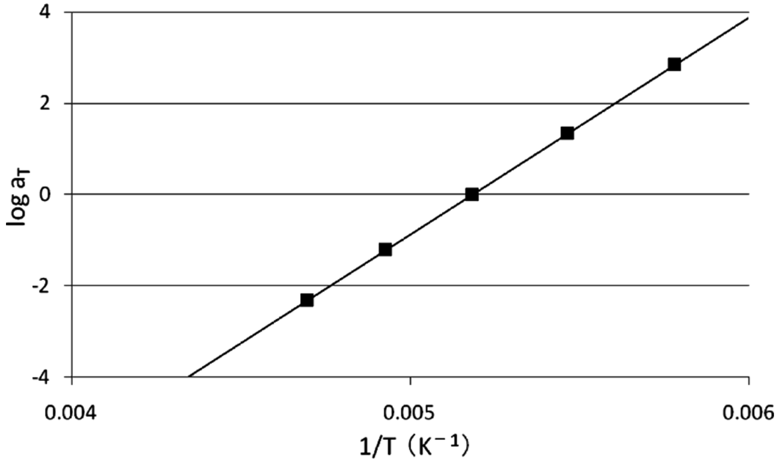


FIGURE 9 Plot of the shift factor $\log a_T$ of Figure 7.

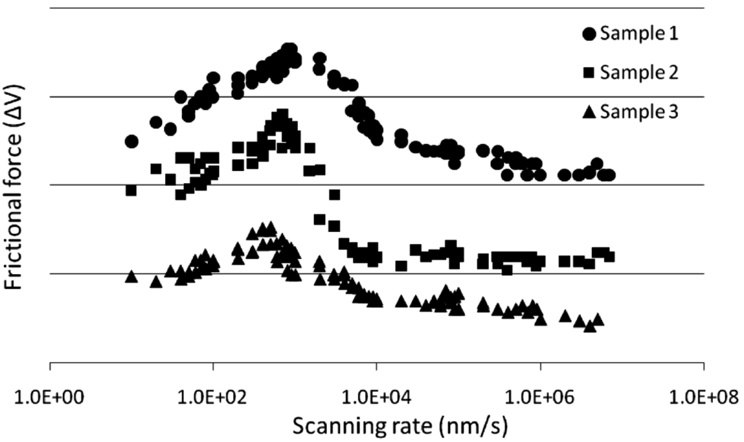


FIGURE 10 Master curve from −60 to −100°C of Samples 1–3.

vertical direction for better viewing. The results for SIS/tackifier system of Samples 1–3 are shown by the peak shifts to a lower scanning rate as the tackifier content increases. These tendencies correspond to the behavior of the Tgs shown in Fig. 2, where the Tg of the miscible system increases with increasing tackifier content.

Therefore, we can see that the frictional force on the PSA surface is dominated by the viscoelastic properties of the PSA, where frictional behavior on the adhesive surface has a tendency similar to that of the bulk of PSAs [4].

If this method can be applied to the surface of all materials, the frictional force might be quantifiable.

3.5. Relationship Between the Scanning Rate-Frictional Force Curve and the Failure Mode

Surface observations after the measurements of frictional forces were carried out to determine the failure mode caused by scanning the surface of the PSA with the probe tip. Figure 11 shows the surface topographic image and the relationship between the failure mode and the master curve for Sample 2 after the measurements of frictional force, respectively.

In the surface topographic image, the hole in the center is an impact scar created when the probe approached the surface. In the region [A] where the rate is high, a scanning trace is not found on the surface. In the region [B] where is the rate is low, it is very clear that scanning traces are found on the surface.

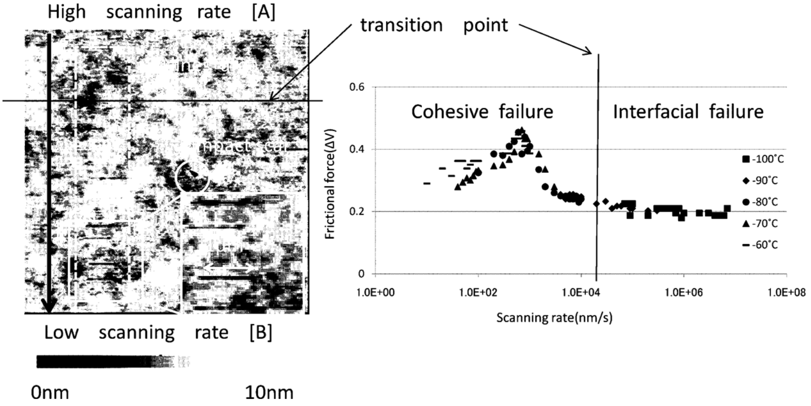


FIGURE 11 The surface topographic image after the measurement of frictional force for Sample 2 at −80°C and the master curve for Sample 2.

The scanning distance is 1000 nm. There are 20 scanning traces between the region [A] and the region [B]. This forms one scanning rate-frictional force curve. The shape image of Sample 2 at −80°C is shown in Fig. 11. Figure 11 shows five scanning traces of low scanning rate in the [B] area where scanning trace remains have been expanded. Similar to macro adhesive failures, which include interfacial failure, cohesive failure, and stick-slip even in nano failure on the surface, interfacial failure occurs in the higher scanning rate region [A] and cohesive failure in the lower scanning rate region [B]. The depth of this scanning trace is from 10 to 20 nm. This is irrelevant to the thickness of the film which is about 30 μ.

From the master curve shown in Fig. 11, it was found that the interfacial failures are observed at high scanning rate in the scanning rate-frictional force curve and the cohesive failures are observed at low scanning rate. Furthermore, the transition point from interfacial failure to cohesive failure is located in a little higher rate region of the peak of the frictional force. We do not know why the type of failure changes in the peak of the master curve, which is common in macro adhesive failure. In addition, around the transition point, stick-slip was observed.

4. CONCLUSION

The PSA's surface properties and phase compatibility were investigated in the SIS/tackifier system used as a model pressure sensitive adhesive. The tackifier having a good compatibility with PI was used. The following results were obtained:

1. The peak appeared in the scanning rate-frictional force curve shifted to a lower scanning rate with decreasing temperature. It can be said that the frictional force reflects rheological behavior of the PSA surface.
2. In the case of the polyisoprene and Tackifier A miscible system, the tendency of a peak to shift to a lower scanning rate was observed in the scanning rate-frictional force curve with increasing tackifier content. However, with the polyisoprene and Tackifier B immiscible system, the peak of the scanning rate-frictional force curve was not shifted. As a result, probably the Tackifier B and polystyrene of SIS were a miscible blend. We concluded that the frictional force is influenced by the viscoelastic properties of the PSA.
3. The master curve can be drawn from the scanning rate-frictional force curve by changing the temperature and velocity. As a result, it was indicated that the time-temperature superposition principle of the viscoelastic behavior of a general polymeric material can be applied to the surface of the adhesives.
4. The high scanning rate resulted in interfacial failure, while the low scanning rate resulted in cohesive failure. The transition point from interfacial failure to cohesive failure is located in a little higher rate region of the peak of the friction force.

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