

# Shear Creep Resistance of Styrene–Isoprene–Styrene (SIS)-Based Hot-Melt Pressure-Sensitive Adhesives

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**ABSTRACT:** The effects of the properties of substrates and tackifier on the shear creep of SIS-based HMPSAs were investigated. The holding power ( $t_b$ ) and shear adhesion failure temperature (SAFT) were measured. The relationship between the complex viscosity and the holding power was examined. The holding power and SAFT values of the triblock SIS blends were higher than those of the diblock-containing SIS blends, perhaps because blends using triblock SIS have higher crossover temperature and complex viscos-

ity than those using diblock-containing SIS. Higher levels of aromatic resin-modified aliphatic tackifier and rosin ester were found to decrease the holding power of the HMPSAs. This maybe due to the fact that rosin ester and aromatic-modified aliphatic resin are compatible with both the ends and midblocks of SIS. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 825–831, 2006

**Key words:** adhesives; shear; creep; viscosity

## INTRODUCTION

The shear resistance of PSAs can be measured either statically or dynamically. Currently, static shear test methods use a constant load and require longer test times than do dynamic shear test methods. These tests require a very long measurement time. Better results are obtained with the hot shear test, where the cohesion of the sample is measured at an elevated temperature. The dynamic shear test measures the cohesion of the sample in a tensile tester under increasing load (force). If a hot shear test is carried out in such a way that the test temperature is gradually raised, and if the temperature at which the bond fails is taken as a characteristic value, specialists refer to this as the dead load hot strength test or shear adhesion failure temperature (SAFT). There are other shear test methods that measure neither the time until debonding nor the temperature of the debonding, but rather the deformation of the sheared sample (i.e., the slip of the sample is measured after a given time).<sup>1–3</sup>

To understand the reason for a failure caused by creep, it is important to identify whether it is a cohesive failure (nearly the same amount of adhesive on both sides) or an adhesive failure (residue on one side only). In the first case, the adhesive is too soft or

undercured, whereas, in the second case, it may be too hard or overcured. Furthermore, there may be a weak boundary layer on one surface. Sometimes structured patterns of the adhesive are found on the surface. This is an indication of a fracture resulting from stress concentrations.<sup>4,5</sup>

Many publications have shown the relation between the key properties of PSAs, such as peel resistance and tack, and the viscoelastic characteristics measured by dynamic mechanical analysis (DMA). The events responsible for the creep of PSAs occur at a much lower frequency range. A difference also exists between the creep failure and creep damage of a joint. Creep failure is the complete or partial separation of a bonded structure. Creep damage can occur when the deformations due to creep affect the use of the bonded object.<sup>1,5,6,7</sup>

In this study, we investigated the effects of the properties of the substrates on the shear creep of SIS-based HMPSAs. The holding power ( $t_b$ ) and shear adhesion failure temperature (SAFT) were measured. The relationship between the complex viscosity and the holding power was also examined.

## EXPERIMENTAL

### Materials

The SIS (styrene–isoprene–styrene) materials selected for this study comprised one diblock-containing SIS and one triblock SIS. The diblock-containing SIS was Kraton D1107 (diblock contents 15 wt. %, styrene 15

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TABLE I  
Polymer Characterization Data

Trade name	Types	Styrene content (wt. %) <sup>a</sup>	Diblock content (wt. %) <sup>a</sup>	$M_w^b$	$M_n^b$	$M_w/M_n^b$	$T_g$ (°C)	Manufacturer
Kraton D1107	Linear SIS	15	15	129,000	106,000	1.21	-61.0	Kraton Polymer
Vector 4111	Linear SIS	18	<1	114,000	108,000	1.06	-61.0	ExxonMobil Chemical Co.

<sup>a</sup> Data supplied by the manufacturer.

<sup>b</sup> Determined by GPC.

<sup>c</sup> Determined by DSC.

wt. %, made by Kraton polymer), and the triblock SIS was Vector 4111 (diblock < 1%, styrene 18 wt. %, made by ExxonMobil Chemical Co.). The polymer characterization data are listed in Table I.

The tackifiers selected for this study included one type of rosin ester and four types of synthetic hydrocarbon resins. The rosin ester was GA-100 (Nichimen Corp.), and the synthetic hydrocarbon resins were Hikorez A-1100S (C-5, Kolon Chemical Co. Ltd.), Regalite R-125 (Hydrogenated C-9, Eastman Chemical Co.), Quintone U-185 (C5-C9, Nihon Zeon Corp.), and Sukorez SU-100 (Hydrogenated DCPD, Kolon Chemical Co. Ltd.). The properties of the tackifiers are listed in Table II.

### Preparation of HMPSAs

The hot-melt pressure-sensitive adhesives (HMPSAs) were blended in an internal mixer at 170–180°C. An antioxidant, Irganox 1010, was used as a thermal stabilizer. The SIS/tackifier blend ratios were 30/70, 40/60, 50/50, and 60/40 by weight.

The PSA specimens were prepared by melt-coating onto a PET film with an average thickness of 75  $\mu\text{m}$ , using an automatic film applicator with a hot-plate (Kee-Pae Trading Co.) operated at 150°C. A No. 9 bar coater (wetting thickness = 20.6  $\mu\text{m}$ ) was used.

### Complex viscosity

The complex viscosities of the blends were determined using an ARES (Advanced Rheometrics Expan-

sion System, Rheometric Scientific Inc., in NICEM at Seoul National University) in 8 mm parallel plate mode. A typical scan covered the range from -40°C to 120°C.

### Holding power

To examine the effects of the surface properties on the holding power, seven different substrates were used. The substrates were stainless steel (SUS), PE (polyethylene), PP (polypropylene), PVC (polyvinylchloride), Bakelite, Teflon, and glass.

The HMPSA specimen was pressed onto SUS (stainless steel) (bonding area of 25 mm  $\times$  25 mm) by two passes of a 2-kg rubber-roller. The specimen was maintained at room temperature for 1 h. The holding power (break time,  $t_b$ ) was measured at three different temperatures (50, 70, and 90°C) and a load of 1 kg.

### Shear adhesion failure temperature (SAFT)

The shear adhesion failure temperature is a measure of the ability of an HMPSA to withstand an elevated temperature under a constant force, which pulls the HMPSA tape downward from a vertically placed test substrate in a direction parallel to the surface of bonding.<sup>2</sup>

To examine the effects of the surface properties on the holding power, seven different substrates were used. The substrates were stainless steel (SUS), PE, PP, PVC, Bakelite, Teflon, and glass.

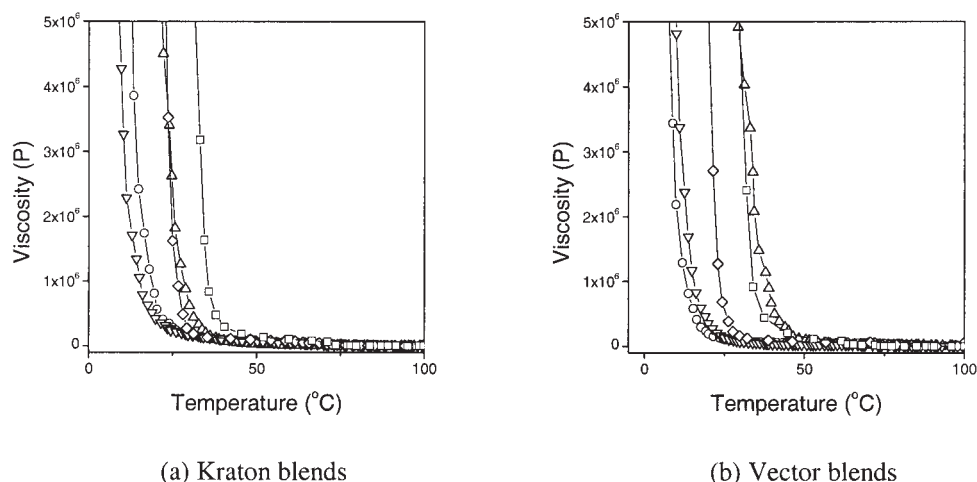
TABLE II  
Tackifier Properties

Trade name	Types	Softening point (°C) <sup>a</sup>	$M_w^b$	$M_n^b$	$M_w/M_n^b$	$T_g^c$ (°C)	Manufacturer
GA-100	Rosin ester	95 $\mu$ 105	860	530	1.61	46.6	Nichimen Corp.
Hikorez A-1100S	Aliphatic hydrocarbon	98	950	380	2.48	45.7	Kolon Chemical Co.
Regalite R-125	Hydrogenated Aromatic hydrocarbon	123	820	370	2.21	68.0	Eastman
Quintone U-185	Modified C5	86	1580	480	3.30	39.0	Zeon Corp.
Sukorez SU-100	Hydrogenated dicyclopentadiene	105	200	100	1.91	56.3	Kolon Chemical Co.

<sup>a</sup> Determined by Ring and Ball methods. Data supplied by the manufacturer.

<sup>b</sup> Determined by GPC.

<sup>c</sup> Determined by DSC.



**Figure 1** Complex viscosities of SIS/tackifier (40/60) blends; (○) Hikorez A 1100 S, (△) Regalite R 125, (▽) Quintone U 185, (◇) Sukorez SU 100, (□) GA-100.

The HMPSA specimen was pressed onto SUS (stainless steel) (bonding area of 25 mm × 25 mm) by two passes of a 2-kg rubber-roller. A load of 1 kg was attached to one end of the lap shear, while the bonded area was adhered to the stainless steel substrate. The temperature was raised in increments of 0.4°C/min.

## RESULTS AND DISCUSSION

### Complex viscosity

Rheology is used to predict a material's response to differing mode of flow and deformation at any point from the processing step through its final end use. The complex viscosity is one rheology property defined by:

$$|\eta^*| = |G^*| / \omega$$

where  $G^*$  is the complex modulus.<sup>8</sup>

The complex viscosity of the SIS/tackifier (40/60) blends is shown in Figure 1.

As shown in this Figure, the complex viscosities of the SIS/tackifier blends decreased substantially in the range 25–50°C. The complex viscosity for the SIS/Regalite R 125 blend decreases rapidly at the highest temperature and that of SIS/Quintone U 185 blend decreases at the lowest temperature.

In our previous study,<sup>9</sup> we investigated the relationship between the complex viscosity and the holding power. According to the results of this study, the complex viscosities of the SIS-based HMPSAs decreased substantially in the range 60–80°C. The complex viscosities of the triblock SIS-based HMPSAs decrease at the highest temperature.

### Holding power

#### Effects of substrates

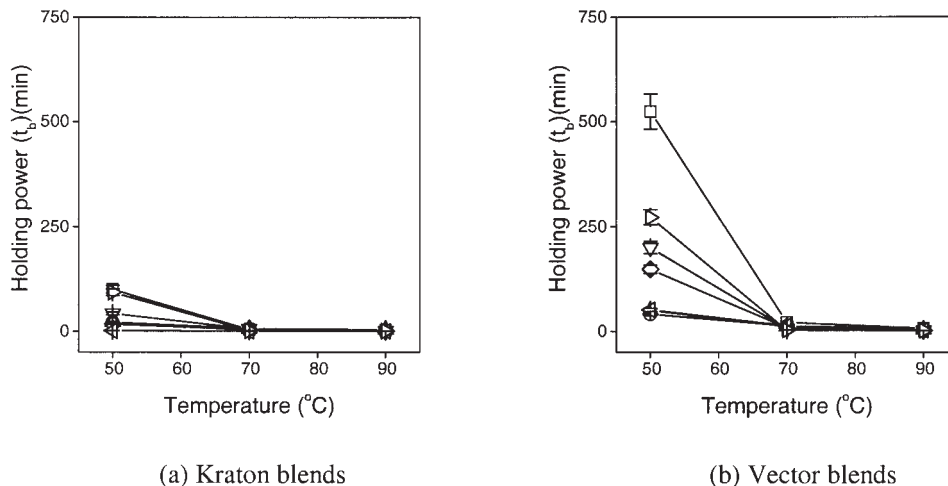
The holding power ( $t_b$ ) of the SIS/Hikorez A 1100S (40/60) blends is shown in Figure 2.

The substrates used in this study were classified into three groups (high holding power, medium holding power, and low holding power). High holding power was observed in the case of stainless steel (SUS). Medium holding power was observed in the case of glass, Bakelite, and PVC, and low holding power was observed in the case of PE, PP, and Teflon. A classification was obtained using surface tension as the distinguishing factor.

In terms of the results for peel strength, PP had medium peel strength, but also had low holding power in this study. The holding power ( $t_b$ ) is measured for the case where cohesive failure occurs, and therefore the value is usually independent of the substrates. However, in this study, complicated failure modes were evident. Failures on low surface tension substrates were observed to be in the interfacial mode and that on high surface tension substrates were observed in general to be cohesive or mixed mode.

In our previous study,<sup>10</sup> we investigated the effect of the properties of the polyolefin substrates on the holding power of HMPSAs. The HMPSAs were composed of SIS/tackifier/plasticizer (40/60/10). According to the results of this study, the holding power of the HMPSAs on PE substrates was higher than that on PP substrates. These results are similar to those of the current study.

Hata et al.<sup>11</sup> investigated the relationship between the holding power ( $t_b$ ) and the sliding friction coefficient of pressure-sensitive adhesives. They reported that, for two series of PSAs, the holding power,  $t_b$ , was



**Figure 2** Holding power of SIS/Hikorez A 1100S (40/60) blends; (□) SUS, (○) PE, (△) PP, (▽) PVC, (◇) Bakelite, (◁) Teflon, (▷) Glass.

correlated with the sliding friction coefficient,  $\mu$ , in the low velocity region. The holding power of a PSA must be closely related to the  $\mu$  value of the material in the low velocity region, as they are both dependent on the rubbery plateau modulus.

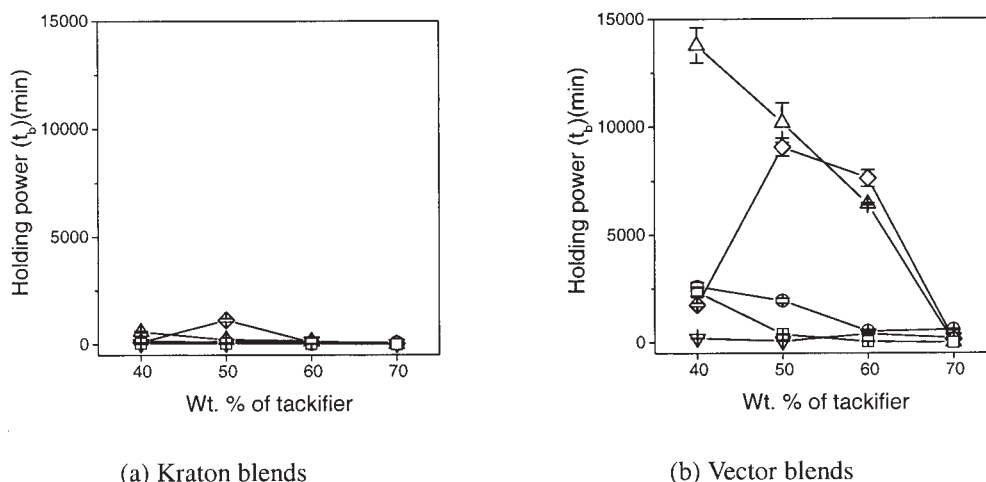
Effects of tackifiers

The holding power of the SIS/tackifier blends on the SUS substrate at various tackifier contents are shown in Figure 3.

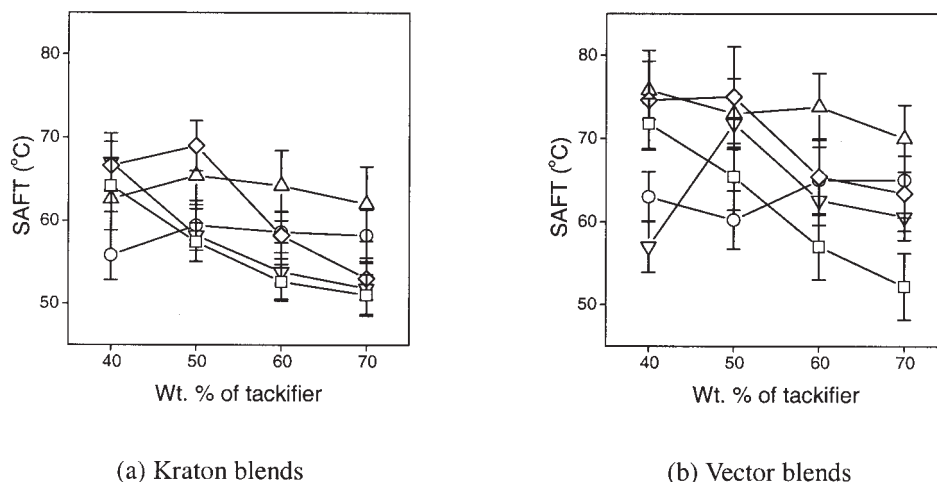
As shown in this Figure, the holding power decreased as the tackifier content increased, except for SIS/Sukorez blends. Also, the holding power of the Vector 4111 blends was higher than that of the Kraton D 1107 blends. This is due to the characteristics of the tackifier and the SIS.

Generally, increasing the tackifier content decreases the shear holding power of a PSA. A tackifier acts as an antiplasticizer at high concentrations and as a plasticizer at low concentrations. If a PSA is made from a block copolymer in which one of the blocks phase-separates from the other, and if the separated phase is glassy, then the phase-separated material acts as a crosslink. Thus, in general, block copolymer PSAs are not crosslinked during processing and, therefore, can potentially be re-melted with the retention of their properties.<sup>1,3</sup>

Cohesion increases with increasing molecular weight. Longer molecules do not impart higher strength, because their various segments act independently of each other. SIS block copolymers undergo oxidative degradation at elevated temperatures by a mechanism which leads predominantly to scission of the polymer



**Figure 3** Holding power (at 50°C) of SIS/tackifier blends on SUS substrate; (○) Hikorez A 1100 S, (△) Regalite R 125, (▽) Quintone U 185, (◇) Sukorez SU 100, (□) GA-100.



**Figure 4** Shear adhesion failure temperature of SIS/tackifier blends on SUS substrates; (○) Hikorez A 1100S, (△) Regalite R 125, (▽) Quintone U 185, (◇) Sukorez SU100, (□) GA-100.

chains. This leads to a fall in molecular weight and a resulting decrease in viscosity and holding power.<sup>1,12</sup>

The composition of the adhesive (i.e., its nature and molecular weight) influences the shear. When a high shear mixer is used, the degradation depends on the mixing environment. In contact with the open air, degradation occurs rapidly and polymer breakdown is observed. A dramatic reduction in melt viscosity and holding power results from even partial degradation.

The shear depends on the molecular weight and its distribution. A broad MWD polymer may have a lower cohesive strength than one with a narrow MWD and a lower molecular weight. The shear resistance is improved by increasing the melting point of the resin.<sup>1,3,12</sup>

Because triblock SIS (Vector 4111) has higher cohesion than diblock-containing SIS (Kraton D 1107), Vector 4111/tackifiers blends have higher holding power than Kraton D 1107/tackifier blends.<sup>13,14</sup>

### Shear adhesion failure temperature (SAFT)

The SAFT values of the SIS/tackifier blends are shown in Figure 4. As shown in this Figure, higher levels of Quintone U 185 and GA-100 decrease the holding power of the HMPSA. Also, the SAFT values of the Vector 4111 blends were higher than those of the Kraton D 1107 blends. These results are similar to those obtained in the case of the holding power.

Rosin ester and aromatic-modified aliphatic resin are compatible with both the ends and midblocks of these polymers and tackify the entire molecule. They increase the  $T_g$  value of the rubber midblock and decrease the  $T_g$  of the polystyrene endblock. This generates tack while limiting the high temperature resis-

tance of the adhesive due to the “softening” of the end blocks.<sup>3,7,15</sup>

Nakajima et al.<sup>2</sup> investigated the relationship between the SAFT value and the viscoelastic properties of HMPSAs using three types of SIS material.

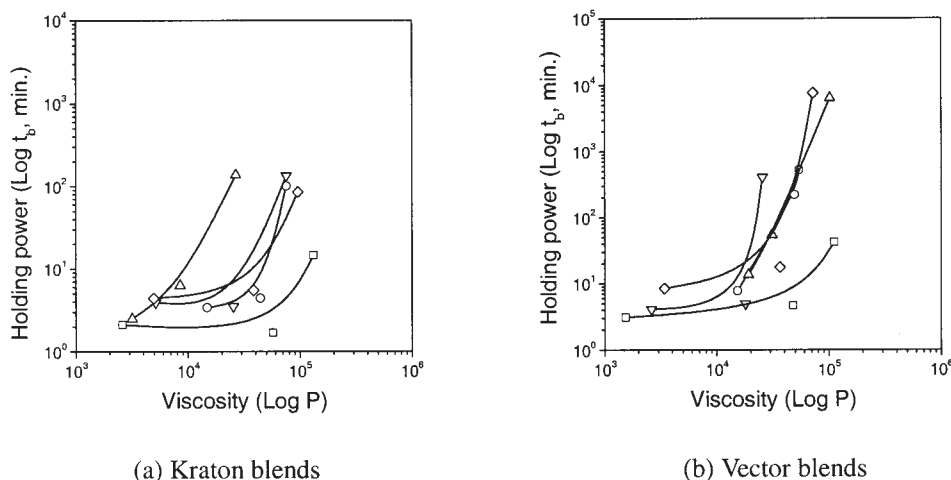
According to their study, the SAFT was related to the crossover temperature, in the region where  $G' = G''$  at the higher temperature end of the rubbery plateau. The SIS material with a higher polystyrene wt. % exhibited the highest SAFT and crossover temperature. However, in the cases of the other two materials, they exhibited different failure temperatures, while the crossover temperatures were the same. This demonstrates that the crossover temperature is not the only factor that determines adhesive behavior. The difference in the elastic modulus between these materials is expected to have an influence on the failure behavior.

### Relationship between holding power and complex viscosities

The relationship between the holding power and the complex viscosity of the SIS/tackifier blends is shown in Figure 5. As shown in this Figure, the complex viscosity was closely related to the holding power.

The holding power is defined as the time a pressure-sensitive adhesive-coated film holds under a defined shear load. During the preparation of HMPSAs, the compositions of the base polymer and the tackifiers have an effect on the holding power of the resultant HMPSA. Because of the sensitivity of hot-melt PSAs to elevated temperature, the viscosity of the HMPSA plays a significant role in determining the holding power of the HMPSA.<sup>2-4,14</sup> The relationship between holding power and complex viscosity was similar to the case of steady flow viscosity.





**Figure 5** Relationship between holding power and complex viscosity of SIS/tackifier (40/60) blends; (○) Hikorez A 1100S, (△) Regalite R 125, (▽) Quintone U 185, (◇) Sukorez SU100, (□) GA-100.

In our previous study,<sup>9</sup> we investigated the relationship between complex viscosity and holding power. According to the results of this study, the complex viscosities of the SIS-based HMPSAs decreased substantially in the range 25–50°C. The decrement observed for the triblock SIS-based HMPSAs was larger than that observed for the diblock-containing SIS-based HMPSAs. Also, the complex viscosities were closely related to the holding power.

#### Schematic illustration

Schematic illustrations of the shear creep of the SIS-based HMPSAs are shown in Figures 6 and 7. As shown in the Figures, the substrates used in this study were classified into three groups (high holding power, medium holding power, and low holding power).

Also, the holding power and SAFT values of the triblock SIS blends were higher than those of the diblock-containing SIS blends. Higher levels of aromatic resin-modified aliphatic tackifier and rosin ester

were found to decrease the holding power of the HMPSAs.

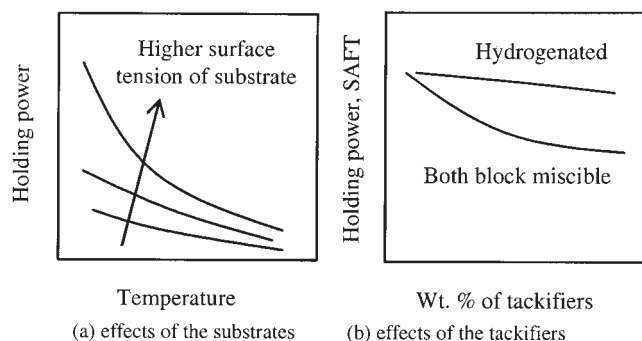
#### CONCLUSIONS

The effects of the properties of the substrates on the shear creep of the SIS-based HMPSAs were investigated. The holding power ( $t_b$ ) and shear adhesion failure temperature (SAFT) were measured. The relationship between the complex viscosity and the holding power was also examined.

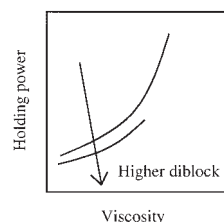
The substrates used in this study were classified into three groups (high holding power, medium holding power, and low holding power).

High holding power was observed in the case of SUS. Medium holding power was observed in the case of glass, bakelite, and PVC, and low holding power was observed in the case of PE, PP, and Teflon. A similar classification was obtained using surface tension as the distinguishing factor. Interfacial failure mode was observed on low surface tension substrates.

Also, the holding power decreased as the tackifier content increased. The holding power and SAFT values of the triblock SIS blends were higher than those of the diblock-containing SIS blends. This may be due to



**Figure 6** A schematic illustration of the effects of the properties of the substrates and tackifiers on the holding power of the SIS-based HMPSAs.



**Figure 7** A schematic illustration of the relationship between the holding power and the complex viscosity of the SIS-based HMPSAs.

blends using triblock SIS having higher crossover temperature and complex viscosity than those using diblock-containing SIS.

Higher levels of aromatic-modified aliphatic resin (Quintone U 185) and rosin ester (GA 100) were found to decrease the holding power of the HMPSAs. This is may be due to rosin ester and aromatic-modified aliphatic resin being miscible with both the ends and midblocks of these polymers.

It is thought that they increase the  $T_g$  value of the rubber midblock and decrease the  $T_g$  value of the polystyrene endblock.<sup>16</sup> This generates tack while limiting the high temperature resistance of the adhesive due to the softening of the end blocks.

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