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## Tack and fracture energy of tackified SIS (styrene-isoprene-styrene)-based hot-melt pressure sensitive adhesives (HMPSAs)

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**Abstract**—The relationship between probe tack and fracture energy for SIS (styrene-isoprene-styrene)-based HMPSAs (hot-melt pressure-sensitive adhesives) made using various SIS and tackifiers was investigated. Generally, HMPSAs made using low- $T_g$  tackifiers have higher probe tack than using high- $T_g$  tackifiers, except in the case of Sukorez SU 100. In the case of Kraton blends, blends made using Quintone U 185, Hikorez A 1100S and Sukorez SU 100 exhibit a maximum probe tack at 60 wt% tackifier content, while the blends made using GA-100 and Regalite R 125 exhibit a maximum probe tack at 40 wt% tackifier content. In the case of the Vector blends, similar results are observed, except that those HMPSAs made using Hikorez A 1100S and Sukorez SU 100 have a maximum probe tack at 50 wt% tackifier content. Because tri-block SIS (Vector 4111) has a higher cohesion than the diblock containing SIS (Kraton D 1107), Vector 4111/tackifier blends exhibit a maximum tack at higher tackifier contents than Kraton D 1107/tackifier blends. In terms of the fracture energy of blends, similar results were observed. Generally, the fracture energy ( $w$ ) of the SIS-based HMPSAs was closely related to the maximum probe tack. Because of the effects of failure mode on fracture energy and probe tack, there is some variation in the fracture energy between the different blends, because of their different failure modes.

**Keywords:** SIS (styrene-isoprene-styrene); tackifier; hot-melt pressure-sensitive adhesives (HMPSAs); phase diagram; miscibility; probe tack; fracture energy of blends.

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## 1. INTRODUCTION

Tack is the ability of a PSA to create a bond spontaneously under no or minimal external contact pressure [1]. While various empirical rules have been expounded regarding the phenomenon of tack, its precise mechanism is still not satisfactorily understood. The elementary processes of the tack phenomenon are the bonding and debonding processes between the adhesive and the substrate [2]. The contribution of each of these is believed to vary according to the measurement method and ambient conditions, which make it very complex and difficult to quantify tack on a scientific basis. Many studies have been done on tack measurement and analysis methods [3–6].

Among the various methods, which have been proposed, probe tack can best be evaluated by bringing the smooth end of a cylindrical probe into contact with the adhesive and then plotting the stress/strain curve produced when the probe is pulled away [2, 7].

Zosel [8] proposed that tack should be defined as the adhesive fracture energy, determined with adhesive joints which had been formed under conditions of low contact pressure and short contact time. The adhesive fracture energy exhibits a maximum in the temperature range just above the glass transition region. In this temperature range, the mechanical behavior is determined by evaluating the intermolecular interactions.

In the probe tack test, fibrillation occurs with tacky and soft PSAs, while such fibrillation does not occur with brittle PSAs. This phenomenon is related to the failure mode and has an effect on the fracture energy measured.

Brown *et al.* [7] investigated the micromechanisms underlying the tack of PSAs using SIS/liquid tackifier systems. They identified 4 different micromechanisms leading to the separation of the probe from the PSA film, which they defined as types 1, 2, 3 and 4. Each one of these micromechanisms corresponds to a specific type of stress–strain curve.

In this study, we investigated the relationship between the probe tack and fracture energy of SIS based HMPSAs using various SIS materials and tackifiers.

## 2. EXPERIMENTAL

### 2.1. Materials

The SIS (styrene-isoprene-styrene) materials selected for this study were a diblock containing SIS and a tri-block SIS. The diblock containing SIS was Kraton D1107 (diblock content 15 wt%, styrene 15 wt%, made by Kraton Polymer, Houston, TX, USA), and the tri-block SIS was Vector 4111 (diblock <1%, styrene 18 wt%, made by ExxonMobil). The polymer characterization data are given in Table 1.

The tackifiers selected for this study were rosin ester and four different synthetic hydrocarbon resins. The rosin ester was GA-100 (Nichimen, Japan), and the synthetic hydrocarbon resins were Hikorez A-1100S (C-5, Kolon Chemical, Incheon,

**Table 1.**

Polymer characterization data

Trade name	Type	Styrene content (wt%) <sup>a</sup>	Diblock content (wt%) <sup>a</sup>	$M_w^b$	$M_n^b$	$M_w/M_n^b$	$T_g^c$ (°C)	Manufacturer
Kraton D1107	Linear SIS	15	15	128 928	106 282	1.21	-61.0	Kraton Polymer
Vector 4111	Linear SIS	18	<1	114 395	107 614	1.06	-61.0	ExxonMobil

<sup>a</sup> Data supplied by the manufacturer.<sup>b</sup> Determined by GPC.<sup>c</sup> Determined by DSC.**Table 2.**

Properties of tackifiers

Trade name	Type	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	95–105	857	532	1.61	46.6	Nichimen
Hikorez A-1100S	Aliphatic hydrocarbon	98	946	382	2.48	45.7	Kolon Chemical
Regalite R-125	Hydrogenated Aromatic hydrocarbon	123	816	369	2.21	68.0	Eastman Chemical
Quintone U-185	Modified C5	86	1580	478	3.30	39.0	Zeon
Sukorez SU-100	Hydrogenated dicyclopentadiene	105	200	105	1.91	56.3	Kolon Chemical

<sup>a</sup> Determined by the Ring and Ball method. Data supplied by the manufacturer.<sup>b</sup> Determined by GPC.<sup>c</sup> Determined by DSC.

South Korea), Regalite R-125 (Hydrogenated C-9, Hercules), Quintone U-185 (C5-C9, Nihon Zeon, Japan) and Sukorez SU-100 (Hydrogenated DCPD (Dicyclopentadiene), Kolon Chemical). The properties of the tackifiers are shown in Table 2.

## 2.2. Preparation of HMPSAs

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

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

### 2.3. Thermal properties

The glass transition temperatures ( $T_g$  values) were measured using a differential scanning calorimeter (DSC, TA Instruments model Q-1000, in NICEM at Seoul National University). The samples were first cooled to  $-80^\circ\text{C}$ , then heated to  $150^\circ\text{C}$  at a heating rate of  $5^\circ\text{C}/\text{min}$  (first scan). They were then immediately quenched to  $-80^\circ\text{C}$  and kept at this temperature for 5 min. The samples were then reheated to  $150^\circ\text{C}$  at a heating rate of  $5^\circ\text{C}/\text{min}$  (second scan). The  $T_g$  defined in this study was obtained from the second scan to assure reproducible thermograms free from thermal history effects.

### 2.4. Phase diagram

The phase diagrams of the blends were examined by visual observation. The blends were coated onto glass slides. The films on the glass slides were maintained at  $30^\circ\text{C}$  for 12 h to attain phase equilibrium and then visually observed to see whether they were transparent or opaque at this temperature. The same procedures were repeated by raising the temperature in a stepwise manner at  $5^\circ\text{C}$  at each 12-h interval up to  $190^\circ\text{C}$  in an air circulation oven.

### 2.5. Probe tack and fracture energy

The probe tack test was conducted using a Texture Analyzer (TA-XT2i, Stable Micro Systems, UK) with a polished stainless steel cylindrical probe with a diameter of 5 mm. Measurements were carried out at separation rates of 0.1, 0.5, 1, 5 and 10 mm/s under a constant pressure of  $100\text{ g}/\text{cm}^2$  and a dwell time of 1 s.

## 3. RESULTS AND DISCUSSION

### 3.1. Thermal properties

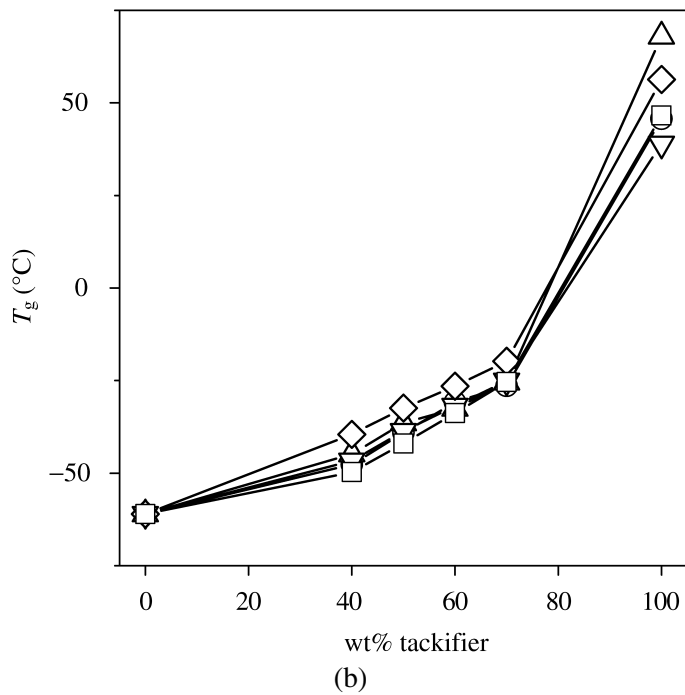
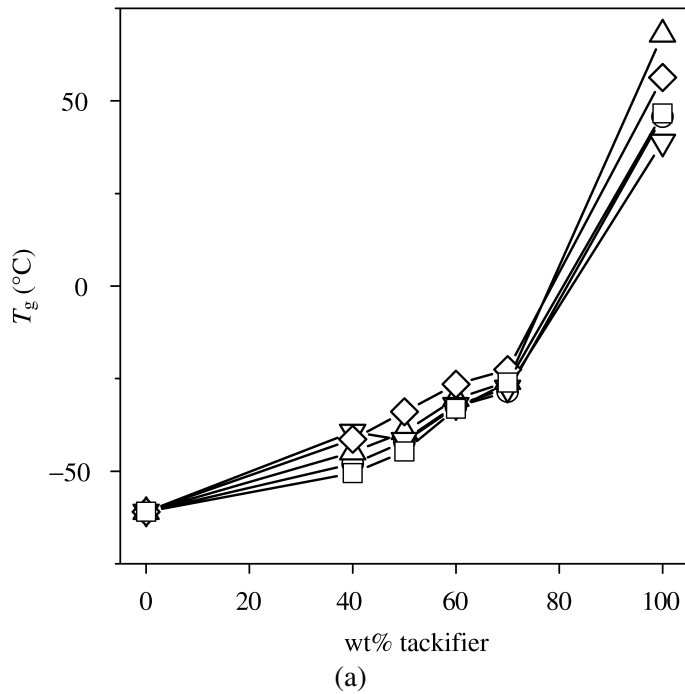
The thermal properties of the HMPSAs are shown in Fig. 1.

According to previous studies [9, 10], miscible blends have composition-dependent  $T_g$  values.

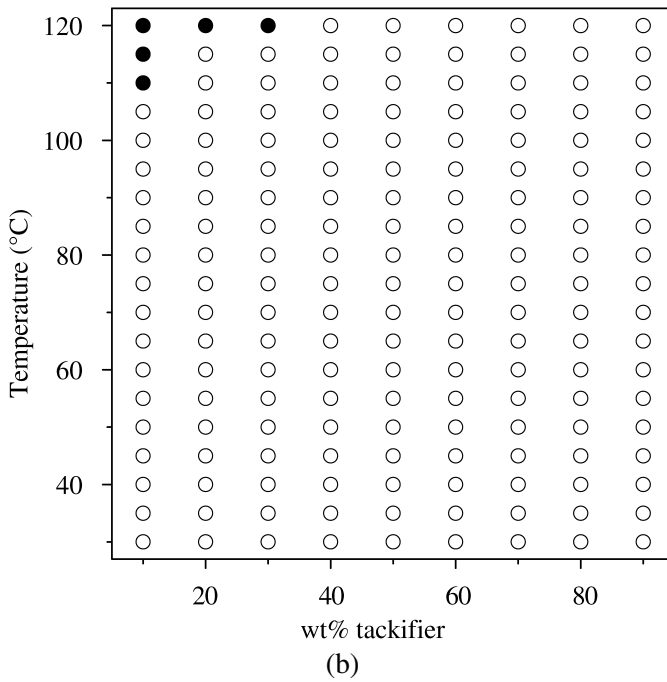
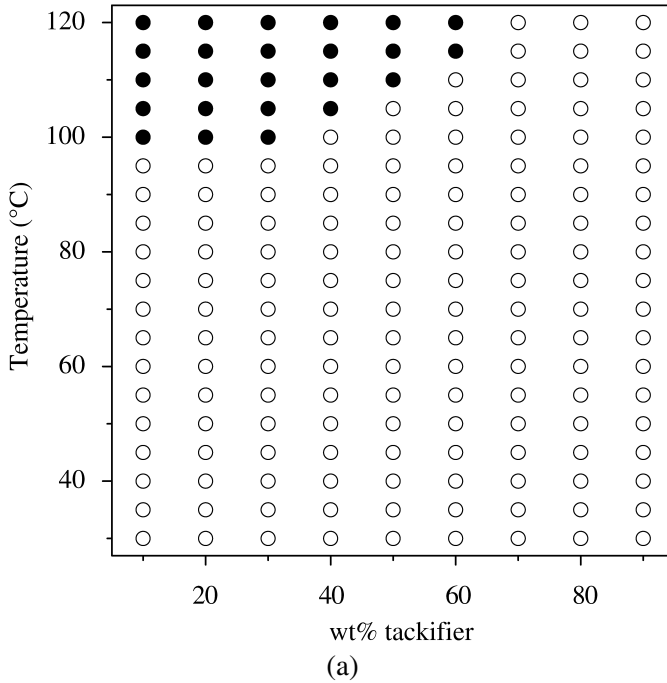
In all of the blends, only one well-defined glass transition in between the glass transitions of the pure components was detected and it changed gradually depending on the composition. The existence of a single composition-dependent  $T_g$  is evidence that SIS materials used in this study (Kraton D 1107 and Vector 4111) were miscible with the tackifiers used in this study (Hikorez A 1100 S, Regalite R 125, Quintone U 185, Sukorez SU 100, and GA-100) below the  $T_g$ .

### 3.2. Phase diagram

Phase diagrams of the Kraton D 1107/Hikorez A 1100S and Vector 4111/Hikorez A 1100S blends are shown in Fig. 2. All of the blend systems show phase diagrams



**Figure 1.**  $T_g$  by DSC of SIS/tackifier blends ( $\circ$  Hikorez A 1100S,  $\Delta$  Regalite R 125,  $\nabla$  Quintone U 185,  $\diamond$  Sukorez SU 100,  $\square$  GA-100). (a) Kraton D 1107 blends, (b) Vector 4111 blends.



**Figure 2.** Phase diagrams of Hikorez A 1100S blends (○ transparent (miscible), ● opaque (immiscible)). (a) Kraton D 1107 blends, (b) Vector 4111 blends.

of the lower critical solution temperature (LCST) type. The critical temperatures of the Kraton D 1107/tackifier blends are in the range of 100–110°C, while those of the Vector 4111/tackifier blends are in the range of 110–125°C. The critical temperatures of the Vector 4111/tackifier blends were slightly higher than those of the Kraton 1107/tackifier blends. As shown in Fig. 2, the SIS materials used in this study (Kraton D 1107 and Vector 4111) are miscible with the tackifier Hikorez A 1100 S at temperatures below the  $T_g$ .

### 3.3. Probe tack

The probe tack values of the SIS/tackifier (40:60) blends at various separation rates are shown in Fig. 3.

In the case of the Kraton D 1107 blends, the order of probe tack was Quintone U 185 (Softening Point, SP 85°C) > Sukorez SU 100 (SP 105°C) > Hikorez A 1100S (SP 98°C) > GA-100 (SP 105°C) > Regalite R 125 (SP 123°C). In the case of the Vector 4111 blends, similar results were observed. As shown in Fig. 3, generally speaking, the low softening point tackifiers have higher probe tack values than the high softening point tackifiers, except in the case of Sukorez SU 100.

As shown in Fig. 3, for those blends with high tack values (over 1000 g at a separation rate of 10 mm/s), the tack value increased as the separation rate increased, while for those blends with low tack values (under 1000 g at separation rate of 10 mm/s), the tack value increased as the separation rate decreased.

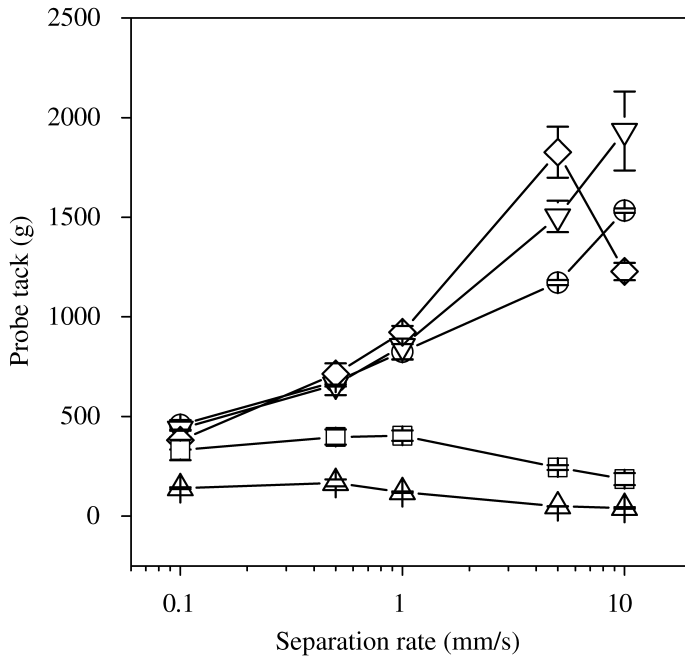
The probe tack values of the SIS/tackifier blends at various tackifier contents are shown in Fig. 4.

In the case of the Kraton blends, those blends made using Quintone U 185, Hikorez A 1100S and Sukorez SU 100 show a maximum probe tack at 60 wt% tackifier content, while those blends made using GA-100 and Regalite R 125 show a maximum probe tack at 40 wt% tackifier content. In the case of the Vector blends, similar results are observed, except for those blends made using Hikorez A 1100S and Sukorez SU 100, which have a maximum probe tack at 50 wt% tackifier content.

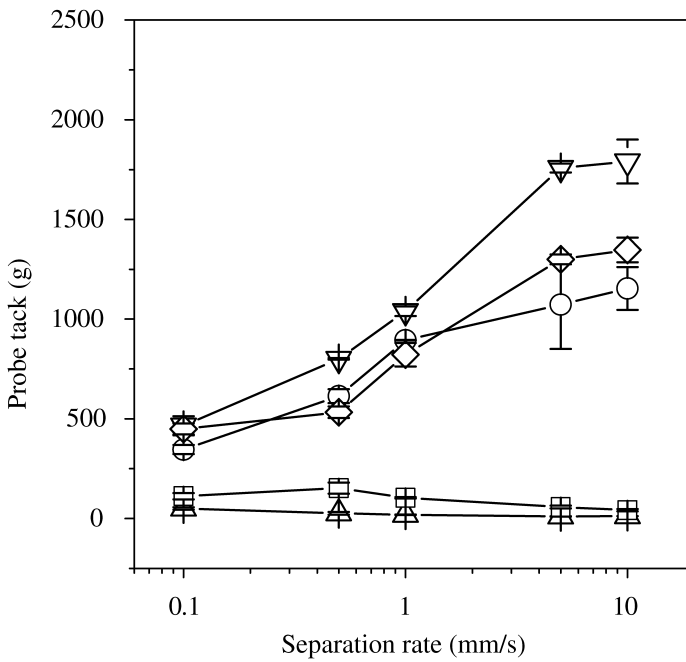
The blend made with low di-block content tends to exhibit better cohesive properties, but the blend made with high di-block content elastomer exhibits low viscosity causing better wetting properties and good tack [11]. Therefore, Vector 4111/tackifier blends (made with low di-block content) exhibit maximum tack values at higher tackifier contents than Kraton D 1107/tackifier blends (made with high di-block content).  $\tan \delta$  increases linearly with increasing di-block content, whereas the inherent elastic response ( $G'$ ) of the tri-block co-polymer network is diminished and the corresponding inelastic or loss modulus response ( $G''$ ) is increased [12].

Kim *et al.* [13] measured the probe tack of many blends of acrylic co-polymers with tackifiers. In their study, the probe tack master curve of the miscible PSA systems shifted toward the lower separation rate side and, at the same time, the peak height increased as the tackifier content increased. This is due to the fact



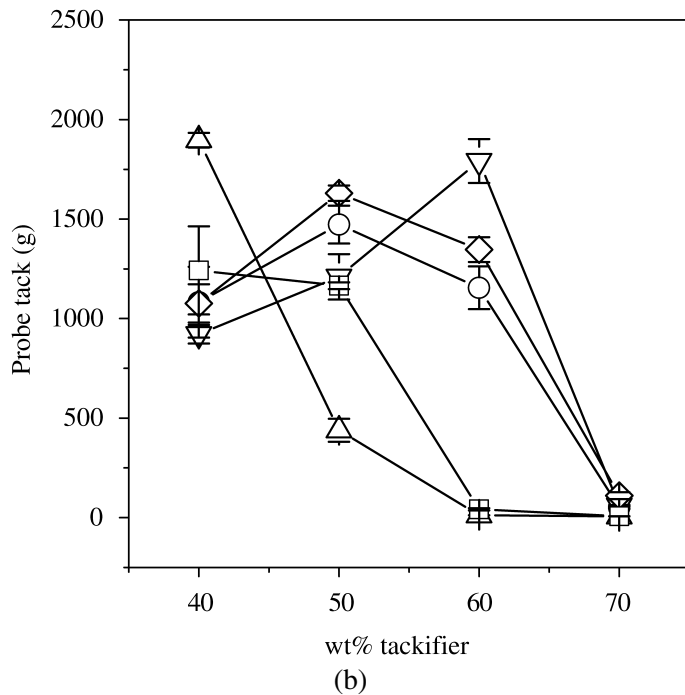
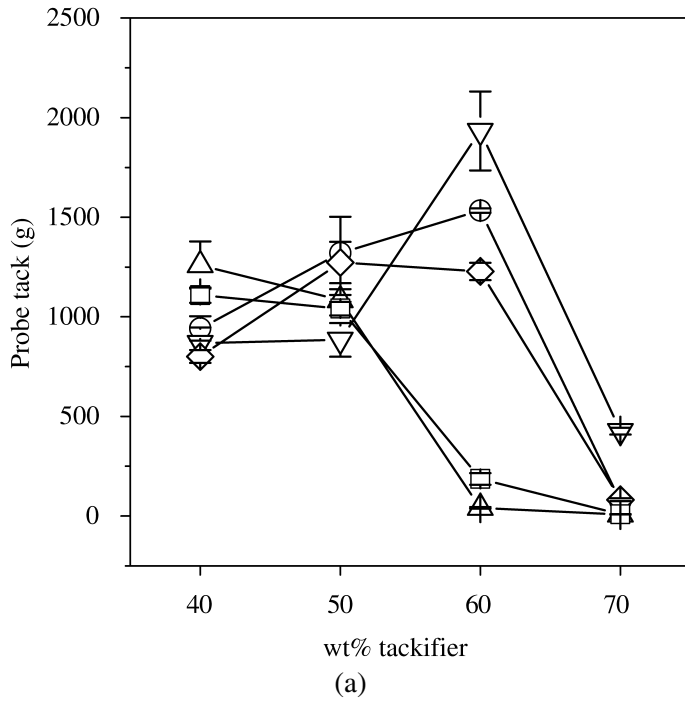


(a)



(b)

**Figure 3.** Probe tack of SIS/tackifier (40:60) blends as a function of separation rate (○ Hikorez A 1100S, △ Regalite R 125, ▽ Quintone U 185, ◇ Sukorez SU 100, □ GA-100). (a) Kraton D 1107 blends, (b) Vector 4111 blends.



**Figure 4.** Probe tack of SIS/tackifier blends as a function of tackifier content (○ Hikorez A 1100S, △ Regalite R 125, ▽ Quintone U 185, ◇ Sukorez SU 100, □ GA-100). (a) Kraton D 1107 blends, (b) Vector 4111 blends.

that the tackifier resin incorporation results in the modification of the viscoelastic properties, as well as of the surface tension of the PSAs.

In the case of the immiscible systems, in which the lower and upper  $T_g$  values remain constant, a peak value of the probe tack was not observed within the range of separation rates used in this experiment [13, 14].

Creton and Lakrout [5] observed the same tendency and interpreted their results as follows. When the cylinder is pulled away, first a uniform deformation occurs, but then cavities develop at the adhesive surface and begin to expand.

Since a maximum stress appears during this initial stage, while the strain is still low, it displays a tendency similar to linear viscoelasticity. However, towards the end of the pull away process, fibrillation occurs.

The dependence of the tack on molecular weight is demonstrated by the aging of SIS rubbers. In this case, chain scission occurs and tack increases. In general, resins with a softening point below about 50°C impart tack, but give poor cohesive strength; while resins with a softening point above 70°C give good cohesive strength but poor tack [15].

### 3.4. Fracture energy

The fracture energies of the SIS/tackifier (40:60) blends at various separation rates are shown in Fig. 5. The results show a similar trend to that obtained in the case of the probe tack.

In the case of the Kraton 1107 blends, the order of fracture energy was Quintone U 185 > Sukorez SU 100 > Hikorez A 1100S > GA-100 > Regalite R 125. In the case of the Vector 4111 blends, similar results were observed.

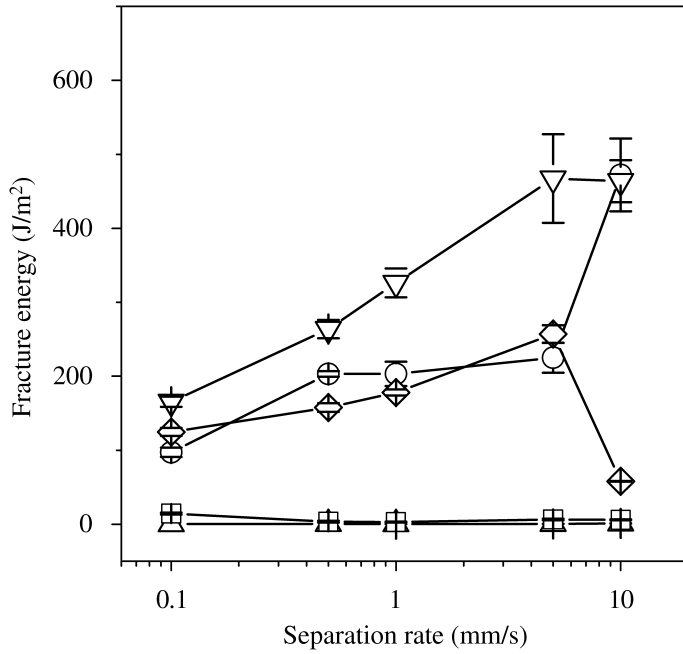
Generally, the fracture energy of blends was closely related to the maximum probe tack. Because of the effects of failure mode on both fracture energy and probe tack, there was some variation in the fracture energies of the blends, because of their different failure modes.

Kim *et al.* [13] reported similar results with acrylic PSAs. The fracture energy of blends for acrylic PSAs was closely related to the miscibility between the components.

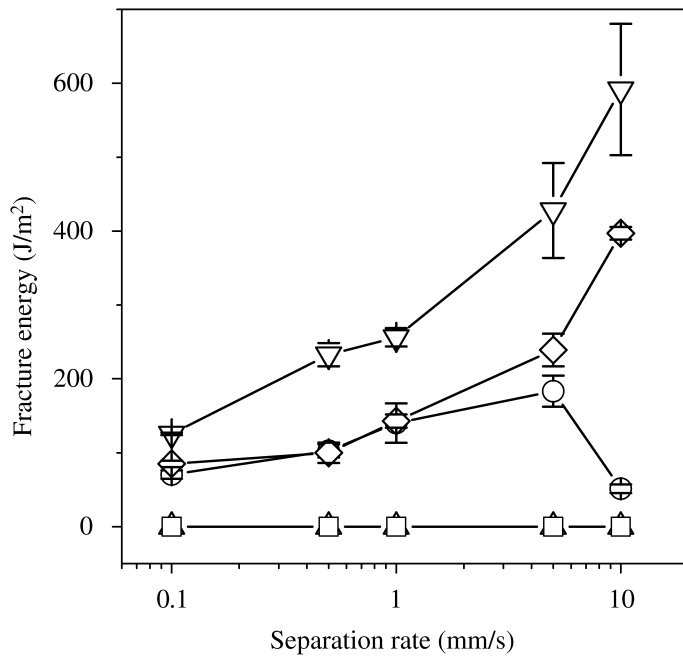
The fracture energies of the SIS/tackifier blends at various tackifier contents are shown in Fig. 6. The results were similar to those obtained in the case of the probe tack.

In the case of the Kraton blends, blends made using Quintone U 185, Hikorez A 1100S and Sukorez SU 100 show a maximum fracture energy at 60 wt% tackifier content, while blends made using GA-100 and Regalite R 125 show a maximum fracture energy at 40 wt% tackifier content. In the case of the Vector blends, similar results were observed.

Brown *et al.* [7] reported the stress–strain curves of SIS-based PSAs. They defined 4 different mechanisms of tack which they referred to as types 1, 2, 3 and 4. In type 1, initial cavitation occurs at the interface. Types 2 and 3 were marked by initial cavitation in the bulk materials rather than at the interface. In

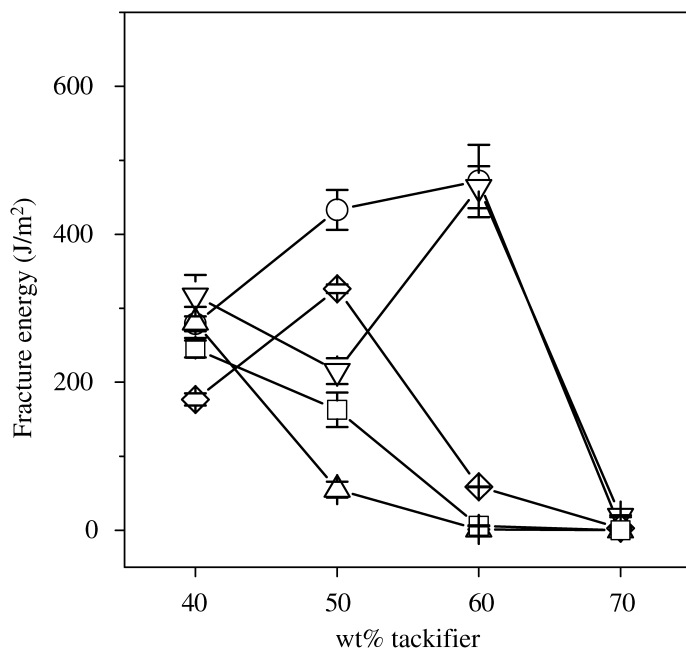


(a)

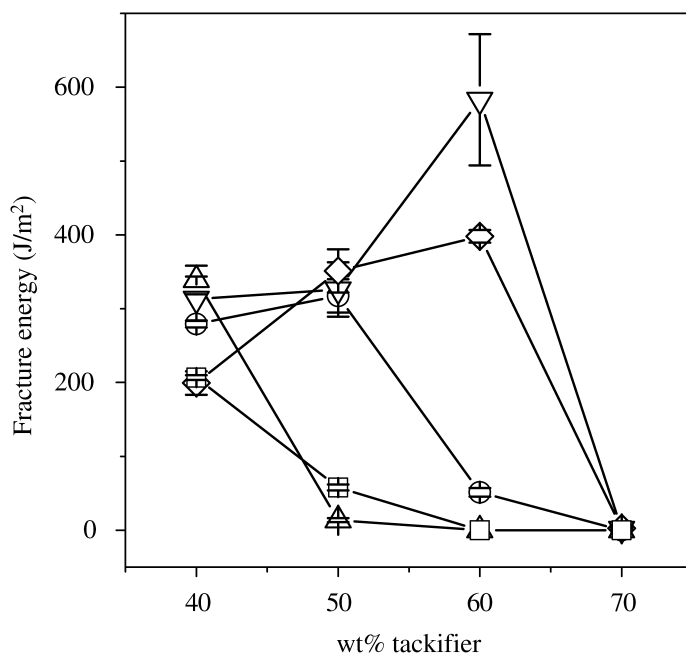


(b)

**Figure 5.** Fracture energy of SIS/tackifier (40/60) blends as a function of separation rate (○ Hikorez A 1100S, △ Regalite R 125, ▽ Quintone U 185, ◇ Sukorez SU 100, □ GA-100). (a) Kraton D 1107 blends, (b) Vector 4111 blends.

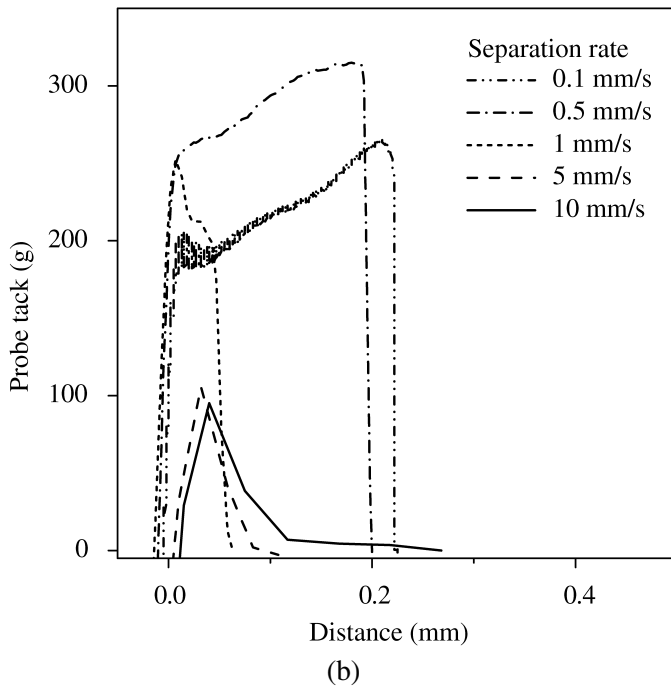
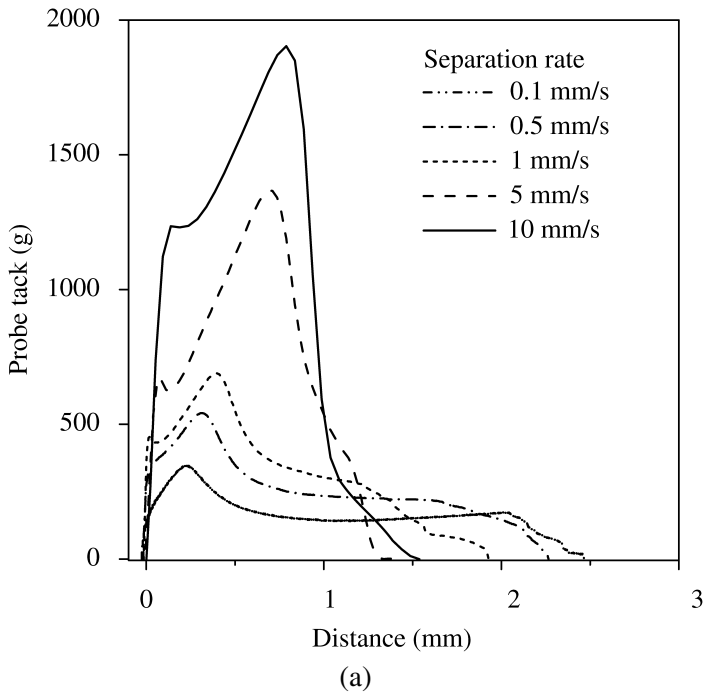


(a)



(b)

**Figure 6.** Fracture energy of SIS/tackifier blends as a function of tackifier content (○ Hikorez A 1100S, △ Regalite R 125, ▽ Quintone U 185, ◇ Sukorez SU 100, □ GA-100). (a) Kraton D 1107 blends, (b) Vector 4111 blends.



**Figure 7.** Probe tack test curves of SIS/Hikorez A 1100S (40:60) blends as a function of separation rate. (a) Kraton D 1107 blends, (b) Vector 4111 blends.

going from mechanism 1 to mechanism 4, the observed tendency was a transition from interfacial cracks to interfacial cavitation to bulk cavitation. In acrylic-based PSAs, mechanisms 2 and 3 have never been observed.

In our study, HMPSAs with a low fracture energy exhibit a curve which is similar to type 1. While, HMPSAs with a high fracture energy exhibit a curve which is similar to type 2 or 3.

The probe tack test curves of the Kraton D 1107/Hikorez A 1100S (40:50) and Kraton D 1107/Regalite R 125 (40:60) blends are shown in Fig. 7. Figure 7a corresponds to fibrillation, while Fig. 7b corresponds to deformation. This is due to the Kraton D 1107/Hikorez A 1100S blends being softer than the Kraton D 1107/Regalite R 125 blends.

#### 4. CONCLUSIONS

The relationship between the probe tack and the fracture energy of SIS-based HMPSAs using various SIS materials and tackifiers was investigated.

For blends with high tack values (over 1000 g at a separation rate of 10 mm/s), the tack value increased as the separation rate increased, while for blends with low tack values (under 1000 g at separation rate of 10 mm/s), the tack value increased as the separation rate decreased.

In the case of the Kraton blends, blends made using Quintone U 185, Hikorez A 1100S and Sukorez SU 100 exhibit a maximum probe tack at 60 wt% tackifier content, while blends made using GA-100 and Regalite R 125 exhibit a maximum probe tack at 40 wt% tackifier content. In the case of the Vector blends, similar results were observed except that Hikorez A 1100S and Sukorez SU 100 exhibited maximum probe tack values at 50 wt% tackifier content.

In terms of the fracture energy, similar results were observed. Generally speaking, the fracture energy ( $w$ ) of the SIS-based HMPSAs was closely related to the maximum probe tack.

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