PSA Performances and Viscoelastic Properties of SIS-Based PSA Blends with H-DCPD Tackifiers

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ABSTRACT: Hotmelt pressure sensitive adhesives (PSAs) usually contain styrenic block copolymers like styrene–isoprene–styrene (SIS), SBS, SEBS, tackifier, oil, and additives. These block copolymers individually reveal no tack. Therefore, a tackifier is a low molecular weight material with high glass transition temperature (T_g), and imparts the tacky property to PSA. The SIS block copolymer with different diblocks was blended with hydrogenated dicyclopentadiene (H-DCPD tackifier), which has three kinds of T_g. PSA performance was evaluated by probe tack, peel strength, and shear adhesion failure temperature. PSA is a viscoelastic material, so that its performance is significantly related to the viscoelastic properties of PSAs. We tested the viscoelastic properties by dynamic mechanical analysis and the thermal properties by differential scanning calorimeter to investigate the relation between viscoelastic properties and PSA performance. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2839–2846, 2006

Key words: pressure sensitive adhesive; hotmelt; tackifier; tack; peel; SAFT

INTRODUCTION

Pressure sensitive adhesives (PSAs) are usually used in the form of tapes. There are many processes involved in the manufacture of PSA products such as the selection of raw materials, coating in substrates, aging, etc. For the coating process, the PSA ingredients should have the ability to flow. PSAs can be coated onto the substrate by melting, dissolving, and dispersing. The method of dissolving in organic solvent causes environmental problems, so attention has been focused on the dispersion of hotmelt PSA.

Hotmelt PSA is a 100% solid material which exists in the solid state at room temperature, but in the liquid state at high temperature.[1] Hotmelt PSA can be coated at high temperature, and gains its cohesive strength at room temperature. It has the benefits of aggressive tack, good peel strength, bonding ability to rough surfaces, good water resistance, heavy coat weight, and acceptable economics.

Hotmelt PSAs are derived from an elastomeric material such as styrenic copolymer, rubber, butyl, silicone, and acrylic polymer. The elastomer provides the flexibility and cohesive strength of PSA compounded with tackifier, pigments, plasticizer, and antioxidant.[2] Styrene–isoprene–styrene (SIS) block copolymer provides a long open time for hotmelt formulations, and so is widely used in the manufacture of hotmelt

PSAs.[3] SIS is composed of a polyisoprene block trapped between two polystyrene domains. The styrene block is in its glassy state at room temperature, while the isoprene has a rubbery behavior. In other words, SIS is composed of rigid PS domains dispersed in a rubbery and dense network of isoprene entangled molecules.[4] The selective options are the molecular weight of the isoprene midblock, the molecular weight of the styrene endblock, and the coupling efficiency. From this, a family of SIS block copolymers can be developed from soft to firm.

PSA in this research was prepared with SIS copolymer, which is widely used in hotmelt PSA manufacture, and hydrogenated dicyclopentadiene (H-DCPD) resin. The two copolymers were pure triblock copolymer and triblock copolymer containing diblock. The tackifier comprised three types of resin with different glass transition temperatures (T_g). We researched the relationship between the viscoelastic properties and composition of PSA, and adhesion properties of PSA based on SIS copolymer.

EXPERIMENTAL

Materials

SIS block copolymer was used as base polymer of the hotmelt PSAs. Vector 4111 is a pure triblock and Kraton D1107 is a triblock containing 15% diblock. The detailed information of SIS block copolymer is shown in Table I. H-DCPD resin was used as the

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TABLE I
Characteristics of SIS Copolymers

Trade name	Structure	Styrene content	Diblock content	T_g by DSC	Company
Kraton D1107	Linear SIS	15%	15%	−60.6	Kraton Polymer
Vector 4111	Linear SIS	18%	< 1%	−60.6	Exxon Mobil Chemical

tackifier. The tackifier resins were SU90, SU110, and SU130 (Kolon Chemical, South Korea). T_g of tackifier was characterized by differential scanning calorimeter (DSC) and complete information is presented in Table II. To reduce the thermal degradation of the hotmelt adhesives, 0.25 parts of antioxidant (Irganox 1010, Ciba Geigy) was used as a thermal stabilizer.

Preparation of hotmelt PSAs

PSAs were blended in an internal mixer at about 170°C. The SIS/tackifier blend ratios were 30/70, 40/60, 50/50, 60/40, and 70/30 by weight. The PSA specimens were prepared by melt coating onto a polyester film with an average thickness of 75 μm, using an automatic film applicator with hot plate (Kee-Pae Trading, South Korea) at 150°C. The specimens were then stored at room temperature for over 1 week.

Instrumental analysis

Differential scanning calorimeter

DSC analysis was carried out using a TA Instrument DSC Q 1000 (NICEM at Seoul National University) with 4–6 mg sample. The samples were cooled from room temperature to −80°C and then heated to 180°C at a heating rate of 10°C/min under a nitrogen atmosphere. They were next cooled to −80°C and kept at this temperature for 5 min, after which they were reheated again to 180°C at a heating rate of 10°C/min (second scan). T_g defined in this study was obtained from the second scan to assure reproducible thermograms free from thermal history effects.

Dynamic mechanical analysis

The viscoelastic properties (storage modulus, loss tangents, and complex viscosities) of the PSAs were determined using RDA III (Rheometric Scientific, in the Reliability Assessment Center of Chemical Materials, Korea Research Institute of Chemical Technology) in the 8 mm parallel plate mode utilizing a temperature sweep over the range from −80 to 130°C at constant strain (0.05%) and frequency (1 Hz). The gap of parallel plates was about 1 mm.

Probe tack

The probe tack was tested using a Texture Analyzer (Micro Stable Systems, TA-XT2i) with a 5-mm diameter stainless steel cylinder probe. The measurements were carried out at a separation rate of 60 mm/min under a constant pressure (100 gf) and a dwell time (1 s.). In the debonding process, the probe tack results were obtained at the maximum debonding force.

180° Peel test

The stainless steel substrate was cleaned with acetone. Then, the PSA specimen was pressed onto the stainless steel substrate using two passes of a 2 kg rubber roller and stored at room temperature for over 12 h. The 180° peel strength of the PSA specimens was measured after being coated onto the polyester film. The cross-head speed was 300 mm/min at room temperature. The average force in the debonding process was the peel strength.

Shear adhesion failure temperature

The shear adhesion failure temperature (SAFT) indicates the resistive ability under a constant shear load at an elevated temperature. The specimen was pressed onto a stainless steel substrate by a 2 kg rubber roller. The load attached to the specimen was 1 kg and the heating rate was 0.4°C/min. The SAFT results indicated the temperature at which the bonding failed.

RESULTS AND DISCUSSION

Viscoelastic properties

Viscoelastic materials like PSAs exhibit a combination of elastic and viscous behavior. Generally, PSA viscoelastic properties refer to the time and temperature dependence of mechanical behaviors such as

TABLE II
Characteristics of H-DCPD Resins

Trade name	Softening point (°C)	T_g by DSC (°C)	Molecular weight
SU90	85–95	39.1	450
SU110	110–115	64.3	510
SU130	126–135	75.4	700
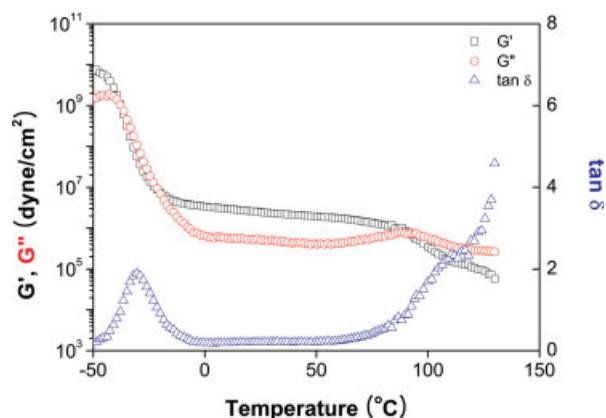
Figure 1 Viscoelastic property–temperature curves of PSA (Kraton : SU110 = 7 : 3). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 3 Loss modulus–temperature curves of PSA as a function of tackifier content (Kraton : SU110). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tack, peel strength, and holding power. The PSA performance involves both the bonding and debonding, and these phenomena reveal different behaviors as a function of temperature or frequency.

Figure 1 shows the viscoelastic behavior of one sample based on Kraton copolymer and tackifier as a function of temperature. At low temperature, PSA is in the glassy state and is too brittle and stiff to bond to the substrate. As the temperature increases, the storage modulus drops near T_g and tan δ peaks. The general PSA shows a rubbery plateau region at room temperature. The plateau modulus is related to the molecular weight between entanglements. At higher temperature, the PSA sample starts to melt and enters into the terminal region. This region is important in the processing of hotmelt PSA by influencing the properties of blending, flow property, open time, and set time.

Figure 2 Storage modulus–temperature curves of PSA as a function of tackifier content (Kraton : SU110). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

We measured the storage modulus (G'), loss modulus (G''), and tan δ over the range of temperature. The results presented in Figure 2 show that the storage modulus is related to the tackifier content of DCPD. At around −50°C, the storage modulus is too high to bond another substance. The variation of T_g is related with the tackifier content. The T_g of PSA show the increasing tendency as tackifier content increase. And storage modulus at plateau region drops as tackifier content increase. Tobing and Klein investigated relation molecular parameter and adhesive performance of acrylic PSAs.[5] Entanglement molecular weight (M_e) is one of the most critical molecular parameters related to PSA performance. The tackifier caused low shear holding power because of the lack of the entanglement, but increased tack and peel strength because of viscoelastic energy dissipation and more in intimate contact with substrates.

Figures 3 and 4 show the curves for loss modulus and tan δ, respectively. SIS block copolymers generally have two T_gs of isoprene and styrene. Since SIS block copolymers are microphase-separated materials, they have T_g near −50°C of the isoprene phase and at 100°C of the styrene domain. In Figure 3, the T_g of isoprene is prominent but that of styrene is not obviously revealed. This phenomenon is due to the small amounts of styrene in PSA. Chu tested the viscoelastic properties of PSA based on block copolymer, and suggested that styrene's T_g of PSA based on block copolymer is not revealed in thermal analysis for styrene content less than 14%.[6] Nevertheless, the loss modulus between 70 and 100°C showed little peaks related to the styrene domain. In Figure 4, the curve shows a sharper slope from 70 to 100°C with increasing tackifier content. On the basis of previous data, the H-DCPD resins are miscible with both rubbery phase and styrene domain.
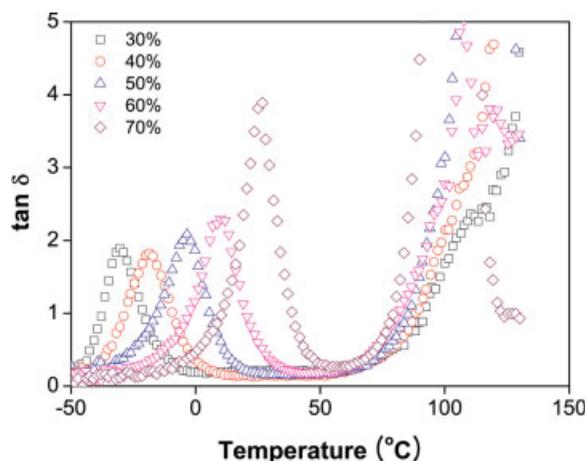
Figure 4 The tan δ–temperature curves of PSA as a function of tackifier content (Kraton : SU110). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 6 The tan δ–temperature curves of PSA as a function of T_g of tackifier. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Dynamic mechanical analysis (DMA) is an efficient method to characterize the degree of miscibility between polymer and tackifier. A compatible tackifier with midblock affects T_g of midblock, that with endblock affects T_g of styrene endblock, and that with midblock and endblock affects T_g of both phases. Miscibility also affects the plateau modulus according to the compatible phase of the block copolymer.[7] H-DCPD resin sharply increases the T_g of isoprene, and has little connection with the styrene domain. Though the miscibility with styrene domain is low, the H-DCPD resin is miscible with both midblock (major) and endblock (a little).

Figure 5 shows the storage modulus curves for the Kraton/tackifier at various T_g (50/50). Tackifier content and molecular structure are fixed, but the T_g of the tackifier varies. With increasing T_g of tackifier, the T_g of PSA increases (Fig. 5). Though the tackifier content is relevant to the T_g of PSA and plateau modulus, the T_g of the tackifier is related with the T_g of PSA, but the relation with the plateau modulus is slight. The plateau modulus depends on the entanglement of molecular chains. The T_g of the tackifier has less connection to the entanglement of chains, in contrast to the tackifier content.[5]
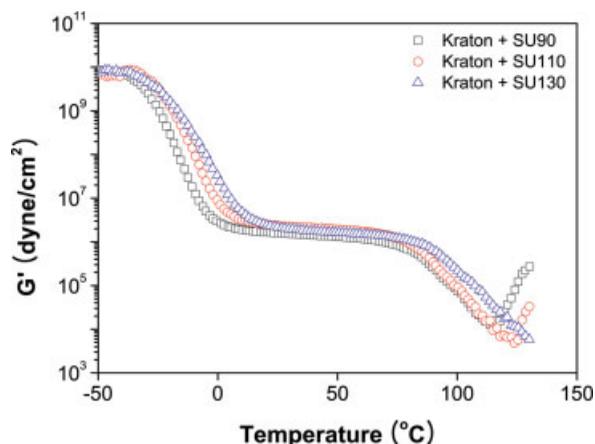
In Figure 6, tan δ indicates the rigidity of the materials. The shifted peak to high temperature shows that the T_g of PSA increases as a function of the T_g of tackifier, and the height of the peak is decreasing as T_g of tackifier increase. The smaller peak height demonstrates that the materials have more elastic property, and less mobility of molecular chains. The molecular weight of SU90, SU110, and SU130 is 450, 510, and 700, respectively, according to data sheet from Kolon Chemical. The high molecular weight of the tackifier interrupts the movement of chains. Therefore, the T_g increases and the height of the peak decreases with increasing tackifier T_g.

Comparison of T_g by DSC and theoretical calculation

PSA properties are known to depend on the T_g of PSA. The T_g of PSA can be measured by various methods such as dilatometry, DSC, and DMA. In this study, the T_g of PSAs was measured by DSC, and compared with the calculated T_g of PSA by Fox equation[8] and Gordon–Taylor equation.[9]

The T_g-composition data can be represented by the Fox equation or the Gordon–Taylor equation. Figure 7 compares the T_g measured by DSC and DMA

Figure 5 Storage modulus–temperature curves of PSA as a function of T_g of tackifier. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
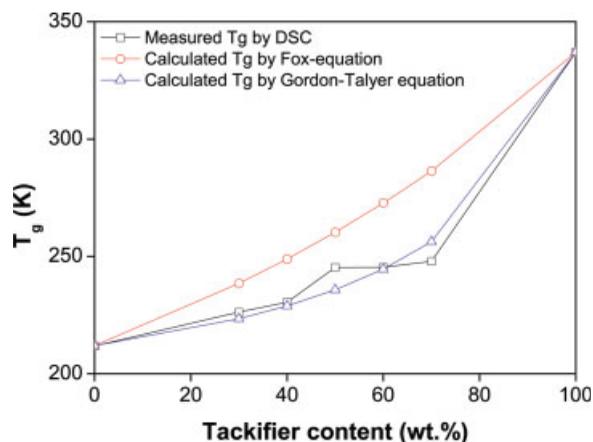
Figure 7 Comparision of T_g between T_g by DSC and T_g calculated by Fox-equation and Gordon–Talyor equation ($\kappa = 0.2$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

with that calculated by the Fox and Gordon–Taylor equations.[10]

The Fox equation is presented below:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2}$$

where T_g is the T_g of PSA, w_1 is the Kraton weight fraction, w_2 is the SU110 weight fraction, T_{g1} is the T_g of Kraton (211.9 K), and T_{g2} is the T_g of SU110 (337 K).

The T_g for hotmelt PSAs calculated according to the Fox equation may yield different results. It has been described that many miscible blend systems exhibit phase separation upon heating, caused by the existence of a lower critical solution temperature. This incompatibility caused by heating may influence the T_g of PSAs.[11]
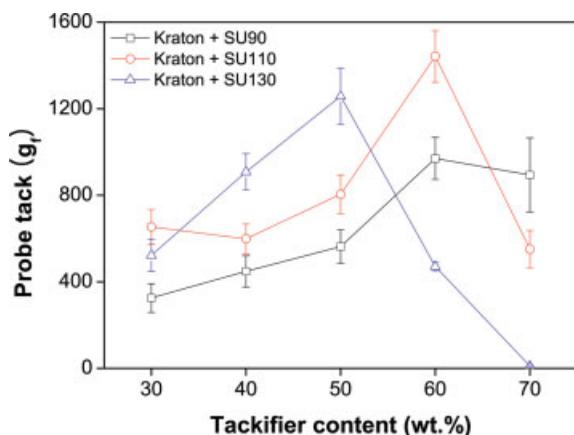
Figure 8 Probe tack of Kraton blends as a function of tackifier content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
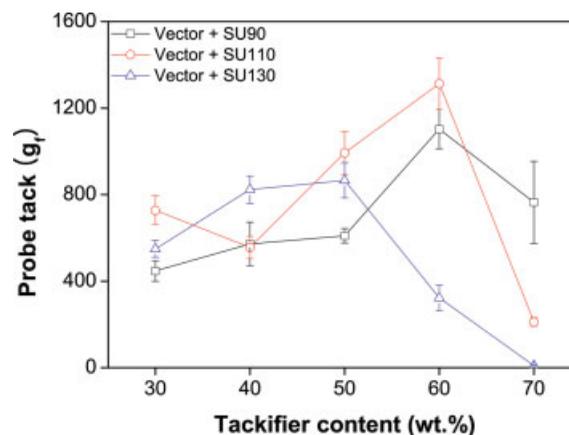
Figure 9 Probe tack of Vector blends as a function of tackifier content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The Gordon–Taylor equation[8] is represented by:

$$T_g = (w_1/T_{g1} + kw_2/T_{g2})/(w_1 + kw_2)$$

T_g is the T_g of PSA, w_1 is the Kraton weight fraction, w_2 is the SU110 weight fraction, T_{g1} is the T_g of Kraton (211.9 K), T_{g2} is the T_g of SU110 (337 K), and κ is the adjusting parameter.

The Gordon–Taylor equation provides a significantly better fit to the DSC data than the Fox equation. The primary reason is that the solid resin is denser than the other components and has a higher T_g than the other components. Therefore, the Gordon–Taylor equation predicts a lower T_g than the Fox equation does, and gives better agreement with the experimental measurements.[12] The adjusting parameter (κ) is related to the degree of curvature of the T_g-composition diagram. The value of κ gives a qualitative measure of the degree of interaction between components in the blend, that is, the higher the value of κ, the higher the degree of interaction.[13]

Probe tack

The probe tack is the major property of the characteristics of PSAs. Relevant experiments are essential to clearly understand the role of various molecular, experimental, or topological parameters on the tack properties of PSAs.[14]

PSA can be made by blending an elastomer and tackifier which has a low molecular weight, so tack is very different according to the tackifier content. Figure 8 is the plot of probe tack versus tackifier content for Kraton blends, and Figure 9 is the tack results for Vector blends. All these series of blends have a maximum peak at 50–60% tackifier resin content. At low tackifier content, the probe tack of PSA is low because of low cohesion. At excessively high
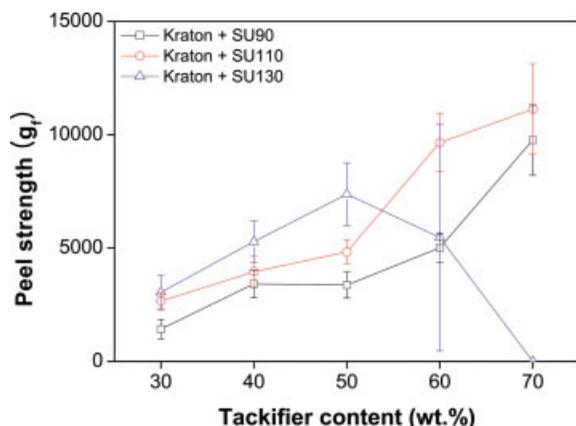
Figure 10 Peel strength of Kraton/tackifier as a function of tackifier content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tackifier content, PSA is too rigid to bond to the surface of the stainless steel probe, so the tack at both low and high tackifier content is relatively low.

Many researchers explained the change in tack properties with different tackifier content by the formation of a two-phase system.[15–17] At low tackifier content, resin is completely soluble in elastomer. Then, the elastomer is saturated with resin and the second phase with resin develops. Since the second phase has a lower viscosity than the elastomer phase, the tack property is raised. The maximum peak of probe tack indicated that the second phase had developed until the maximum resin content became soluble with the elastomer phase. Further increases in tackifier content caused the phase inversion in the matrix from the elastomer phase to the resin phase. The matrix phase with resin had no tack property and wettability.

The tackifier contents which showed the maximum peak varied with the T_g of the tackifier. PSA with a high T_gs tackifier shows a peak at lower tackifier content in Figures 8 and 9. The tackifier with high T_g, such as SU130, has a higher molecular weight than the others. Such a high-molecular-weight tackifier interrupts the mobility of PSA more than a low-molecular-weight tackifier does. Therefore, the secondary resin phase can comprise a lower content of tackifier with high T_g.

Peel strength

The peel strength for the blends of Kraton blends is shown in Figure 10, and the peel strength for PSA based on Vector elastomer is shown in Figure 11. The peel strength of both Kraton and Vector blends generally increased with increasing tackifier content. The tackifier provides the necessary flow property to PSA. As the tackifier content increases, PSA has

sufficient flow ability to wet a substrate. The peel strength gradually increases with increasing tackifier content. At tackifier content in the region of 30–50%, PSA with high T_g tackifier showed high peel strength. The addition of high T_g tackifier caused the loss of deformability, but gave high cohesion to PSA.

At high tackifier content of 60–70%, the peel strength shows unstable tendency. This behavior is a stick-slip behavior observed in Figures 10 and 11, which increased the deviation value of the peel strength. The stick-slip behavior occurred because PSA is brittle at high tackifier content.[18] A rapid drop in peel strength was observed for 70% tackifier content in Kraton/SU130(3/7), Vector/SU110(3/7), and Vector/SU130(3/7). First of all, PSA with high tackifier content showed the lowest peel strength in all blends. In Figures 8 and 9, these blends showed a probe tack lower than that of the others because of the phase inversion between elastomer and resin. Hence, the PSA samples did not become attached to the substrates.

The peak location of peel strength shifts to lower tackifier content with increasing tackifier content in Figures 10 and 11. This behavior is shown in miscible blends. The increasing T_g of PSA due to the tackifier affects the location of the peak. The shift in the peak location of the peel strength was observed in not only this article, but also in previous studies.[19,20] The peel strength in PSA made from NR and tackifier showed the peak shift with pulling rate,[19] and also with tackifier content.[20]

Shear adhesion failure temperature

Shear adhesion failure temperature (SAFT) determines the upper working limit temperature of a tape under static shear load. The SAFT results of Kraton and Vector blends are shown in Figures 12 and 13.
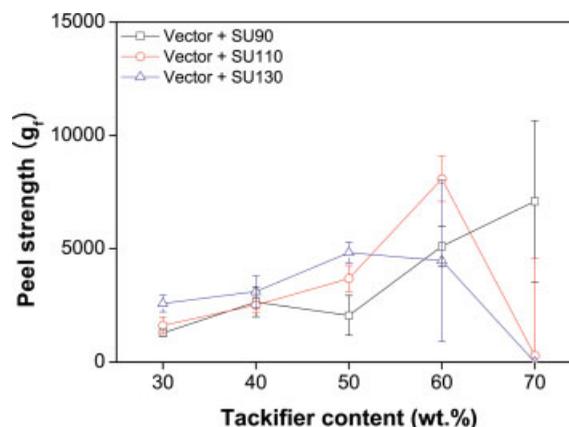
Figure 11 Peel strength of Vector/tackifier as a function of tackifier content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The SAFT values of the Vector blends were higher than those of the Kraton blends on the whole. The Vector polymer is an SIS triblock copolymer, whereas the Kraton polymer is an SIS triblock copolymer with 15% diblock content. Because of the diblock, the SAFT results showed different behavior. Diblock copolymer makes semicontinuous network in contrast with the continuous network by triblock. Tobing and Klein showed the comparison between acrylic emulsion and acrylic solvent PSA.[5] The emulsion showed lower shear holding power than that of solvent PSA because of polymer network difference. This result suggests that the diblock content is related to the viscoelastic properties in the low frequency region.

Gilbert et al. investigated the rheological properties of hotmelt PSAs based on styrene–isoprene copolymer.[21] At the same styrene content in the SIS copolymer, the storage modulus in the terminal zone tended to decrease with increasing diblock content in the blend, and the plateau modulus of SIS with diblock was lower than that of pure SIS. Nakajima et al. suggested that to determine which viscoelastic properties are related to SAFT, the first step was to examine the crossover temperature.[22] Crossover temperature is the critical temperature at which the viscous response (G'') becomes dominant over the elastic response (G'). However, the crossover temperature alone is insufficient for analysis of SAFT because the SAFT behavior belongs to the large deformation that is different from the very small deformation of DMA.

CONCLUSIONS

It is important to investigate the degree of miscibility between SIS block copolymer and tackifier, and this degree was measured in the present article by visco-

Figure 13 SAFT of Vector/tackifier blends as a function of tackifier content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

elastic properties. The H-DCPD resins are miscible with the isoprene phase of SIS copolymer, and also show a little miscibility with styrene domain. For the miscible blends, the T_g of PSA showed increased tendency with increasing tackifier content and the plateau modulus dropped with increasing tackifier content.[23] The T_g and molecular weight of the tackifier exerted a greater effect on the T_g of PSA than that of the plateau modulus.

The tackifier content, molecular weight, and T_g markedly affected the PSA performance. The probe tack increased with increasing tackifier content, but was reduced at high tackifier content. The peak location of the maximum probe tack value shifted toward a low tackifier content according to the T_g of the tackifier. The effect of tackifier content on the peel strength showed similar behavior to that of the probe tack. At high tackifier content, peel strength showed stick-slip behavior due to the rigidity of PSA. SAFT showed good heat resistance at a tackifier content of 40–60%, while Vector blends without diblock showed better SAFT results than Kraton blends did.

Figure 12 SAFT of Kraton/tackifier blends as a function of tackifier content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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