

The aromatic hydrocarbon resins with various hydrogenation degrees Part 2. The adhesion and viscoelastic properties of the mixtures of resins and block copolymers

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Abstract

The adhesion and viscoelastic properties, and the order-to-disorder transition temperature (T_{ODT}) were investigated for the mixture of polydiene-based block copolymers/hydrogenated aromatic resins (HRs) with various degrees of hydrogenation (DHs). The block copolymers employed were commercially available ones: (1) polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) copolymer (Kraton D1102; Shell Development Co.); and (2) polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) copolymer (Vector 4211; Dexco Co.). HRs with various DHs were synthesized via the hydrogenation of an aromatic C-9 hydrocarbon resin by monitoring the amounts of hydrogen added and the reaction times.

We found that viscoelastic properties, such as plateau modulus and glass transition, depend predominantly on the miscibility between polystyrene (PS) block and HRs as well as that between polybutadiene (PB) (or polyisoprene (PI)) block and HRs, which in turn are strongly affected by the DH in an HR. At lower values of DH, HRs are associated with PS end block; thus tack properties become negligible, although the plateau modulus increases greatly.

The tack properties depended remarkably on the miscibility between HRs and elastomeric mid-block in the block copolymers. With increasing DH, tack properties of the mixture of Kraton D1102/HRs increased up to DH = 0.7, reached a maximum at DH = 0.7 and finally decreased. However, tack properties of the mixture of Vector 4211/HRs increased steadily up to DH = 0.951 which is the largest value in this study. This is because the miscibility between PI block and HR increases steadily with increasing DH, which is explained by the difference in the solubility parameter.

When the weight fraction of HRs is less than 0.5, the T_{ODT} s of the mixture having either Kraton D1102 or Vector 4211 and HR always decreased with the increasing amount of HR due to the lower molecular weight of HR. Interestingly, the T_{ODT} s of both the mixture systems was the smallest at DH ~ 0.3 when the weight fractions of HR in the mixture were 0.1 and 0.3. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Hydrogenated C-9 resin; Tack properties; Viscoelastic properties

1. Introduction

Various kinds of elastomers based on polydiene-based block copolymers, e.g. polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) copolymer and polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) copolymer, have been widely used for pressure-sensitive adhesives (PSAs) and hot-melt adhesives. Owing to poorer tack properties of elastomers themselves, ‘tackifying resins’, for instance, aliphatic C-5 resins, aromatic C-9 resins, hydrogenated

derivatives of C-5 and C-9 resins, and rosin derivatives, are added to elastomers [1]. Readers are referred to the recent monograph [2] in order to understand in detail tackifying resins and PSAs.

According to ASTM D1878, tack in PSAs is defined by “the property of a material that enables it to form a bond of measurable strength immediately upon contact with another surface”. The tack of a mixture of a block copolymer and a tackifying resin depends predominantly on the wettability onto the substrate and the debonding force from the substrate. The wettability would be a function of the surface roughness and plateau modulus of the mixture. The smaller the plateau modulus ($G_{N,mixture}^0$) of the mixture of a block copolymer and a tackifying resin, the easier the blend wets

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Table 1
The molecular characteristics of block copolymers employed in this study

Sample code	Block Molecular weight ($\times 10^3$) ^a	M_w/M_n ^b	wt% of PS block ^c	Microstructure of diene block (mol%) ^c			
				1,2	3,4	<i>trans</i> -1,4	<i>cis</i> -1,4
Kraton D1102	9.0S-45B-9.0S	1.20 ^d	28.6	9.9	–	42.9	47.2
Vector 4211	11.3S-52.4I-11.3S	1.16	30.0	–	7.4	23.7	68.9

^a Weight-average molecular weight determined by a lower angle laser light scattering apparatus and nmr spectroscopy.

^b Determined by GPC.

^c Determined by ¹H NMR spectroscopy.

^d The broad molecular distribution is due to the existence of about 20 wt% of uncoupled diblock.

on the substrate. According to the Dahlquist criterion [3], $G_{N,mixture}^0$ should be less than approximately 3×10^5 Pa in order to exhibit good tack. However, the lower plateau modulus is not alone sufficient for exhibiting higher tack, because the debonding force would be very small for this case. Thus, one must have PSAs showing a larger dissipating energy at the debonding step.

It has been reported that the tack properties and the performance of adhesive in a PSA depend upon the bulk viscoelastic properties of PSA [4–7] as well as the miscibility between the constituent components of PSA [8–13]. According to Akiyama and coworkers [8–10], the most favorable miscibility between PB copolymer consisting of 1,2 and 1,4 microstructures and terpene resins (or their hydrogenated ones) was observed when the mole fraction of 1,2-microstructure in the PB copolymer was ~ 0.5 . Fujita et al. [11–13] and Hayashi et al. [14–16] reported the effects of miscibility on the peel strength and the tack property of natural rubber, and acrylic based PSAs, respectively. The miscible systems exhibit higher peel strength and tack value compared with immiscible ones.

The miscibility between an elastomer and a tackifying resin can be expressed with the interaction parameter depending on temperature and molecular weight. When tackifying resins with different chemical structures and different molecular weights are employed in PSAs, each effect on the miscibility, which in turn affects tack properties of PSAs, is not independently investigated. In order to investigate each effect independently, tackifying resins having different molecular structures but the same molecular weight (or vice versa) can be selected. One candidate of this purpose is the partially hydrogenated aromatic resins with various degrees of hydrogenation (DHs). In this situation, the miscibility between a block copolymer and a resin is varied with DH. Similar approach was carried out very recently by Hashimoto et al. [17] who employed the mixture of an SI block copolymer and another block copolymer consisting of PS block and partially hydrogenated PI (HPI) or fully hydrogenated PI (PEP). As DH increased, the miscibility between PEP block and HPI increased; thus the mixture does not show a macrophase separation.

In the former paper [18], we investigated the miscibility of hydrogenated aromatic C-9 hydrocarbon resin (HR) with

PB and PS homopolymers. It was found that an HR has best miscibility with PB homopolymer at a DH ~ 0.7 and that the tack properties exhibited the largest, which suggests that tack depended directly upon the miscibility between HR and PB. In this paper, we have investigated in detail adhesion properties of the mixtures of SBS/HRs and SIS/HRs with various DHs, and these properties are discussed with viscoelastic properties of the mixtures. Also, the order-to-disorder transition temperature of those blends was investigated.

2. Experimental section

2.1. Materials

The block copolymers used in this study were commercially available ones: (1) SBS copolymer (Kraton D1102; Shell Development Co.); and (2) SIS copolymer (Vector 4211; Dexco Co.). The weight average molecular weight (M_w) and the molecular weight distribution (M_w/M_n) were determined by low angle laser light scattering method, and gel permeation chromatography (GPC, Waters Co.) on the basis of the calibration curve made by polystyrene standards, respectively. The molecular characteristics of the block copolymers are summarized in Table 1. The weight fraction of the PS block in two block copolymers and microstructures of polydiene blocks were measured by nuclear magnetic resonance spectroscopy (Bruker DRX 500). It is seen in Table 1 that the weight fraction of PS block in Kraton D1102 is almost the same as that in Vector 4111.

The details for the molecular characteristics of C-9 resin and the hydrogenation reaction of C-9 resin were described in the former paper [18].

2.2. Rheological properties

The samples were prepared by dissolving a predetermined amount of a block copolymer and an HR in toluene in the presence of an antioxidant (Irganox1010, Ciba-Geigy Group). The solvent was slowly removed in a fume hood at room temperature for a week, then completely removed in a vacuum oven at 65°C for three days.

Dynamic temperature sweep experiments from ca. -110 to 140°C at a heating rate of 3°C/min were performed using

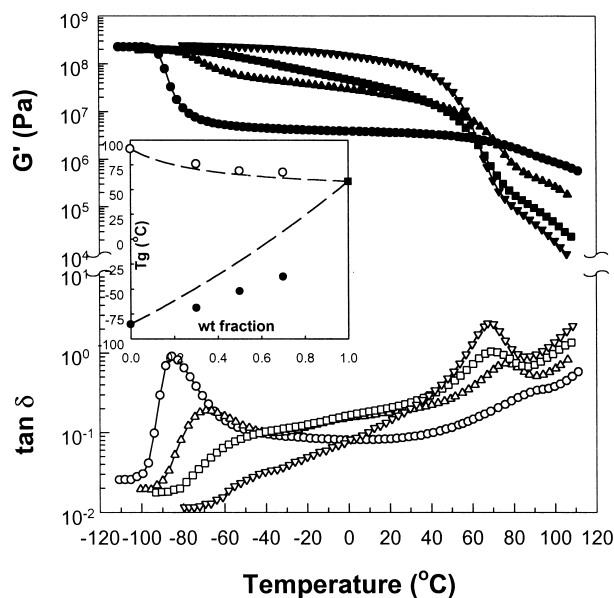


Fig. 1. Plot of $\log G'$ (filled symbols) and $\tan \delta$ (open symbols) versus temperature for Kraton D1102/neat C-9 resin. Weight fractions of Kraton D1102 in the mixture are: (●,○) 1.0; (▲,△) 0.7; (■,□) 0.5; and (▼,▽) 0.3.

a Rheometrics Dynamic Spectrometer (RDS-II, Rheometrics) in the parallel plates mode of 8 mm diameter. The angular frequency (ω) and strain amplitude (γ_0) were 10 rad/s and 0.3–3%, respectively. The sample gap between the plates was ca. 1.5 mm.

Using an Advanced Rheometrics Expansion System (ARES, Rheometrics) in the parallel plate mode of 25 mm diameter, the order-to-disorder transition temperature (T_{ODT}) for the mixtures of Kraton D1102/HRs and Vector

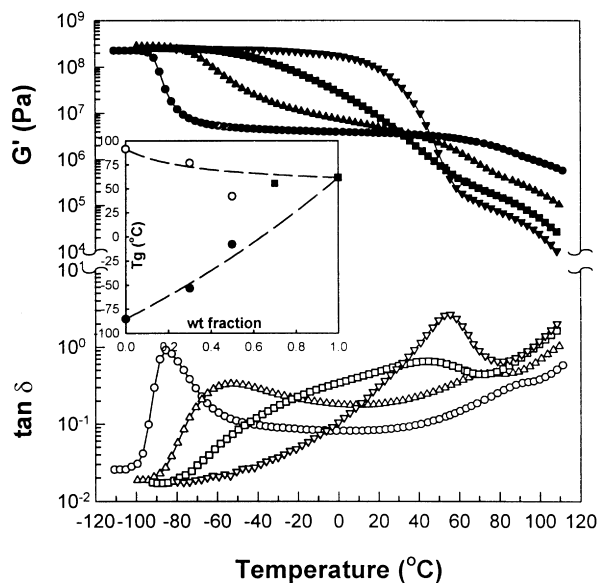


Fig. 2. Plot of $\log G'$ (filled symbols) and $\tan \delta$ (open symbols) versus temperature for Kraton D1102/HR-298. Weight fractions of Kraton D1102 in the mixture are: (●,○) 1.0; (▲,△) 0.7; (■,□) 0.5; and (▼,▽) 0.3.

4211/HRs is determined as the temperature where a rapid drop was observed in storage modulus (G') during heating run at a heating rate of 1°C/min, $\omega = 0.2$ rad/s and $\gamma_0 = 5\%$. These conditions lie in the linear viscoelastic regime.

2.3. Adhesion properties

The adhesive layer consisting of various blend compositions of a block copolymer and a tackifying resin was prepared by solution coating (50wt% in solid in toluene) onto a poly(ethylene terephthalate) backing film having a thickness of 52 μm , followed by the quick removal of the solvent using a convection oven at 100°C for 5 min. The complete removal of the solvent was carried out in a fume hood at room temperature for 5 days. The thickness of the adhesive layer is 150 μm for the probe tack test and 20 μm for the peel adhesion test. According to ASTM D2979, we employed the probe tack tester (TE6002, Sangyo Co.), which is regarded as being one of the most reliable methods as described in the former paper [18].

Peel strength was evaluated by measuring the tensional force required for the removal of the PSA film toward 180° from an adherent according to ASTM D903, PSTC-1. (Pressure-Sensitive Tape Council). This experiment was performed with the 25 mm width of a specimen at the cross-head speed of 300 mm/min. The sample for measuring peel strength was annealed at 80°C for 10 min after it was applied to the stainless steel substrate with a surface roughness height of 0.05 μm (SUS 304) using a standard hand-roller of 2 kg. All experiments were carried out at 23 \pm 0.5°C and a relative humidity of ca. 40%.

2.4. Synchrotron small angle X-ray scattering

The SAXS measurements with synchrotron radiation sources were conducted at the 3C2 beam line in the Pohang Light Source (PLS), Korea [19,20]. The primary beam was monochromatized with a couple of Si(111) single crystals at a wavelength of 0.1598 nm (the photon energy of X-ray is 7.76 keV), and then it was focused on a detector plane by a bent cylindrical mirror. An one-dimensional position-sensitive detector (Diode-Array PSD; Princeton Instruments Inc.; Model ST-120) with a distance of each diode of 25 μm was used. The sample thickness was 1 mm. After annealing a specimen having either Kraton D1102 or Vector 4211 and HRs at ca. $T_{ODT} - 40^\circ\text{C}$ for 10 min, SAXS profiles of the specimen were measured at various temperatures up to ca. $T_{ODT} + 30^\circ\text{C}$ during heating at a rate of 3°C/min.

The predetermined value of T_{ODT} of a specimen, which was measured by temperature sweep experiment of G' , as described in the previous section, was used as a reference. The exposure time at each measurement was 10 s. We subtracted the scattering intensity of an empty cell with two pieces of thin polyimide (Kapton) films from that of the samples by taking into account the transmittance of X-rays through the samples. A contribution of the thermal diffuse scattering (TDS) arising from the density fluctuations

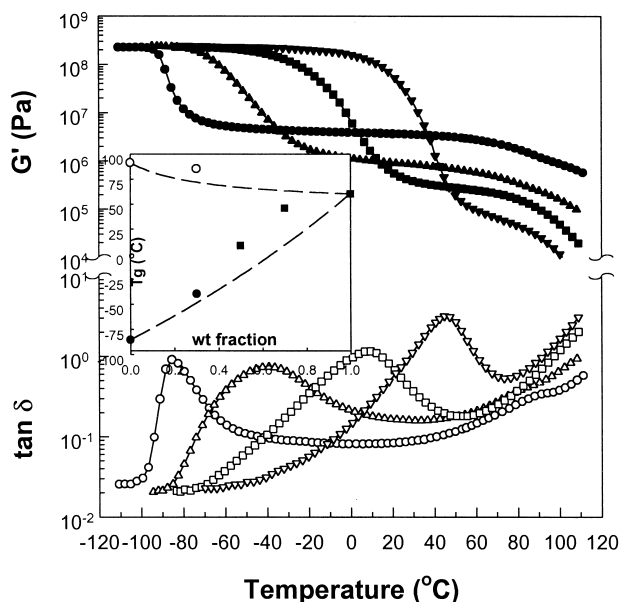


Fig. 3. Plot of $\log G'$ (filled symbols) and $\tan \delta$ (open symbols) versus temperature for Kraton D1102/HR-699. Weight fractions of Kraton D1102 in the mixture are: (●,○) 1.0; (▲,△) 0.7; (■,□) 0.5; and (▼,▽) 0.3.

was further subtracted. We approximated that the intensity at the high q region, where the scattering intensity is independent of q , is identical to the intensity level of TDS. Here, q is the magnitude of the scattering vector, $q = (4\pi/\lambda) \sin(\theta/2)$, where λ and θ are the wavelength of the X-rays and the scattering angle, respectively. The obtained scattering intensities were not converted to absolute units.

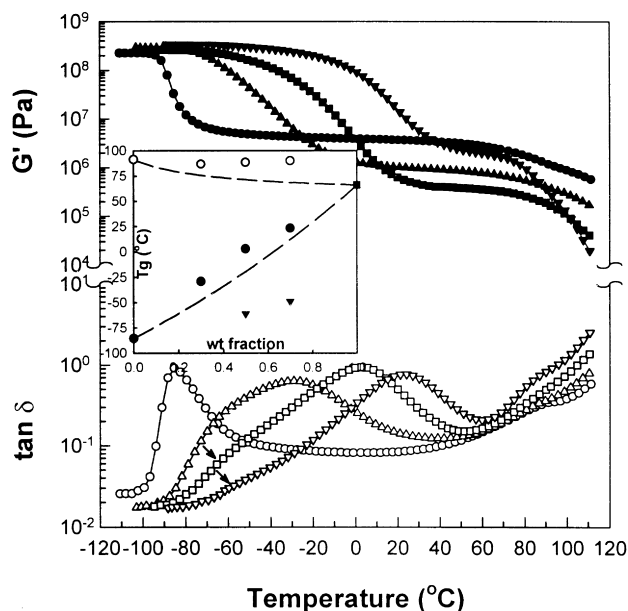


Fig. 4. Plot of $\log G'$ (filled symbols) and $\tan \delta$ (open symbols) versus temperature for Kraton D1102/HR-951. Weight fractions of Kraton D1102 in the mixture are: (●,○) 1.0; (▲,△) 0.7; (■,□) 0.5; and (▼,▽) 0.3.

3. Results and discussion

3.1. Viscoelastic properties for the mixtures of block copolymers and HRs

3.1.1. Kraton D1102/HRs

Temperature sweep experiments of $\log G'$ and $\tan \delta$ are given in Fig. 1 for the mixtures of Kraton D1102/neat C-9 resin. Those plots for Kraton D1102/HR-298, Kraton D1102/HR-699 and Kraton D1102/HR-951 systems are given in Figs. 2–4, respectively. The plateau modulus ($G'_{N,mixture}$) of each blend system was evaluated by the G' value at $\tan \delta_{min}$. However, when $\tan \delta_{min}$ was not clearly observed, $G'_{N,mixture}$ was taken as G' at $T = (T_{g,L} + T_{g,H})/2$. Here, $T_{g,L}$ and $T_{g,H}$, at which each $\tan \delta$ becomes a maximum, correspond to the glass transition of the mid-block phase and the end-block phase, respectively. The plots of $T_{g,L}$ and $T_{g,H}$ versus the amount of HR are added in the inset of each figure. Also, the predicted $T_{g,H}$ s are given as the upper dashed line in the inset, using the assumption that HRs were associated entirely with PS end-block in the block copolymer. The predicted $T_{g,L}$ s are given as the lower dashed line in the inset, using the assumption that HRs were associated entirely with PB mid-block in the block copolymer. The T_g of the mixture consisting of a block copolymer and a tackifying resin can be predicted by the Fox equation [21]:

$$1/T_{g,m} = w_a/T_{g,a} + w_b/T_{g,b} \quad (1)$$

where $T_{g,m}$, $T_{g,a}$, $T_{g,b}$ are the glass transition temperatures for the mixture and each constituent component, and w_a and w_b are the weight fractions of constituent components. For the calculation of $T_{g,L}$, w_a is the weight fraction of the PB (or PI) block in total rubberic phase and $T_{g,a} = T_g$ of PB (or PI), $T_{g,b} = T_g$ of an HR. Thus, $w_a = 1 - w_b$ is given by

$$w_a = 1/[1 + \rho_b(1 - \phi)/(\rho_a(1 - f)\phi)] \quad (2)$$

where ρ_a and ρ_b are the densities of PB (or PI) mid-block and HR, respectively; f the volume fraction of PS block in the block copolymer and ϕ is the volume fraction of a block copolymer in the mixture. The values of T_g of neat C-9 resin, HR-299, HR-699, and HR-951 were 58, 62, 61, and 66°C ($\pm 2^\circ\text{C}$), respectively.

It can be seen in Fig. 1 that for the mixture of Kraton D1102/neat C-9 resin, $G'_{N,mixture}$ increased with the increasing amount of neat C-9 resin. The $T_{g,L}$ corresponding to the PB block phase in the mixture was slightly shifted toward higher temperature, while the $T_{g,H}$ corresponding to the PS block phase in the mixture decreased gradually as the amount of neat C-9 resin increased. It is also seen in the inset of Fig. 1 that the experimentally obtained $T_{g,L}$ s deviated from the prediction given by Eq. (1), while the experimentally obtained $T_{g,H}$ s were close to the prediction. These results imply that the neat C-9 resin was more miscible with the PS block than with the PB block in Kraton D1102. In a former paper [18], we clearly showed that

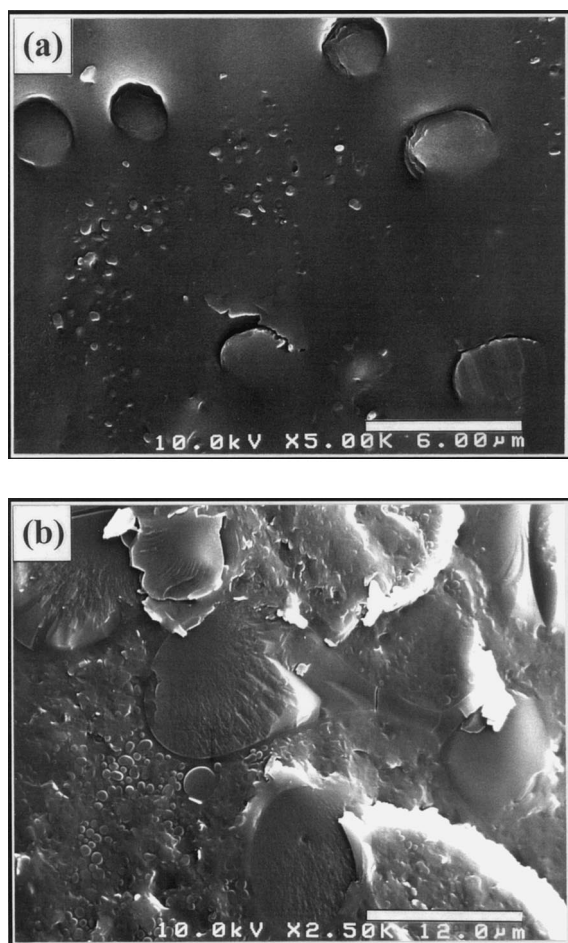


Fig. 5. Field emission SEM images for (a) (50/50)(wt/wt) Kraton D1102/HR-951 blend, (b) (30/70)(wt/wt) Kraton D1102/HR-951 blend.

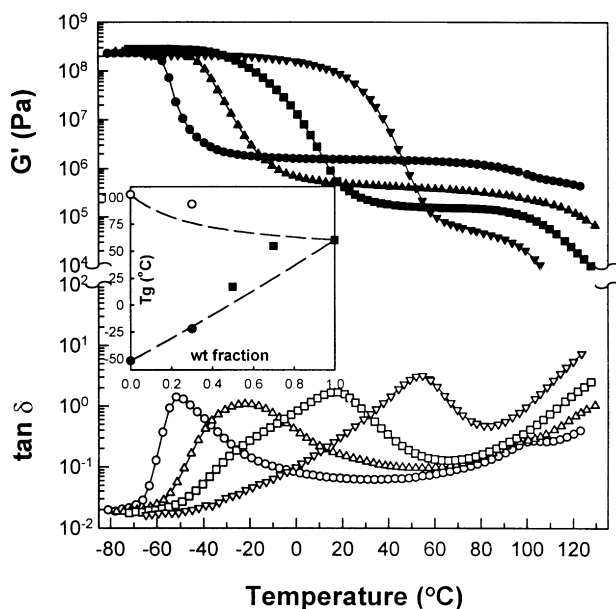


Fig. 6. Plot of $\log G'$ (filled symbols) and $\tan \delta$ (open symbols) versus temperature for Vector 4211/HR-699. Weight fractions of Vector 4211 in the mixture are: (●,○) 1.0; (▲,△) 0.7; (■,□) 0.5; and (▼,▽) 0.3.

neat C-9 resin was completely miscible with PS even if the molecular weight of PS was as high as three millions. However, the mixture of PB and neat C-9 resin showed a phase diagram with the upper critical solution temperature.

For Kraton D1102/HR-298 blend, $G_{N,mixture}^0$ increased with the increasing amount of HR-298 as given in Fig. 2, which is similar to the behavior of Kraton D1102/neat C-9 resin blend. For the 70/30 (wt/wt) Kraton D1102/HR-298 blend, $T_{g,L}$ and $T_{g,H}$ were shifted toward higher temperature and lower temperature compared with T_g s of PB and PS block. This suggests that HR-298 could be miscible with both the PB and the PS block in Kraton D1102 because of the low molecular weight of the PB block. But, from Ref. [18], the miscibility between HR-298 and PS was better than that between HR-298 and PB. For the 50/50 (wt/wt) Kraton D1102/HR-298 blend, two broad peaks in $\tan \delta$ were observed. However, when the amount of HR-298 was further increased to 70%, this blend exhibited only one single T_g . From the results given in Figs. 1 and 2, it is concluded that the miscibility between HR-298 and the PB block is better than that between neat C-9 resin and the PB block in Kraton D1102.

It can be seen in Fig. 3 for Kraton D1102/HR-699 blend that $G_{N,mixture}^0$ decreased with the increasing amount of HR-699, which is of an opposite trend to the Kraton D1102/neat C-9 resin and Kraton D1102/HR-298 systems. $T_{g,L}$ s of all compositions were shifted toward higher temperature over the range investigated. Also $T_{g,H}$ of the 70/30 (wt/wt) SBS/HR-699 blend was a little shifted towards lower temperature. But, $T_{g,H}$ of the blend with more than 50% of HR-699 in a blend was not detected. Interestingly, from the inset of Fig. 3, experimentally determined $T_{g,L}$ s were larger than the predictions. This is because of the fact that when the weight fraction of HR-699 in the mixture is larger than 0.5, micro-phase-separated PS domains do not exist anymore, as found by the SAXS measurement [22]. Thus, $T_{g,L}$ of the blend was affected by the presence of PS chains with higher T_g , implying that an increase in $T_{g,L}$ would be larger than the predicted value.

From Fig. 4, we noted that the addition of HR-951 decreased $G_{N,mixture}^0$ of the Kraton D1102/HR-951 blend with less than 50% of HR-951, but it increased with a further increase in the amount of HR-951. There are two possible reasons why the modulus of the mixtures increased with an increasing amount of tackifying resin: one is that the tackifying resin is miscible with the PS end-block in the block copolymer, as shown in Figs. 1 and 2, and the other is that the tackifying resin forms a macroscopically separated phase. From the inset in Fig. 4, two $T_{g,L}$ s are observed for the blends with more than 50% of HR-951 although the lower one marked by the arrow in $\tan \delta$ is not distinct. But, 50/50 (wt/wt) Kraton D1102/HR-951 blend showed clearly a macrophase separation, as shown in Fig. 5. The domain size of this blend was ca. $2 \mu\text{m}$, which is ca. 6 times smaller than that for 30/70 (wt/wt) Kraton D1102/HR-951

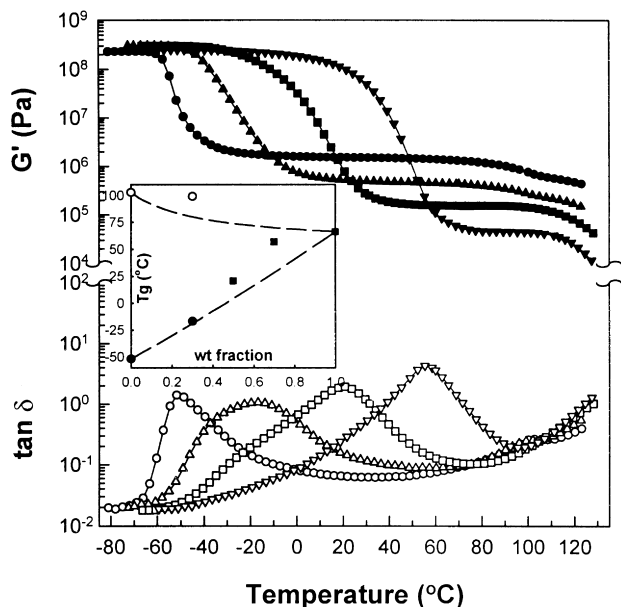


Fig. 7. Plot of $\log G'$ (filled symbols) and $\tan \delta$ (open symbols) versus temperature for Vector 4211/HR-951. Weight fractions of Vector 4211 in the mixture are: (●,○) 1.0; (▲,△) 0.7; (■,□) 0.5; and (▼,▽) 0.3.

blend. Thus, compared with the latter blend, some of HR-951 in the former would be associated with the PB block in Kraton D1102; thus $G_{N,mixture}^0$ is not increased drastically. But, this value was 3.78×10^5 Pa, which is larger than that (2.69×10^5) of 50/50 (wt/wt) Kraton D1102/HR-699 (see Fig. 3). Further, $T_{g,H}$ s do not change with an increasing amount of HR-951. This implies that the miscibility between the PS block and HR-951 is quite poor compared with that between the PS block and HR-699. Also, the miscibility between the PB block and HR-951 is not good. As discussed in the former paper [18], the favorable interaction between PB and HR is not always increased with increasing DH, rather the most favorable miscibility between PB and HR is found at $DH \sim 0.7$. Therefore, for the Kraton D1102/HR-951 system, the miscibility between the PB block and HR-951 and that between the PS block and HR-951 is poor, although the miscibility of the former seems to be better compared with the latter system. Thus, macrophase separation occurred for this system, as shown in Fig. 5. Here, we just demonstrate the existence of macrophase separation using a field emission scanning electron microscope (Hitachi S4200). The details of the microdomain structures in the matrix taken by TEM are discussed in a separate paper [22].

On the basis of the results given in Figs. 1–4, it was concluded that the miscibility between HRs and the PS block in Kraton D1102 decreased steadily with the increasing DH, while the miscibility between HRs and the PB block increased up to $DH \sim 0.7$ but decreased with further increasing DH. This is in excellent agreement with the turbidity result demonstrated in Ref. [18].

3.1.2. Vector 4211/HR resin systems

Temperature sweep experiments of $\log G'$ and $\tan \delta$ are given in Figs. 6 and 7 for the mixtures of Vector 4211/HR-699 and Vector 4211/HR-951, respectively. The temperature sweep experiments of G' for the mixtures of Vector 4211/neat C-9 resin and Vector 4111/HR-298 blend are not shown here due to the space limit. But, the $G_{N,mixture}^0$ of two mixtures increased with an increasing amount of neat C-9 resin or HR-298. The behaviors of G' and $\tan \delta$ for the mixtures of Vector 4211/neat C-9 resin, and Vector 4211/HR-298 blend are similar to those for Kraton D1102/neat C-9 resin (Fig. 1), and Kraton D1102/HR-298 (Fig. 2), respectively. Also, $G_{N,mixture}^0$ of Vector 4211 is about 3 times lower than that of neat Kraton D1102, because G_N^0 of PI homopolymer is about 3 times lower than that of the PB homopolymer and very similar volume fractions of the PS block between the two block copolymers. However, for mixtures of Vector 4211/neat C-9 resin as the amount of neat C-9 resin increased, $T_{g,LS}$ was hardly shifted toward high temperature, while $T_{g,H}$ was shifted gradually toward lower temperature. These results led us to conclude that the miscibility between the PB block and neat C-9 resin is better than that between the PI block and neat C-9 resin. This is attributed to the fact that the difference in the solubility parameter (δ) in $(\text{J}/\text{cm}^3)^{1/2}$ between PI and neat C-9 is 2.67, which is larger than that (1.67) between PB and neat C-9. Previously, using Hoy's group contribution method [23], we reported that $\delta = 18.29$ for PB, $\delta = 17.29$ for PI, $\delta = 19.35$ for PS, $\delta = 19.96$ for neat C-9 resin, and $\delta = 17.85$ for HR-1000, respectively [18]. Notice that the values of δ for PB and PI are estimated using the linear combination of each microstructure in PB and PI. Further, the miscibility between the PS block in Kraton D1102 and neat C-9 resin seems to be better than that between the PS block in Vector 4211 and neat C-9 resin, because the M_w of PS block in the former is 1.2 times smaller than that in the latter (see Table 1).

It can be seen in Fig. 6 for Vector 4211/HR-699 blend that $G_{N,mixture}^0$ decreased with increasing amount of HR-699. $T_{g,LS}$ were shifted toward higher temperature over the range investigated. But, $T_{g,H}$ of 70/30 (wt/wt) blend composition was a little shifted toward lower temperature, but no peak was detected when the weight fraction of HR-699 in the mixture was larger than 0.5. This behavior is very similar to the Kraton D1102/HR-699 system (Fig. 3). Therefore, when DH is about 0.7, the miscibility between HR and PS block in Vector 4211 is much poorer than that between HR and PI (or PB) block.

From Fig. 7, $G_{N,mixture}^0$ gradually decreased with increasing amount of HR-951, which is a similar behavior in Vector 4211/HR-699 blend; also, the T_g behavior of Vector 4211/HR-951 blend was very similar to that of Vector 4211/HR-699 blend. However, $T_{g,H}$ of 70/30 (wt/wt) Vector 4211/HR-951 blend was a little higher than that of 70/30 (wt/wt) Vector 4211/HR-699 blend, because the miscibility between PS block and HR decreased with increasing DH.

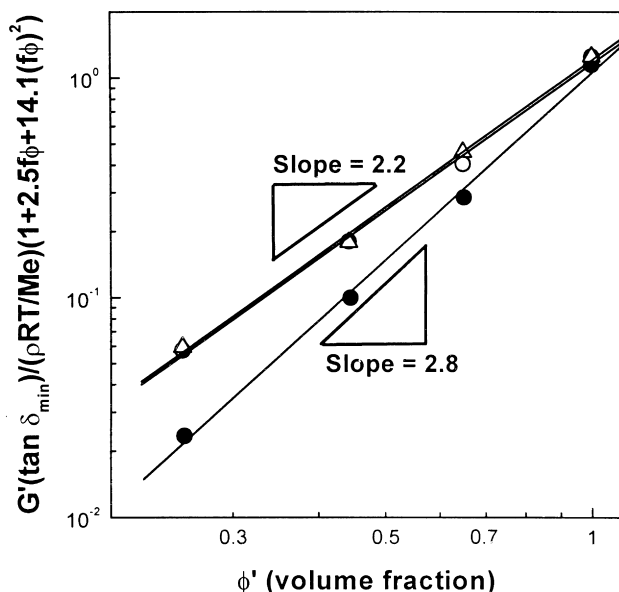


Fig. 8. Plots of $G'(\tan \delta_{\min})/(\rho RT/M_e)(1 + 2.5f\phi + 14.1(f\phi)^2)$ versus the volume fraction of the polydiene block (ϕ') in the mid-block associated phase for the mixtures of (●) Kraton D1102/HR-699; (○) Vector 4211/HR-699; (△) Vector 4211/HR-95.

This behavior is quite different compared with Kraton D1102/HR-951 (see Fig. 4), where the macrophase separation occurred when the weight fraction of HR-951 in the mixture was higher than 0.5. This different behavior between Vector 4211 and Kraton D1102 is also explained by the solubility parameter difference between PI and HR-951 compared with PB and HR-951. In other words, the miscibility between PI and HR is gradually increased with the increasing DH; however, that between PB and HR

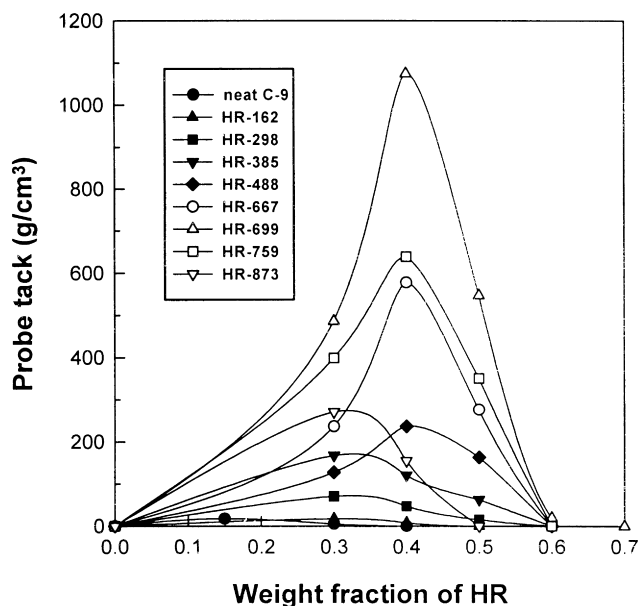


Fig. 9. Probe tack versus weight fraction of HR resins for the blends of Kraton D1102/HRs with various DHs.

exhibits a maximum at $DH \sim 0.7$. Also, the miscibility between PS and HR is gradually reduced with increasing DH.

It is noted from Figs. 6 and 7 that when the weight fraction of HR-699 (or HR-951) in the mixture is larger than 0.5, only a single T_g corresponding to $T_{g,L}$ is observed, and the experimental values of $T_{g,L}$ are higher than that predicted by the Fox equation. This is a similar phenomenon in the Kraton D1102/HR-699 system (see Fig. 3). As explained previously, this is because of the fact that when the weight fraction of HR-699 in the mixture is larger than 0.5, microphase-separated PS domains do not exist anymore, as found by the SAXS measurement [22]. Thus, $T_{g,L}$ of the blend was affected by the presence of PS chains with higher T_g , implying that $T_{g,L}$ would be larger than the predicted value shown in the inset.

Now, we consider $G_{N,mixture}^0$ of Kraton D1102/HR-699, Vector 4211/HR-699, and Vector 4211/HR-951 blend depending upon the volume fraction of the block copolymer (ϕ) in the mixture. The plateau modulus of the elastomeric phase $G_{N,mixture}^0$ in the mixture of SIS (or SBS) copolymer and a tackifying resin with the volume fraction of block copolymer ϕ can be predicted as follows. The polystyrene microdomains in the block copolymer may be regarded as a filler dispersed in a continuous elastomeric matrix, Holden [24] estimated $G_{N,block}^0$ for A-B-A triblock copolymer systems:

$$G_{N,block}^0 = (\rho RT/M_e)(1 + 2.5f + 14.1f^2) \quad (3)$$

where M_e is the entanglement molecular weight of polydiene block (PI or PB), ρ the density of the polymer, R the universal gas constant, and T is the absolute temperature. When a tackifying resin is regarded as a diluent, the plateau modulus of the mixture scales as [25]:

$$G_{N,mixture}^0 = (\phi')^\alpha (G_{N,block}^0)^\alpha \quad (4)$$

where $(G_{N,block}^0)^\alpha$ is the plateau modulus of the block copolymer in the presence of a tackifying resin and given by Eq. (3) when f is replaced by $f\phi$. The scaling constant α in Eq. (3) has a value between 2.25 and 2.5 [25]. Here, ϕ' is the volume fraction of the polydiene block in the mid-block associated phase, and is given by $\phi' = (1-f)\phi/(1-f\phi)$. When a clear plateau region in the temperature sweep experiment of G' is not observed, $G_{N,mixture}^0$ of the mixture can be determined by the G' value at the minimum value of the loss tangent ($\tan \delta_{\min}$) [26].

From the above two equations, $G_{N,mixture}^0$ is given by:

$$G_{N,mixture}^0 \approx G'(\tan \delta_{\min}) = (\phi')^\alpha (\rho RT/M_e) \times (1 + 2.5f\phi + 14.1(f\phi)^2) \quad (5)$$

In deriving Eq. (5), it is assumed that all of the tackifying resins should be associated with the polydiene phase of the block copolymer. This assumption would be valid for the three blend systems (namely, Kraton D1102/HR-699,

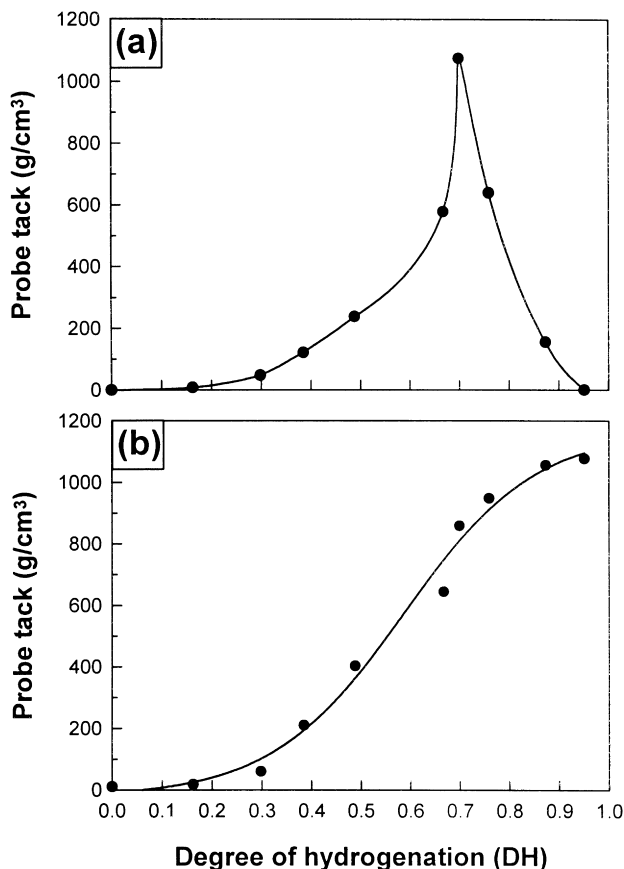


Fig. 10. (a) Probe tack versus DH for (60/40) (wt/wt) Kraton D1102/HRs blends. (b) Probe tack versus DH for (70/30) (wt/wt) Vector 4211/HRs blends.

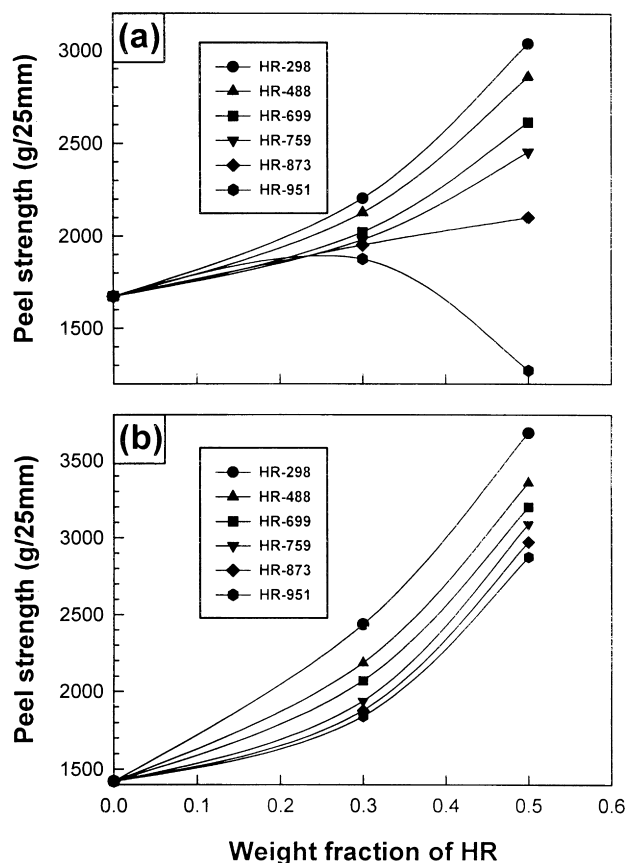


Fig. 12. Peel strength versus weight fraction of HRs with various DHs for (a) Kraton D1102/HRs and (b) Vector 4211/HRs.

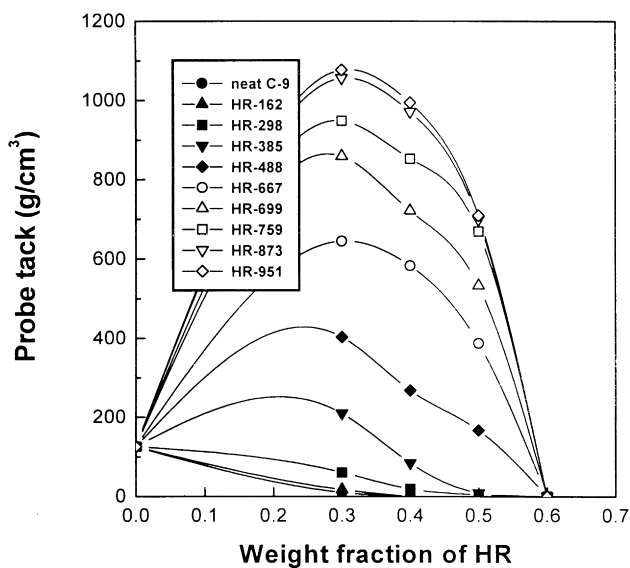


Fig. 11. Probe tack versus weight fraction of HR resins for the blends of Vector 4211/HRs with various DHs.

Vector 4211/HR-699, and Vector 4211/HR-951), where the miscibility between PB (or PI) and each HR is much better than that between PS and corresponding HR. It is seen from Fig. 8 that the behavior of $G_{N,mixture}^0$ was successfully described by Eq. (5) with the exponent $\alpha = 2.2$ for Vector 4211/HR-699 and Vector 4211/HR-951, and $\alpha = 2.8$ for Kraton D1102/HR-699. Here, we used M_e of PB = 1543, and M_e of PI = 5097 [27]. Thus, the values of G' ($\tan \delta_{min}$) for neat block copolymers are slightly larger than the predicted ones using Eq. (4) with $\phi' = 1$. A large α for Kraton D1102/HR-699 system compared with two other systems is attributed to the fact that the amount of HR-699 being associated with the PB block in Kraton D1102 is smaller than that with the PI block in Vector 4211 due to the smaller PS block in Kraton D1102. As described in Ref. [18], PS homopolymer with $M_w = 198,000$ and HR-699 blend showed a UCST of 224°C, while PS homopolymer with $M_w = 7800$ and HR-699 is completely miscible. Thus, as the M_w of the PS block decreases, the miscibility between the PS block in Kraton D1102 and HR-699 would be increased. In this situation, ϕ' in Kraton D1102/HR-699 should be smaller than that shown in Fig. 8, which implies that α of Kraton D1102/HR-699 system should be smaller than 2.8. However, we consider that the upper limit value of α with 2.8 is not too

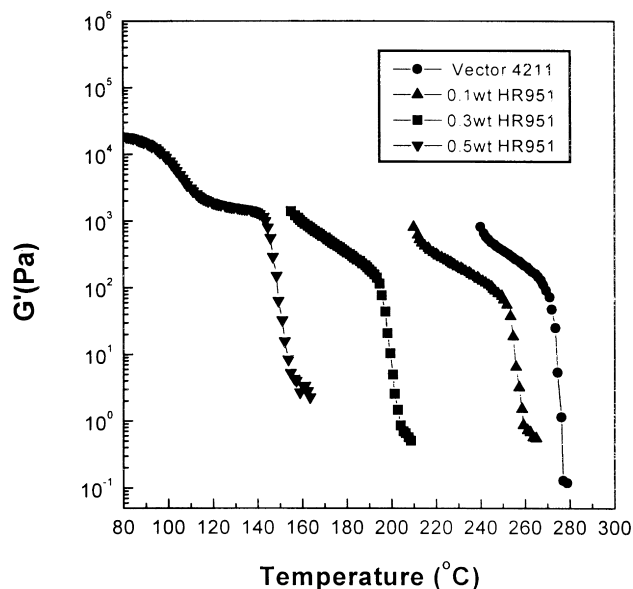


Fig. 13. Temperature sweep in G' for various compositions of Vector 4211/HR-951 blend. The weight fractions of HR-951 in the blend are: (●) 0; (▲) 0.1; (■) 0.3; and (▼) 0.5.

large. Previously, Kraus et al. [28] reported that the values of α for the mixtures of SIS and SBS with hydrogenated rosin ester (or C-5) resins are 2.82 and 2.62, respectively. But, Kim et al. [29] reported that the α values for SIS and SBS with mid-block associating tackifying resins are 2.1 and 2.16, respectively.

3.2. Adhesion properties for the mixture of block copolymers and HRs

Fig. 9 gives the plots of the probe tack versus weight fraction of HRs for Kraton D1102/HRs with various DHs. The maximum tack at a given blend (namely at a given DH) was observed at a weight fraction of HRs of 0.4. However, the maximum tack, although it is small, occurs at a weight fraction of HRs of 0.3 for $DH \leq 0.385$ and $DH = 0.873$, implying a limited miscibility between the PB block and HRs. When $DH > 0.873$, no detectable tack is observed due to poorer miscibility between the PB block and HRs. Notice that the maximum tack value of a blend is related to the viscoelastic properties (G' , G'' and $\tan \delta$) at a measured temperature (23°C). Thus, even if a blend shows the minimum $G'_{N,mixture}$, this blend does not necessarily exhibit the maximum tack properties. Interestingly, at a fixed value (0.4) of the weight fraction of HR, probe tack increased up to $DH = 0.7$ where it exhibited the maximum, and then decreased with increasing DH, as shown in Fig. 10(a). These results could be interpreted by the fact that tack value is mainly related to the miscibility between the PB block and HRs. This is consistent with the former results [18] that the maximum miscibility of PB homopolymer/HRs occurred at $DH \sim 0.7$.

Fig. 11 gives plots of the probe tack versus the

weight fraction of HRs for Vector 4211/HRs with various DHs. The maximum tack at a given blend (namely at a given DH) was observed at a weight fraction of 0.3, except for HRs with DHs lower than 0.298 where the miscibility between PI block and HRs is far poorer than HRs with DH larger than 0.298. Interestingly, at a fixed value (0.3) of the weight fraction of HR, probe tack increased up to HR-951 with increasing DH, although the increase in probe tack was not large at higher DHs, as shown in Fig. 10(b). From the results of Figs. 9–11, the probe tack depends predominantly on the miscibility between the elastomeric phase of PB (or PI) in Kraton D1102 (or Vector 4211) block copolymers and HRs. Also, the weight fraction of HRs exhibiting a maximum tack among all blend compositions in the mixture of Vector 4211/HRs is 0.3, which is smaller than that (0.4) in the mixture of Kraton D1102/HRs. This is because $G'_{N,mixture}$ for the former is smaller than that of the latter at a given weight fraction of HRs in the mixtures, thus, the smaller amount of HRs is needed for the former.

Fig. 12(a) and (b) gives the plots of peel strength versus weight fraction of HRs for Kraton D1102/HRs and Vector 4211/HRs with various DHs. We could not increase the weight fraction higher than 0.5 due to the existence of cohesive or grassy failure. As DH increased, the aromatic characters changed to aliphatic; therefore, peel strength with the polar surface of stainless steel plate was decreased gradually. The smaller value for 50/50 (wt/wt) Kraton D1102/HR-951 compared with 70/30 (wt/wt) composition shown in Fig. 12(a) is because of the macrophase separation from the poor miscibility between the PB block and the HR-951 as well as the poor miscibility between the PS block and the HR-951 (see Fig. 5). It is reported [11–13] that the peel strength of macrophase-separated systems becomes very low.

3.3. The order-to-disorder transition for the mixtures of block copolymers and HRs

To determine whether the tack properties depend upon the microdomain structure of the mixture of a block copolymer and a tackifying resin, we investigated the microdomain structure and the order-to-disorder transition temperature (T_{ODT}) of the mixtures. We found from the synchrotron SAXS results that both Kraton D1102 and Vector 4211 have hexagonally packed cylindrical (HEX) microdomains and the domain spacings (D) at room temperature for the two block copolymers are 26.1 and 28.1 nm, respectively [30]. Temperature sweep experiments of G' for Vector 4211/HR-951 with four different weight fractions of HR-951 (0, 0.1, 0.3, and 0.5) are given in Fig. 13. The T_{ODT} of each blend was determined at a temperature when G' drops precipitously, for instance 271°C for neat Vector 4211. We also found that $\log G'$ versus $\log G''$ plots of these blends give the essentially same T_{ODTs} measured by the temperature sweep experiment [30], as

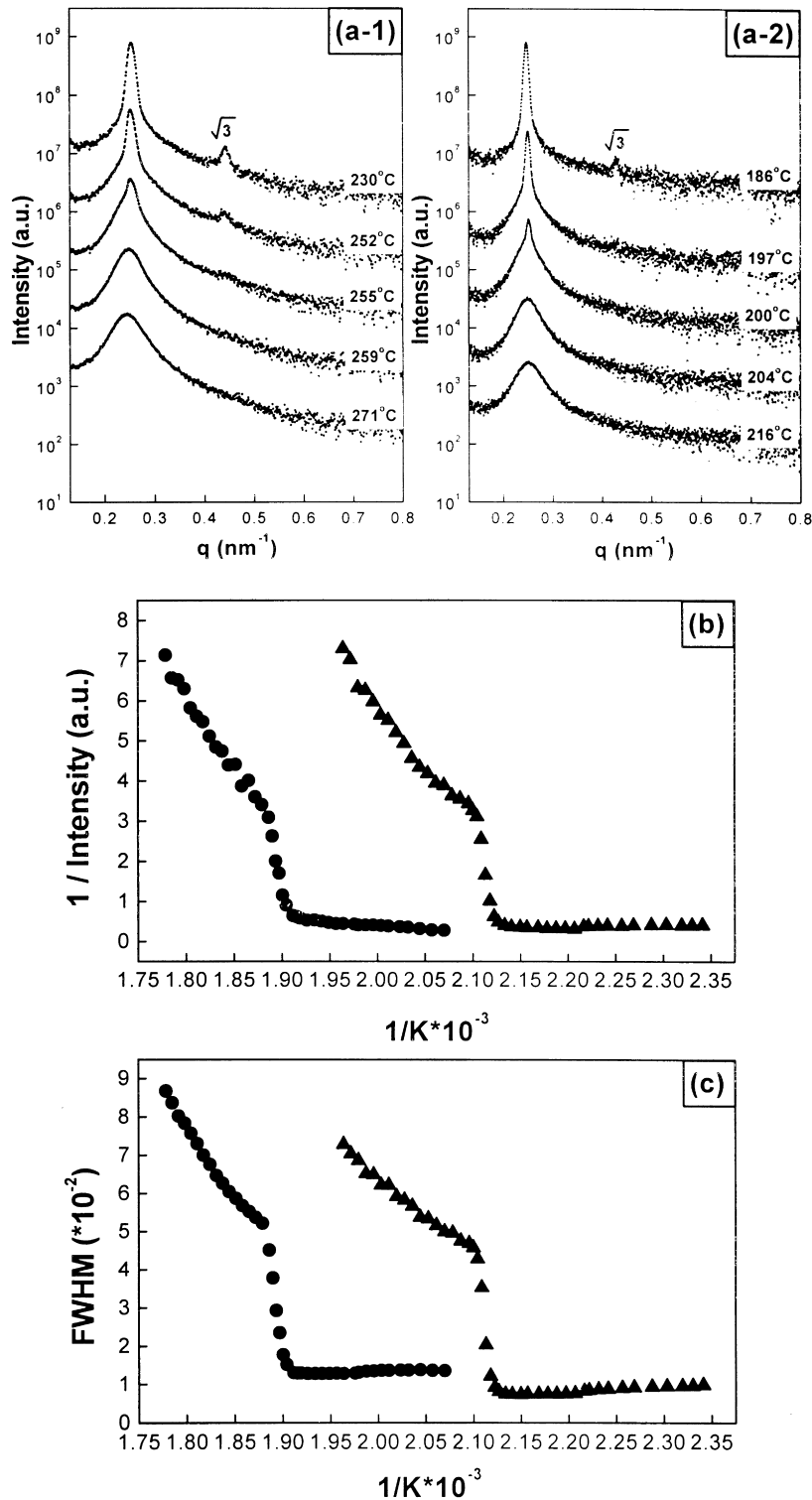


Fig. 14. (a) The SAXS profiles of 90/10 (wt/wt) composition (a-1) and 70/30 (wt/wt) composition (a-2) of Vector 4211/HR-951 at different temperatures. The plots of the inverse scattering intensity (b) and the FWHM (c) of the first order peak versus inverse temperature. Symbols (●) and (▲) in Figs. 15(b) and (c) are 90/10 and 70/30 (wt/wt) compositions, respectively.

the volume fraction of the PS block in Vector 4211 is 0.26, which is not asymmetric composition. For a block copolymer with very asymmetric composition having body centered cubic spherical (BCC) microdomains (say

$f < 0.15$), the T_{ODT} measured by the temperature sweep in G' would be different from that measured by plots of $\log G'$ versus $\log G''$ [31–34]. From Fig. 13, T_{ODT} decreased gradually with an increasing amount of HR-951. This is because of

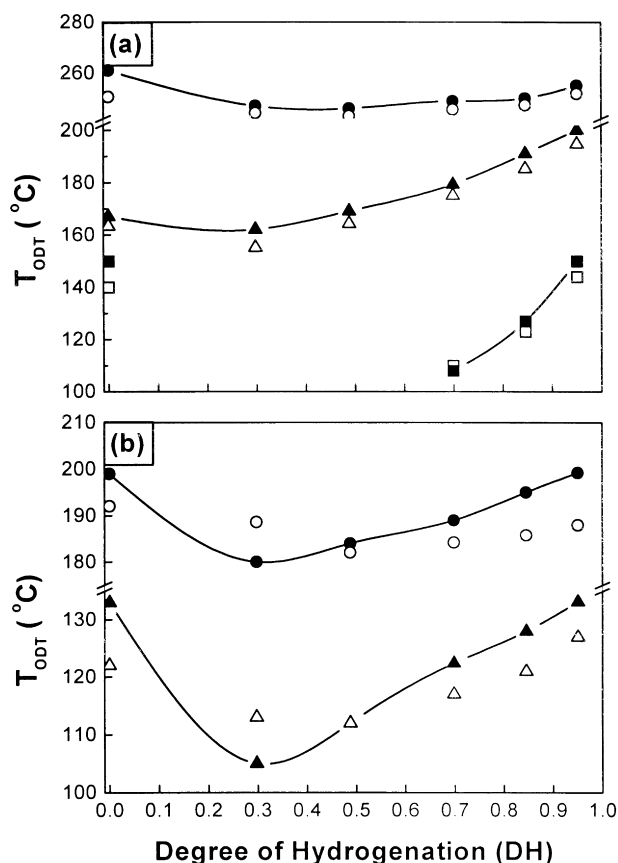


Fig. 15. The variations of the T_{ODT} s for (a) Vector 411/HRs and (b) Kraton D1102/HRs with DH at different blend compositions determined by SAXS (●;▲;■) and rheology (○;△;□). (●;○) 90/10 (wt/wt); (▲;△) 70/30 (wt/wt); and (■;□) 50/50 (wt/wt) Vector 4211 (or Kraton D1102)/HRs blends.

the lower molecular weight of HR-951 in addition to the good miscibility between HR-951 and PI block in Vector 4211.

The overall SAXS profiles with temperatures are given in Fig. 14(a) for two blend compositions (90/10 and 70/30 (wt/wt)) of Vector 4211/HR-951. Also, plots of the inverse of the scattering intensity and the full-width at half-maximum (FWHM) of the first-order peak versus the inverse of temperature are given in Fig. 14(b) and (c), respectively. Two blend composition of 90/10 and 70/30 (wt/wt) Vector 4211/HR-951 have HEX microdomains due to the existence of $\sqrt{3} q^*$ at lower temperatures (see Fig. 14(a-1) and (a-2)). From Fig. (a-1), this peak start to disappear at 255°C and it disappears completely at 259°C. With this result and the fact that the inverse SAXS intensity and FWHM precipitously increased at 255°C, as shown in Fig. 14(b) and (c), we estimate the T_{ODT} of 90/10 (wt/wt) Vector 4211/HR-951 as 255°C. Also, 70/30 (wt/wt) blend composition has a similar transition behavior to the 90/10 (wt/wt) composition, except the lower value (200°C) of T_{ODT} compared with the latter. Further, the T_{ODT} s of these two blends are almost the same as those determined from rheology (see Fig. 13).

On the basis of the above methods, the change in the T_{ODT} of the three blend compositions (90/10, 70/30, and 50/50

(wt/wt)) of Vector 4211/HR blends with DH is given in Fig. 15(a). We found that 50/50 (wt/wt) Vector 4211/neat C-9 resin as well as 70/30 (wt/wt) compositions of Vector 4211/neat C-9 resin and Vector 4211/HR-298 has lamella microdomains. This is because most resins are dissolved into the PS block, thus the overall weight fraction of PS increased to 0.65 and 0.51, respectively, for 50/50 and 70/30 (wt/wt) compositions. But, except for these three, all blend systems showed HEX microdomains. This suggests that even if at $DH = 0.951$ where almost all HRs are associated with the PI block, the overall weight fraction of PS in the 70/30 (wt/wt) Vector 4211/HRs becomes 0.21; thus, there is very little chance to change HEX microdomains to body-centered cubic microdomains. At a given DH, the T_{ODT} would decrease with the increasing amount of HRs. This is attributable to the smaller M_w of HR. However, very interestingly, the minimum T_{ODT} occurred at $DH = 0.3$ for the two blend compositions (90/10 and 70/30 (wt/wt) Vector 4211/HRs).

We also found that 70/30 (wt/wt) Kraton D1102/neat C-9 resin has lamellar microdomains, and, except for C-9 resin, all blend systems of Kraton D1102/HRs showed HEX microdomains. It is pointed out that 70/30 (wt/wt) Kraton D1102/HR-298 has HEX microdomains, while 70/30 (wt/wt) Vector 4211/HR-298 has lamellar microdomains. This is because, even though the interaction between the PS block in Kraton D1102 and HR-298 is more favorable than that between the PB block and HR-298, some portions of the HR-298 are dissolved into the PB block. However, as described previously, almost all HR-298 is dissolved into PS phase for 70/30 (wt/wt) Vector 4211/HR-298. Thus, the total PS phase for 70/30 (wt/wt) Kraton D1102/HR-298 does not become large enough to exhibit lamellar microdomains. The T_{ODT} of Kraton D1102/HR measured by SAXS was slightly larger than that determined by rheology. It should be pointed out that the PB would be cross-linked at higher temperatures [35]; thus the measured T_{ODT} of Kraton D1102 in this study might not be very accurate. Nevertheless, the cross-linking was negligible at T_{ODT} s as given in Fig. 15(b) for 90/10 (wt/wt) and 70/30 (wt/wt) Kraton D1102/HRs.

At a given DH, the T_{ODT} would decrease with increasing amount of HRs. Also, similar to Vector 4211/HRs, the minimum T_{ODT} occurred at $DH = 0.3$. When we considered only the stability limit [36–38] for the microphase separation, predicted by the mean field theory with the interaction parameters between PS/HR and PB/HR reported in Ref. [18], the minimum T_{ODT} occurred at $DH = 0.3$ for the two blend compositions (90/10 and 70/30 Kraton D1102/HRs (and Vector 4211/HRs)). In this calculation, the interaction parameter is simply assumed to be zero when there is no turbidity between the blend. The detailed predictions of the T_{ODT} of the blends will be reported later [22].

4. Conclusions

In this study, we have shown that viscoelastic properties,

such as plateau modulus and glass transition, depends predominantly on the miscibility between PS and HR as well as PB (or PI) and HRs, which is strongly affected by DH in HR. At lower values of DH, HRs are associated with the PS end block; thus tack properties become negligible although the plateau modulus increased considerably. Further, using SAXS experiment, the mixture of Kraton D1102 (or Vector 4211)/neat C-9 resin has lamellar microdomain.

We found that the tack properties depended on the miscibility between HRs and the elastomeric mid-block in the block copolymers. In other words, the tack value of the mixture of Kraton D1102/HR exhibits a maximum at $DH = 0.7$ (HR-699) where the plateau modulus decreases gradually with increasing amount of HR-699 resin. This is well consistent with the previous result [18] that the maximum miscibility between PB and HR occurred at $DH = 0.7$. However, tack properties of the mixture of Vector 4211/HR increased steadily up to HR-951, because the miscibility between PI and HR increases steadily with increasing DH. These results are consistent with the prediction by the solubility parameter approach. Thus, even if the diene of C-4 is slightly changed to that of C-5, the miscibility between the block copolymer and a tackifying resin changes significantly; thus large different tack properties are expected.

The T_{ODT} s of the mixture having either Kraton D1102 or Vector 4211 always decreased with the increasing amount of a given HR due to the lower M_w of HR. Interestingly, the decrease in T_{ODT} s of the mixtures was the largest at $DH \sim 0.3$ when the weight fraction of HR was 0.1 and 0.3.

Acknowledgements

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