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Interphase transfer of tackifier between poly(butadiene) and poly(styrene-*co*-butadiene)

Vu Anh Doan · Shogo Nobukawa · Shigeki Ohtsubo · Toshio Tada · Masayuki Yamaguchi

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Abstract The interphase transfer behavior of poly(styrene-*co*-α-methyl styrene), which is known as a tackifier in rubber industry, is investigated using poly(butadiene) rubber (BR) and poly(styrene-*co*-butadiene) rubber (SBR). The films of pure rubbers and the blends with the tackifier were prepared by a solution-cast method using toluene as a solvent. Two sheets composed of different rubbers, in which the tackifier was mixed at least in one rubber sheet, were piled together and annealed beyond the glass transition temperature T_g of the tackifier. The transfer phenomenon of the tackifier between the sheets was evaluated by the peak shift in the tensile loss modulus E'' curve, ascribed to T_g of the rubbers, which was measured by the dynamic mechanical analysis. Moreover, crystallization temperature of BR was also employed as a measure of the transfer, because the tackifier retards the crystallization of BR. It is found that the tackifier moves from one rubber to another during annealing procedure to reduce severe localization. When the content is the same in each rubber, the tackifier immigrates from BR to SBR, suggesting a better miscibility with SBR. This behavior is attributed to the small difference in the solubility parameter between SBR and the tackifier as compared to that between BR and the tackifier.

V. A. Doan · S. Nobukawa · M. Yamaguchi (✉)
School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan
e-mail: m_yama@jaist.ac.jp

S. Ohtsubo · T. Tada
Sumitomo Rubber Industries, Ltd., 1-1-2 Tsutsui, Chuo, Kobe 651-0071, Japan

Introduction

Among synthetic elastomers, styrene butadiene rubber (SBR), and butadiene rubber (BR) are the first and second largest in terms of volume usages [1], respectively. One of the most important applications for both rubbers is tires. SBR is known to offer good wet skid and traction properties of tires, whereas BR exhibits high elasticity, good abrasion resistance, and tread wear performance. BR shows extremely good physical properties at low temperature due to its low glass transition temperature, leading to one of the main components of winter tires [1, 2]. Moreover, it is widely known that both rubbers are often mixed together.

Fujimoto and Yoshimiya [3] investigated the miscibility between SBR and BR by dynamic mechanical and dielectric loss analyses. According to them, SBR/BR blend shows homogeneous structure after mill-mixing for few minutes. Marsh et al. [4] used the electron microscope technique to observe the morphology of SBR/BR blend and found a similar result. On the contrary, Ougizawa et al. [5] firstly revealed that BR/SBR blends show the upper critical solution temperature which is around 150 °C. Therefore, they are immiscible at room temperature in the equilibrium state, irrespective of the blend ratio.

In the rubber industry, a tackifier plays important roles in various properties. For example, adding a tackifier into rubber compounds improves the tensile strength and adhesive strength. Moreover, the dispersion of fillers and wetting behavior with the filler surface are modified by a tackifier [1, 2, 6–14].

Among tackifiers for rubbers, poly(styrene-*co*-α-methyl styrene) is known to provide mechanical hysteresis at 0 °C and thus enhances the wet traction for tires while remaining the dynamic mechanical properties at higher temperature, i.e., in the range from 25 to 100 °C. Interestingly, the addition of the tackifier together with a large amount of silica particles leads to the reduction of rolling resistance [15, 16].

It is widely accepted that structure and properties of rubber blends are strongly affected by the distribution and migration behavior of fillers and additives. Therefore, numerous researches have been focused on the distribution of fillers such as carbon black (CB) [17–20], silica particle (Si) [21–25], nano-clay [26, 27], and carbon nanotube (CNT) [28, 29] in rubber blends. Basically, the localization of particles in rubber blends occurs to minimize the overall free energy of the system. Moreover, it has been understood that rubber molecules absorbed on fillers, called "bound rubber," play an important role in localization of the filler. For example, Kawazoe and Ishida [18] found that the selective absorption of acrylonitrile butadiene rubber (NBR) on CB surface is responsible for the localization of CB in NBR phase in SBR/NBR blends. Therefore, control of the amount of bound rubber is an important technique. Ono et al. [21] found that the amount of bound rubber in a composite with silica particles is strongly dependent on the mixing temperature.

When the initial distribution of fillers is not favored from the viewpoint of free energy, the filler transfer occurs. Yoon et al. [28] firstly demonstrated that CNT immigrates from one polymer to another. Moreover, Gouldel et al. [29] revealed that the interfacial transfer is enhanced when the aspect ratio of CNT is high. This phenomenon can be explained by the large surface area of CNT.

The distribution and migration of curatives have also attracted the attention of many researchers, because they directly affect the vulcanization rate and cross-link density [30–37]. Usually, the distribution and diffusion of sulfur and accelerators in rubber blends are determined by the solubility parameter in each phase [30–32]. Gardiner [35] demonstrated that most curatives tend to immigrate from a rubber with less polar to another during mixing, because most curatives are polar compounds. Torregrosa-Coque et al. [37] studied the influence of the temperature on surface properties of sulfur-vulcanized SBR. They found that paraffin wax and zinc stearate move out onto the rubber surface, leading to the lack of adhesion.

However, less attention has been paid for the distribution and migration behavior of tackifiers in rubber blends. Although some researches have been published on the structure and properties of rubber blends containing a tackifier [38–44], the distribution state of the tackifier has not been understood in detail.

In this research, interphase transfer of a tackifier between BR and SBR is studied. As a tackifier, an oligomeric copolymer composed of styrene and α-methyl styrene is employed. Furthermore, our preliminary study on the interphase transfer of fillers is referred to decide the experimental technique [29, 45].

Experimental

Materials

The materials used in this research were SBR, BR, and the tackifier, i.e., an oligomeric copolymer mainly composed of styrene and α-methyl styrene. All of them are commercially available. The average molecular weight was determined by a gel permeation chromatography as polystyrene standard and the values are summarized in Table 1. SBR was obtained by solution polymerization. The styrene content is 27 % and vinyl content is 59 %. The *cis*-content in BR is 94.8 % and vinyl fraction is 0.5 %. The composition of the tackifier is as follows; 41.5 % of styrene, 53.2 % of α-methyl styrene, and 5.3 % of 1-methylethylbenzene.

Sample preparation

Various amounts of the tackifier were mixed with SBR and BR in toluene. After stirring for 6 h at room temperature, the solution was poured onto a Teflon plate and left at room temperature for 72 h to allow the solvent to evaporate slowly and completely to obtain the smooth films. Thickness of the films is about 300 μm. Films of a pure rubber were also prepared by the same method.

For annealing experiments, a film containing the tackifier was piled with another film of a different rubber. After making a perfect contact between the films under an applied slight pressure by manual operation, the samples were annealed without pressure at 100 °C for 120 h in an oven. This procedure was originally developed for the study on filler transfer [29, 45]. A similar experiment was conducted using the piled sheets composed of rubbers containing 15 phr of the tackifier in each phase. Before annealing procedure, nitrogen gas was filled in the oven to avoid thermal oxidation.

In order to examine the dynamic mechanical properties of the tackifier, a film of pure tackifier was prepared using a compression-molding machine at 190 °C under 10 MPa for 3 min. The thickness of the film is about 1 mm.

Table 1 Molecular weights of raw materials

	M_n	M_w	M_w/M_n
BR	3.3×10^5	6.5×10^5	2.0
SBR	1.5×10^5	4.9×10^5	3.2
Tackifier	6.8×10^2	1.1×10^3	1.6

Polystyrene standard

M_n number average molecular weight, M_w weight average molecular weight

Measurements

Thermal properties of rubber/tackifier blends were analyzed using a differential scanning calorimeter (DSC) (Mettler, DSC 820) under a nitrogen atmosphere. Approximately, 10 mg of each sample was encapsulated in a standard aluminum pan. The samples were cooled from room temperature to −80 °C at a cooling rate of 5 °C/min to evaluate crystallization behavior. The DSC measurements were carried out using the piled sheets before and after annealing procedure.

Moreover, the pure tackifier was heated from room temperature to 250 °C at a heating rate of 5 °C/min and then cooled down to room temperature at a cooling rate of 2 °C/min. The second heating scan was carried out at the same rate with the first one after keeping at room temperature for 3 min.

Temperature dependence of dynamic tensile moduli was evaluated by a dynamic mechanical analyzer (UBM, DVE3). The frequency was 10 Hz and the heating rate was 2 °C/min. A rectangular specimens were employed for the measurement.

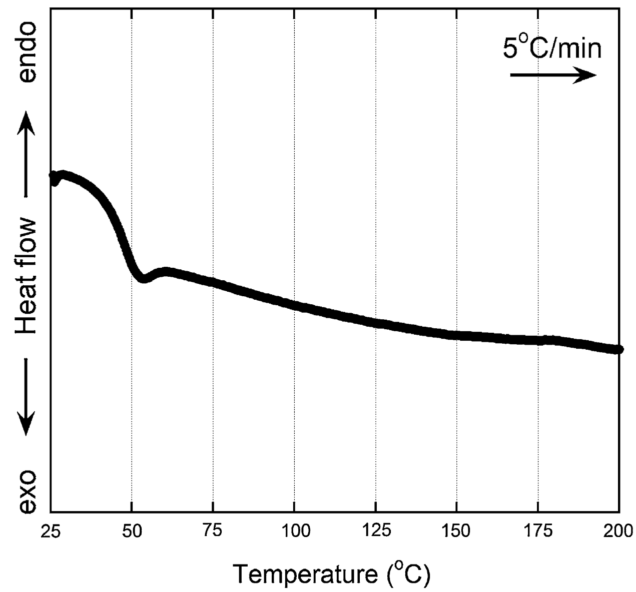

Fig. 1 DSC curve of second heating run for pure tackifier at 5 °C/min

Results and discussion

Characteristics of tackifier

Figure 1 shows the DSC heating curve from the second scan of the tackifier at a heating rate of 5 °C/min. In order to erase the thermal history, the sample is heated to 250 °C as the first scan and cooled at a rate of 2 °C/min to room temperature.

The curve shows that the glass transition temperature T_g of the tackifier is located at 50 °C. Moreover, no endothermic peak due to melting is detected. The result indicates that the tackifier is a fully amorphous material.

The temperature dependence of the dynamic tensile moduli such as tensile storage modulus E', loss modulus E'', and loss tangent *tan* δ at 10 Hz for the tackifier is shown in Fig. 2. The sample is cooled from room temperature to −100 °C in the machine, and then the measurement is started.

As seen in the figure, E'' shows the peak around 55 °C. Correspondingly, E' falls off sharply at this temperature. These results indicate that T_g of the tackifier is 55 °C at this frequency, which is in good agreement with the DSC data mentioned above. However, the T_g obtained in this study seems to be significantly low, compared to T_g's of polystyrene and poly(α-methyl styrene) reported elsewhere [46]. This phenomenon is attributed to the difference in molecular weight. A number of chain ends having marked mobility due to free volume in low molecular weight materials are responsible for the low T_g [47], which is confirmed by the results reported by Rietsch et al. [48].

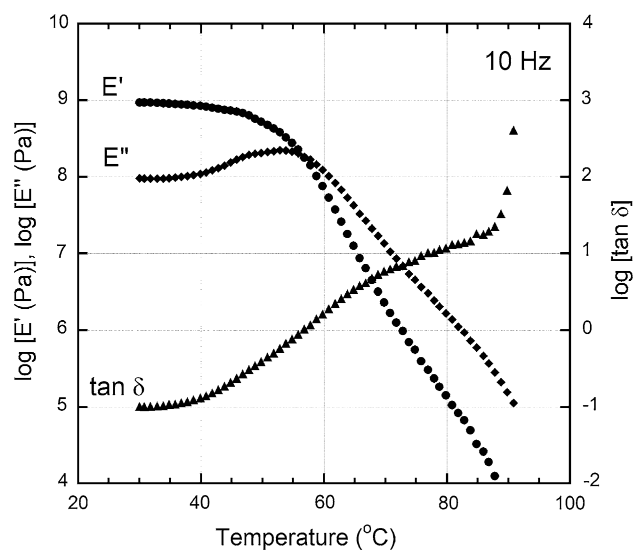

Fig. 2 Temperature dependence of (*circles*) storage modulus E', (*diamonds*) loss modulus E'' , and (*triangles*) loss tangent *tan* δ for pure tackifier at 10 Hz

Characteristics of rubbers containing tackifier

The effect of the tackifier on the thermal and dynamic mechanical properties of the rubbers is studied before investigation of interphase transfer of the tackifier.

It is well-known that BR is a semi-crystalline polymer [1, 46, 49] and shows crystallization during cooling process. In order to clarify the effect of the tackifier on the crystallization behavior of BR, DSC measurements are performed. Figure 3 shows the DSC cooling curves from room temperature at a rate of 5 °C/min for BR containing various amounts of the tackifier.

As seen in the figure, the crystallization temperature T_c of the pure BR is −32 °C, which is in agreement with the literature data [1, 46]. Furthermore, it is clearly demonstrated that addition of the tackifier greatly retards the crystallization. Consequently, the crystallization of the blends containing the tackifier occurs at lower temperature. It is reasonable because the tackifier acts as a diluent. Therefore, BR has to expel the tackifier molecules for the crystallization to occur, which results in the lowering of the crystallization temperature.

Figure 4 shows the peak temperature of the crystallization at the DSC cooling run, plotted against the tackifier content. The crystallization temperature decreases monotonically with the tackifier content when the amount of the tackifier is smaller than 20 phr. The results indicate that the tackifier content in BR can be estimated by the crystallization temperature.

Figure 5a and b show the temperature dependence of tensile storage modulus E' and loss tangent *tan* δ at 10 Hz for SBR and BR, respectively, containing various amounts of the tackifier.

The figures show that the peak of *tan* δ is clear and narrow for SBR as compared to that of BR. This is reasonable because SBR is a fully amorphous polymer. Moreover, the peaks for both BR and SBR shift toward a higher temperature by the addition of the tackifier, because T_g of the tackifier is 55 °C as shown in Fig. 2. The shape of the relaxation peak of SBR with the tackifier is almost the same as that for the pure SBR. It indicates that the distribution of relaxation time is not greatly changed, suggesting a good miscibility between them. A rubbery region is also clearly observed for BR, with and

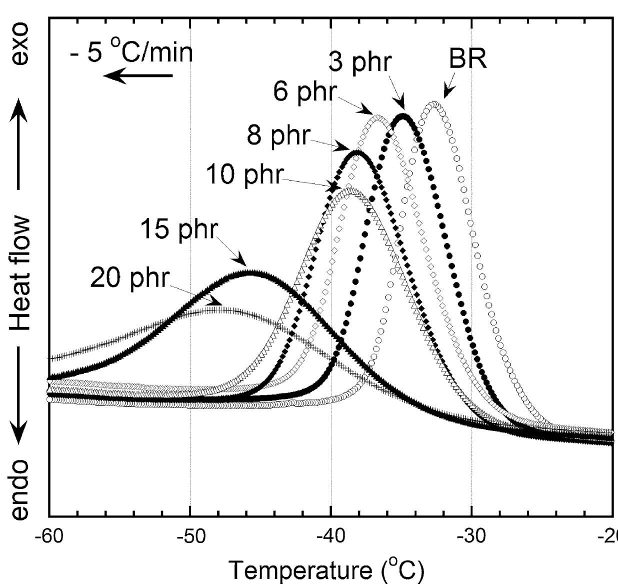

Fig. 3 DSC cooling curves for pure BR containing various amounts of the tackifier at 5 °C/min

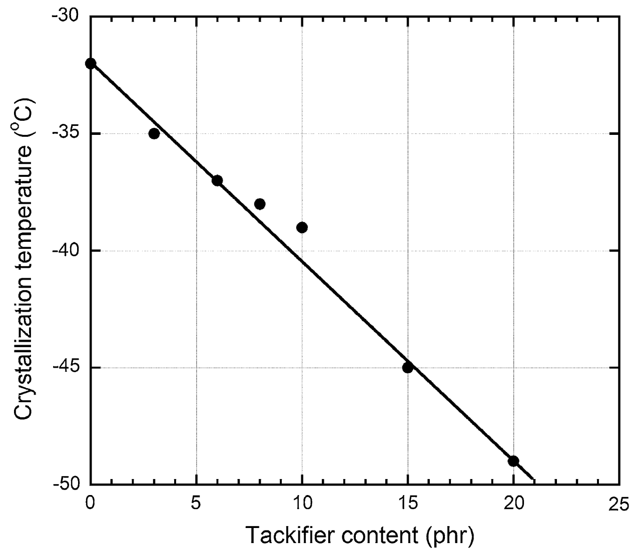

Fig. 4 Relation between the crystallization temperature and the tackifier content in BR

without the tackifier. The plateau modulus decreases slightly by the addition of the tackifier. The plasticizing effect of the tackifier is responsible for this behavior. In the case of BR with the tackifier, the shape of E'' peak due to T_g is not affected by the tackifier. This will be attributed to the difference in the crystallization state of BR, although the exact reason is not clear at present. Of course, E' in the rubbery region is higher than that for SBR due to the crystallinity.

Interphase transfer of the tackifier between BR and SBR

The transfer phenomena of the tackifier between BR and SBR are evaluated by the dynamic mechanical properties of the laminated sheets composed of a pure rubber and another rubber containing 20 phr of the tackifier. Since the measurements are performed using the piled sheets with parallel geometry, the same strain is applied to both sheets. Consequently, the response from the SBR sheet having higher modulus is dominant for the dynamic mechanical spectra, although the thickness of each sheet is almost the same. The immigration of the tackifier is examined by comparing the dynamic mechanical spectra of the samples before and after annealing procedure.

Figure 6a and b show the temperature dependence of dynamic tensile moduli of the piled sheet composed of (a) pure BR and SBR containing 20 phr of the tackifier and (b) pure SBR and BR containing 20 phr of the tackifier.

As seen in the figure, two peaks of *tan* δ are clearly detected for all samples. The peak at −100 °C is attributed to T_g of BR, while the one located around 0 °C is assigned to the T_g of SBR. The contribution of the melting of BR crystals will not affect, at least, *tan* δ significantly. It is

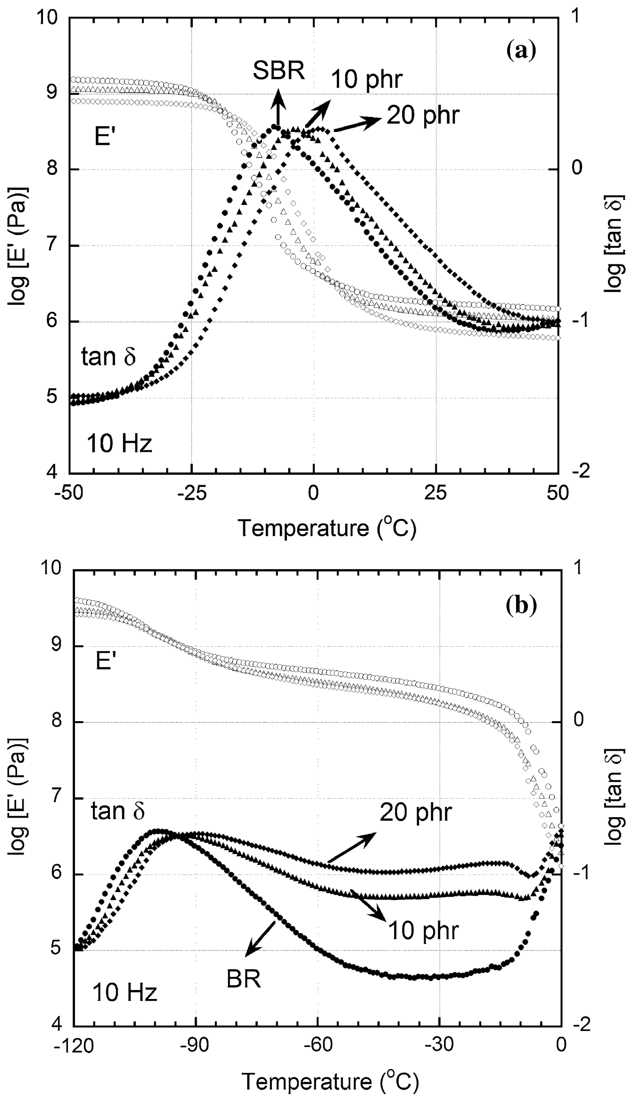

Fig. 5 Temperature dependence of (*open symbols*) storage modulus E' and (*closed symbols*) loss tangent *tan* δ at 10 Hz for **a** SBR and **b** BR containing various amounts of the tackifier

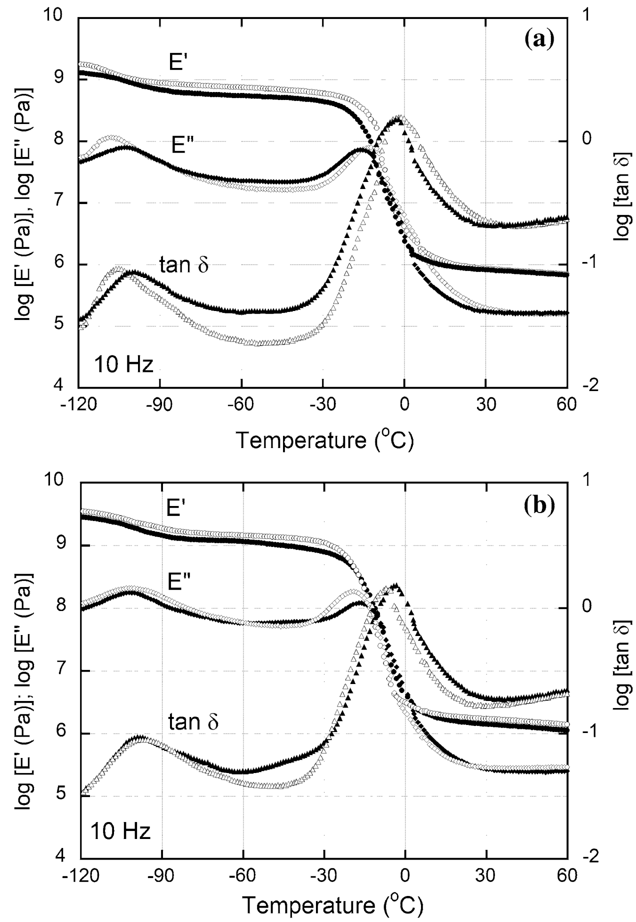

Fig. 6 Temperature dependence of (*circles*) storage modulus E', (*diamonds*) loss modulus E'' and (*triangles*) loss tangent *tan* δ of the piled sheet composed of **a** pure BR and SBR containing 20 phr of the tackifier and **b** pure SBR and BR containing 20 phr of the tackifier; (*open symbols*) before and (*closed symbols*) after annealing

generally understood that the dynamic mechanical properties are less sensitive to crystallization and/or melting as compared to glass transition, which is confirmed in Fig. 5. Although a slight shoulder at −15 °C in Fig. 6a would be ascribed to the melting of BR, the dynamic mechanical response beyond −10 °C is dominated by the SBR sheet because of the higher modulus.

Figure 6a shows the dynamic mechanical spectra for the piled sheets composed of pure BR and SBR/tackifier (100/20). It is found that the peak temperature of *tan* δ of BR is shifted to higher temperature and that of SBR is to lower temperature by the applied annealing procedure. The result suggests that the tackifier moves from SBR to BR.

A similar phenomenon is observed in the piled sheets composed of pure SBR and BR/tackifier as shown in Fig. 6b. The peak shifts due to the annealing are also detected, although the direction of the immigration is opposite to that in Fig. 6a. Moreover, it seems that the peak temperature of BR phase is not affected greatly by applied annealing procedure. The crystallization condition, which will be changed by the annealing, can be responsible for the phenomenon, although the detailed mechanism is unknown.

The transfer phenomenon of the tackifier is confirmed by the DSC measurements. The DSC cooling curves of the piled sheets before and after the annealing are shown in Fig. 7. The cooling is performed from room temperature at a rate of 5 °C/min.

It is known that the tackifier delays the crystallization of BR as discussed previously. Therefore, the transfer of the tackifier from SBR to BR shifts the crystallization of BR to a lower temperature, and vice versa.

The results correspond with the dynamic mechanical spectra. Furthermore, it can be concluded that the concentration gradient plays a decisive role in the interphase transfer phenomenon of the tackifier.

In order to further clarify the miscibility between the rubbers and tackifier, additional experiments are conducted with the piled sheets composed of rubbers containing the same amount of the tackifier. The content of the tackifier in each rubber is 15 phr. Figure 8 shows the DSC cooling curves from room temperature for the laminated sheets before and after the annealing.

It is found from the figure that the T_c of the sample increases from −45 to −42 °C after the annealing procedure. The increase in T_c is attributed to the transfer of the tackifier from BR to SBR, suggesting that the tackifier prefers to SBR. Although the interdiffusion of SBR into BR has a capability to retard the crystallization of BR, it has no influence on the T_c shift at this experiment because of extremely small diffusion constants of the rubbers.

The compatibility between the tackifier and rubbers can be discussed by solubility parameter. The solubility parameters of polystyrene [50] and poly(α-methyl styrene) [51] are known to be 18.75 and 18.4 (MPa$^{1/2}$), respectively. According to Coleman and Painter [52], the solubility parameter of a random copolymer is calculated as follows;

$$\delta_{\text{copolymer}} = \phi_1\delta_1 + \phi_2\delta_2 \tag{1}$$

where ϕ_i and δ_i are the volume fraction and solubility parameter of the i-comonomer, respectively.

Following the equation, the solubility parameter for PS-αMSt is estimated to be 18.55 (MPa$^{1/2}$). On the other hand, the solubility parameters of SBR [53] and BR [54] are known to be 17.39 and 16.2 (MPa$^{1/2}$), respectively. As a result, it is reasonable for the tackifier to prefer to SBR rather than BR.

Considering the relationship between crystallization temperature of BR and the concentration of the tackifier as shown in Fig. 4, the result indicates that about 11 phr of the tackifier remains in the BR sheet after the annealing procedure, implying that around 4 phr is transferred to SBR.

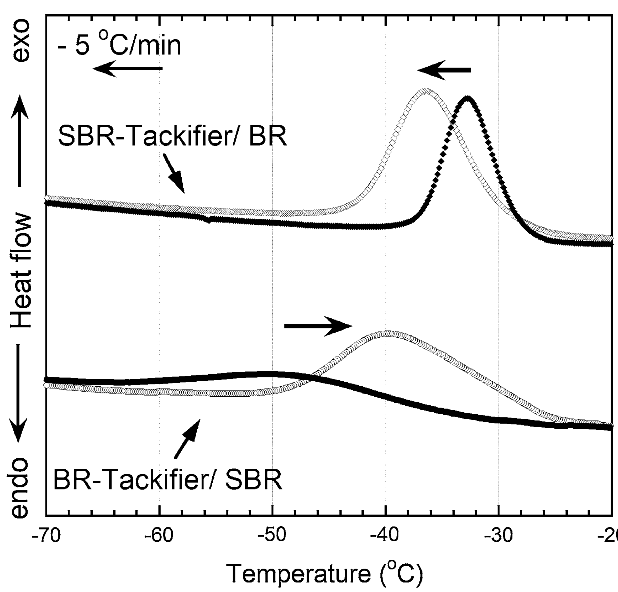

Fig. 7 DSC cooling curves of the piled sheets composed of (*circles*) BR and SBR containing 20 phr of the tackifier and (*diamonds*) SBR and BR containing 20 phr of the tackifier; (*closed symbols*) before and (*open symbols*) after annealing

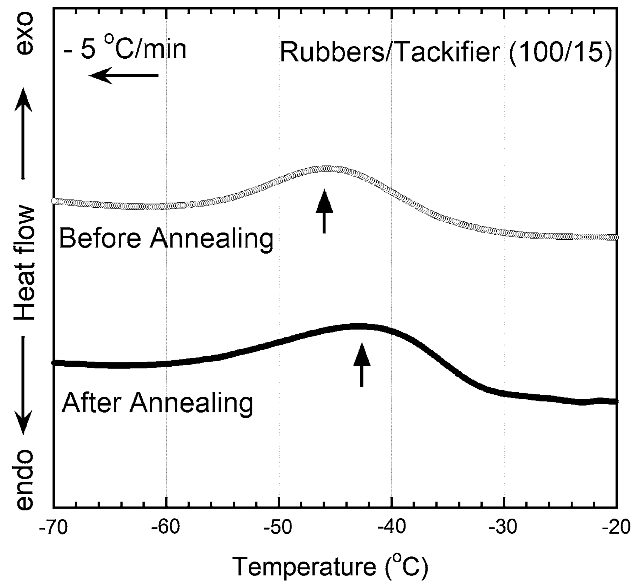

Fig. 8 DSC cooling curves of the piled sheets composed of rubbers containing 15 phr of the tackifier in each sheet; (*open*) before and (*closed*) after annealing procedure

Conclusion

The interphase transfer between SBR and BR for an oligomeric copolymer composed of styrene and α-methyl styrene, which is used as a tackifier in the rubber industry, is studied by means of dynamic mechanical analyzer and differential scanning calorimeter. The dynamic mechanical spectra are evaluated using the piled sheet composed of one rubber and another containing the tackifier. Since the strain is applied in parallel geometry, T_g of each sheet is estimated. The T_g shift after annealing procedure provides the information on the interdiffusion of the tackifier. DSC measurements also give the information on the tackifier transfer because the crystallization temperature of BR is significantly sensitive to the tackifier content. It is revealed from this study that the tackifier prefers to SBR over BR, which can be explained by the difference in the solubility parameter.

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