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Phase behavior and pressure sensitive adhesive properties in blends of poly(styrene-*b*-isoprene-*b*-styrene) with tackifier resin

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Abstract

Phase behavior of poly(styrene-*b*-isoprene-*b*-styrene) (SIS)/tackifier resin blends were investigated by thermal analysis, morphological observation and cloud point measurements. In the heating process, the blends showed lower critical solution temperature phase transition at around 150°C and upper critical solution temperature (UCST) phase transition at around 200°C. However, in the cooling process, only UCST phase transition was observed in the SIS/tackifier resin blends. In addition, it was found that properties of the pressure sensitive adhesive in SIS/tackifier resin blends were changed with annealing temperature corresponding to the phase behavior. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer blends; Pressure sensitive adhesive; Dynamic mechanical analysis

1. Introduction

Polymer blends have been applied in various fields such as rubber, fiber and adhesive industry [1–3]. Among them, in the pressure adhesive (PSA) industry, the technique of polymer blending has been applied extensively to control PSA properties, such as tackiness, peel adhesion and holding power [4,5].

It is well known that PSA properties of the polymer blends are affected by dynamic mechanical properties depending on blend composition and miscibility of the systems. Especially in the rubber-based PSA, the miscibility of the systems are of great importance since it is constructed by blending rubbery polymers, such as polyisoprene with tackifier resin [6,7]. Then, the focus has been on miscibility and pressure sensitive adhesive properties of blend PSA in polybutadiene with various tackifier resins [8–12]. In the binary mixtures of a homopolymer and a tackifier resin, the problem of phase behavior is only between the base polymer and the tackifier resin. On the other hand, in PSA using block copolymer, such as a hot-melt PSA, as a base polymer the phase behavior in the system is complicated due to complex phase behavior in the block copolymer itself [13–19]. Further, it is well known that microscopic and macroscopic phase morphologies have significant effects on PSA properties of block copolymer based PSA [18–21]. In this study, we investigate phase behavior and PSA properties of PSA using SIS as a base polymer.

2. Experimental

2.1. Materials and PSA preparation

Samples used in this study were: SIS as a base polymer and hydrogenated terpene resin, Piccolyte S-115, as a tackifier resin (PIC); supplied from Tonex Co., Ltd. and Yasuhara Chemical Co., Ltd., respectively. SIS and PIC were weighed to the desired composition and then dissolved in toluene. The solution was mechanically stirred until it became clear. After the solution became transparent, the toluene was evaporated on a release liner. The resulting PSA films were dried at 40°C for 1 week under reduced pressure.

2.2. Differential scanning calorimetry

For just cast SIS/PIC blends, Differential scanning calorimetry (DSC) measurements were performed using a Du Pont 910 differential scanning calorimeter under dry N_2 atmosphere at a heating rate of $10\,^\circ\mathrm{C/min}^{-1}$ between -100 and 110°C.

2.3. Dynamic mechanical analysis

For the PSA samples annealed at 100 and 120°C for 1 h,

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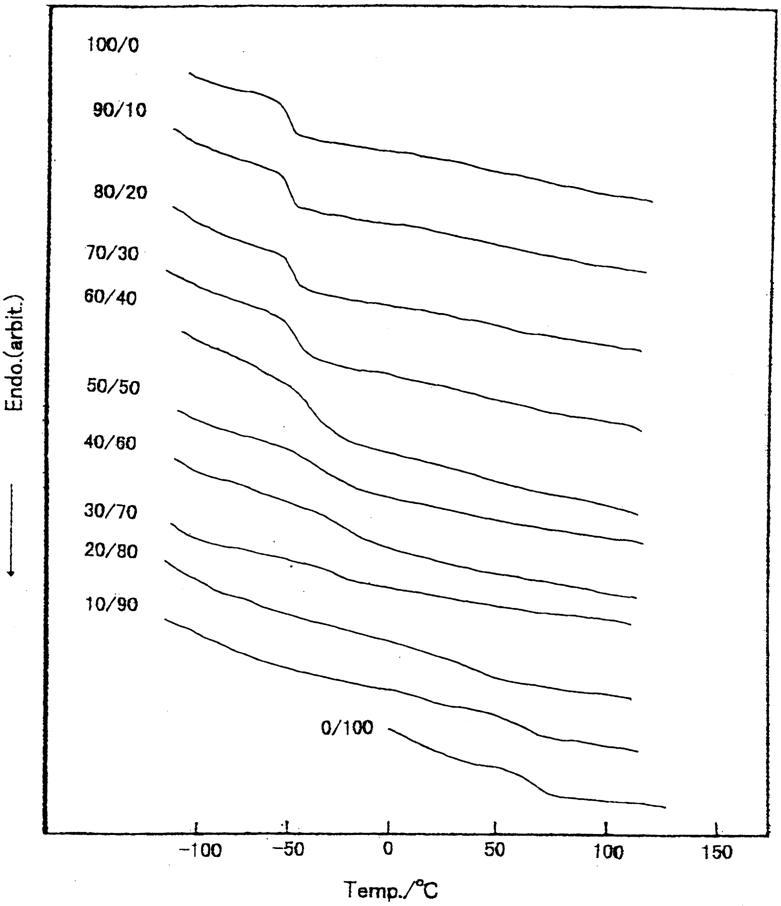

Fig. 1. DSC thermograms for just cast SIS(0)/PIC blends.

Dynamic mechanical analysis measurements were carried using a SEIKO Instrument Inc. DMS-200 dynamic mechanical spectrometer. All the measurements were performed at a heating rate of 1 °C/min^{-1} and a frequency of 1 Hz in tension mode.

2.4. Optical microscopy and cloud point measurements

Optical microscopy and cloud point measurements were performed using a Nikon S-Ke optical microscope equipped with a heating stage. PSA films were put on a glass plate and then set on the heating stage. Temperature of the heating stage was varied every 5 °C from 80 to 220°C. Cloud points were determined as the onset temperatures at which the phase separated structure appeared in the heating process and disappeared in the cooling process.

2.5. Transmission electron microscopy

Transmission electron microscopy (TEM) observations were performed using a Hitachi H-700H transmission electron microscope. Samples were embedded in epoxy resin and cut into 100 nm thickness using a Sorval MT-1 ultramicrotome.

2.6. PSA properties

PSA samples were annealed at certain temperature between 40 and 150°C for 1 h. Then, the samples were cooled gradually to room temperature. J-Dow ball tack, holding power, and peel adhesion were measured as PSA properties. The measurements were performed following JIS Z-0237 at 25°C. The peel adhesion of SIS/PIC blends to stainless steel was carried out at 180° using a Toyo Balldwin Co., Ltd. TENSIRON/UTM-4-100.

3. Results and discussion

3.1. Phase behavior

Fig. 1 shows DSC thermograms measured in second heating process for as-cast SIS(0)/PIC blends. Single glass transition is detected between the glass transition temperatures for the polyisoprene block in SIS(0) and PIC. This result suggests that SIS and PIC are miscible in a just dried state. Generally, in miscible polymer blends, compositional dependence of the glass transition temperature (T_g) of

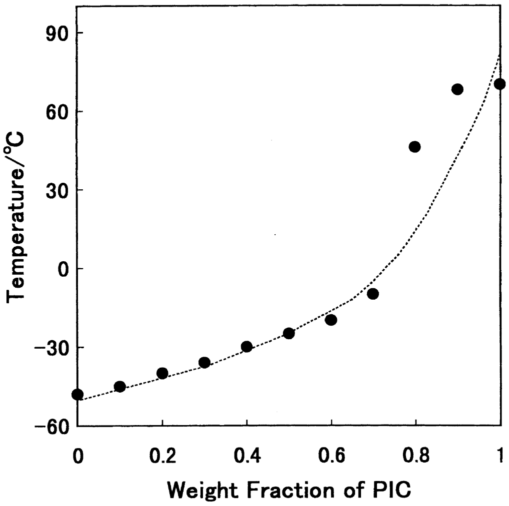

Fig. 2. Compositional dependence of glass transition temperature for SIS(0)/PIC blends.

polymer blends shows negative deviations from additive rule of T_gs of each component polymer.

Fig. 2 shows plots of T_g as a function of blend composition. The T_g is elevating systematically with increasing contents of PIC in SIS(0)/PIC blends. In addition, the compositional dependence of T_g shows negative deviation from additivity between T_gs of the polyisoprene block in SIS(0) and PIC. Therefore, it is concluded that the polyisoprene block is miscible with PIC in a just dried state. Since it is well known that miscibility of polymer mixtures are sensitive to variation of temperature, we investigated phase behavior in SIS/PIC blends as a function of temperature.

Fig. 3 shows plots of cloud points in temperature–composition plane obtained in the heating process. In the low temperature region, SIS/PIC blends take a homogeneous state in the visible scale. With increasing temperatures, SIS(0)/PIC = 90/10-30/70 (w/w) and SIS(42)/PIC = 90/10-50/50 (w/w) (see Table 1 for their molecular characteristics) blends undergo phase separation above 160°C. Further, above 220°C for SIS(0)/PIC blends and 200°C for SIS(42)/PIC blends, the blends take a homogeneous state again in the visible scale. Therefore, in the heating process, the SIS/PIC blends show both lower critical solution temperature (LCST) at 160°C and UCST at about 210°C. It is well known that polymer blends in the just dried state include various hystereses that originated during the process of solvent evaporation. Therefore, the loop-type phase diagrams in Fig. 3 might indicate non-equilibrium and irreversible phase behavior. The cloud point measurements are also performed in the cooling process.

Fig. 4 shows cloud points of SIS/PIC blends obtained in the cooling process. SIS(0)/PIC = 90/10-30/70 (w/w) and SIS(42)/PIC = 90/10-50/50 (w/w) blends show phase separation at about 220 and 210°C, respectively. This result corresponds to the result obtained in the heating process.

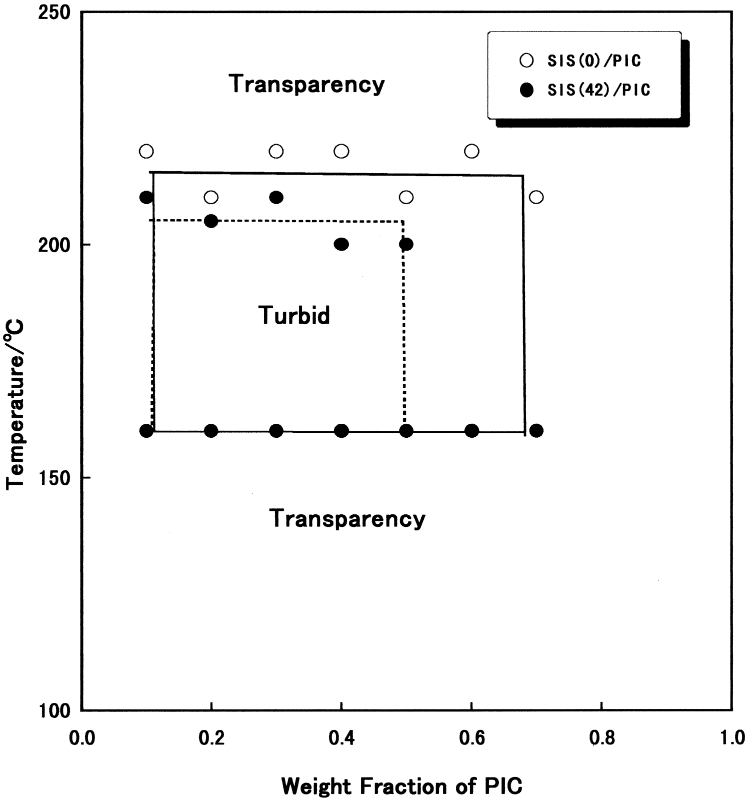

Fig. 3. Plots of cloud points detected in heating process against blend composition for just cast SIS/PIC blends.

Table 1
Molecular characteristics of SIS

Abbreviations	Diblockmer content (wt%)	Styrene contents (wt%)	$\overline{M_n} \times 10^{-5}$	$\overline{M_w} \times 10^{-5}$
SIS(0)	0	18	1.3	1.7
SIS(42)	42	15	–	–

Since the phase transition shows thermal reversibility, the UCST type phase behavior in SIS/PIC blends is regarded as thermal equilibrium phase transition. On the other hand, LCST type phase transition, observed around 160°C in the heating process is not observed in the cooling process. Therefore, the apparent phase transition at 160°C is regarded as a non-equilibrium state caused in sample preparation.

In polymer blends containing a block copolymer, it is expected that heterogeneous structures would appear in various scales. Phase structures in A and B regions in Fig. 4 for SIS(0)/PIC blends are observed by an optical microscope (OM) and a TEM, respectively. Fig. 5 indicates OM and TEM photographs observed at A and B regions of Fig. 4, respectively. In the A region, a macroscopic heterogeneous domain structure is observed corresponding to cloud point measurements in the cooling process. On the other hand, in the B region, a mesoscopically heterogeneous structure is observed using the TEM. The white area in the TEM photograph corresponds to the domain constructed by a polystyrene block of SIS(0). Therefore, there is the microphase structure originated during the microphase separation of SIS in the optically transparent state of SIS(0)/PIC blends. This result suggests that polystyrene block is strongly segregated from polyisoprene block in SIS and PIC.

It is interesting to note that optically homogeneous states of just dried SIS/PIC blends are maintained up to 160°C as shown in Fig. 3. However the temperature, 160°C, is much higher than T_g of polystyrene block in SIS which is the highest T_g in SIS/PIC blends. The polystyrene block is considered to be strongly segregated in optically homogeneous states below 160°C (Fig. 3). Therefore, the strongly segregated polystyrene block prevents macroscopic diffusion of PIC. It is thought that the homogeneous state in just dried SIS/PIC blends is maintained up to 160°C. The polyisoprene block and PIC are expected to show phase separation tendency due to thermodynamic instability of the miscible state. Hence, dynamic mechanical analysis is applied to SIS/PIC blends annealed at several temperatures between 100 and 160°C.

Fig. 6 shows change in the tan δ spectra for SIS(0)/PIC = 40/60 (w/w) blends annealed at 100 and 120°C. The peaks shown in Fig. 6 indicate α-relaxation corresponding to glass transition of a mixture of polyisoprene block and PIC. The blend annealed at 100°C shows a single peak corresponding to the apparent miscible state. On the other hand, SIS(0)/PIC = 40/60 (w/w) blend annealed at 120°C shows an obvious shoulder at the peak. The shoulder is regarded as the appearance of heterogeneity in the region constructed by polyisoprene with PIC in SIS(0)/PIC blends. It is considered that the SIS(0)/PIC = 40/60 (w/w) blend tends towards phase separation. Since the phase behavior in SIS(42)/PIC blends is very much like that of SIS(0)/PIC blends, a similar result is obtained for SIS(42)/PIC blends. Fig. 7 indicates change in tan δ spectra for SIS(42)/PIC = 40/60 (w/w) blend annealed at 100 and 120°C. Similar to the results of SIS(0)/PIC blends, a shoulder suggesting the tendency of phase separation is recognized for the SIS(42)/PIC blends annealed at 120°C, nevertheless the blend annealed at 100°C shows a single peak. Hence, it is suggested that just dried SIS/PIC blends

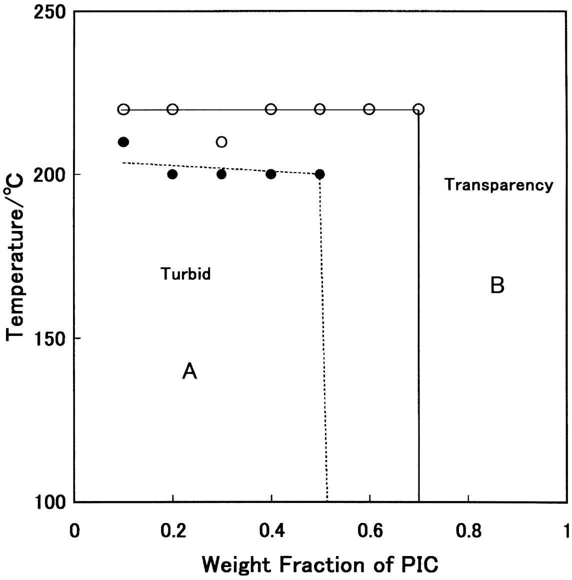

Fig. 4. Plots of cloud points detected in cooling process for SIS/PIC blends.

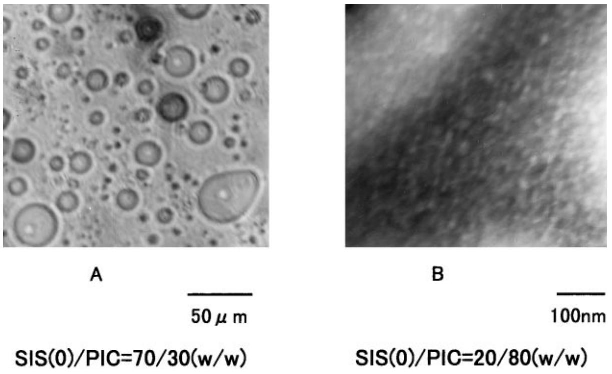

Fig. 5. OM and TEM photographs for SIS(0)/PIC blends at A and B states, respectively.

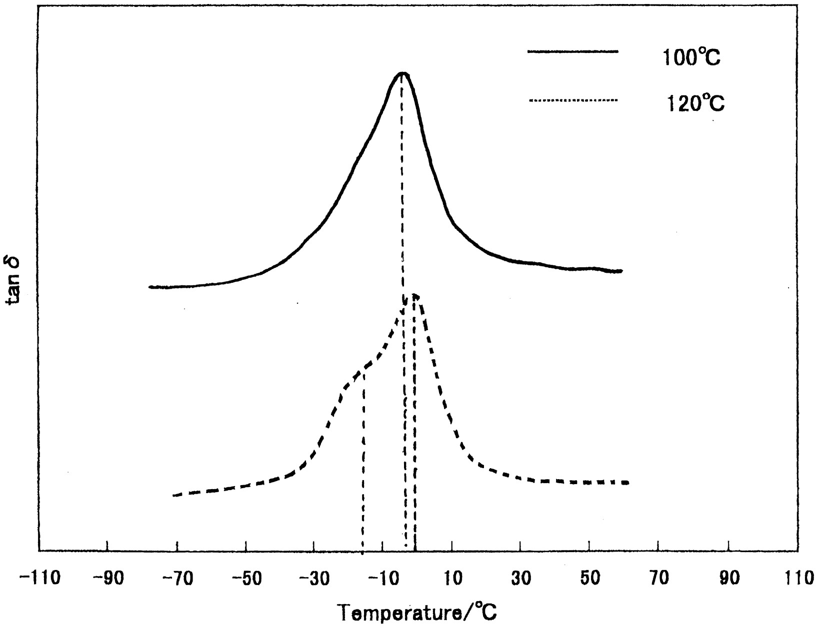

Fig. 6. tan δ spectra for SIS(0)/PIC = 40/60 (w/w) blend annealed at 100 and 120°C.

tend towards phase separation even below 160°C, which is the apparent LCST for SIS/PIC blends.

3.2. PSA properties

PSA properties for just cast SIS/PIC blends are listed in Table 2. As shown in Figs. 6 and 7, the state of mixing in just dried SIS/PIC blends varies with varying annealing temperatures up to 160°C. Therefore, it is considered that the change in the state of mixing in SIS/PIC blends with varying annealing temperature and time causes drastic variation of tack properties of the PSA films based on SIS/PIC blends. In this study, we discuss the effects of annealing temperature on PSA properties of SIS-based PSA. Hence the annealing time is kept constant (1 h) for all PSA samples.

Fig. 8 shows change in ball tack value for SIS(0)/PIC blends with varying annealing temperatures. The ball tack values of SIS(0)/PIC = 80/20 and 70/30 (w/w) blends are almost invariant with variation of annealing temperature.

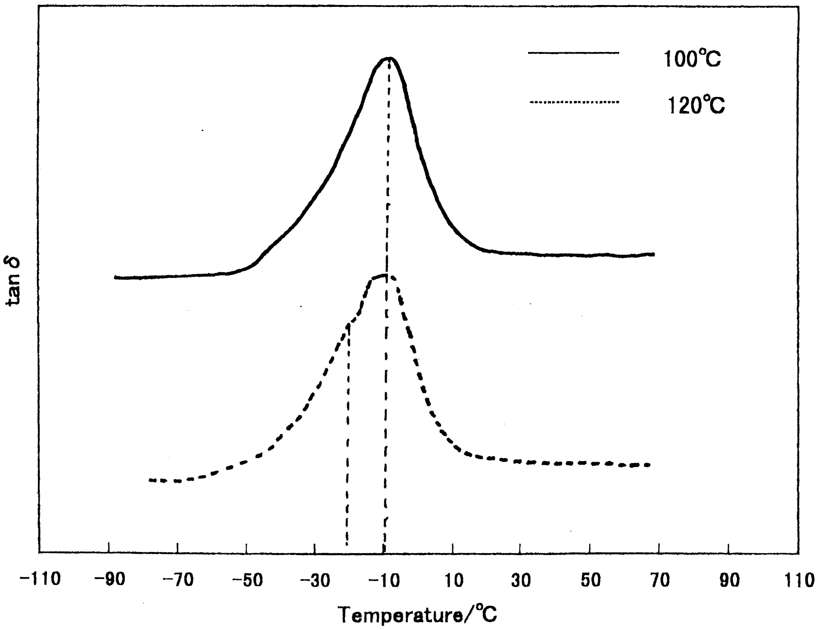

Fig. 7. tan δ spectra for SIS(42)/PIC = 40/60 (w/w) blend annealed at 100 and 120°C.

Table 2
PSA properties of SIS/PIC blends. (NC: non creep >35–000 s)

Weight fraction of PIC	0.2	0.3	0.4	0.5	0.6	0.7
SIS(0)/PIC blends						
Ball tack no.	8	8	4	<1	<1	<1
Holding power/s	NC	NC	NC	NC	NC	10 800
Peel strength/(g/25 mm)	660	710	770	1360	280	8
SIS(42)/PIC blends						
Ball tack no.	9	8	7	1	<1	<1
Holding power/s	NC	NC	NC	NC	NC	10–800
Peel strength/(g/25 mm)	810	540	1020	900	550	–

On the other hand, in SIS(0)/PIC = 60/40 (w/w) blend, the ball tack value increases continuously with increasing annealing temperatures from 40 to 120°C. Further, in SIS(0)/PIC = 50/50, 40/60, and 30/70 blends, although the ball tack values are almost constant with annealing from 40 to 100°C, they increase drastically when the blends are annealed at 120°C (temperature at which a shoulder in the peak of tan δ spectra for SIS/PIC blends appears obviously). Since the phase behavior and change of tan δ spectra with varying annealing temperature in SIS(0)/PIC blends are closely similar to those of SIS(42)/PIC blends, a similar dependence of annealing temperature in ball tack value for SIS(42)/PIC blends is expected.

Fig. 9 shows variation in ball tack values for SIS(42)/PIC blends with varying annealing temperatures. SIS(42)/PIC = 80/20, 70/30, and 60/40 (w/w) blends show a relatively high ball tack value regardless of variation of annealing temperature. On the other hand, ball tack of SIS(42)/PIC = 50/50, 40/60, and 30/70 (w/w) blends annealed between 40 and 120°C have significantly low values that increase drastically at 120°C. The annealing temperature between 100 and 120°C corresponds to the molten state in SIS/PIC blends. Since the homogeneous state of just cast samples is caused by the process of PSA preparation, the state of mixing of SIS/PIC blends is varied with varying annealing temperatures in molten state. To investigate the state of mixing of SIS/PIC blends, dynamic mechanical analysis is performed for SIS/PIC blends annealed between 100 and 120°C.

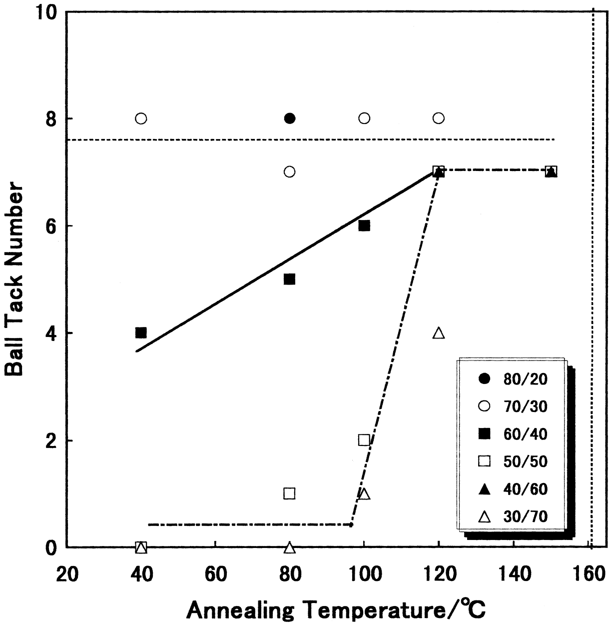

Fig. 8. Change in ball tack value for SIS(0)/PIC blends with variation of annealing temperature.

4. Concluding remarks

It is found that just cast SIS/PIC blends show both LCST and UCST type phase transition in the heating process. Further, it is observed by cloud point measurements in cooling process that the LCST of the systems are apparent phase transitions. However, the apparent miscible states of SIS/PIC blends are maintained till 160°C, which is the temperature above glass transition of polystyrene block. It is also found that the PSA properties of just cast SIS/PIC blends are changed by varying annealing temperatures up to the apparent LCST due to changes in the state of mixing.

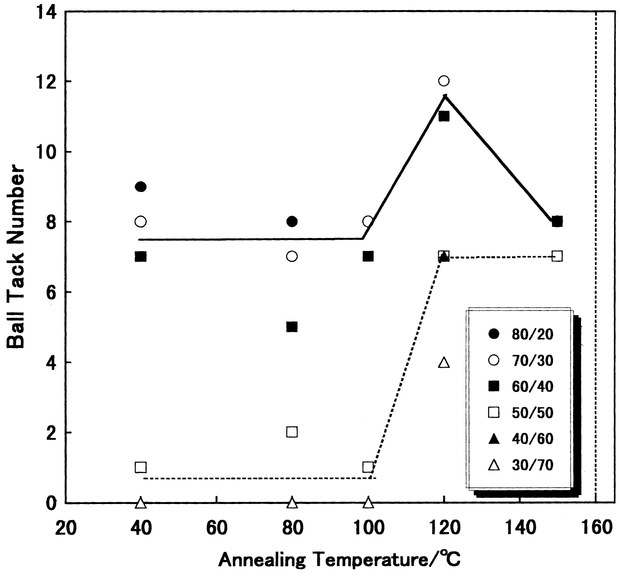

Fig. 9. Change in ball tack value for SIS(42)/PIC blends with variation of annealing temperature.

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