The Journal of Adhesion

Miscibility and Probe Tack of Acrylic Pressure Sensitive Adhesives—Acrylic Copolymer/Tackifier Resin Systems

Hyun-Joong Kim[a]; Hiroshi Mizumachi[a]

[a] Division of Chemistry of Polymeric Materials, Department of Forest Products Science, Faculty of Agriculture, The University of Tokyo, Tokyo, JAPAN

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HYUN-JOONG KIM and HIROSHI MIZUMACHI

Division of Chemistry of Polymeric Materials,
Department of Forest Products Science, Faculty of Agriculture,
The University of Tokyo, Bunkyo-Ku, Tokyo 113, JAPAN

Miscibility between acrylic copolymers and tackifier resins are investigated in terms of phase diagrams, and the probe tack of the blends are measured as a function of both temperature and rate of separation in order to obtain the master curves. It is found that the probe tack of the pressure sensitive adhesives are closely related to the miscibility between the components. The master curves of the miscible blends shift along the X(rate)-axis according to the change of T_g of the bulk materials with a gradual variation of the peak heights. However, those of the immiscible blends will not shift along the X(rate)-axis, but the magnitude will decrease with increase of a dispersed phase.

KEY WORDS: acrylic PSA; tackifier resin; miscibility; probe tack; master curves; polymerblends; glass transition temperature; phase diagrams

INTRODUCTION

There are several types of pressure sensitive adhesives, such as rubber-based pressure sensitive adhesives, block copolymer (SIS, SBS, SEBS, etc.)-based pressure sensitive adhesives, acrylic pressure sensitive adhesives and others.[1] The former two are blends of rubbery polymers and oligomeric tackifier resins, and the third type of pressure sensitive adhesive has been acrylic copolymers without any added ingredients. Recently, however, there are many cases where the acrylic polymers are blended with some tackifier resins in order to modify the practical performance of these materials as pressure sensitive adhesives. We wish to study some of the mechanical properties of these materials to clarify the extent of miscibility between the components, because it is a fundamental factor for structure formation in the materials.

Miscibility between elastomeric polymers and tackifiers has been studied by many researchers, especially in the field of rubber-based pressure sensitive adhesives[2–5] and block copolymer-based pressure sensitive adhesives,[6–10] although there are few studies where the phase diagrams are shown. However, no researchers have systematically studied the miscibility in acrylic pressure sensitive adhesives in relation to their practical performance. Kim and Mizumachi[11,12] studied the miscibility between poly (butyl acrylate-co-acrylic acid) and some tackifier resins, and analyzed the phase

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diagrams according to the Flory-Huggins theory. In a subsequent paper, they reported on the relation between the peel strength of the acrylic pressure sensitive adhesives and the miscibility between the components. In the case of miscible blends, incorporation of tackifier resin results in the modification of the bulk properties of the blends. However, in the case of an immiscible blend when two phase exist in the system, the absolute value of peel strength of an immiscible acrylic PSA decreases as the amount of the dispersed phase increases.

There have been few studies on the relationship between the phase diagrams and probe tack of PSAs. Therefore, in this study, probe tack of some pressure sensitive adhesive systems are investigated and the dependence of the master curves of the probe tack on the miscibility is discussed.

EXPERIMENTAL

Materials

The acrylic copolymers used in this study are listed Table I, where the average molecular weight is also shown. All these samples were kindly supplied by Toyo Ink Manufacturing Co. in the form of ethyl acetate/toluene solution (84.6/15.4 by wt.%). The tackifier resins were a hydrated terpene resin, "Clearon K-4090", a terpene phenolic copolymer (phenol 25%), "YS Polystar T-130", an esterified rosin, "Superester A-100" and a partially polymerized rosin, "Polypale", which were kindly supplied by Yasuhara Chemical Co. Ltd., Arakawa Chemical Co. Ltd., and Hercules Co. Ltd., respectively. Their characteristics are listed in Table II. They were dissolved in ethyl acetate (50/50 by volume %).

TABLE I
Acrylic Copolymers*

Code	Composition of Copolymers (mol %)	M_n	M_w	$T_g(°C)$
NO. 1	Butyl Acrylate/Acrylic Acid (97/3)	112,000	417,600	−42
NO. 2	Butyl Acrylate/Acrylic Acid (90/10)	110,800	241,900	−21
NO. 3	2-Ethyl Acrylate/Butyl Acrylate/			
	Vinyl Acetate/Acrylic Acid (39/21/37/3)	80,000	399,000	−40

*: Toyo Ink Manufacturing Co. Ltd.

TABLE II
Tackifier Resins

Tackifier Resins	M_n	M_w	S.P.*	Modification of Resins
Superester A—75 (R)(1)	900	1,100	75	Disproportionation of Abietic Acid
Polypale (R)(2)	1,300	2,000	102	Partially Polymerized Rosin
YS Polystar T—130 (T)(2)	1,000	1,300	131	Terpene Phenolic copolymer (Phenol 25%)
Clearon K—4090 (T)(3)	1,000	1,500	89	Hydrogenated Terpene

(R): Rosin, (T): Terpene, *: Softening Point (°C)
(1): Arakawa Chemical Industry Co. Ltd., (2): Hercules Co. Ltd., (3): Yasuhara Chemical Co. Ltd.

Blend Preparation

All the blends of acrylic copolymers with tackifier resins, with blend ratios of 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80 and 10/90 by weight, were prepared by casting from ethyl acetate/toluene solutions. The solutions were kept at room temperature for 24 days to ensure complete dissolution. Also, the samples for DSC and Rheovibron studies were prepared by removing the solvent slowly at room temperature for 24 hours. All the samples were dried at 80°C for 24 hours, and then dried in a vacuum oven at 110°C for 48 hours to remove residual solvent completely.

T_g Measurements

The glass transition temperatures (T_g) of various samples were measured with a Perkin-Elmer DSC-7 differential scanning calorimeter with a heating rate of 40°C/min. The glass transition temperature reported in this study was obtained from the second scan to assure reproducible thermograms free from thermal history effects. In all cases T_g was taken as the intersection of the extrapolated low temperature base line with the tangent to the heat capacity rise endotherm. In order to get supplemental information on transition of the blends, dynamical mechanical properties were measured as a function of temperature at a fixed frequency of 110 Hz using a Rheovibron Dynamic Mechanical Spectrometer, Model DDV-II, made by Toyo Baldwin Co. Ltd. Detailed methods were described previously.[12]

Phase Diagrams

Solutions of the blends were coated on glass slides and, after removing the solvent completely from the samples, they were kept at a fixed temperature for 48 hours to attain equilibrium, and then visually observed to see whether they were transparent or opaque. The same procedures were repeated by changing the temperature stepwise from 50 to 170°C, and the phase diagrams were drawn. Phase diagrams were given in our previous paper;[12] however, some of them are reproduced in the figures which appear later in this paper in order to compare the miscibility between the components of the pressure sensitive adhesives and the rheological characteristics of the probe tack.

Preparation of PSA film

PSA specimens for the probe tack tests were prepared by coating ethyl acetate solutions of the blends of acrylic copolymers and tackifier resin onto corona-treated polythelene terephthalate (PET) film of 25 μm average thickness, using or laboratory coating device. The thickness of the PSA tape was adjusted to 20 μm by a film thickness gauge. The PSA tape thus obtained was kept at room temperature in a hood for 24 hours to remove most of the solvent very slowly and then dried at 80°C for 12 hours and 120°C for 12 hours in a circulating-air oven.

Dried PSA tape was pressed onto release coating paper using a 2 kg rubber-roller. The tapes were then seasoned at 20°C and 65% RH for more than 14 days.

Measurement of Probe Tack (tack force)

The Probe Tack Tester (TAC-II, Rhesca Co. Ltd) provides a measure of the tackiness of a PSA or the PSA's ability to wet-out a surface instantaneously. The test is conducted on a probe Tack Tester with a polished stainless steel probe 2 mm in diameter, which is designed to measure the maximum force (peak) required to break the adhesive bond (grams per square centimeter) when the probe is placed in contact with a flat film at controlled rates of separation, temperatures, contact pressures, and dwell times. Measurements were carried out at five different temperatures (20, 30, 40, 50 and 70°C), and at five different rates of separation (2.5, 5, 30, 120 and 600 mm/min) under a constant pressure of 100 gf/cm^2 and a dwell time of 3 seconds. Test results are the average of four measurements under the same conditions.

RESULTS AND DISCUSSION

Probe Tack (tack force) of Miscible Acrylic PSAs

The tack depends on a number of experimental parameters such as contact time (or dwell time), contact pressure, rate of separation and temperature. The tack force should increase with rising contact pressure and contact time. Both effects were examined using a sample of acrylic copolymer No. 3/Polypale (8/2), which is a completely miscible pressure sensitive adhesive system, and the data shown in Figure 1 were obtained. The tack force increases drastically with contact time and a plateau is reached in about 18 seconds. However, when the contact pressure increases, the probe tack keeps on increasing. Our results are in agreement with the investigation of Sherriff et al.,[13] who measured the tack within a contact time of 20 seconds. Increase of the contact time increases the tack force because the adhesive is allowed to flow for a longer time and to make greater contact with the probe surface. Kamagata et al.[14] studied tack of rubber-based PSAs, and reported that when contact time is very short, the contact between adherend and adhesive is imperfect. The T_g of the resin-rich phase is higher than of the elastomer-rich phase, and though the viscosity of the system as a whole is very low, the viscosity of the resin-rich phase is high when testing at room temperature and therefore wetting is incomplete.

In this study, contact time and contact pressure were fixed at 3 seconds and 100 gf/cm^2, respectively.

Figure 2 illustrates the temperature- and rate-dependence of acrylic copolymer NO. 1. The master curves of the probe tack for acrylic copolymer NO. 1 and blends with Polypale were obtained by applying the time (rate)-temperature superposition principle[15] to a series of data, which are also shown in the same figure. The probe tack linearly decreases with temperature and increases with rate of separation. The temperature dependence of the shift factor for acrylic copolymer NO. 1/Polypale systems is shown in Figure 3. The activation energies obtained from the master curves are 7, 8, 9, 5 and 6 kcal/mol for unmodified acrylic copolymer NO. 1 and blends of acrylic copolymer NO. 1 and Polypale with a resin content of 10, 20, 30 and 40 %, respectively. These blends showed a single composition-dependent T_g as shown in Figure 4a (lower), which is considered to be a confirmation of the fact that acrylic copolymer
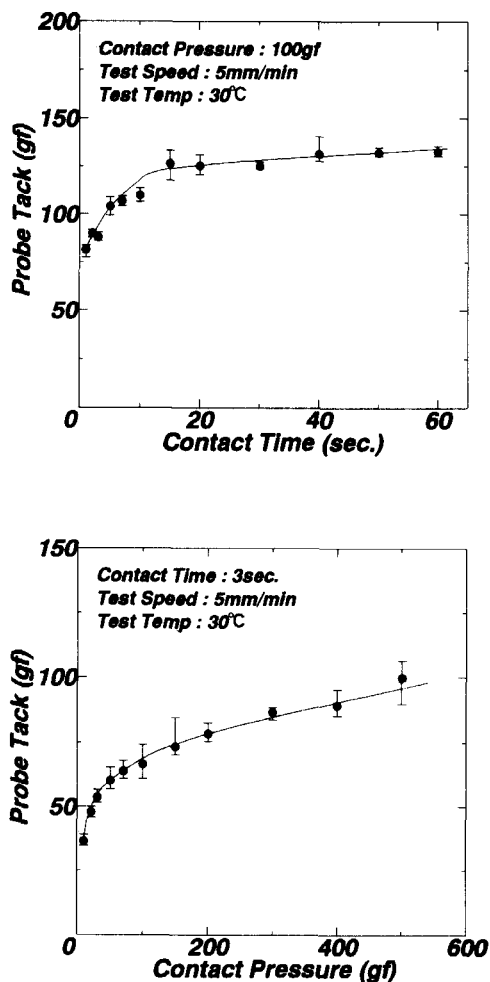
FIGURE 1   The plot of contact time and contact pressure against probe tack of acrylic copolymer NO. 3 and Polypale (8/2) system.

NO. 1 and Polypale are miscible with each other below the T_g of the blends. The blends were transparent upon further heating until they were heated above the cloud point where they became opaque because of phase separation. The phase diagram of a lower critical solution temperature (LCST) type is drawn in Figure 4a (upper). The skewness of the phase diagram toward the high Polypale concentration side arises from the difference in the molecular weight of the two components.[16] The overall master curves of a series of acrylic copolymer NO. 1/Polypale system are shown in Figure 4b. As the content of Polypale increases, the probe tack increases. However, in the case where the Polypale content is 40%, the tack reaches a maximum (or a peak) at about 1×10^{-2} (cm/sec.) and then decreases to zero as the rate of separation increases further. The probe tack of unmodified acrylic copolymer NO. 1 is smaller than that of the blends
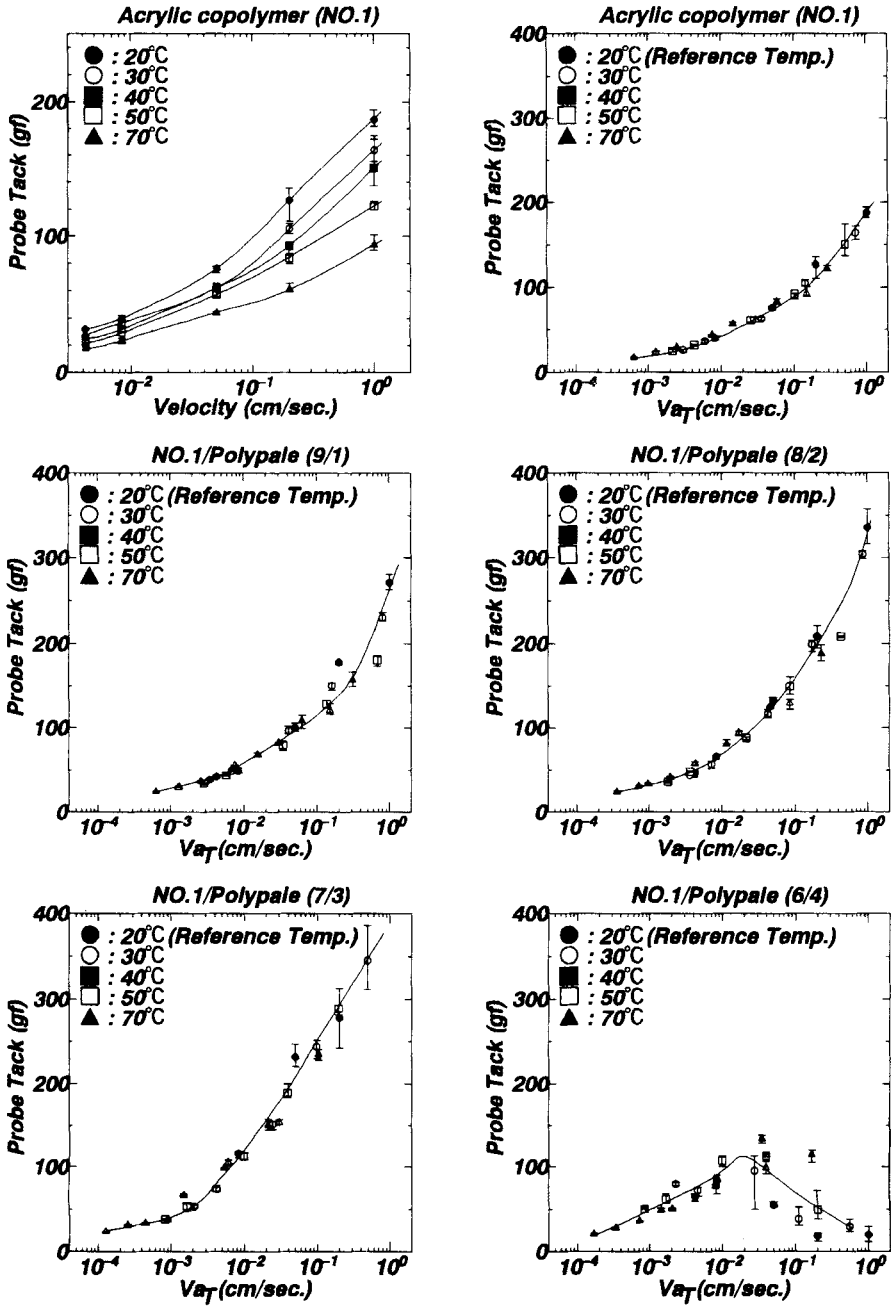
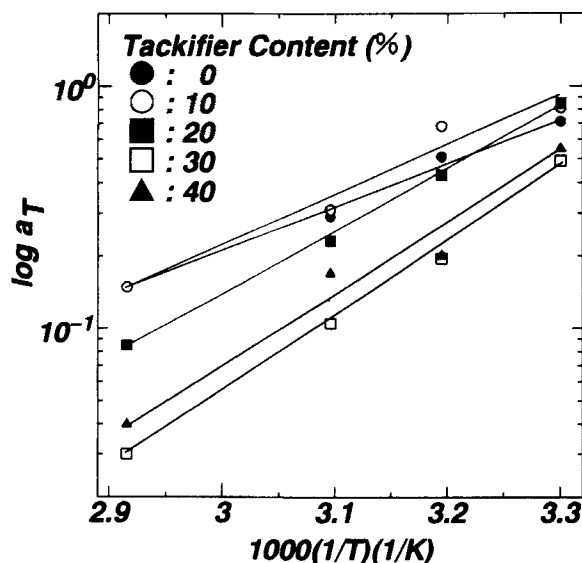FIGURE 2   Master curves of acrylic copolymer NO. 1 and Blends.

FIGURE 3   Arrhenius plot of acrylic copolymer NO. 1 and Polypale system.

within the entire velocity range in this study, except for blends of 40% content of Polypale in the higher separation rate region. Among these systems, maximum probe tack is obtained when acrylic copolymer NO. 1 is blended with 30% content of Polypale. Similar studies were done by Wetzel and coworkers,[2] but they did not investigate the phase diagrams of the PSA systems and they did not measure the PSA performance (probe tack) as a function of temperature and rate of separation. Figure 5a shows a T_g-composition curve (lower) and a phase diagram (upper) of the blend of acrylic copolymer NO. 3 and Superester A-75. All of the solution-cast films of the blends with different compositions were optically clear. At a temperature of about 100°C or lower, they were transparent and no indication of phase separation was observed. For the miscible acrylic copolymer/tackifier resin blends where specific interactions may be expected, one predicts that a single glass transition temperature should be observed. Our DSC analysis shows that the T_g of these blends elevates gradually with increase in tackifier as expected for miscible systems. However, phase separation is observed at elevated temperature within some composition region, which means that the phase diagram of this system is of the LCST type as shown in Figure 5a (upper).

The master curves of a series of blends of acrylic copolymer NO. 3 and Superester A-75 system are shown in Figure 5b. The maximum probe tack is obtained when acrylic copolymer NO. 3 is blended with Superester A-75 at 30% within the velocity region of this experiment. In the case of this system, the peak appears at $3-7 \times 10^{-2}$ (cm/sec.) for 40% content of Superester A-75, and at $1-2 \times 10^{-2}$ (cm/sec.) for 50% content of Superester A-75. The peak shifts to lower rate of separation as the content of tackifier resin increases, i.e. as T_g of the blends elevates. The probe tack of the blends of the copolymer and tackifier resin is greater than that of the pure copolymer. But in the
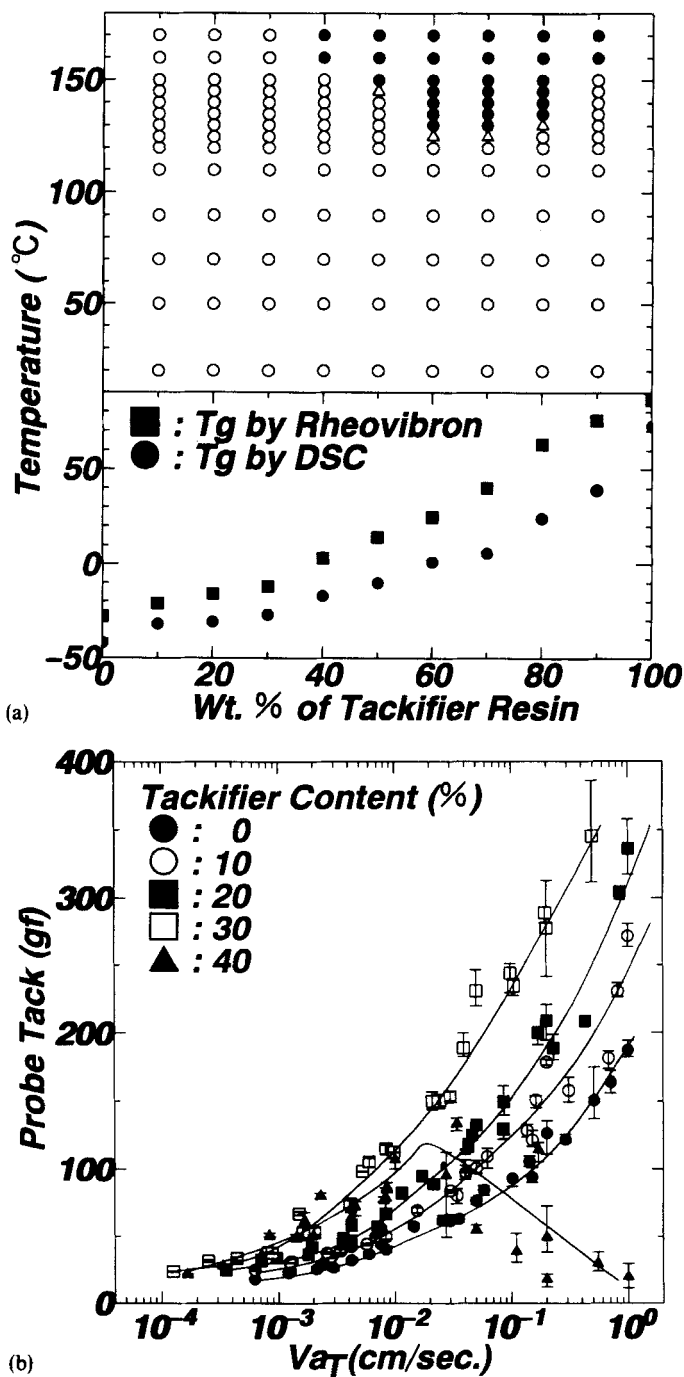
(a)

(b)

FIGURE 4   (a) Phase diagram and T_g-composition, ○: transparent (miscible), ●: opaque (immiscible) and △: intermediate state, and (b) master curves of probe tack of the blends of acrylic copolymer NO. 1 and Polypale.
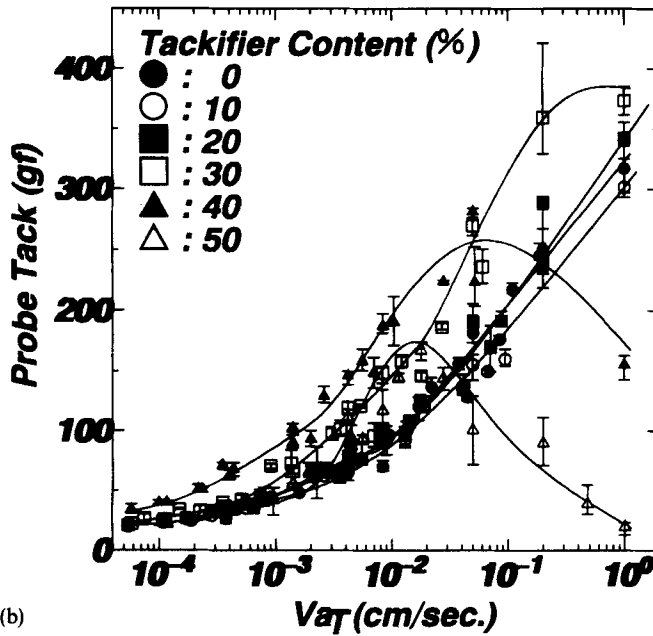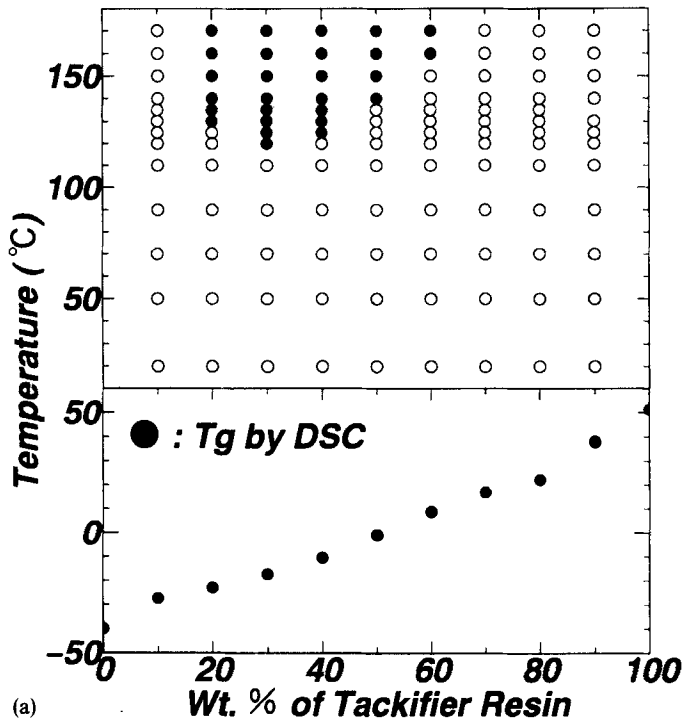
FIGURE 5 (a) Phase diagram and T_g-composition, and (b) master curves of probe tack of the blends of acrylic copolymer NO. 3 and Superester A-75 system.

case of 10% content of Superester A-75, the probe tack is slightly lower than for the pure copolymer in the higher velocity region.

A T_g-composition curve and a phase diagram of the acrylic copolymer NO. 3 and Polypale system are shown in Figure 6a. The blends show a single glass transition temperature by DSC over the entire blend composition range. This is evidence that the amorphous phase in these blends is a single phase where components are molecularly mixed. The overall master curves of the acrylic copolymer NO. 3 and Polypale system are shown in Figure 6b. In the case of miscible blends, a peak is obtained in all the blends but, in the unmodified acrylic copolymer NO. 3, no peak is found within the velocity region of this study. The peaks for individual blends are observed at 1–2×10^{-1}, 4–9 $\times 10^{-2}$, 1–2 $\times 10^{-2}$, and 4–5 $\times 10^{-3}$ (cm/sec.) for 10%, 20%, 30% and 40% content of Polypale, respectively, and the maximum value of the tack decreases rapidly as tackifier concentration increases. The peak in these blends shifts to a lower rate of separation as the content of tackifier resin increases.

Figure 7a shows a T_g-composition curve and a phase diagram of the acrylic copolymer NO. 3 and YS Polystar T-130 system. All the blends of the acrylic copolymer NO. 3/YS Polystar T-30 system exhibit a single T_g which is located between those of the components. Consequently, it can be concluded that the blends are completely miscible systems. In other words, segments of the two components mix with each other. A concave curve is obtained when T_g is plotted as a function of the weight fraction of tackifier resin (Figure 4a, 5a, 6a and 7a). This concavity is generally found in polymer/polymer blends wehre a strong interaction between the segment pairs is expected to be present.[11,17,18] Master curves of the probe tack for a series of the blends of acrylic copolymer NO. 3 and YS Polystar T-130 system are shown in Figure 7b. A peak in the master curve is observed when acrylic copolymer NO. 3 is blended with tackifier resin. The peak is located at 2×10^{-1} and $2-3 \times 10^{-2}$ (cm/sec.) for a YS Polystar T-130 content of 10 and 20%, respectively. Generally the probe tack vs. log(Va$_T$) curve shifts toward the lower velocity side in a manner similar to the peel strength P vs. log(V) curve and this is in agreement with theoretical prediction.[19,20] Similar phenomena were also studied by Aubrey et al.[21] and Class and Chu,[7–9] where the rheological aspects of performance of natural rubber-based PSAs were investigated.

Probe Tack of Immiscible Acrylic PSAs

In Figure 8a (lower) the T_g's of the acrylic copolymer NO. 1/Clearon K-4090 blends are plotted against composition, where T_g's were determined by DSC and Rheovibron. Two glass transition temperatures were observed in each of the blends. The T_g's are close to those of acrylic copolymer NO. 1 and Clearon K-4090. Moreover, all the films of the blends were cloudy. The results show that acrylic copolymer NO. 1 is immiscible with Clearon K-4090 at any concentration. The phase diagram of acrylic copolymer NO. 1/Clearon K-4090 blends, in Figure 8a (upper), shows that the blends are cloudy in most of the composition regions and temperatures of the experiments in this study. Master curves of the probe tack for a series of blends of the acrylic copolymer NO. 1 and Clearon K-4090 system are shown in Figure 8b. In the case of immiscible blends,
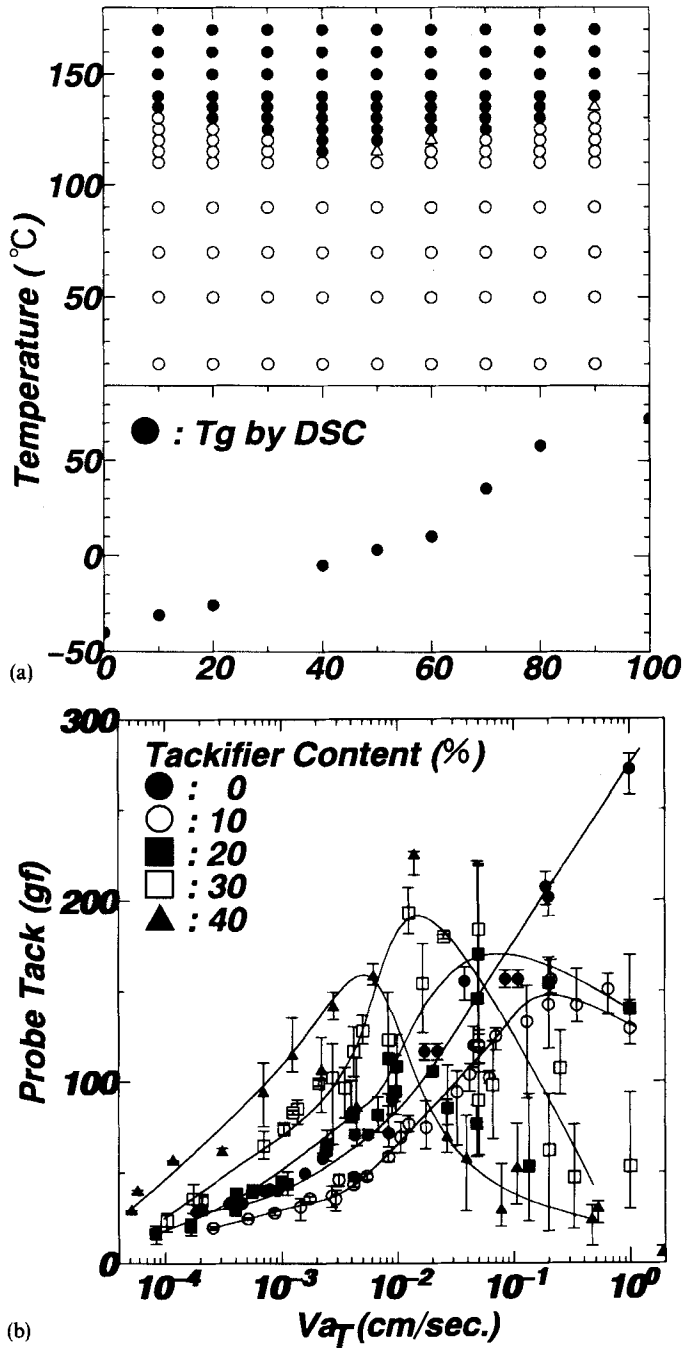
FIGURE 6 (a) Phase diagram and T_g-composition, and (b) master curves of probe tack of the blends of acrylic copolymer NO. 3 and Polypale system
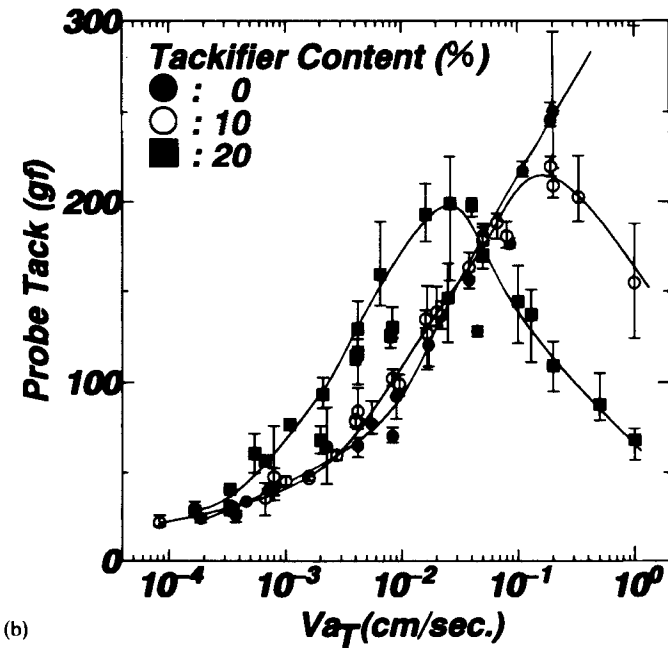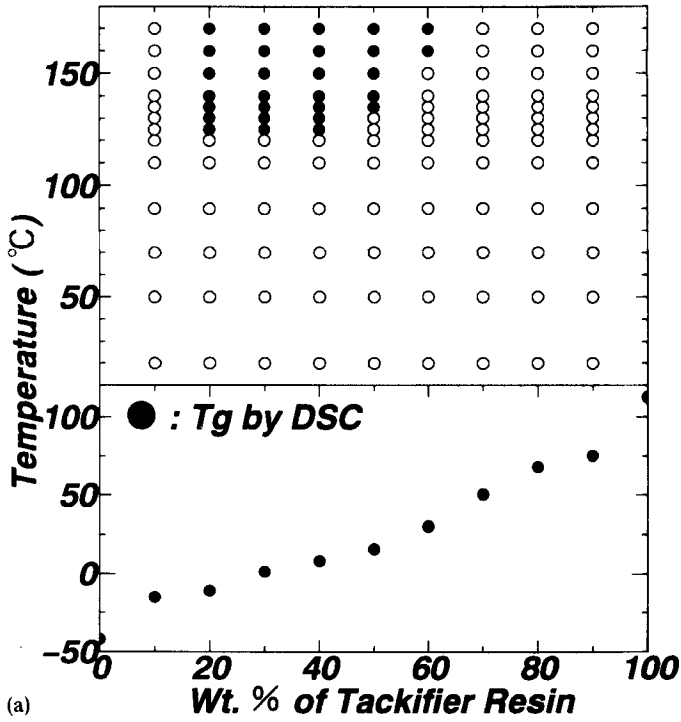
(a)

(b)

FIGURE 7   (a) Phase diagram and T_g-composition, and (b) master curves of probe tack of the blends of acrylic copolymer NO. 3 and YS Polystar T-130 system.
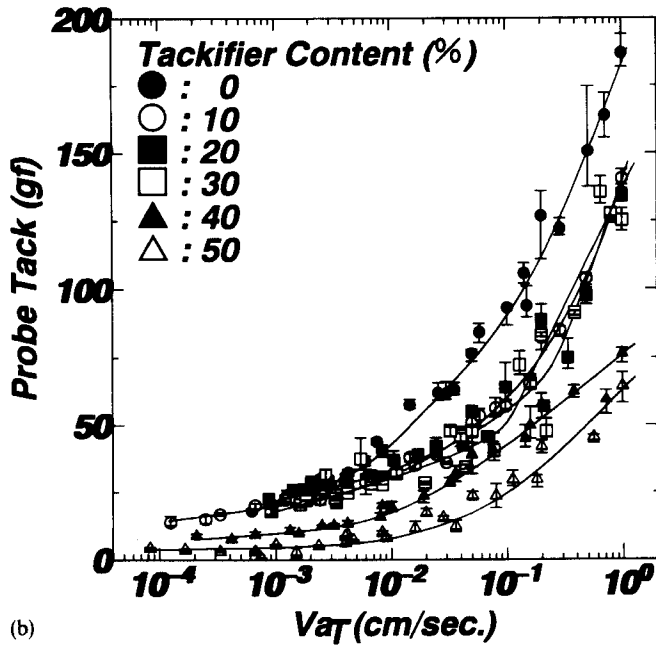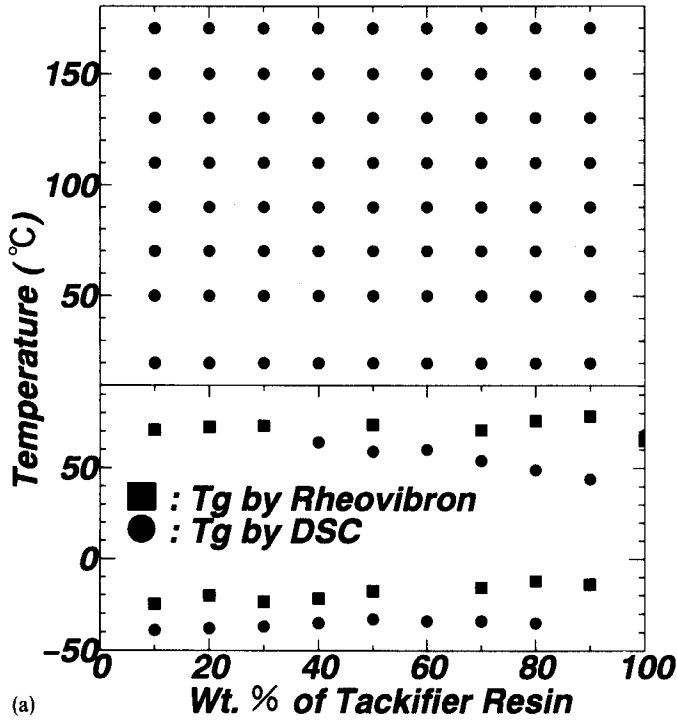
FIGURE 8 (a) Phase diagram and T_g-composition, and (b) master curves of probe tack of the blends of acrylic copolymer NO. 1 and Clearon K-4090 system.

the probe tack of unmodified acrylic copolymer NO. 1 is much greater than that of the blends. Probe tack of the blends of acrylic copolymer NO. 1 with Clearon K-4090 remarkably decrease as Clearon K-4090 content increases, and no peak is observed in the velocity region of this study. These trends are remarkably different from those given in the corresponding figures for miscible blends. Acrylic copolymer NO. 1 cannot be modified by incorporation of these tackifier resins. This feature is similar to our previous study of peel strength of immiscible blends, where it was pointed out that performance of a PSA depends mostly upon the dynamic mechanical properties of the matrix phase, and the resin-rich phase acts as a filler, reducing the performance.[12,22]

The T_g-composition curves and a phase diagram of acrylic copolymer NO. 2/Clearon K-4090 blends are shown in Figure 9a (lower and upper, respectively). On the basis of the DSC data on glass transition temperatures and film opaqueness, the blends are found to be completely immiscible over nearly the whole composition region. Master curves of the probe tack for acrylic copolymer NO. 2 and Clearon K-4090 system are shown in Figure 9b. This system is also similar to Figure 9b in respect to the fact that the probe tack of unmodified acrylic copolymer is much greater than that of the blends.
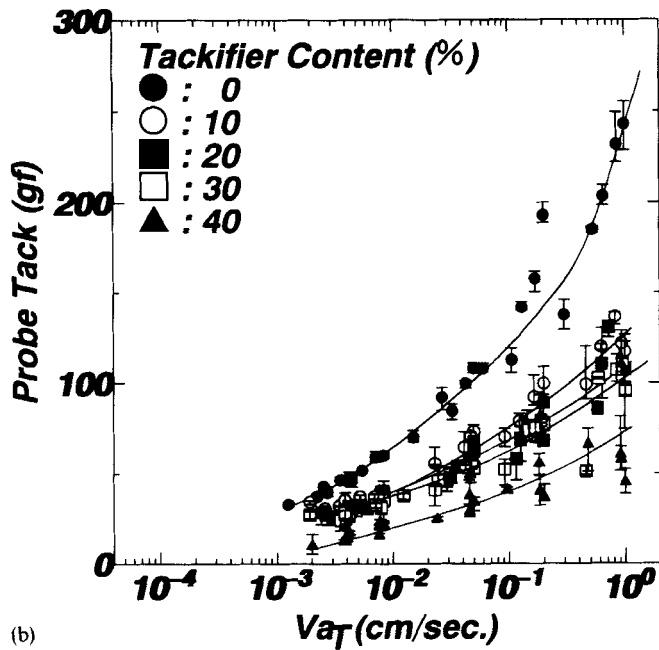
The T_g-composition curves and a phase diagram of acrylic copolymer NO. 3/Clearon K-4090 blends are shown in (Figure 10a) (lower and upper, respectively). These blends are also completely immiscible over the entire composition range, judging from the double T_g and opaqueness of the blends which is similar to the case of Figure 8a and 9a. Master curves of the probe tack for the acrylic copolymer NO. 3 and Clearon K-4090 system are shown in Figure 10b. There are also the blends of a completely immiscible system.

Probe Tack of Acrylic PSAs, the Components of which are Miscible within Some Composition Region

Acrylic copolymer NO. 2 and Superester A-100 are miscible with each other within some composition region and immiscible outside of this region, as shown in Figure 11a (lower and upper). On the basis of DSC results, a single T_g appears when the tackifier content is between 0% to 20–30%, but two distinctly separated T_g's appear at higher tackifier content. This is not precisely in agreement with the phase diagram of the system given in the same figure. But the blend system is certainly miscible at a Superester A-100 content of 10% or lower. Master curves of the probe tack for a series of blends of acrylic copolymer NO. 2 and Superester A-100 system are shown in Figure 11b. Probe tack of the blend at a Superester A-100 content of 10%, where a uniform phase exists, is much greater than that of the unmodified acrylic copolymer NO. 2. Probe tack of the blend at a Superester A-100 content of 20% is also greater than that of unmodified acrylic copolymer NO. 2. Consequently, the probe tack of the miscible blend is greater than that of polymer without tackifier resin, especially in the lower velocity region (Figure 4b, 5b, 6b and 7b). But the probe tack of the blend at higher Superester A-100 content, where phase separation has occurred, is smaller than that of acrylic copolymer NO. 2 without tackifier resin, as predicted in another immiscible system. These results are in agreement with our previous study that some discontinu-
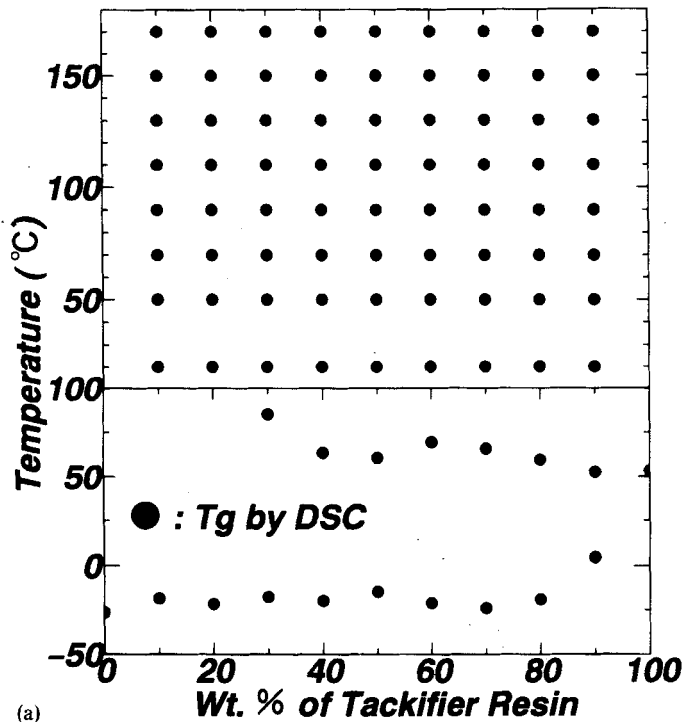
(a)

(b)

FIGURE 9   (a) Phase diagram and T_g-composition, and (b) master curves of probe tack of the blends of acrylic copolymer NO. 2 and Clearon K-4090 system.
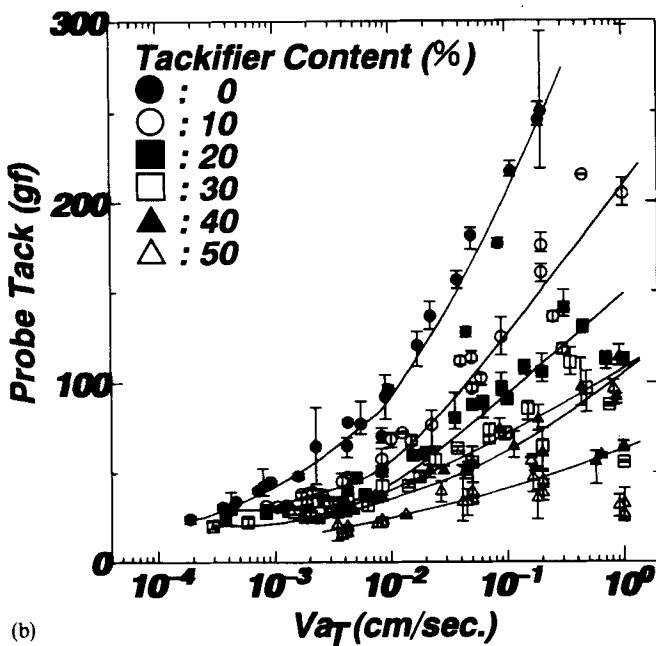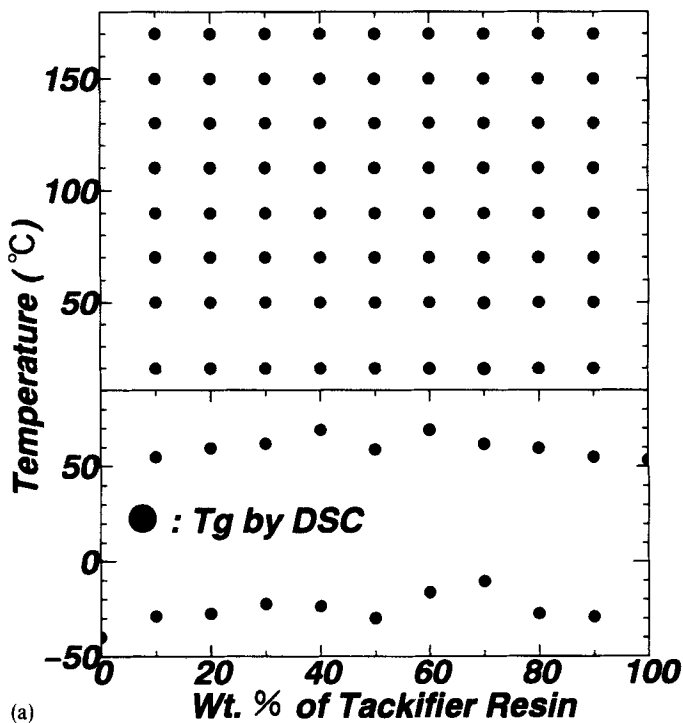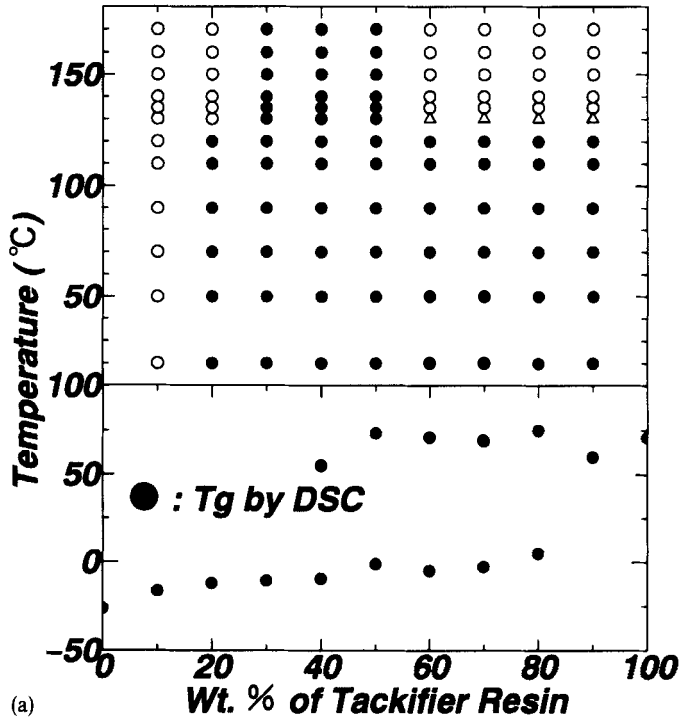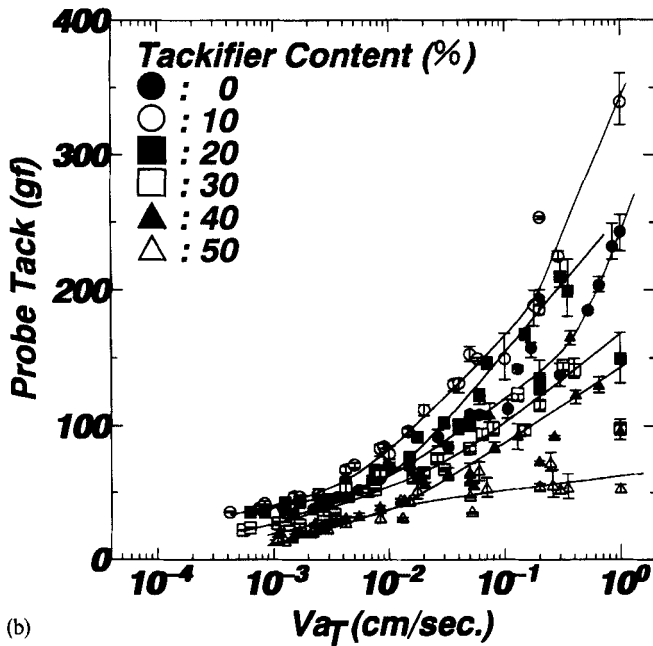
FIGURE 10   (a) Phase diagram and T_g-composition, and (b) master curves of probe tack of the blends of acrylic copolymer NO. 3 and Clearon K-4090 system.

FIGURE 11   (a) Phase diagram and T_g-composition, and (b) master curves of probe tack of the blends of acrylic copolymer NO. 2 and Superester A-100 system.

ous drops are found not only in tack and peel strength, but also in probe tack at around the concentration at which the phase structure changes.[12,22]

A schematic illustration of the probe tack for miscible acrylic pressure sensitive adhesives is shown in Figure 12. Suppose we have a uniform PSA, and measure the probe tack over a very wide range of separation rate. Then we get a curve having a peak at some separation rate (V_{peak}). Cohesive failure occurs at a separation rate (V) lower than V_{peak}, and interfacial failure occurs when $V > V_{peak}$. When $V < V_{peak}$, the probe tack value depends solely upon mechanical properties of the bulk PSA materials. But when $V > V_{peak}$, the probe tack value depends not only upon the mechanical properties of the bulk PSA, but also upon the surface chemical properties of both PSA and adherends. For example, the peak height will be expected to decrease as γ_c of the adherend decreases. If the interfacial properties of the materials are the same even when the blend ratio changes, then we only have to think of the horizontal shift of the master curves, because T_g of the miscible PSA systems will vary systematically by incorporation of tackifier resins. In our study, the master curve of the probe tack of the miscible PSA systems shifts toward the lower rate side and, at the same time, the peak height decreases as tackifier content increases. This means that incorporation of tackifier resin results in modification of the viscoelastic properties and also the surface tension of the PSAs.

A schematic illustration of the probe tack for immiscible acrylic pressure sensitive adhesives is shown in Figure 13. In the case of immiscible systems, which keep a constant T_g value, the peak of the probe tack is not observed in the range of separation rate in this experiment. But it is considered that the peak of the probe tack will appear at the same separation rate outside of our experimental range and the magnitude will decrease with increase of tackifier content as shown in Figure 8b, Figure 9b and Figure 10b.
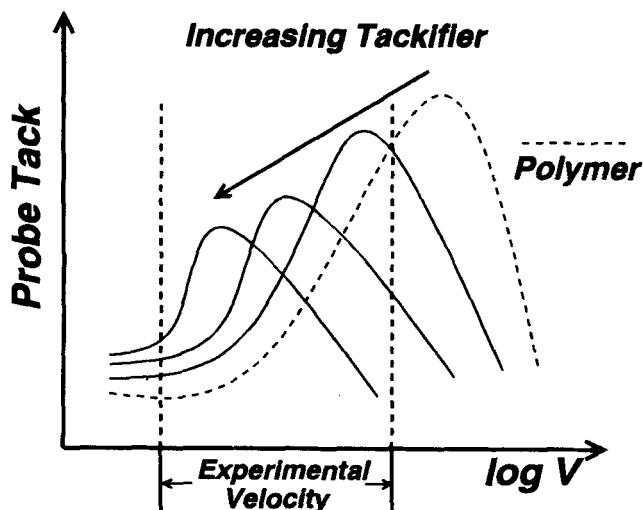

FIGURE 12   Schematic representation of PSA performance for miscible blends.
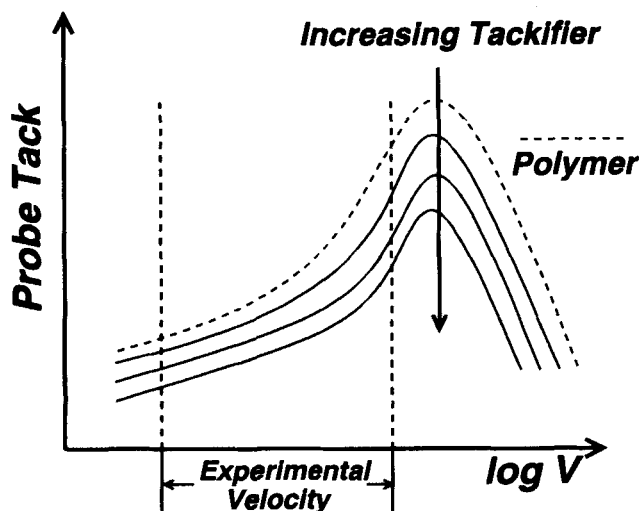
FIGURE 13   Schematic representation of Psa performance for immiscible blends.

CONCLUSION

Because most pressure sensitive adhesives are blends of rubbery polymers and oligomeric tackifier resins, it is very important to investigate the relationship between the miscibility of the components and the practical performance.

In this study, phase diagrams of the blends of acrylic copolymers and tackifier resins are examined, and it is found that there are four types of phase diagrams: miscible type, LCST type, UCST type and immiscible type. The probe tack of these types are measured as a function of both temperature and rate of separation, and master curves are obtained by applying the time (rate)-temperature superposition principle.

In the case of systems where the components are miscible with each other at any blend ratio in the temperature range of the probe tack tests, a single T_g was found which varies gradually with the composition, and the master curve of the probe tack shifts along the X(rate)-axis with a gradual change of peak height. In the case of systems where the components are not miscible at all, double T_g's were observed which do not vary greatly with composition, and it is supposed that the peak of the master curve of the probe tack will not shift along the rate axis and the magnitude will decrease with increase of tackifier content. Physical properties and practical performance of the blends with a two-phase structure depend mostly on the matrix phase, and a dispersed phase will act as a kind of filler.

Finally, in the case of systems where the components are miscible within a restricted range of composition, and immiscible outside this range, intermediate behavior is found.

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