

# Miscibility and Shear Creep Resistance of Acrylic Pressure-Sensitive Adhesives: Acrylic Copolymer and Tackifier Resin Systems

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## SYNOPSIS

The miscibility between an acrylic copolymer and a tackifier resin was investigated in terms of phase diagrams, glass transition temperatures ( $T_g$ 's), and dynamic mechanical properties of blends. Shear creep resistance (holding power,  $t_b$ ) of the blends was measured as a function of both temperature and stress ( $\sigma_0$ ) in order to obtain the master curves. It was found that the shear creep resistance of the pressure-sensitive adhesives (PSAs) was closely related to the miscibility between the components and viscoelastic properties of the blends. The master curve of the miscible blends shifts toward a longer time scale as the amount of tackifier resin in the blend is increased as a result of the modification of the bulk properties, and their behavior greatly depends on the glass transition temperature ( $T_g$ ) and storage modulus ( $G'$ ) of the blends. However, the master curve of immiscible blends where two phases exist in the system does not shift greatly toward a longer time scale, because  $T_g$  and the storage modulus of the blend do not change greatly. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Resistance to creep is a very important property of pressure-sensitive adhesives (PSAs). Generally, the requirements come from end uses. For example, tapes used for book mending or envelope sealing may never be subjected to severe stress, and masking tapes supporting protective paper aprons in automotive painting during backing cycles may need resistance to relatively short-term creep at elevated temperature. Also, when objects are attached to walls with double-faced tapes, or when cartons are sealed with packaging tapes, resistance to long-term creep is of vital importance.<sup>1</sup>

The shear creep test indicates the resistance of an adhesive to shearing force. It is measured by the "static" shear test which determines the time (holding time or break time,  $t_b$ ) required to pull a defined area of a tape on a test panel under a constant shear force.<sup>2</sup> The behavior of an adhesive tape

in a shear test is strongly governed by the viscoelastic response of the PSAs. The shear test is a creep test carried to high deformation.

Generally, shear creep resistance is related to a low-rate process. According to the time-temperature superposition principle, the high-temperature region corresponds in effect to the low-frequency (rate) region of a frequency test run at a constant temperature. Macosko<sup>3</sup> and Chang<sup>4</sup> pointed out that frequencies lower than  $10^{-2} \text{ s}^{-1}$  (100 s or longer) would correspond roughly to the onset of creep in a shear creep test.

In our previous studies,<sup>5-8</sup> we examined the degree of miscibility between the components in some acrylic PSAs and reported on the dependence of the peel strength and probe tack of the acrylic PSAs on the miscibility between the components.

There have been few studies on the relationship between miscibility and the shear creep resistance of acrylic PSAs. Therefore, in this study, the influence of the dynamic mechanical properties of acrylic PSAs upon shear creep resistance is examined in relation to the miscibility between the components of the PSAs.

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**Table I Acrylic Copolymers**

Code	Composition (Mol %) <sup>a</sup>	$M_n$	$M_w$	$T_g^b$
1	BA/AA (100/0)	79,300	291,600	-36
2	BA/AA (97/3)	112,300	417,600	-42
3	BA/AA (95/5)	187,600	362,100	-29
4	BA/AA (93/7)	154,000	302,500	-23
5	BA/AA (90/10)	110,800	241,900	-21
6	BA/AA (85/15)	9600	15,900	-17

<sup>a</sup> Toyo Ink Manufacturing Co.<sup>b</sup> Measurements by DSC (°C).

## EXPERIMENTAL

### Materials

The polymers used are a homopolymer of butyl acrylate (BA) and a series of copolymers consisting of BA and acrylic acid (AA) with varying composition: BA/AA = 97/3, 95/5, 93/7, 90/10, and 85/15 by mol %. These monomers were polymerized in ethyl acetate and the solutions were kindly supplied by Toyo Ink Manufacturing Co. Their characterization data are listed in Table I.

Tackifier resins are hydrated terpene resin, "Clearon K-4090," esterified rosin with glycerol, "Superester A-100," and partially polymerized rosin, "Polypale," which were kindly supplied by Yasuhara Chemical Co., Arakawa Chemical Co., and Hercules Co., respectively. Their characterizations are listed in Table II.

The molecular weight of the acrylic polymers and tackifier resins was measured by gel permeation chromatography (GPC) using a Shodex KF-802, -803, -804, -805 column with tetrahydrofuran (THF) at 40°C.

### Preparation of Blends

The acrylic polymers and tackifier resins were blended in ethyl acetate solution in various blend

ratios: 90/10, 90/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, and 10/90. After ensuring that the solutions are uniform and transparent for more than 24 h, filmy samples of 20  $\mu\text{m}$  thickness were prepared by casting them onto glass plates. The samples were kept at 80°C for 24 h and then evacuated at 110°C for 48 h to remove the solvent from the samples.

### Measurement of $T_g$ Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Properties

The  $T_g$  of the blends was measured by a Perkin-Elmer DSC-7 equipped with a thermal analysis data station with a helium purge. Samples of 9–18 mg were encapsulated in the standard aluminum pans. The samples were first cooled to -100°C, then heated to 150°C at a heating rate of 40°C/min (first scan). Also, they were immediately quench cooled to -100°C at a cooling rate of 200°C/min and kept at this temperature for 5 min. The samples were then reheated to 150°C at a heating rate of 40°C/min (second scan). The  $T_g$  of the blends reported in this study was obtained from the second scan to assure a reproducible thermogram free from thermal history effects. The  $T_g$  was taken as the midpoint.

To obtain supplemental information on the transition of the blends, dynamic mechanical properties of the filter papers impregnated with the blends were measured as a function of temperature at a fixed frequency of 110 Hz using a Rheovibron, Model DDV-II, made by Toyo Baldwin Co. The detailed method was described in a previous article.<sup>5</sup>

Dynamic viscoelastic properties of the blends were determined by a dynamic mechanical spectrometer RDS-II (Rheometrics Inc.) in the parallel plate mode (8 mm diameter plates with a 2 mm gap). From temperature scans from the glassy region to flow at a fixed angular frequency ( $\omega$ ) of 69.08 rad/s, the dynamic storage modulus ( $G'$ ) and loss tangent ( $\tan \delta$ ) were evaluated as a function of temperature.

**Table II Tackifier Resins**

Tackifier Resin	$M_n$	$M_w$	SP <sup>a</sup>	$T_g^b$	Modification of Resins
Superester A-100 <sup>c</sup>	1000	1200	100	71	Disproportionated acetic acid
Polypale <sup>d</sup>	1300	2000	102	73	Partially polymerized rosin
Clearon K-4090 <sup>e</sup>	1000	1500	89	53	Hydrogenated terpene

<sup>a</sup> Softening point (°C).<sup>b</sup> Measurements by DSC (°C).<sup>c</sup> Arakawa Chemical Industry Co.<sup>d</sup> Hercules Co.<sup>e</sup> Yasuhara Chemical Co.

## Phase Diagrams

The blends were coated on a glass slide at about a 40  $\mu\text{m}$  thickness with a glass rod. After drying in a vacuum oven at 110°C for 48 h, they were visually observed to see whether they were transparent or opaque at this temperature. The same procedures were repeated by changing the temperature in a stepwise manner up to 170°C in an air-circulation oven. In most cases, phase diagrams could not be drawn above 180°C due to discoloration of the tackifier resin.

## Measurement of Shear Creep Resistance (Holding Power)

PSA tapes for shear creep resistance were prepared by coating ethyl acetate solutions of the blends of acrylic copolymers with the tackifier resin onto corona-treated poly(ethylene terephthalate) (PET) film of 25  $\mu\text{m}$  average thickness, using our laboratory's coating device. The thickness of the PSA tapes was adjusted to about 20  $\mu\text{m}$  by film thickness gauge. The PSA tapes thus obtained were kept at room temperature in a hood for 24 h to remove most of the solvent very slowly and then in an oven at 80°C for 12 h and at 120°C for 12 h in an air-circulation oven.

The dried PSA tapes were pressed onto a release coating paper by a 2 kg rubber roller. Then, they were seasoned at 20°C and 65% relative humidity for more than 14 days.

The holding time is a measure of the ability of a PSA to withstand pressure from another substrate under a constant stress ( $\sigma_0$ ) at a certain temperature, which pulls the PSA tape downward from a vertically placed test substrate in a direction parallel to the surface of bonding. In this study, aluminum was used as a substrate. The aluminum substrate was cleaned

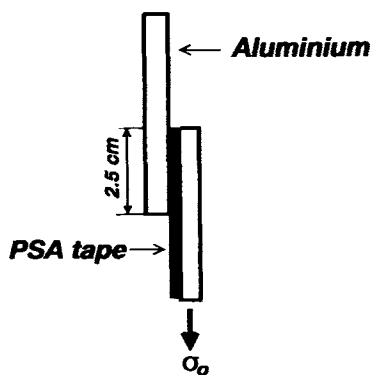


Figure 1 Measurement of shear creep resistance ( $t_b$ ).

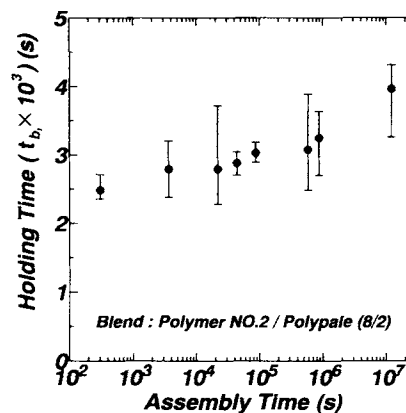


Figure 2 Plot of holding time ( $t_b$ ) against assembly time of the blends of acrylic copolymer 2 and Polypale (8/2) at 20°C.

with acetone and then with trichloroethylene beforehand. PSA tapes were pressed onto aluminum by a 2 kg rubber roller passing over twice after conditioning for 24 h at 20°C and 65% relative humidity. Test samples were prepared to form a bonding area of  $2.5 \times 2.5$  cm. Also, they were loaded at a various levels of stress ( $\sigma_0$ ) and at four different temperatures (30, 40, 50, and 60°C), as shown in Figure 1. The time to slip completely (holding time,  $t_b$ ) was recorded as the failure time by Model CP6-L-500 of Orientec Co.

## RESULTS AND DISCUSSION

### Shear Creep Resistance of Miscible Acrylic PSAs

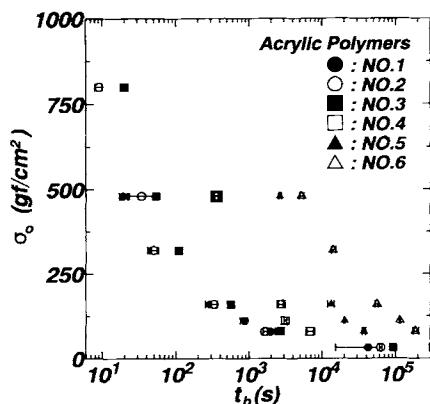
A typical plot of holding time ( $t_b$ ) against assembly time of a blend of acrylic copolymer 2 and Polypale (8/2), which is a completely miscible PSA system, is shown in Figure 2. The shear creep resistance (holding time) increases gradually with increasing assembly time. In this study, all assembly sets of samples have been kept approximately for 24 h at 20°C and 60% RH before measurements.

Figure 3 illustrates the plot of stress (loading,  $\sigma_0$ ) against holding time ( $t_b$ ) of acrylic polymers at 30°C. As loading ( $\sigma_0$ ) decreases, holding time ( $t_b$ ) increases. Also, as AA concentration increases, the holding time gradually increases. However, holding time increases sharply when the content of AA is larger than 10%.

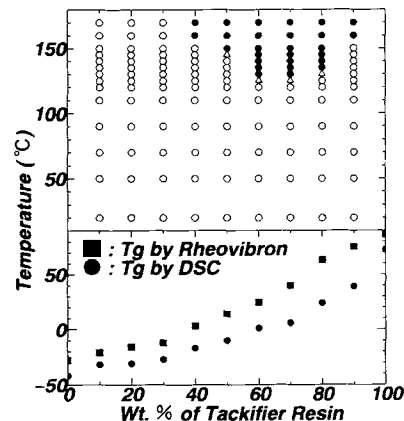
The acrylic copolymer 2 and the Polypale system showed a single composition-dependent  $T_g$  as shown in Figure 4 (lower), which is considered to be a confirmation of the fact that acrylic copolymer 2 and

Polypale are miscible with each other below the  $T_g$  of the blends. The blends were transparent while they were heated up to 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 4 (upper).

Figure 5 illustrates the temperature-dependence of the  $\sigma_0$ - $t_b$  curves of the acrylic copolymer 2 and 2/Polypale (9/1) system. The master curves of the shear creep resistance for acrylic copolymer 2 and the blends are obtained by applying the time-temperature superposition principle<sup>9</sup> to a series of data. The shear creep resistance (holding time,  $t_b$ ) linearly decreases with temperature and also decreases with stress ( $\sigma_0$ ) in both acrylic copolymer 2 and the blends. The temperature dependence of the shift factor ( $a_T$ ) for the blends of acrylic copolymer 2 and Polypale is shown in Figure 6. The activation energies ( $E_a$ ) obtained from the shift factors are relatively low values of 7, 10, 5, 8, and 5 kcal/mol for the blends of acrylic copolymer 2 and Polypale with a resin content of 10, 20, 30, and 40%, respectively. The values of activation energy ( $E_a$ ) by shear creep resistance is similar to those by probe tack of the 5–10 kcal/mol level in a previous article.<sup>7</sup> The overall master curves of a series of the blends of acrylic copolymer 2 and Polypale are shown in Figure 7. As the content of Polypale increases, the holding time ( $t_b$ ) increases. In the case of Polypale content of 40%, the holding time ( $t_b$ ) increased sharply. The holding time ( $t_b$ ) of acrylic copolymer 2 is shorter than that of the blends all over the region. It is evident that the performances of shear creep resistance as well as peel strength<sup>7</sup> and probe tack<sup>8</sup> in miscible systems of acrylic PSAs are modified systematically by incorporation of a tackifier resin.



**Figure 3** Plot of  $\sigma_0$  against  $t_b$  of acrylic polymers at 30°C.



**Figure 4** Phase diagram and  $T_g$ -composition of the blends of acrylic copolymer 2 and Polypale: (○) Transparent (miscible); (●) opaque (immiscible); (△) intermediate.

### Shear Creep Resistance of Immiscible Acrylic PSAs

Figure 8 (lower) shows the  $T_g$ -composition curve of the blends of acrylic copolymer 2 and Clearon K-4090, where  $T_g$  was measured by DSC and Rheovibron. Two glass transition temperatures ( $T_g$ 's) are observed in the whole composition range. The  $T_g$ 's are close to those of acrylic copolymer 2 and Clearon K-4090 sample. The results show that acrylic copolymer 2 is immiscible with Clearon K-4090 at any blend ratio. The phase diagram of acrylic copolymer 2 and Clearon K-4090 is shown in Figure 8 (upper). The blend films were cloudy over nearly the entire composition region and experimental temperature region. The temperature dependence of the shift factor ( $a_T$ ) for the blends of acrylic copolymer 2 and Clearon K-4090 is shown in Figure 9. The activation energies ( $E_a$ ) obtained from the master curves are 13, 8, 9, and 15 kcal/mol for the blends of acrylic copolymer 2 and Clearon K-4090 of 9/1, 8/2, 7/3, and 6/4, respectively. The overall master curves of a series of the blends of acrylic copolymer 2 and Clearon K-4090 are shown in Figure 10. As the content of Clearon K-4090 increases, the holding time ( $t_b$ ) increases. However, the degree of increasing of holding time ( $t_b$ ) for the blends of acrylic copolymer and Clearon K-4090 is much smaller than those for the blends of acrylic copolymer 2 and Polypale. The holding time ( $t_b$ ) of acrylic copolymer 2 is also shorter than that of the immiscible blends all over the region. Therefore, it is evident that miscible systems can be modified more efficiently than can immiscible systems by incorporation of a tackifier resin in shear creep resistance.

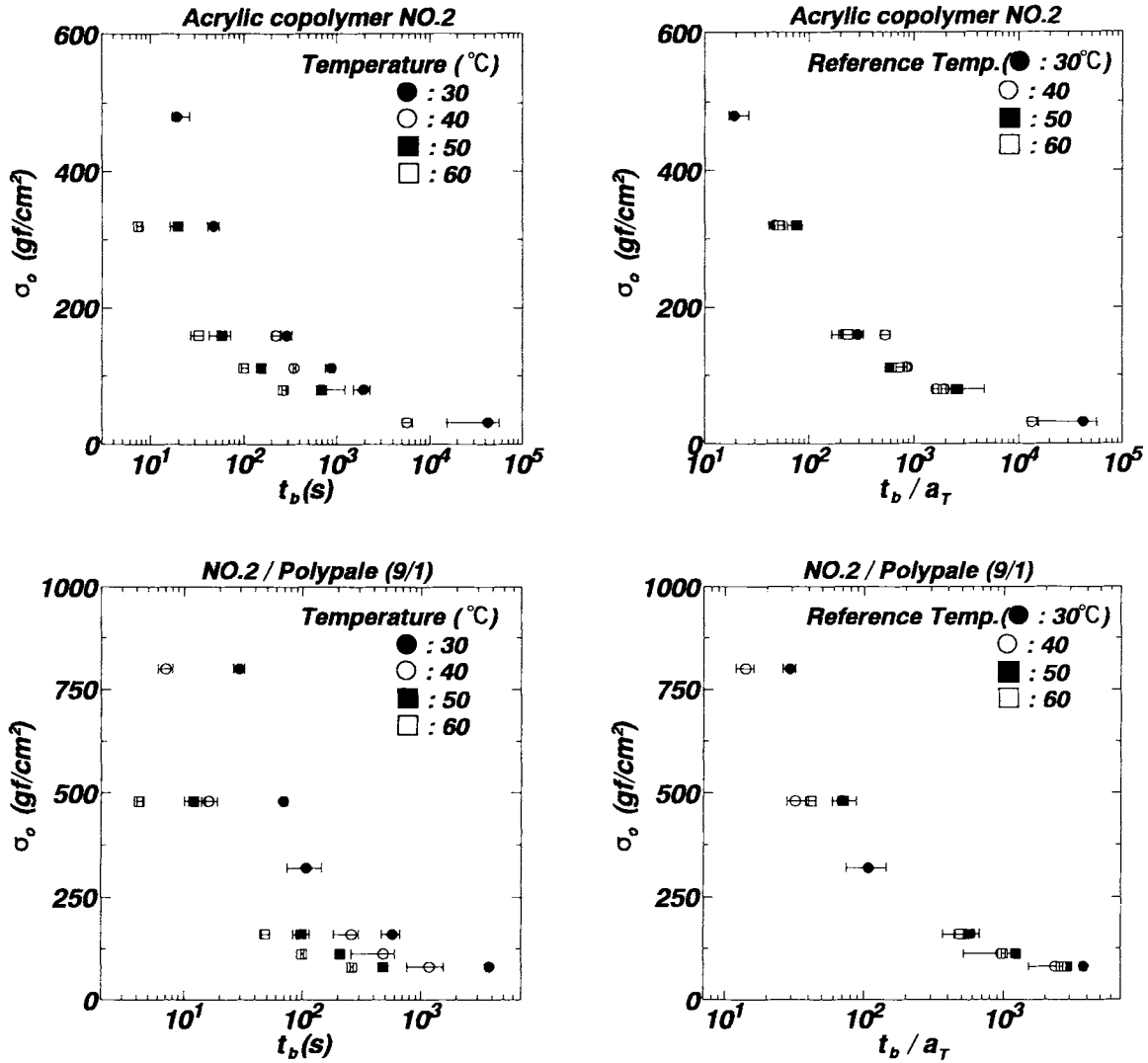


Figure 5 Plot of  $\sigma_0$  against  $t_b$  and master curve of acrylic copolymer 2 and blends of acrylic copolymer 2 and Polypale (9/1).

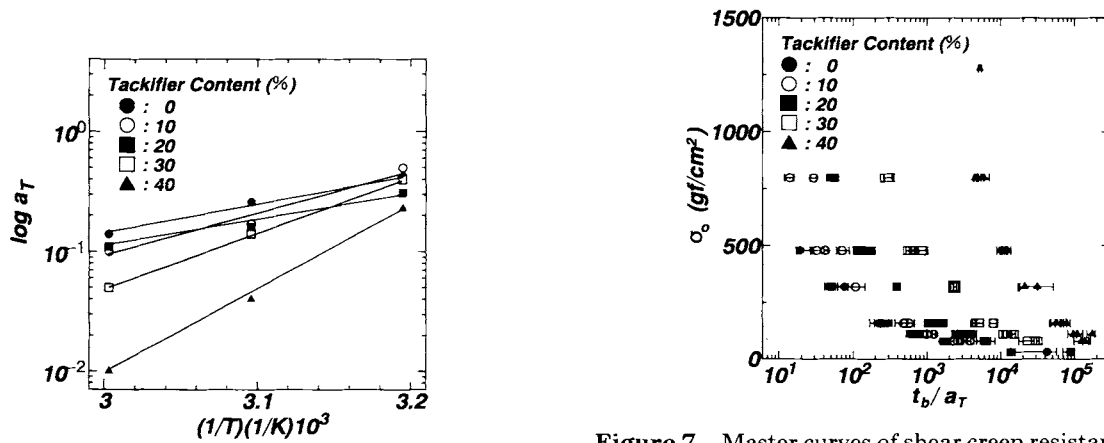


Figure 6 Arrhehinus plot of the blends of acrylic copolymer 2 and Polypale.

Figure 7 Master curves of shear creep resistance of the blends of acrylic copolymer 2 and Polypale. Reference temperature is at 30°C.

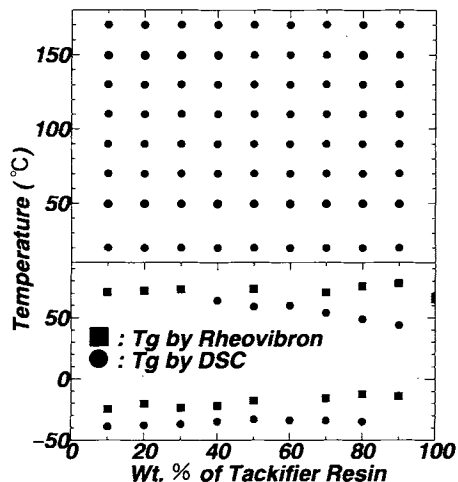


Figure 8 Phase diagram and  $T_g$ -composition of the blends of acrylic copolymer 2 and Clearon K-4090. The symbols are the same as in Figure 4.

**Shear Creep Resistance of Acrylic PSAs, Components of Which Are Miscible Within Some Composition Region**

In such systems as the blends of acrylic copolymer 2 and Superester A-100, the two components are miscible within some composition region and immiscible outside this region, just as shown in Figure 11. In the Rheovibron data, a single  $T_g$  appears when the Superester A-100 content is between 0 and 50%, but two distinctly separated  $T_g$ 's appear at higher Superester A-100 content. Although a single  $T_g$  appears in DSC data all over the composition range, we can distinctly find the second transition in the Rheovibron data. Also, this is consistent with the phase diagram of the systems given in the same figure (upper), where it is shown that phase separation occurs at room temperature when Superester A-100

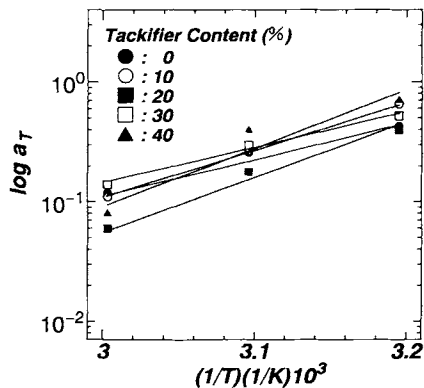


Figure 9 Arrhenius plot of the blends of acrylic copolymer 2 and Clearon K-4090.

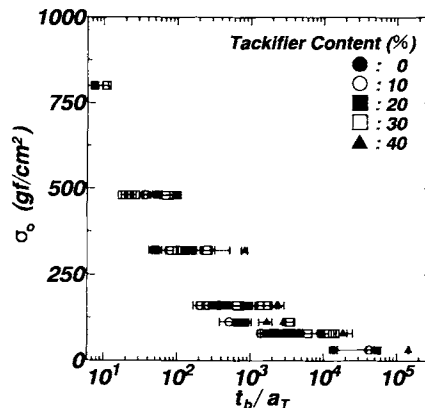


Figure 10 Master curves of shear creep resistance of the blends of acrylic copolymer 2 and Clearon K-4090. Reference temperature is at 30°C.

is more than 50%. This system exhibits a phase diagram of the upper critical solution temperature (UCST) type, i.e., the components are immiscible at elevated temperature, but phase separation occurs at low temperature, which is often found in the blends of a polymer/oligomer system. Figure 12 illustrates the plot of stress (loading,  $\sigma_0$ ) against holding time ( $t_b$ ) of the blends of acrylic copolymer 2 and Superester A-100 at 30°C. As the content of Superester A-100 increases, the holding time ( $t_b$ ) increases. This tendency of the blends of acrylic copolymer 2 and Superester A-100 is similar to that of miscible system within a miscible region.

**Shear Creep Resistance and Dynamic Mechanical Properties of Acrylic PSAs**

The mechanical behavior of the acrylic polymers and the blends with the tackifier resin was investigated

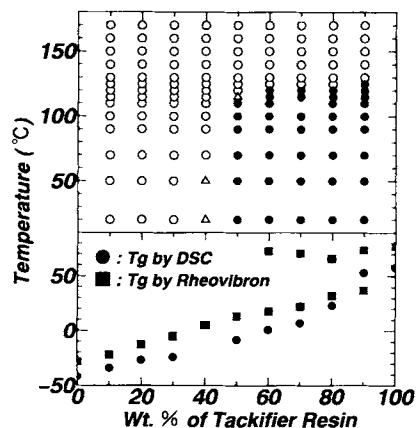


Figure 11 Phase diagram and  $T_g$ -composition of the blends of acrylic copolymer 2 and Superester A-100. The symbols are the same as in Figure 4.

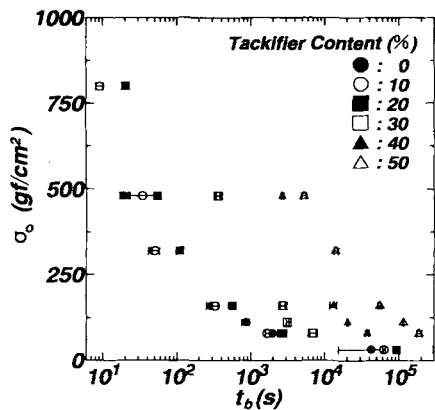


Figure 12 Plot of  $\sigma_0$  against  $t_b$  of the blends of acrylic copolymer 2 and Superester A-100 at 30°C.

with a dynamic mechanical analyzer, which determines the dynamic storage modulus ( $G'$ ) and loss tangent ( $\tan \delta$ ) as a function of temperature.

Figure 13 shows the storage modulus and loss tangent of acrylic polymers of BA and AA. Zosel et al.<sup>10</sup> investigated the dynamic mechanical properties of BA/AA copolymers and blends of poly (butyl acrylate) with poly (acrylic acid) in emulsion PSAs. The storage modulus ( $G'$ ) curve in Figure 13 shows an increase in  $G'$  with an increasing amount of AA in the copolymer, which corresponds to the increased shear creep resistance, as shown in Figure 3.

Figure 14 shows the storage modulus and loss tangent of the acrylic copolymer 2 and Polypale systems. In the curve for the blends,  $T_g$  for the blends gradually increased with increasing tackifier content, which is indicative of complete miscibility, as shown in Figure 4.

The storage modulus ( $G'$ ) and loss tangent ( $\tan$

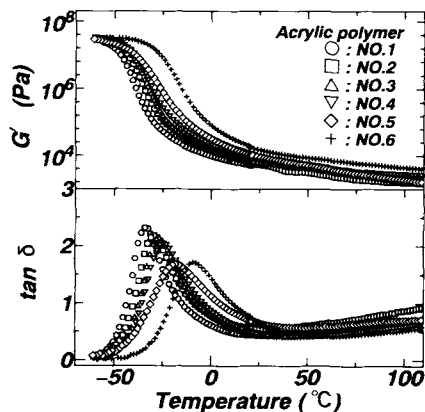


Figure 13 Dynamic storage modulus ( $G'$ ) and loss tangent ( $\tan \delta$ ) vs. temperature of acrylic polymers.

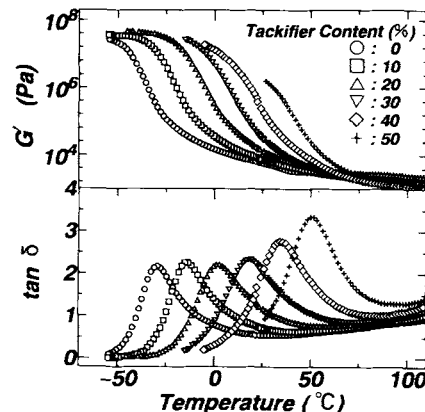


Figure 14 Dynamic storage modulus ( $G'$ ) and loss tangent ( $\tan \delta$ ) vs. temperature of the blends of acrylic copolymer 2 and Polypale.

$\delta$ ) of the blends of acrylic copolymer 2 and Clearon K-4090 are shown in Figure 15 as a function of temperature. The two-step descent of the storage modulus of the blend and the two peaks of the loss tangent especially in higher concentration of the tackifier resin correspond to the  $T_g$  of the pure acrylic copolymer 2 and Clearon K-4090. The initial peak in  $\tan \delta$  shifts only about 6–12°C. Thus, the appearance of double loss tangent peaks is characteristic of an immiscible blend.<sup>11,12</sup> The higher-temperature peak corresponds to a phase which is rich in tackifier resin, while the lower-temperature peak corresponds to the continuous phase which is rich in acrylic copolymer. Of course, it is possible that some low molecular weight resin dissolved in the continuous phase. These blends were opaque and contained “island”-like structures of one phase embedded in a matrix of the second phase.

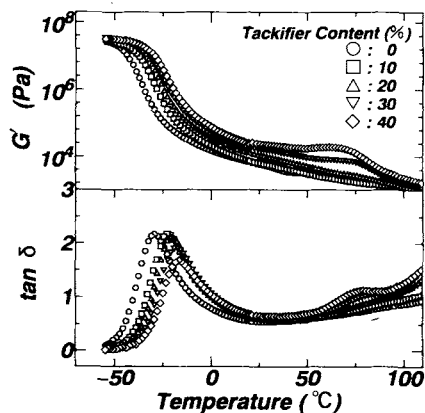
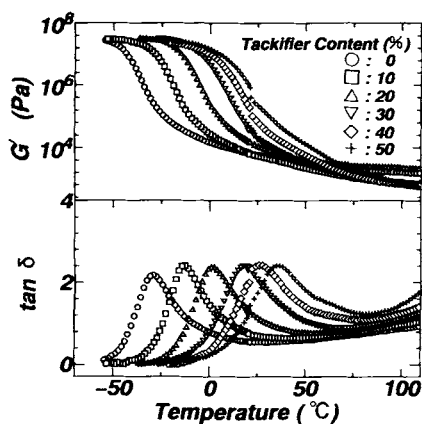


Figure 15 Dynamic storage modulus ( $G'$ ) and loss tangent ( $\tan \delta$ ) vs. temperature of the blends of acrylic copolymer 2 and Clearon K-4090.

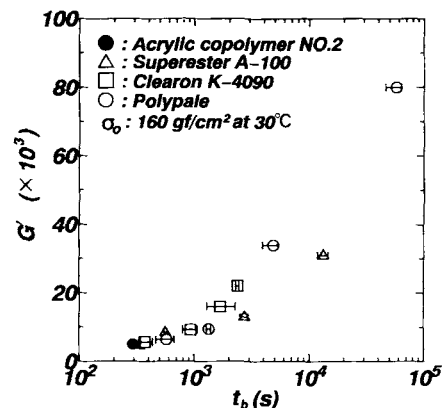
Figure 16 shows the storage modulus and loss tangent of acrylic copolymer 2 and Superester A-100. The  $T_g$  for the blends gradually increased with increasing Superester A-100. Also, Figure 11 shows that this system is miscible within 50% of tackifier resin.

The plot of storage modulus ( $G'$ ) against holding time ( $t_b$ ) of systems is shown in Figure 17 at 30°C. In the case of miscible systems, the storage modulus increases to a great extent with increasing tackifier content, and at the same time, the holding time ( $t_b$ ) shifts greatly toward a longer time scale. The dependence of holding time upon storage modulus of immiscible blends seems similar to that of miscible blends. However, the storage modulus of immiscible blends does not increase greatly and, hence, the holding time does not shift greatly along the time-scale axis as tackifier content increases.

Although the correlation between  $G'$  and  $t_b$  of systems at 30°C shows a similar tendency irrespective of whether the system is in a miscible state or not, as shown in Figure 17, it is clearly shown in Figure 18 that there is a significant difference between the correlation between  $G'$  and  $t_b$  for miscible blends and that for immiscible blends. In case of miscible blends,  $G'$  (at 40°C) varies from  $3.5 \times 10^3$  to  $2.0 \times 10^4$  (Pa), and  $t_b$  (at 40°C), from  $2.1 \times 10^2$  to  $1.3 \times 10^4$  (s) as tackifier increases up to 40%. But in case of immiscible blends,  $G'$  (at 40°C) varies from  $3.5 \times 10^3$  to  $1.9 \times 10^4$  (Pa), and  $t_b$  (at 40°C) does not exceed  $1.7 \times 10^2$  (s), which is reflecting the fact that the tackifier does not modify the physical properties of the matrix phases. It is very interesting to notice that although  $G'$  (at 40°C) values of miscible or immiscible blends for 40% tackifier



**Figure 16** Dynamic storage modulus ( $G'$ ) and loss tangent ( $\tan \delta$ ) vs. temperature of the blends of acrylic copolymer 2 and Superester A-100.

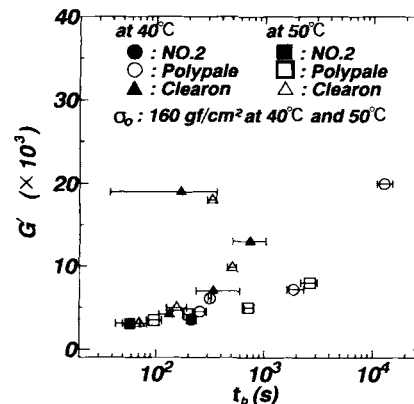


**Figure 17** Plot of  $G'$  and  $t_b$  of the blends of acrylic copolymer 2 and tackifier resins at 30°C.

content is almost the same the holding time is very different.

## CONCLUSION

Miscibility between an acrylic copolymer and a tackifier resin was investigated in terms of phase diagrams and glass transition temperatures. Shear creep resistance (holding power,  $t_b$ ) of the blends were measured as a function of both temperature and stress ( $\sigma_0$ ) in order to obtain a master curve. It was found that the shear creep resistance of the pressure-sensitive adhesives (PSAs) was closely related to the miscibility between the components and viscoelastic properties of the PSA. The master curve of  $\sigma_0$ - $t_b$  plot for the miscible blends shifts toward a longer time scale as the amount of tackifier resin in the blend increases as a result of the modification of the bulk properties, such as glass transition tem-



**Figure 18** Plot of  $G'$  and  $t_b$  of the blends of acrylic copolymer 2 and tackifier resins at 40 and 50°C.



perature ( $T_g$ ) and storage modulus ( $G'$ ) of the blends. However, in the case of immiscible blends where two phases exist in the system, little shift toward longer time is found because the physical properties of the matrix phase are not modified by incorporation of the tackifier. It is pointed out in this study that the practical performance of PSAs is greatly influenced by the miscibility between the components.

We would especially like to thank Masao Inoue and the Konishi Co. Ltd. for the measurement of dynamic mechanical properties of PSA with the Rheometrics RDS-II throughout this work.

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