Miscibility and Fracture Energy of Probe Tack for Acrylic Pressure-Sensitive Adhesives: Acrylic Copolymer/Tackifier Resin Systems

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ABSTRACT: The relationship between the miscibility of acrylic pressure-sensitive adhesive (PSA) and the fracture energy (W) (Jm^{-2}) of the probe tack was investigated, wherein the master curve of W was compared with that of the maximum force ($\sigma_{\max}$) (gf) of the probe tack. It was ascertained that W of acrylic PSA was closely related to the miscibility between the components (acrylic copolymer and tackifier resin). In the case of the miscible blend system, the master curve of W shifted toward the lower rate side and, at the same time, the magnitude decreased as the tackifier resin content increased. The degree of the shift of W was extremely smaller than that of $\sigma_{\max}$. In the case of the immiscible blend system, the master curve of W remarkably decreased as the tackifier resin content increased, which suggests the fact that W of the PSA depended on the dynamic mechanical properties of the matrix phase and that the resin-rich phase acted as a kind of filler, thus reducing the practical performance. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 581–587, 1998

Key words: acrylic pressure-sensitive adhesive (PSA); tackifier resin; miscibility; probe tack

INTRODUCTION

Most pressure-sensitive adhesives (PSAs) 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.

Kim and Mizumachi[1] investigated the miscibility between acrylic copolymers and tackifier resins in terms of phase diagrams, and measured the maximum force ($\sigma_{\max}$) (gf) of the probe tack of the blends as a function of both temperature and rate of separation to obtain the master curves. They concluded as follows. $\sigma_{\max}$ of acrylic PSA was closely related to the miscibility between the components (acrylic copolymer and tackifier resin). In the case of systems where the components were miscible with each other, a single T_g was found that varied gradually with composition. The master curve of $\sigma_{\max}$ was a convex curve having a peak at some separation rate (V_{peak}). The master curve shifted toward the lower rate side and, at the same time, the peak height decreased as the tackifier resin content increased. Cohesive failure oc-

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Table I Acrylic Copolymers[a]

Code	Composition of Copolymers (mol %)	M_n	M_w	T_g[b] (°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/vinyl acetate/acrylic acid (56/41/3)	80,500	279,100	−37
No. 4	2-Ethyl acrylate/butyl acrylate/vinyl acetate/acrylic acid (39/21/37/3)	80,000	399,000	−40

[a] Toyo Ink Manufacturing Co., Ltd.

[b] By differential scanning calorimetry measurements.

curred at a separation rate (V) lower than V_{peak}, and interfacial failure occurred when $V > V_{\text{peak}}$. These facts meant that incorporation of the tackifier resin resulted in modification of the viscoelastic properties of the PSAs. In the case of systems where the components were not miscible at all, double T_g's were observed that did not vary greatly with composition, and it was supposed that the peak of the master curve of $\sigma_{\max}$ did not shift along the rate axis, and only the magnitude decreased with increasing of the tackifier resin content. Physical properties and practical performance of the blends with a two-phase structure depended mostly on the matrix phase, and a dispersed phase would act as a kind of filler.

On the other hand, Zosel[2–5] developed an instrument, which was similar to the Polyken Probe Tack Tester, to determine the adhesive fracture energy (W) (J m^{-2}) and to study the stress-strain behavior during bond separation. Zosel took notice of the energy dissipation in the polymer during debonding. W was obtained by integration of the force (F) *versus* time curve over the separation phase and dividing by the probe area (A). F *versus* time curve could be transformed into a common stress–strain curve. The sample thickness (d) and the separation velocity (v) were known, and the tensile stress $\sigma = F/A$ and the tensile strain $\varepsilon = vt/d$. So that, $W = (1/A) \int Fvdt = d \int \sigma d\varepsilon$. He described that W showed a maximum of about 50 to 70°C above the glass transition temperature of polymers. However, no person has studied the relationship between the miscibility of PSA and W. Therefore, in this study, the relationship between the miscibility of acrylic PSA and W was investigated. We also discussed the difference between the dependence of miscibility on W and that of $\sigma_{\max}$. Because, in most practical cases, the probe tack is expressed in terms of $\sigma_{\max}$.

EXPERIMENTAL

Materials

Acrylic copolymers used in this study are listed in Table I, where the average molecular weight is also shown. All of these samples were kindly supplied by Toyo Ink Manufacturing Co., Ltd. (Tokyo, Japan) in the form of ethyl acetate/toluene solution (84.6/15.4, wt %). The tackifier resins were an esterified rosin "Superester A-75," an esterified rosin "Superester A-100," a partially polymerized rosin "Polypale," and a hydrated polyterpene resin "Clearon K-4090" that were kindly supplied by Arakawa Chemical Industries, Ltd., Hercules, Inc., and Yasuhara Chemical Co., Ltd., respectively. Their characteristics are listed in Table II. They were dissolved in ethyl acetate (50/50, vol. %).

Blend Preparation

All blends of acrylic copolymers with tackifier resins, with a blend ratio of 90/10, 80/20–10/90 by weight, were prepared by blending in ethyl acetate/toluene solutions. The solutions were kept at room temperature for 24 h to ensure complete dissolution.

Preparation of PSA Film

PSA specimens for the probe tack tests were prepared by coating ethyl acetate/toluene solutions of the blends of acrylic copolymers and tackifier resin onto corona-treated polyethylene terephthalate film of 25 μm average thickness, using our 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 h to remove most of the solvent very slowly and then dried at 80°C for 12 h and 120°C for 12 h 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% relative humidity for more than 14 days.

Measurement of Fracture Energy of Probe Tack

The Probe Tack Tester (TAC-II, Rhesca Co., Ltd.) was used to measure W of PSA. The test was con-

Table II Tackifier Resins

Tackifier Resins	M_n	M_w	Softening Point (°C)	Modification Resins
Superester A-75 (R)[a]	900	1,100	75	Disproportion of abietic acid esterified by glycerol and diethylene glycol
Superester A-100 (R)[a]	1,000	1,200	100	Disproportion of abietic acid esterified by glycerol
Polypale (R)[b]	1,300	2,000	102	Partially polymerized rosin
Clearon K-4090 (T)[c]	1,000	1,500	89	Hydrogenated terpene

R, rosin; T, terpene.
[a] Arakawa Chemical Industries, Ltd.
[b] Hercules, Inc.
[c] Yasuhara Chemical Co., Ltd.

ducted on the Probe Tack Tester with a polished stainless-steel probe 2 mm in diameter, which was designed to measure F *versus* time required to break the adhesive bond at controlled rates of separation, temperatures, contact pressures, and dwell times. Measurements were conducted 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^{-1}) under a constant pressure of 100 gf cm^{-2} and a dwell time of 3 s. Test results were the average of four measurements under the same conditions. W was obtained by integrating F *versus* time curve dividing 600 parts along the time (X) axis. $W = (1/A)\int Fvdt$, where A is probe area, F is force, and v is rate of separation. The master curves of W were obtained by applying the time (rate)-temperature superposition principle to a series of data.

RESULTS AND DISCUSSION

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 generally increases with an increase of contact pressure and contact time.[1,4,7] In this study, contact time and contact pressure were fixed to 3 s and 100 gf cm^{-2}, respectively.

Fracture Energy of Probe Tack for Miscible Acrylic PSAs

The master curves of W for acrylic copolymer no. 1 and blends with Polypale are shown in Figure 1, and they are summarized in Figure 2. The two components were miscible with each other within the temperature range of the probe tack tests. The phase diagram was of the lower critical solution temperature (LCST) type (T_c = 120°C).[1] As the content of Polypale increased, the T_g of the blends increased (Polypale 0%: −42°C, 10%: −32°C, 20%: −31°C, 30%: −27°C, and 40%: −17°C).[1] The master curve of W shifted toward the lower rate side and, at the same time, the magnitude decreased as the tackifier resin content increased. This feature was similar to that of $\sigma_{\max}$ described by Kim and Mizumachi.[1] However, a degree of the shift of W was extremely smaller than that of $\sigma_{\max}$. In the case where the tackifier resin content was 40%, $\sigma_{\max}$ reached a peak at about 1×10^{-2} (cm s^{-1}),[1] whereas W reached a peak at about 1×10^{-1} (cm s^{-1}). Cohesive failure occurred at a separation rate (V) lower than V_{peak}. Within the rate region of this experiment, mainly cohesive failure occurred. In this region, W did not change greatly as the tackifier resin content increased. This may correspond to the difference of the activation energies. The activation energies obtained from the Arrhenius plots of the shift factors for the master curves of $\sigma_{\max}$ were 7, 8, 9, 5, and 6 (kcal mol^{-1}) for neat acrylic copolymer no. 1 and blends of acrylic copolymer no. 1/Polypale with the tackifier resin content of 10, 20, 30, and 40%, respectively,[1] whereas those obtained from the master curves of W were 5, 3, 3, 3, and 7 (kcal mol^{-1}) for neat acrylic copolymer no. 1 and blends of acrylic copolymer no. 1/Polypale with the tackifier resin content of 10, 20, 30, and 40%, respectively.

The master curves of a series of acrylic copolymer no. 4/Superester A-75 system are summarized in Figure 3. The two components were miscible with each other within the temperature range

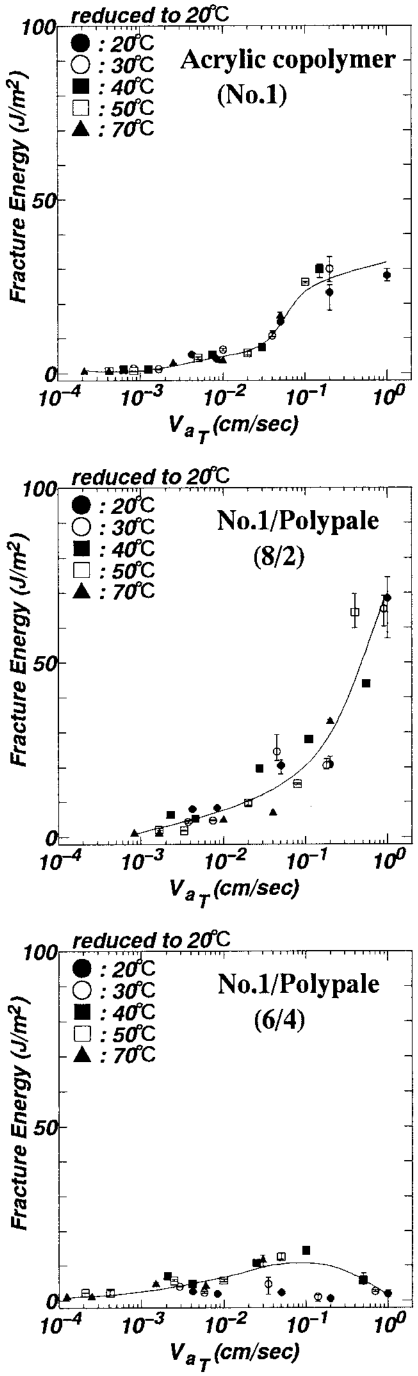

Figure 1 Master curves of fracture energy for blends of the acrylic copolymer (no. 1: butyl acrylate/acrylic acid = 97/3) and the Polypale system.

of the probe tack tests. The phase diagram was of the LCST type (T_c = 120°C).[1] As the tackifier resin content increased, the T_g of the blends increased (Superester A-75 0%: −40°C, 10%: −28°C, 20%: −23°C, 30%: −17°C, 40%: −10°C, and 50%: −1°C).[1] The master curve of W shifted toward the lower rate side and, at the same time, the magnitude decreased as the tackifier resin content increased. However, a degree of the shift of W was extremely smaller than that of $\sigma_{\max}$. In the case where the tackifier resin content was 40%, $\sigma_{\max}$ reached a peak at about 3–7 × 10^{-2} (cm

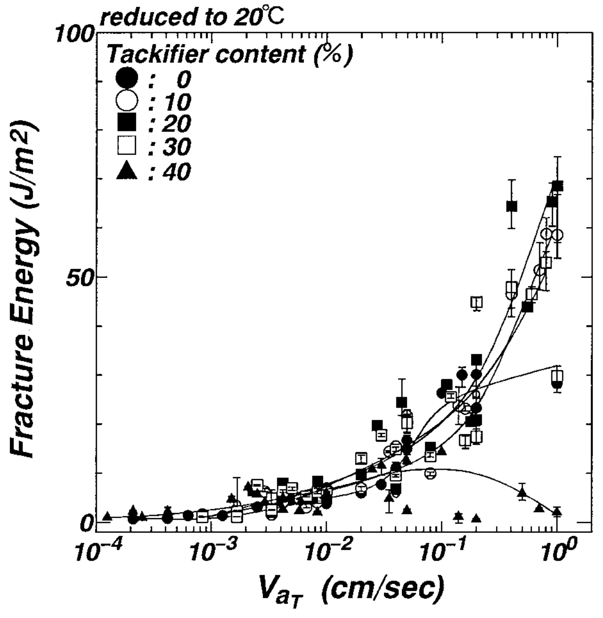

Figure 2 Master curves of fracture energy for blends of the acrylic copolymer (no. 1: butyl acrylate/acrylic acid = 97/3) and the Polypale system.

s^{-1}),[1] whereas W reached a peak at about 2–4 $\times 10^{-1}$ (cm s^{-1}). In the case where the tackifier resin content was 50%, $\sigma_{\max}$ reached a peak at about 1–2 $\times 10^{-2}$ (cm s^{-1}),[1] whereas W reached a maximum at about 2–4 $\times 10^{-1}$ (cm s^{-1}).

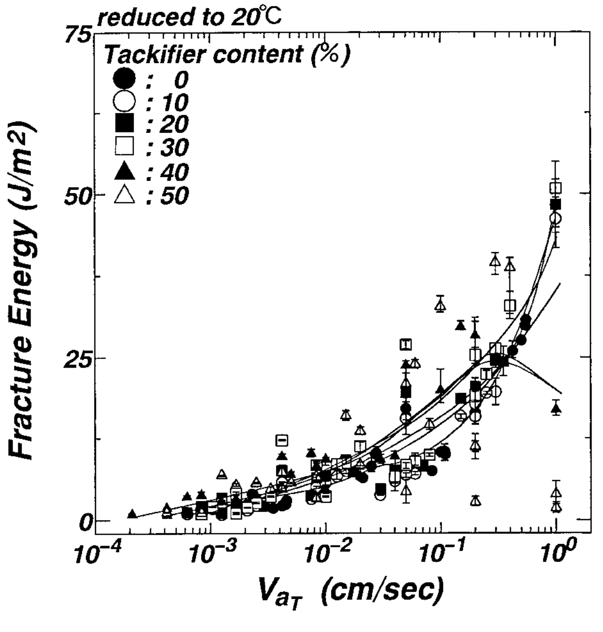

Figure 3 Master curves of fracture energy for blends of the acrylic copolymer (no. 4: 2-ethyl acrylate/butyl acrylate/vinyl acetate/acrylic acid = 39/21/37/3) and the Superester A-75 system.

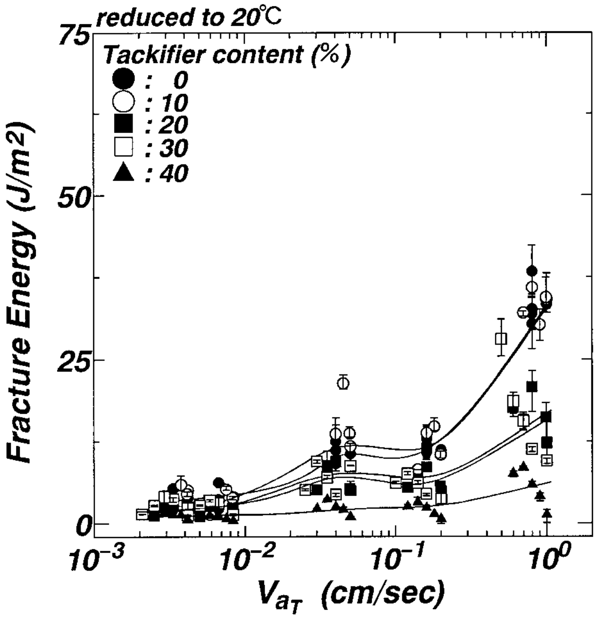

Figure 4 Master curves of fracture energy for blends of the acrylic copolymer (no. 3: 2-ethyl acrylate/vinyl acetate/acrylic acid = 56/41/3) and the Clearon K-4090 system.

Thus, in the case of the miscible blend system, the master curve of W shifted toward the lower rate side and, at the same time, the magnitude decreased as the tackifier resin content increased. This feature was similar to that of $\sigma_{\max}$. However, a degree of the shift of W was extremely smaller than that of $\sigma_{\max}$. At all events, W of acrylic PSA was closely related to the miscibility between the components. This feature was quite similar to those of the holding power,[8] the peel strength,[9,10] and the rolling friction coefficient[11] of acrylic PSA.

Fracture Energy of Probe Tack for Immiscible Acrylic PSAs

The master curves of W for acrylic copolymer no. 3 and blends with Clearon K-4090 are shown in Figure 4. Acrylic copolymer no. 3 and Clearon K-4090 were immiscible with each other within the temperature range of the probe tack tests.[12] Double glass transition temperatures (T_g's) were observed with each of the blends—one was the T_g of the elastomer phase and another was that of tackifier resin phase. Commonly, in case of immiscible blend system, both the T_g of the elastomer phase and that of the tackifier resin phase are constant at any blend ratio. However, in this case, both the T_g of the elastomer phase and that of the tackifier resin phase increased as the tackifier resin content increased (tackifier resin content: 0–40%). The reason was speculated as follows. A tackifier resin consisted of many components. So, if low-molecular weight components of the tackifier resin were soluble in the elastomer phase, T_g could increase. T_g of the elastomer phase were as follows. Clearon K-4090—0%: −37°C, 10%: −30°C, 20%: −23°C, 30%: −19%, 40%: −6°C, 50%: −6°C, 60%: −13°C, 70%: −12°C, 80%: −11°C, and 90%: −12°C.[12] T_g of the tackifier resin phase were as follows. Clearon K-4090—10%: 51°C, 20%: 60°C, 30%: 67%, 40%: 74°C, 50%: 72°C, 60%: 71°C, 70%: 70°C, 80%: 69°C, 90%: 60°C, and 100%: 53°C.[12] T_g's of both the elastomer phase and that of tackifier resin phase were constant as the tackifier resin content up to 40%. The explanation for this result was that each of the blends would be saturated with the low-molecular weight components of the tackifier resin. At all events, double T_g's were observed over the whole range of the tackifier resin content. This fact would be the reason why the no. 3/Clearon K-4090 system is immiscible. In case of the immiscible blend system, *W* of neat acrylic copolymer no. 3 was much greater than that of the blends. *W* of the blends remarkably decreased and did not shift along the rate-axis as the tackifier resin content increased. This trend was remarkably different from those given in the corresponding figures for miscible blend systems. It is evident that *W* of the PSA depends on the dynamic mechanical properties of the matrix phase[8] and that the resin-rich phase acts as a kind of filler, reducing the practical performance.

Fracture Energy of Probe Tack of Acrylic PSAs, the Components of Which Are Miscible within Some Composition Region

There are cases where the components are miscible with each other within some composition region and immiscible outside this region. A typical example is a blend of acrylic copolymer no. 2 and Superester A-100. These components were certainly miscible at the tackifier resin content up to 10%, and immiscible at the tackifier resin content higher than 20% in temperatures of the probe tack tests in this study.[1] T_g appeared in differential scanning calorimetry thermograms are as follows. Superester A-100—0%: −21°C, 10%: −17°C, 20%: −12°C, 30%: −11°C, and 40%: −10, +55°C.[1] T_g of the matrix phase was elevated as the tackifier resin content increased up to 10–20%, whereas in the range where phase separation occurred, it became almost constant. In a strict sense, the tackifier resin consists of many components. Thus, if low-molecular weight components of the tackifier resin are soluble in the matrix phase, T_g of the matrix phase could increase to some extent. If the amount of the resin-rich phase is much smaller than that of the matrix phase, T_g of the resin-rich phase might not observed in the differential scanning calorimetry thermograms. Master curves of *W* for this series of blends are shown in Figure 5. *W* of the blend at the tackifier resin content of 10%, wherein a uniform phase existed, was much greater than that of the neat acrylic copolymer no. 2. *W* of the blend at the tackifier resin content of 20% was also greater than that of neat acrylic copolymer no. 2. Consequently, *W* of the miscible blend was greater than that of polymer without tackifier resin. While *W* of the blend at higher tackifier resin content, where phase separation had occurred, was smaller than that of the neat acrylic copolymer no. 2, it was described as another immiscible system. These results are in agreement with our previous study that some discontinuous drops were found not only in $\sigma_{\max}$,[1] holding power,[8] but also the peel strength[9] at around the concentration at which the phase structure changed.

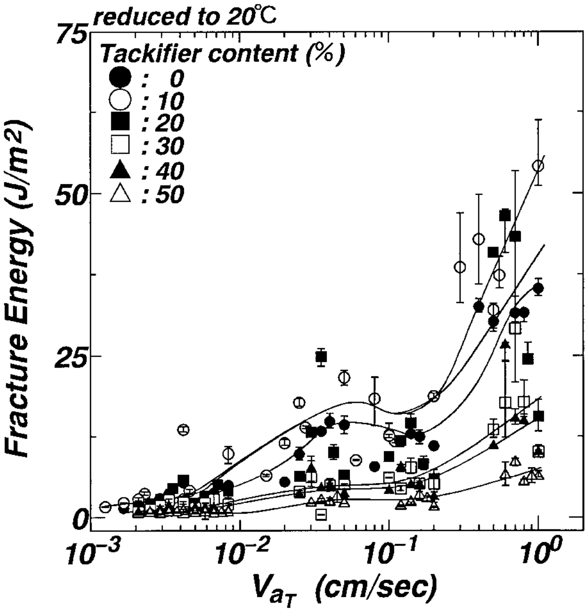

Figure 5 Master curves of fracture energy for blends of the acrylic copolymer (no. 2: butyl acrylate/acrylic acid = 90/10) and the Superester A-100 system.

CONCLUSIONS

1. The fracture energy (W) (J m^{-2}) of the probe tack of acrylic PSA was closely related to the miscibility between the components, just as in the case of the other PSA performance, such as the maximum force ($\sigma_{\max}$) (gf) of probe tack,[1] the peel strength,[9,10] the holding power,[8] and the rolling friction coefficient.[11]
2. In the case of the miscible blend system, the master curve of W shifted toward the lower rate side and, at the same time, the magnitude decreased as the tackifier resin content increases.
3. In the case of the immiscible blend system, the master curve of W did not shift along the rate axis, and the magnitude remarkably decreased as the tackifier resin content increased. It is evident that W of the PSA depends on the dynamic mechanical properties of the matrix phase,[8] and the resin-rich phase acts as a kind of filler, thus reducing the practical performance.
4. The features of W were similar to those of $\sigma_{\max}$. However, in the case of the miscible blend system, a degree of the shift of the former was extremely smaller than that of the latter.

REFERENCES

1. H.-J. Kim and H. Mizumachi, *J. Adhesion,* **49,** 113 (1995).
2. A. Zosel, *Adhesives Age,* **October,** 42 (1989).
3. A. Zosel, *J. Adhesion,* **30,** 135 (1989).
4. A. Zosel, *Advances in Pressure Sensitive Adhesive Technology,* Vol. 1, Satas & Associates, 1992, Chap. 4.
5. A. Zosel, *J. Adhesion,* **34,** 201 (1991).
6. J. D. Ferry, *Viscoelastic Properties of Polymers,* 2nd ed., Wiley, New York, 1970.
7. C. Creton and L. Leibler, *J. Appl. Polym. Sci.,* **34,** 545 (1996).
8. H.-J. Kim and H. Mizumachi, *J. Appl. Polym. Sci.,* **58,** 1891 (1995).
9. H.-J. Kim and H. Mizumachi, *J. Appl. Polym. Sci.,* **56,** 201 (1995).
10. S. Hayashi, H.-J. Kim, and H. Mizumachi, *J. Adhesion Soc. Jpn.,* **31,** 407 (1995).
11. H. Konishi, S. Hayashi, H.-J. Kim, and H. Mizumachi, 20th Annual Meeting of The Adhesion Society, Hilton Head Island, SC, 1997.
12. H.-J. Kim, Ph.D. dissertation, The University of Tokyo, 1995.