

# Poly(butyl acrylate)/Poly(vinylidene fluoride-co-hexafluoroacetone) Blends as Pressure-Sensitive Adhesives

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## SYNOPSIS

The pressure-sensitive adhesive (PSA) properties and dynamic mechanical properties were measured for the poly(butyl acrylate) (PBA)/poly(vinylidene fluoride-co-hexafluoroacetone) [P(VDF-HFA)] blends. The PSA properties of PBA adhesive could be controlled by blending P(VDF-HFA). In order to investigate the relationship between PSA properties and dynamic mechanical properties for PBA/P(VDF-HFA) blends, the master curves of the dynamic mechanical properties, such as storage modulus  $G'$ , loss modulus  $G''$ , and dynamic loss tangent  $\tan \delta$ , were constructed with the temperature-rate superposition principle. The probe tack and peel strength for PBA/P(VDF-HFA) blends were correlated with  $G'$  and  $G''$ . Since the  $G'$  and  $G''$  values increased with increasing P(VDF-HFA) content, the holding power of PBA adhesive could be advanced by blending P(VDF-HFA). © 1997 John Wiley & Sons, Inc.

## INTRODUCTION

An original analysis of chemical and physical factors affecting pressure-sensitive adhesive (PSA) properties was proposed by Dahlquist.<sup>1</sup> He said that the molecular contact between adhesive and adherend is completely established when compressive creep compliance of the adhesive at 1 s is higher than  $10^{-7}$  cm<sup>2</sup>/dyn (Dahlquist criterion). In recent years, the PSA properties (peel adhesion, tack, and holding power) have been interpreted by considering several factors, such as dynamic mechanical properties, surface tension, and miscibility;<sup>2-5</sup> but PSA properties could not be clarified. The values of PSA properties are thought to be influenced by the bonding and debonding processes.

In general, PSA is classified into rubber, acrylic, vinyl ether, and silicone adhesives. Recently, acrylic adhesives have been extensively utilized in industries such as the packaging,

printing, medical, electrical insulation, and automobile industries. The PSA properties of acrylic adhesive have been controlled by blending of tackifiers or dissimilar polymers, by molecular weight and its distribution, and also by copolymerization with polar monomer and curing systems. Particularly, Kim and Mizumachi<sup>6-8</sup> have reported the relationship between miscibility and PSA properties in the blends of acrylic adhesives with various tackifiers.

It is well known that the poly(ethyl acrylate) (PEA), poly(butyl acrylate) (PBA), and poly(2-ethylhexyl acrylate) (P2EHA) have been utilized as the main components of acrylic adhesives because these polymers have low glass transition temperature ( $T_g < -20^\circ\text{C}$ ) and are very flexible at room temperature. On the other hand, poly(vinylidene fluoride-co-hexafluoroacetone) [P(VDF-HFA)] possessing nontackiness, water repellency, and heating and chemical resistance has been known, and the miscibility between P(VDF-HFA) and dissimilar polymers have been investigated.<sup>9-11</sup>

Using attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), and microscopic observation, we<sup>12-15</sup> found that the poly(2-

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**Table I** Molecular Weights and  $T_g$  of Polymers

Polymer	$M_n$	$M_w/M_n$	$T_g$ (°C)
PBA	24700	5.76	-55
P(VDF-HFA)	52000	2.50	-28

ethyl hexyl acrylate-*co*-acrylic acid-*co*-vinyl acetate) [P(2EHA-AA-VAc)]/P(VDF-HFA) blends exhibit surface segregation or gradient structure. Then, tack value of the bottom surface was remarkably larger than that of surface for P(2EHA-AA-VAc)/P(VDF-HFA) (50/50) blend because the P(VDF-HFA) component enriched the upper surface and P(2EHA-AA-VAc) was precipitated at bottom. Therefore, we expected that these blends should be utilized as a new type PSA tapes, without backing film. In our previous study,<sup>16,17</sup> the PSA properties and dynamic mechanical properties were measured for PEA/P(VDF-HFA) blends. Eventually, we found that PSA properties of PEA could be controlled by blending P(VDF-HFA).

In this study, PSA properties (peel adhesion, probe tack, and holding power) and dynamic mechanical properties ( $G'$ ,  $G''$ , and  $\tan \delta$ ) of the PBA/P(VDF-HFA) blends were measured. The master curves of dynamic mechanical properties for PBA/P(VDF-HFA) blends were constructed by means of the temperature-rate superposition principle. Finally, the relationship between PSA properties and dynamic mechanical properties for PBA/P(VDF-HFA) blends was examined by considering bonding and debonding processes.

## EXPERIMENTAL

### Materials

The PBA was prepared by solution polymerization at 70°C for 8 h using benzoyl peroxide as an initia-

tor in toluene. The molecular weights and their distributions and the glass transition temperatures of PBA and the P(VDF-HFA) with 8 mol % HFA content, supplied by Central Glass Co. Ltd. in Japan, are represented in Table I. Molecular weights were determined using a Toso Co. Ltd. CP8000 GPC system in 0.1 wt % THF solution. The samples of the PBA/P(VDF-HFA) blends used for PSA properties were prepared by solution casting from 20 wt % THF solution onto a poly(ethylene terephthalate) (PET) base using the knife coating system. After coating, the films were dried at 90°C for 2 min and kept at  $23 \pm 3^\circ\text{C}$  and  $65 \pm 5\%$  RH for more than a week. The blends were 30  $\mu\text{m}$  thick in their dry state. The specimens were allowed to dry further in a vacuum for seven days at  $40 \sim 60^\circ\text{C}$ . PSA tapes generally consist of adhesive, backing film, and release liner. Film surfaces were covered with the release liner [poly(dimethyl siloxane) coated on paper]. The PSA properties were measured in blends with P(VDF-HFA) contents varied from 0 to 50 wt % region. The blends with more than 50 wt % P(VDF-HFA) contents exhibit nontackiness.

### Measurements

The measurement of the PSA properties were carried out according to Japanese Industry Standard (JIS-Z0237). The peel adhesion of PBA/P(VDF-HFA) blends to stainless steel was performed at 180 degree peel angle using a Toyo Baldwin Co. Ltd. TENSIRON/UTM-4-100. The peel rate was 300 (mm/min). The probe used in probe tack was made of stainless steel. These measurements were carried out at  $23 \pm 3^\circ\text{C}$  and  $65 \pm 5\%$  RH. The holding power was also measured with stainless steel using a Nitto Rika Kogyo Co. Ltd. NDC-100S creep tester at 40°C.

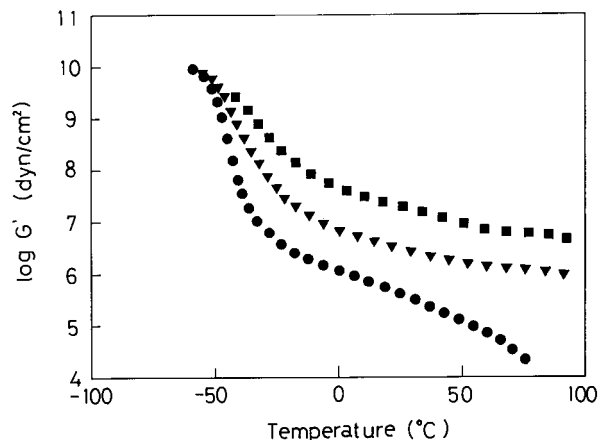
The dynamic mechanical properties of PBA/P(VDF-HFA) blends were carried out with a shearing method using Rheometrics Co. Ltd. Ad-

**Table II** PSA Properties of PBA/P(VDF-HFA) Blends

P(VDF-HFA) Content (wt %)	0	10	20	30	40	50
180 degree peel adhesion <sup>a</sup> (g/25 mm)	1850 <sup>b</sup>	200	80	22	10	—
Probe tack (g/5 mm $\phi$ )	736	745	587	207	39	15
Holding power (s)	178 <sup>b</sup>	1243 <sup>b</sup>	5504 <sup>b</sup>	57531 <sup>b</sup>	—	—

<sup>a</sup> Dwell time 24 h.

<sup>b</sup> CF, cohesive failure of adhesive layer.



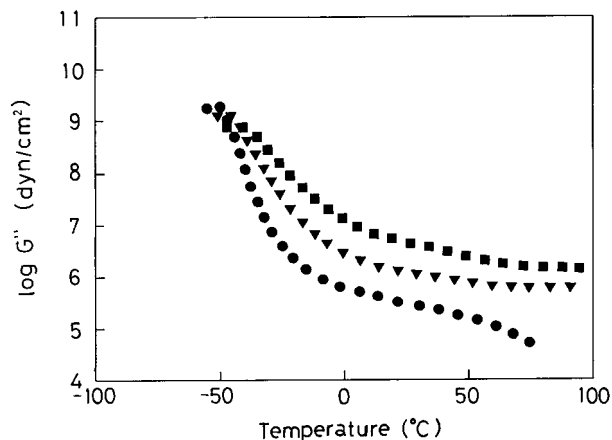
**Figure 1** Temperature dependence of storage modulus  $G'$  of PBA/P(VDF-HFA) blends. Content of P(VDF-HFA) is as follows (wt %): (●) 0; (▼) 20; (■) 40.

vanced Rheometrics Expansion System (ARES). The dynamic mechanical properties, such as storage modulus  $G'$ , loss modulus  $G''$ , and dynamic loss tangent  $\tan \delta$ , were measured in the ranges of  $-60$  to  $100^\circ\text{C}$  and of  $0.5$  to  $500$  (rad/s). The temperature dependence of  $G'$ ,  $G''$ , and  $\tan \delta$  of the PBA/P(VDF-HFA) blends was carried out at  $6.28$  (rad/s) =  $1$  Hz.

## RESULTS AND DISCUSSION

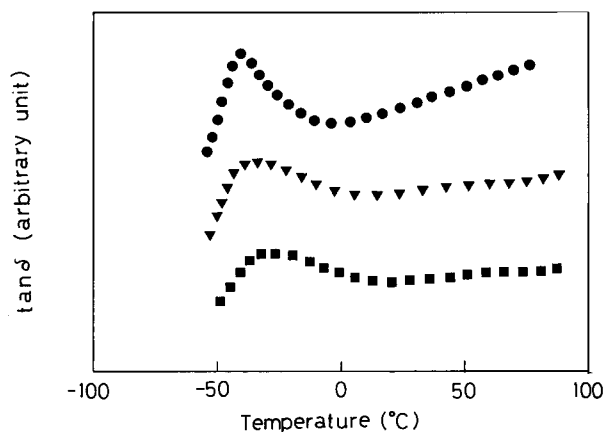
The results of PSA properties for PBA/P(VDF-HFA) blends are represented in Table II. The 180 degree peel adhesion and probe tack decreases with increasing P(VDF-HFA) content. Holding power increases with increasing P(VDF-HFA) content. It is judged that PSA properties of PBA can be controlled by blending P(VDF-HFA). Relatively, the values of probe tack of PBA/P(VDF-HFA) blends are higher than that of PEA/P(VDF-HFA) blends, whereas 180 degree peel adhesion and holding power of PBA/P(VDF-HFA) blends are lower than that of PEA/P(VDF-HFA) blends. We expect that the PSA properties for PBA/P(VDF-HFA) blends are evaluated by dynamic mechanical properties.

Therefore, the temperature dependence of dynamic mechanical properties were investigated for the PBA/P(VDF-HFA) blends. The temperature dependence of  $G'$  of PBA/P(VDF-HFA) 100/0, 80/20, 60/40 blends is shown in Figure 1. The  $G'$  decreases with rising temperature and increases with increasing P(VDF-HFA) content. Since the  $G'$  of PBA suddenly decreased about



**Figure 2** Temperature dependence of loss modulus  $G''$  of PBA/P(VDF-HFA) blends. Content of P(VDF-HFA) is as follows (wt %): (●) 0; (▼) 20; (■) 40.

$50^\circ\text{C}$ , PBA flows in this region. On the other hand, the PBA/P(VDF-HFA) 80/20 and 60/40 blends exhibit the plateau modulus. As shown in Figure 2, the curves of the  $G''$  versus temperature plots are similar to that of the  $G'$  versus temperature plots for PBA/P(VDF-HFA) blends. Figure 3 shows the temperature dependence of  $\tan \delta$  for PBA/P(VDF-HFA) blends. The maximum temperature of  $\tan \delta$  shifts slightly toward higher temperature side with increasing P(VDF-HFA) content and the breadth of  $\tan \delta$ -temperature peak of the 60/40 blend is greater than that of the 100/0 blend. In these blends, a single  $T_g$  was obtained on all differential scanning calorimetry (DSC) thermograms and the homogeneous morphology was observed by scanning electron mi-



**Figure 3** Temperature dependence of dynamic loss tangent  $\tan \delta$  of PBA/P(VDF-HFA) blends. Content of P(VDF-HFA) is as follows (wt %): (●) 0; (▼) 20; (■) 40.

croscopy (SEM) in our previous report.<sup>18</sup> We judge that the PBA/P(VDF-HFA) blends are miscible at low temperature.

Next, the relationship between PSA properties and dynamic mechanical properties for PBA/P(VDF-HFA) blends was examined using the temperature-rate superposition principle. The master curves of  $G'$ ,  $G''$ , and  $\tan \delta$  for the PBA/P(VDF-HFA) 80/20 blend are shown in Figure 4, where the reference temperature is 298 K. Figure 5 shows the relationship between the shift factor  $\log a_T$  and temperature for the PBA/P(VDF-HFA) 80/20 blend. In general, the relationship between  $\log a_T$  and temperature corresponding to the WLF equation is expressed by the following WLF equation<sup>19</sup>:

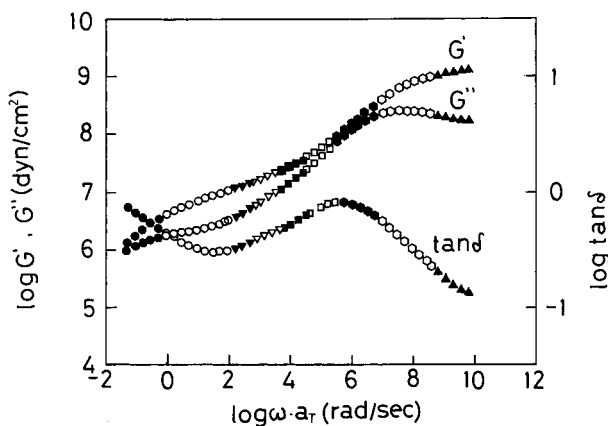
$$\log a_T = [-C_1(T - T_r)]/[C_2 + (T - T_r)] \quad (1)$$

where  $C_1$  and  $C_2$  are constants,  $T$  is temperature, and  $T_r$  is the reference temperature (298 K). The WLF fitting parameters ( $C_1$ ,  $C_2$ ) for PBA/P(VDF-HFA) blends are represented in Table III.

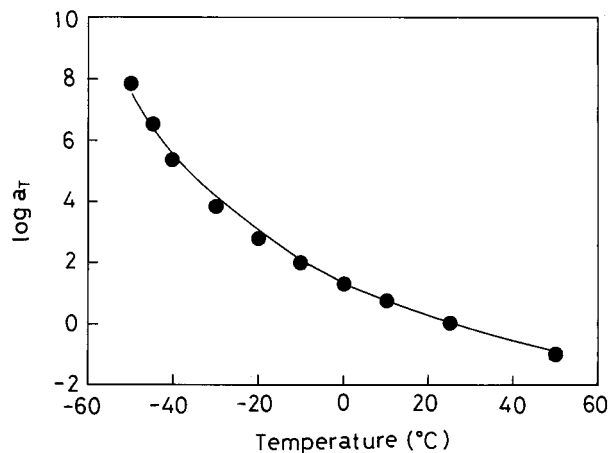
The PSA properties can be evaluated with dynamic mechanical properties, such as  $G'$  and  $G''$ . Because the bonding and debonding processes for PSA tests are strongly dependent on temperature and separation speed.

Tse<sup>20,21</sup> pointed out that the PSA tackiness  $T$  is expressed by considering the bonding and debonding processes of adhesive, as follows:

$$T = W_a \cdot B \cdot D \quad (2)$$



**Figure 4** Master curves of storage modulus  $G'$ , loss modulus  $G''$ , and dynamic loss tangent  $\tan \delta$  for the PBA/P(VDF-HFA) 80/20 blend at 25°C. Temperature (°C) is as follows: (▲) -45; (○) -40; (●) -30; (□) -20; (■) -10; (▽) 0; (▼) 10; (○) 25; (●) 50.



**Figure 5** Shift factor,  $\log a_T$  versus temperature for the PBA/P(VDF-HFA) 80/20 blend.

where  $W_a$  is the work of adhesion between adhesive and adherend,  $B$  is the function of bonding process and depends on the plateau modulus  $G_e$  of adhesive, and  $D$  correlates with debonding process and increases with increasing loss modulus  $G''$  of adhesive. Therefore, parameter  $D$  is influenced strongly by separation speed and temperature. When the  $G_e$  value is equal or lower than  $10^7$  (dyn/cm<sup>2</sup>) (Dahlquist criterion), the  $B$  value should remain constant for PSA tests.<sup>1</sup> That is to say, the extensive molecular contact of adhesive is established on microscopically rough adherend surfaces. In general, adhesives possess the same surface characteristics because their chemical composition is similar. Therefore, the  $W_a$  value should be constant with identical adherend. If the  $G_e$  value of adhesive fulfills the Dahlquist criterion, eq. (2) can be simplified as following equation:

$$T = (\text{constant}) \cdot D \quad (3)$$

By eq. (3), the PSA tackiness  $T$  can be correlated with the only  $G''$ . The characteristic debonding frequency of each adhesive properties is expressed in the following manner.

$$\text{Test frequency} = 2\pi \cdot (\text{separation speed}) / (\text{adhesive thickness}) \quad (4)$$

In this study, the debonding frequency of probe tack and 180 degree peel adhesion are 2100 and 525 (rad/s), respectively. Finally, Tse found that the relationship between  $T$  and  $G''$  for the rubber/tackifier blends is expressed as follows:

**Table III WLF Fitting Parameters ( $C_1$ ,  $C_2$ ) for PBA/P(VDF-HFA) Blends**

P(VDF-HFA) Content (wt %)	0	10	20	30	40	50
$C_1$	5.45	5.48	5.76	7.89	17.20	17.44
$C_2$	127.6	127.6	133.6	126.2	175.3	166.7

$$T = K_1 \cdot \log G''(\omega \cdot a_T) + K_2 \quad (5)$$

where  $\omega$  is the frequency for dynamic mechanical properties, and  $K_1$  and  $K_2$  are the slope and intercept of the  $T$  versus  $\log G''$  plots.

On the other hand, Yang<sup>22</sup> rewrites the PSA tackiness  $T$  of eq. (2) as follows:

$$T \propto W_a \cdot G''(\omega_1) \cdot (A/A_0) \quad (6)$$

where  $\omega_1$  is the debonding frequency, and  $(A/A_0)$  is the kinetic term related to the viscoelastic behavior of adhesive. In PSA tests, the contact area between adhesive and adherend is accomplished through deformation of adhesive under light pressure within 1 s. Thus, the parameter  $A/A_0$  can be calculated by creep compliance  $J(t)$  as in the following equation:

$$A/A_0 = 1 - \exp\{-J(t)\} \simeq J(t) \quad (7)$$

where  $J(t)$  is also expressed in terms of the storage modulus  $G'(\omega_2)$ , as follows:

$$J(t) = [1/G'(\omega_2)] \times \{1/[1 + \tan^2(\delta^2(\omega_2))]\} \\ \simeq 1/G'(\omega_2) \quad \text{for } \tan \delta \ll 1 \quad (8)$$

where  $\omega_2$  is the bonding frequency of adhesive and corresponds to 1 rad/s. For most adhesives,  $\tan \delta \ll 1$  since  $T_g$  is low ( $-20^\circ\text{C}$ ). In eq. (6), the parameter  $W_a$  is calculated by the geometric mean equation as follows:

$$W_a = 2(\gamma_s \cdot \gamma_{ss})^{0.5} \quad (9)$$

where  $\gamma_s$  and  $\gamma_{ss}$  are surface tension of adhesive and adherend (stainless steel  $\sim 44$  dyn/cm), respectively. In this study,  $\gamma_s$  values of the PBA/P(VDF-HFA) blends are calculated by the following equation:

$$\gamma_s = f_{\text{PBA}}^S \cdot \gamma_{\text{PBA}} + f_{\text{P(VDF-HFA)}}^S \cdot \gamma_{\text{P(VDF-HFA)}} \quad (10)$$

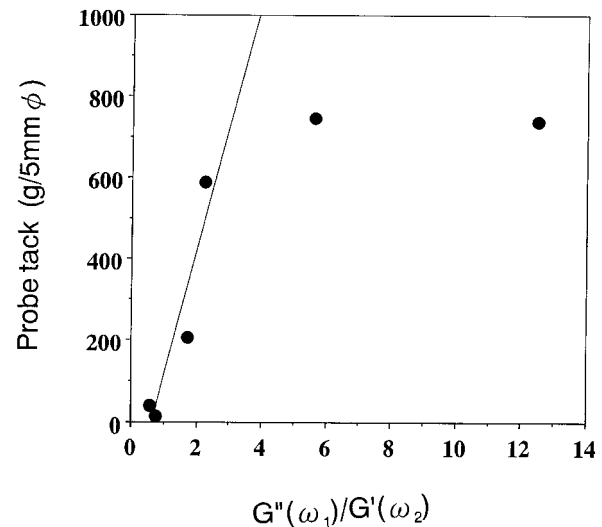
where  $f_{\text{PBA}}^S$  and  $\gamma_{\text{PBA}}$  are surface fraction and surface tension of PBA and  $f_{\text{P(VDF-HFA)}}^S$ , and  $\gamma_{\text{P(VDF-HFA)}}$

are surface fraction and surface tension of P(VDF-HFA), respectively. Using XPS results and surface tension measured in our previous paper,<sup>23</sup> the  $\gamma_s$  values of PBA/P(VDF-HFA) blends used in this article varied from 40.0 to 27.8 (dyn/cm). Since the  $W_a$  values calculated with the geometric mean equation for the PBA/P(VDF-HFA) blends are between 70 and 84 erg/cm<sup>2</sup>, we judged that the variation in the parameter  $W_a$  is very small. Consequently, the PSA tackiness  $T$  for PBA/P(VDF-HFA) blends can be expressed as in the following equation:

$$T \propto G''(\omega_1)/G'(\omega_2) \quad (11)$$

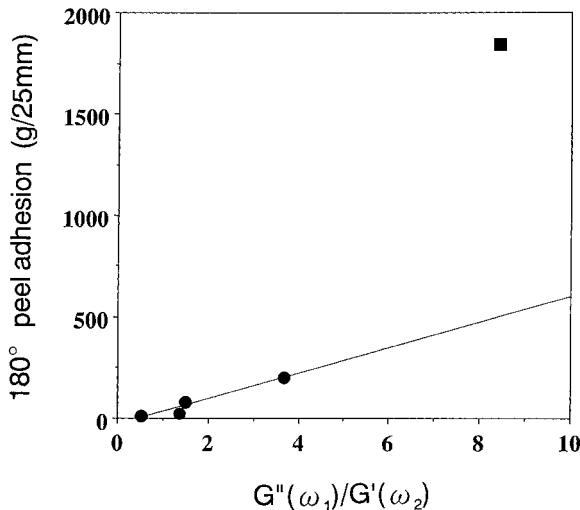
In this study, as the plateau modulus  $G_e$  of the PBA/P(VDF-HFA) 60/40 and 50/50 blends is higher than  $10^7$  (dyn/cm<sup>2</sup>) (Dahlquist criterion), the function of bonding process  $B$  should be considered. Thus, the relationship between PSA tackiness and dynamic mechanical properties for PBA/P(VDF-HFA) blends is investigated with eq. (11), reported by Yang.<sup>22</sup>

The relationship between probe tack and  $G''(\omega_1)/G'(\omega_2)$  for the PBA/P(VDF-HFA) blends are shown in Figure 6. The probe tack value in-

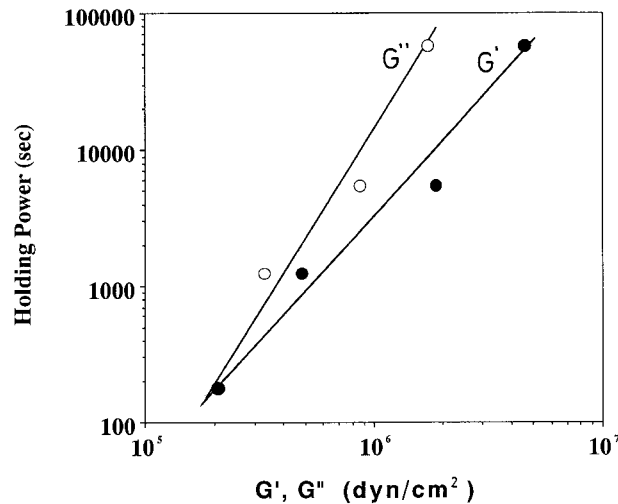


**Figure 6** Relationship between probe tack and  $G''(\omega_1)/G'(\omega_2)$  for PBA/P(VDF-HFA) blends.

creases with increasing  $G''(\omega_1)/G'(\omega_2)$  in the region of  $G''(\omega_1)/G'(\omega_2) = 0$  to 2 region, while the value of probe tack is constant at  $G''(\omega_1)/G'(\omega_2)$  values greater than 6. In this region, our result differs from the result of water-based adhesives reported by Yang.<sup>22</sup> The PBA/P(VDF-HFA) blend ratios exhibiting  $G''(\omega_1)/G'(\omega_2) \geq 6$  corresponded to 100/0 and 90/10. From the results of dynamic mechanical properties for the PBA/P(VDF-HFA) blends, both the  $G'$  and  $G''$  values decreased with decreasing P(VDF-HFA) content. And  $G''(\omega_1)$  and  $G'(\omega_2)$  values for the PBA/P(VDF-HFA) 100/0 and 90/10 blends revealed  $1.35 \times 10^6 \sim 2.80 \times 10^6$  and  $1.60 \times 10^5 \sim 4.98 \times 10^5$  (dyn/cm<sup>2</sup>), respectively. We explain why the value of probe tack is constant at  $G''(\omega_1)/G'(\omega_2) \geq 6$  region. One reason is the magnitude of  $G'(\omega_2)$  at the bonding process. As the  $G'(\omega_2)$  values for the 100/0 and 90/10 blends were markedly lower than Dahlquist criterion, it is presumed that the  $A/A_0$  values for the 100/0 and 90/10 blends are nearly 1 because a complete contact at interface between adhesive and adherend is accomplished. The other reason is the  $G''(\omega_1)$  value at debonding process. Kraus et al.<sup>24</sup> investigated the relationship between probe tack and  $G''$  for the rosin ester tackified block copolymer adhesives. They found that the maximum of probe tack was observed at  $G'' = 1 \sim 2 \times 10^6$  (dyn/cm<sup>2</sup>). These  $G''$  values correspond to the  $G''$  values for the 100/0 and 90/10 blends. Consequently, from above two reasons, we judge that the relationship between  $G''(\omega_1)/G'(\omega_2)$  and probe tack plots for



**Figure 7** Relationship between peel adhesion and  $G''(\omega_1)/G'(\omega_2)$  for PBA/P(VDF-HFA) blends: (●) interfacial failure; (■) cohesive failure of adhesive layer.



**Figure 8** Relationship between holding power and  $G', G''$  at 40°C and 1 Hz for PBA/P(VDF-HFA) blends: (●)  $G'$ ; (○)  $G''$ .

the PBA/P(VDF-HFA) 100/0 and 90/10 blends deviated from the straight line. In other words, for the PBA/P(VDF-HFA) blends, we think that the linear relationship of the probe tack vs.  $G''(\omega_1)/G'(\omega_2)$  plots is obtained at  $G''(\omega_1) > 2.80 \times 10^6$  and  $G'(\omega_2) > 4.98 \times 10^5$  (dyn/cm<sup>2</sup>).

Figure 7 shows the 180 degree peel adhesion vs.  $G''(\omega_1)/G'(\omega_2)$  plots for PBA/P(VDF-HFA) blends. The relationship between 180 degree peel adhesion and  $G''(\omega_1)/G'(\omega_2)$  exhibits the reasonable straight line in the region exhibiting the interfacial failure mode. This result corresponds to the result reported by Yang.<sup>22</sup> On the other hand, the location between the 180 degree peel adhesion and the  $G''(\omega_1)/G'(\omega_2)$  value for PBA deviates from the straight line. It is because the failure mode of 180 degree peel adhesion for only the PBA component exhibited the cohesive failure of adhesive layer. In the interfacial failure mode, we think that the 180 degree peel adhesion can be estimated with the  $G''(\omega_1)/G'(\omega_2)$  values for the PBA/P(VDF-HFA) blends.

As shown in Figure 8, holding power increases monotonically with increasing  $G', G''$  at 1 Hz and 40°C. We think that the holding power can be advanced by blending P(VDF-HFA) into PBA because the  $G'$  and  $G''$  values of P(VDF-HFA) are higher than those of PBA.

## CONCLUSIONS

The PSA properties, such as the 180 degree peel adhesion, probe tack, and holding power of PBA

adhesive could be controlled by blending P(VDF-HFA). The probe tack and 180 degree peel adhesion for PBA/P(VDF-HFA) blends were correlated with the  $G''(\omega_1)/G'(\omega_2)$  value calculated from  $G'$  and  $G''$  on master curves. The probe tack increased with increasing  $G''(\omega_1)/G'(\omega_2)$  in the  $G''(\omega_1)/G'(\omega_2) = 0$  to 2 region, whereas the probe tack values are constant at  $G''(\omega_1)/G'(\omega_2) > 6$ . The relationship between 180 degree peel adhesion and  $G''(\omega_1)/G'(\omega_2)$  exhibited the reasonable straight line in the region exhibiting the interfacial failure mode.

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