Analysis of Holding Power in the Blends of Poly(butyl acrylate) with Poly(vinylidene fluoride-*co*-hexafluoro acetone)

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ABSTRACT: Shear adhesion of pressure-sensitive adhesive tapes was evaluated for the blends of poly(butyl acrylate) with poly(vinylidene fluoride-*co*-hexafluoro acetone). The shear adhesion was determined as the function of the shear strain of pressure-sensitive adhesive tape against elapsed time under the shear stress. Shear adhesion of the blends increased with increasing poly(vinylidene fluoride-*co*-hexafluoro acetone) content. Experimental shear strain data were characterized with dynamic viscosity, stress and shear rate plot, and a generalized viscoelastic model of shear adhesion. However, the experimental data cannot be expressed with these viscoelastic properties. It is believed that shear adhesion is influenced by the viscoelastic properties and other factors (e.g., friction coefficient between adhesive and adherend or cohesive strength of adhesive polymer). © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 727–738, 1998

Key words: blends; dynamic viscosity; pressure-sensitive adhesives; shear adhesion; holding power; viscoelastic model

INTRODUCTION

Holding power[1–4] is a very important property for pressure-sensitive adhesive (PSA) tapes (e.g., book mending, masking, double-faced, and backing tapes). In general, holding power is evaluated as the time required to pull a contacted area between PSA tapes and test panel under a defined shear stress. When the failure occurred in the adhesive layer, this time is expressed as t_c, with the subscript c meaning "cohesion." Therefore, it is thought that the holding power is strongly influenced by the mechanical properties of the adhesive.

Several researchers[5–13] examined the relationship between holding power and mechanical properties. The theoretical analysis of holding power was reported by Saito.[5] He analyzed the holding power with the viscoelastic model composed of modulus, viscosity, and irreversible work of adhesion of interface between adhesive and adherend. The empirical evaluation of holding power with mechanical property has been also reported. Krenceski and Johnson[7] investigated the relationship between holding power and the dynamic viscosity for polyisobutylene adhesives at 0.1 s^{-1}. They reported that the holding power depended on the molecular weight distributions. Dale and coworkers[8] correlated holding power at room temperature and the storage modulus G' at 127°C. Hata and coworkers[11] examined the relationship

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between holding power and the sliding friction coefficient μ. Particularly, they concluded that holding power was closely related to the μ and the rubbery plateau modulus G_e. However, these empirical evaluations seem to be not logical because holding power was related to modulus at arbitrary frequency and temperature. In addition, holding power was evaluated by only t_c. If the elapsed time dependence of shear deformation was measured under the test process of the holding power, the holding power can be elucidated with the mechanical properties of PSA polymers.

Miyagi and Yamamoto[6] developed the device for shear deformation that was determined as a function of elapsed time. Shear deformation can be measured with an error of a micron. Using this device, they found out that the boundary and cohesive deformations occurred under the test. Recently, Zosel[12] also developed a similar device of shear deformation as described by Miyagi and Yamamoto.[6] He investigated the relationship between shear deformation and dynamic viscosity for PSA polymers. It was found that shear deformation can be evaluated with dynamic viscosity for PSA polymers having low or moderate viscosities. However, this evaluation could not be applied to PSA polymers with high viscosity or slight crosslinking.

On the other hand, we[14–16] reported that the PSA properties—such as probe tack, peel adhesion and holding power for poly(ethyl acrylate) and poly(butyl acrylate) (PBA) as PSA polymers—could be controlled by blending poly(vinylidene fluoride-*co*-hexafluoro acetone) [P(VDF-HFA)]. Particularly, we thought that the holding power could be improved by blending P(VDF-HFA) into PBA, because the storage modulus G' and loss modulus G'' values of P(VDF-HFA) are higher than those of PBA. However, shear deformation was not measured in these blends.

In this study, we conducted analysis of holding power for PBA/P(VDF-HFA) blends. The relationship between shear deformation and elapsed time is characterized using dynamic viscosity according to Zosel's[12] method, and the stress and shear rate plot and the generalized viscoelastic model of shear adhesion.

EXPERIMENTAL

Materials

The molecular weights and its distributions and the glass transition temperatures T_g 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. Samples of the PBA/P(VDF-HFA) blends used for holding power were prepared by solution casting onto poly(ethylene terephthalate) base from 20 wt % tetrahydrofuran solution using a knife coating system. After coating, films were dried at 90°C for 2 min and kept at 23 ± 3°C and 65 ± 5% relative humidity for more than 1 week. The blends were 30 μm thick in their dry state. The specimens were further allowed to dry in a vacuum for 7 days at 40–60°C. Film surfaces were covered with the release liner [poly(dimethyl siloxane) coated on paper].

Table I Molecular Weights and T_g of Polymers

Polymer	$\overline{M_n}$	$\overline{M_w}/\overline{M_n}$	T_g (°C)
PBA	27400	5.76	−55
P(VDF-HFA)	52000	2.50	−28

Holding Power

A schematic diagram of the apparatus for shear adhesion is shown in Figure 1. The PSA tape with a 25 mm × 25 mm test area is applied on a stainless-steel plate in sample preparation according to the Japanese Industrial Standard. The dwell time is 1 h. The dead loads are 0.2, 0.5, 0.7, and 1 kg, and test temperature is at 23°C. A block with a core of linear variable differential transformer (LVDT) is put on the PSA tape. Because the core is inserted into a detector of the LVDT, shear deformation of the PSA tape can be detected in the range of 1 μm to 4 mm and is indicated by an electronic gauge. Shear deformation is measured as a function of elapsed time.

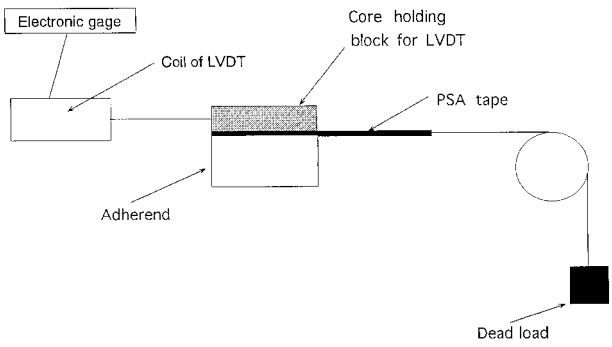

Figure 1 Schematic diagram of the apparatus for shear adhesion.

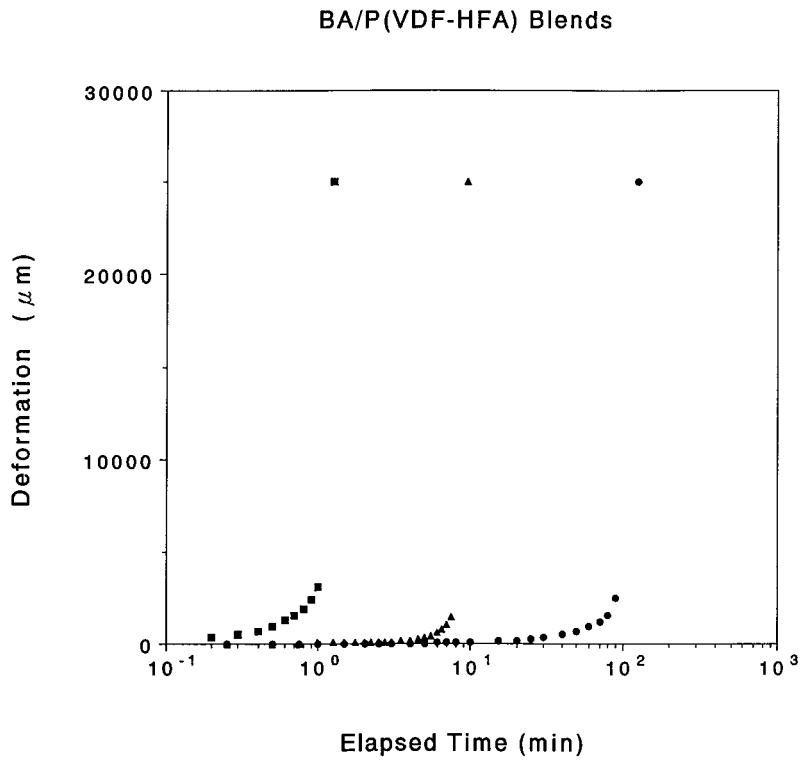

Figure 2 Elapsed time dependence against deformation for the PBA/P(VDF-HFA) blends at 1 kg dead load. P(VDF-HFA) content (wt %): (■) 0, (▲) 10, and (●) 20. BA, butyl acrylate.

Dynamic Viscosity

For the PBA/P(VDF-HFA) blends, the dynamic viscosity η^* is calculated with storage modulus G' and loss modulus G'' as the following equation

$$\eta^* = (G'^2 + G''^2)^{1/2}/\omega \qquad (1)$$

where ω is angular frequency. In this study, the values of G' and G'' in our previous study[16] were used. In the viscous materials, η^* is equal to the steady-state viscosity $\eta(\gamma)$ as follows

$$\eta^*(\omega) = \eta(\gamma), \quad \gamma = d\gamma/dt = \omega \qquad (2)$$

where $d\gamma/dt$ is the shear rate.

RESULTS AND DISCUSSION

Shear deformation as a function of elapsed time for PBA/P(VDF-HFA) blends is shown in Figure 2. The holding power t_c increases, and the curve of shear deformation and elapsed time shift to long time side with increasing P(VDF-HFA) content. It is because the dynamic mechanical properties, such as storage modulus G' and loss modulus G'' of the PBA/P(VDF-HFA) blends, increase with increasing P(VDF-HFA) content.[16] The relationships between shear deformation and elapsed time for PBA and PBA/P(VDF-HFA) (90/10) blend measured at various dead loads are shown in Figures 3 and 4, respectively. The holding power t_c decreases with increasing dead load. In particular, for the PBA sample, t_c is remarkably changed by the dead load. In this study, all samples exhibited cohesive failure of adhesive layer. Delineation of shear deformation-elapsed time relations of PBA/P(VDF-HFA) blends is similar to those of polyisobutylene adhesives reported by Zosel.[12] Therefore, the results of shear adhesion for PBA/P(VDF-HFA) blends were compared with the shear adhesion calculated with the dynamic viscosity η^* according to Zosel's method.[12]

In the shear adhesion test of PSA tape, the test area A decreases with rising the shear deformation Δl from $A_0 = l_0 b$ (start point) to 0 (failure point) as follows

$$A = A_0[1 - (\Delta l/l_0)] \qquad (3)$$

where A_0 is the initial test area, l_0 and b are the

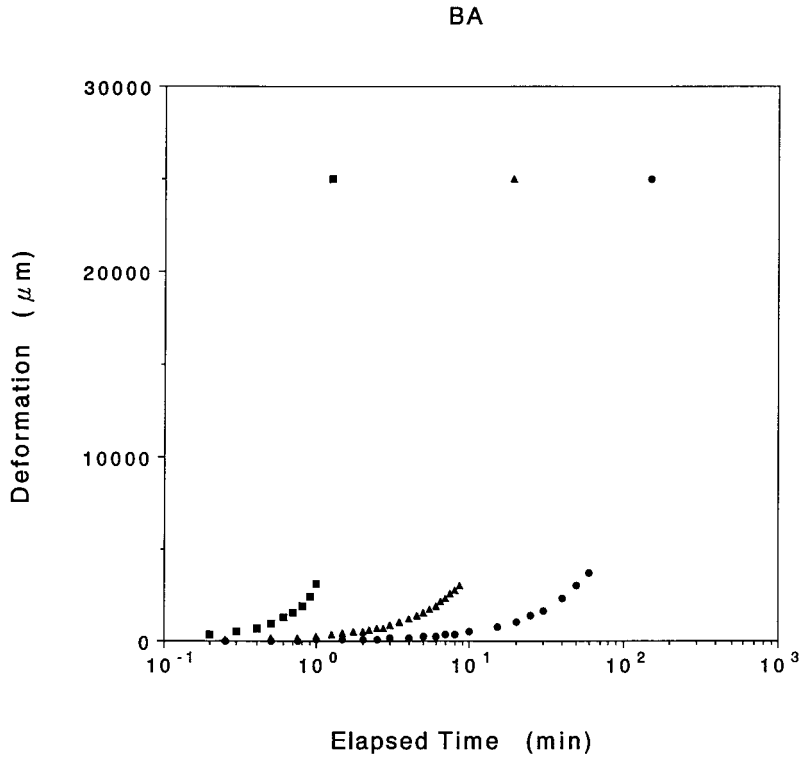

Figure 3 Elapsed time dependence against deformation for PBA. Dead load (kg): (■) 1, (▲) 0.5, and (●) 0.2. BA, butyl acrylate.

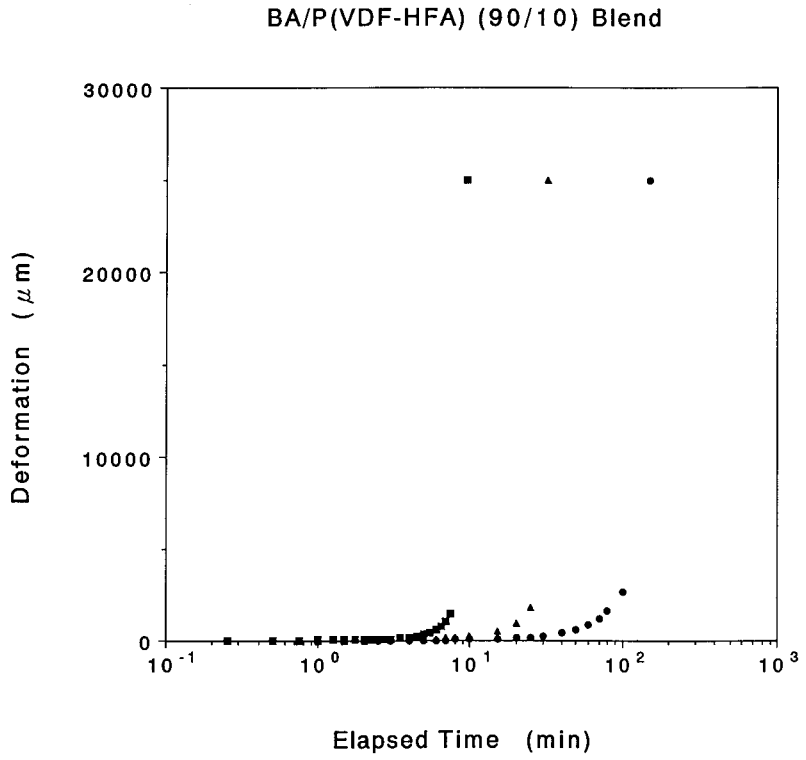

Figure 4 Elapsed time dependence against deformation for the PBA/P(VDF-HFA) (90/10) blend. Dead load (kg): (■) 0, (▲) 10, and (●) 20. BA, butyl acrylate.

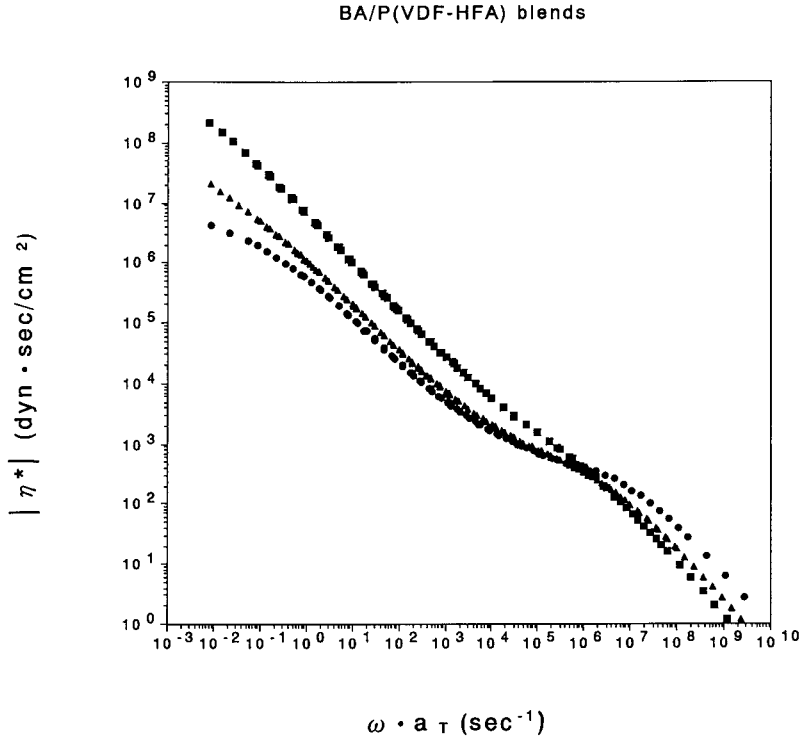

Figure 5 Master curves of dynamic viscosity $|\eta^*|$ and angular velocity ω of PBA/P(VDF-HFA) blends at 23°C. P(VDF-HFA) content (wt %): (●) 0, (▲) 10, and (■) 20. BA, butyl acrylate.

length and width of the test area, respectively. Thus, the shear stress σ increases with increasing Δl as according to the following equation

$$\sigma = \sigma_0/[1 - (\Delta l/l_0)], \quad \sigma_0 = F/A_0 \qquad (4)$$

where σ_0 is the shear stress at starting point and F is the dead load.

To calculate shear adhesion with dynamic viscosity η^*, Zosel[12] limited cohesive failure. From the equation $\sigma = \eta(d\gamma/dt)$, the σ in eq. (4) can be written with the next equation

$$\sigma = \sigma_0/[1 - (\gamma/\gamma_0)], \quad \gamma = \Delta l/d \quad \text{and} \quad \gamma_0 = l_0/d \qquad (5)$$

where γ is the shear strain and d is the thickness of the adhesive layer. Thus, the σ_0 can be regarded as follows

$$\sigma_0 = \eta[1 - (\gamma/\gamma_0)](d\gamma/dt) \qquad (6)$$

Therefore, holding power t_c can be calculated by integration as the following equation

$$t_c = \int_0^{t_1} dt = (A_0/F) \int_0^{\gamma_0} \eta(1 - \gamma/\gamma_0) d\gamma \qquad (7)$$

However, since the integration in eq. (7) cannot be solved, Zosel approximated the shear strain γ *versus* elapsed time t curve as follows

$$t_c = (A_0/F) \sum_{\gamma=1}^{N} \eta_\nu(1 - \gamma_\nu/\gamma_0)\Delta\gamma \qquad (8)$$

First, the dynamic viscosity $|\eta^*(\omega)|$ can be calculated by eq. (1). Next, total shear deformation γ_0 is divided into N intervals $\Delta\gamma$. Finally, every interval of an average viscosity η_ν can be deduced using η *versus* the σ curve. In this study, shear adhesion for PBA/P(VDF-HFA) blends was fitted with the shear strain *versus* elapsed time curve calculated using Zosel's technique described previously.

The master curves of $|\eta^*|$ of PBA/P(VDF-HFA) blends are shown in Figure 5. Zero shear viscosity η_0 for blends increases with increasing P(VDF-HFA) content. We try to compare the experimental shear adhesion with the shear strain and time relation calculated with $|\eta^*|$ data. Figure 6 shows the comparison of measured and cal-

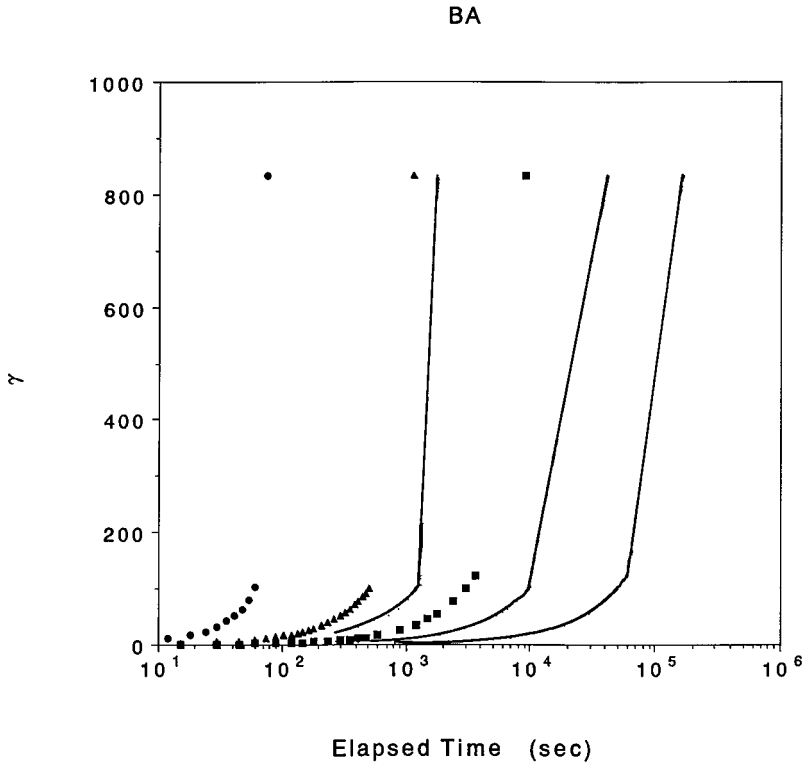

Figure 6 Comparison of measured and calculated shear strain γ and elapsed time for PBA. Dead load (kg): (■) 1, (▲) 0.5, and (●) 0.2. Closed symbols are measured value, and solid line is calculated curve according Zosel's[12] analysis. BA, butyl acrylate.

culated shear strain γ *versus* elapsed time for PBA. The calculated γ *versus* time curves remarkably deviate from experimental data. Measured and calculated holding power t_c is listed in Table II. For all blends, measured t_c differs from calculated t_c. It is considered that the shear adhesion for PBA/P(VDF-HFA) blends cannot be expressed with only $|\eta^*|$ data. In other words, to evaluate shear adhesion, it is necessary that shear adhesion *versus* elapsed time is discussed as the combination of the viscoelastic model and other factors. Next, we propose a new approach to evaluate shear adhesion.

As shown in Figure 7, we express the generalized viscoelastic model of shear adhesion by the four-component model combined with a Maxwell and a Voigt element, one damper element, and other elements. When the dead load is applied to the PSA tape, shear creep deformation of the adhesive polymer expressed with the four-component model occurs. In this state, we assume that cohesive failure do not occur in the adhesive layer. Next, when cohesive failure occurred in the adhesive layer, the shear creep deformation of adhesive, was expressed with the viscoelastic model of damper and other elements. In this study, we re-

Table II Calculated Holding Power t_c of PBA/P(VDF-HFA) Blends

P(VDF-HFA) Content (wt %)	100			90			80
Load (kg)	1	0.5	0.2	1	0.7	0.5	1
$t_{c,\mathrm{exp}}$ (s)	75	1141	9084	569	1918	8933	7509
$t_{c,\mathrm{Zosel}}$ (s)	1721	40551	162106	11449	40295	174117	613223
η_4[a]	6.7×10^3	9.1×10^4	2.8×10^5	2.2×10^4	1.0×10^5	3.2×10^5	7.9×10^5
t_1 (s)	111	3019	23471	367	2393	10450	13768
$t_{c,\mathrm{cal}}$ (s)	111	3019	23516	397	2453	10750	14008

[a] Slope of σ *vs.* $d\gamma/dt$ plots.

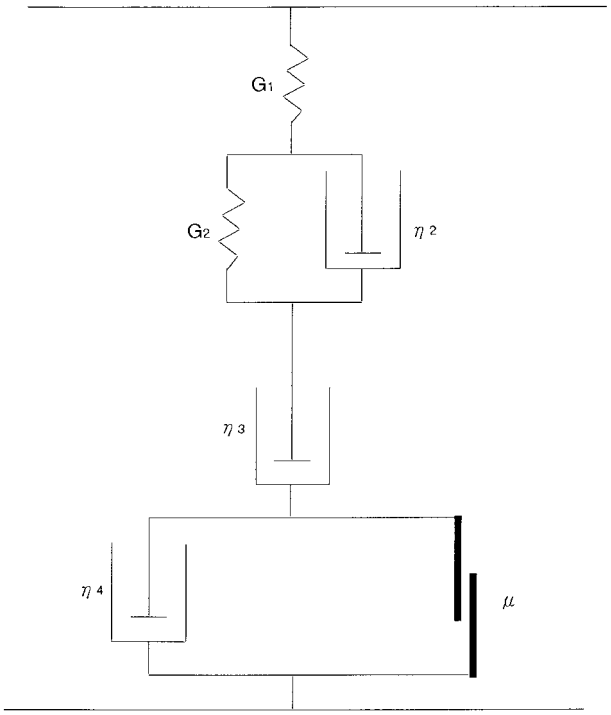

Figure 7 Generalized viscoelastic model of shear adhesion.

garded the friction coefficient μ between adhesive and adherend as the other element. The friction coefficient μ relates to interfacial strength or sliding friction[11] between adhesive and adherend. If the μ-factor does not influence shear adhesion, the viscoelastic model, based on cohesive failure, can be expressed by only damper element η_4. Thus, holding power t_c is expressed with the next equation

$$t_c = t_0 + t_1 \tag{9}$$

where t_0 is the shear deformation time expressed with the four-component model, and t_1 is shear deformation time expressed with damper element η_4 and friction coefficient μ. Shear strain behavior based on the four-component model is expressed as follows

$$\gamma = \sigma_0\{(1/G_1) + [1 - \exp(-t/\tau)]/G_2 + (t/\eta_3)\} \quad \text{for} \quad 0 < t < t_0 \tag{10}$$

On the other hand, the shear strain–time relation expressed with only damper element η_4 can be calculated by the next equation

$$t_1 = \int_0^{t_1} dt = (A_0\eta_4/F)\int_0^{\gamma_0} (1 - \gamma/\gamma_0)d\gamma \quad \text{for} \quad t_0 = t < t_c - t_0 \tag{11}$$

where η_4 can be obtained experimentally as the slope of σ and $d\gamma/dt$ plots. As described previously by Zosel,[12] the integration in eq. (11) cannot be solved. Therefore, we apply the shear strain γ and elapsed time t relation similar to eq. (8) as follows

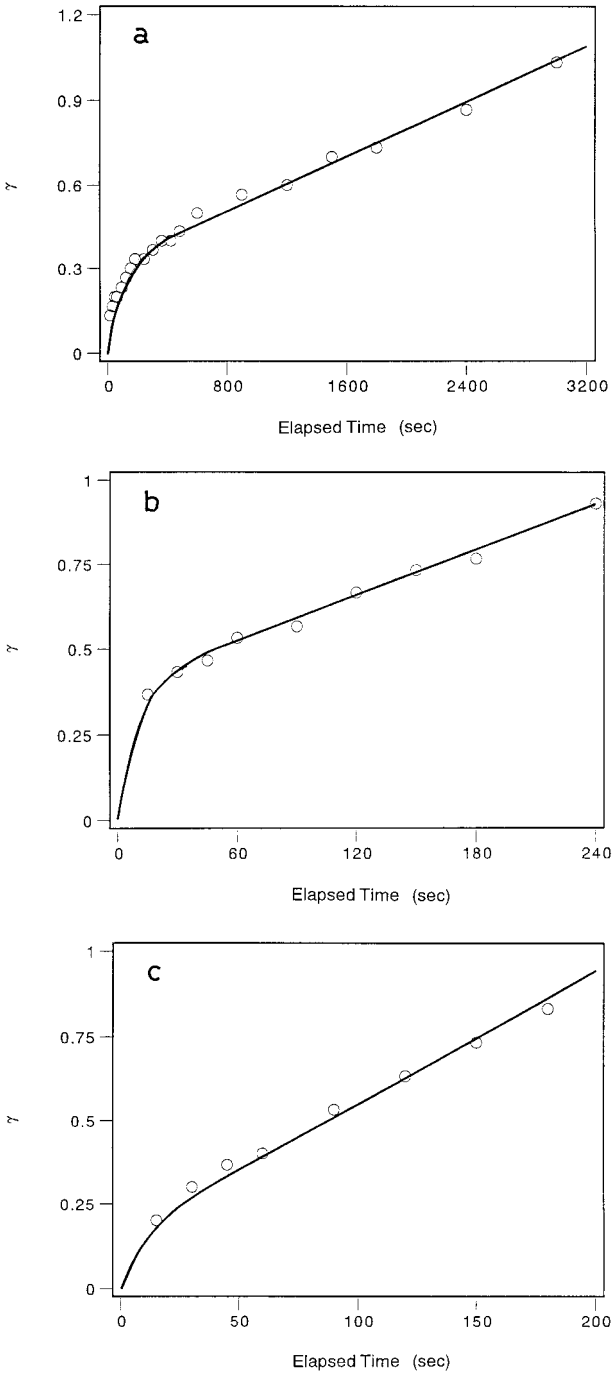

Figure 8 Relationship between shear strain γ and elapsed time. (a) PBA/P(VDF-HFA) (90/10) blend, 0.2 (kg) dead load. (b) PBA/P(VDF-HFA) (90/10) blend, 0.5 (kg) dead load. (c) PBA/P(VDF-HFA) (80/20) blend, 1 (kg) dead load.

Table III Constants of Generalized Viscoelastic Model for PBA/P(VDF-HFA) Blends

	90		80
P(VDF-HFA) Content (wt %)	0.2 Kg Load	0.5 Kg Load	1 Kg Load
G_1 (dyn cm^{-2})	1×10^9	1×10^9	1×10^9
G_2 (dyn cm^{-2})	1×10^5	2×10^5	1×10^6
τ (s)	100	10	10
η_3 (dyn s^{-1} cm^2)	1.3×10^8	3.5×10^7	4×10^7

$$t_1 = (A_0\eta_4/F) \sum_{\gamma=1}^{N} (1 - \gamma/\gamma_0)\Delta\gamma \qquad (12)$$

Figure 8 shows the relationship between shear strain γ and elapsed time of PBA/P(VDF-HFA) blends in the range of $0 < t < t_0$ ($0 < \gamma < 1$). In this study, we determined the t_0 as the time at which the shear deformation reached 30 μm ($\gamma = 1$). In all of samples, the measured γ values fit in the solid curve calculated by eq. (10). The fitting parameters (constants of generalized viscoelastic model) are represented in Table III. The modulus G_2 at the relaxation time τ is close to the storage modulus G' at angular frequency $\omega = 1/\tau$. Therefore, it is suggested that the shear strain behavior for $0 < t < t_0$ region can be evaluated by the four-component model. Next, the relationship between shear stress σ and shear rate $d\gamma/dt$ are examined in the range of t_0 to $t_c - t_0$. The σ *versus* $d\gamma/dt$ plots of PBA are shown in Figure 9. Because the σ increases monotonically with the increasing of $d\gamma/dt$, the value of damper element η_4 can be determined as the slope between σ and $d\gamma/dt$. Figure 10 and Figure 11 show the σ *versus* $d\gamma/dt$ plots for PBA/P(VDF-HFA) (90/10), (80/20) blends, respectively. The σ and $d\gamma/dt$ relations in these blends also exhibit reasonable straight lines. The values of η_4 for all blends are represented in Table II. As the η_4 value increases with increasing the dead load, it is thought that shear adhesion cannot be described by linear viscoelasticity. However, the η_4 values were constant against elapsed time for t_0 to $t_c - t_0$ region. Thus, using these η_4 values, we calculated the shear strain-elapsed time curves for PBA/P(VDF-HFA) blends with eqs. (9) and (12). The comparison of measured and calculated shear strain γ and elapsed time for PBA and PBA/P(VDF-HFA)(90/10), (80/20) blends are shown in Figures 12–14, respectively. In tendency, the calculated curves of γ and t shift to short elapsed time side, compared with the measured γ *versus* t plots. On the other hand, the calculated holding power $t_{c\text{ÅC}\text{cal}}$ is longer than the measured holding power $t_{c,\text{exp}}$.

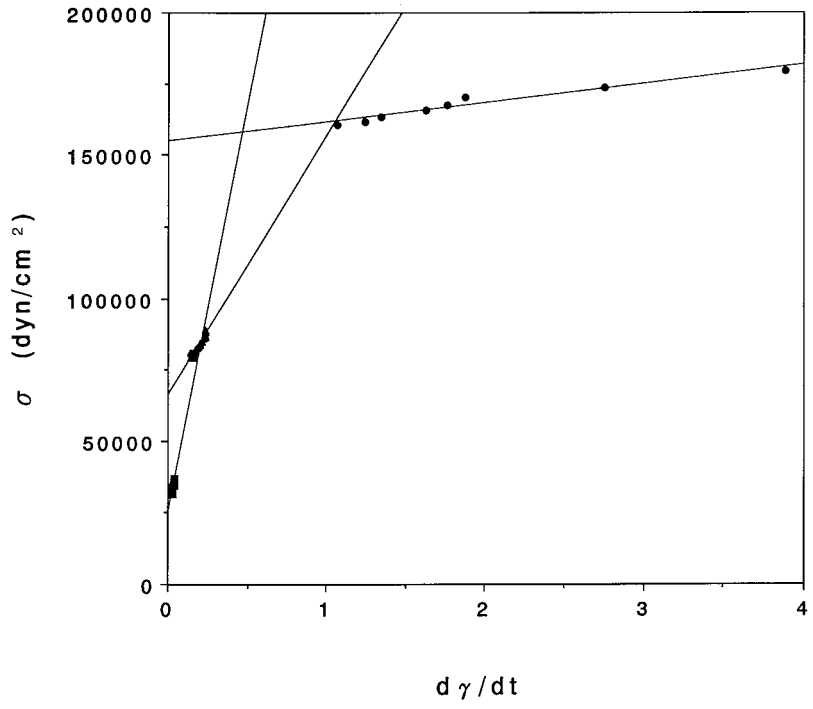

Figure 9 Relationship between shear stress γ and shear rate $d\gamma/dt$ for PBA. Dead load (kg): (■) 0.2, (▲) 0.5, and (●) 1.

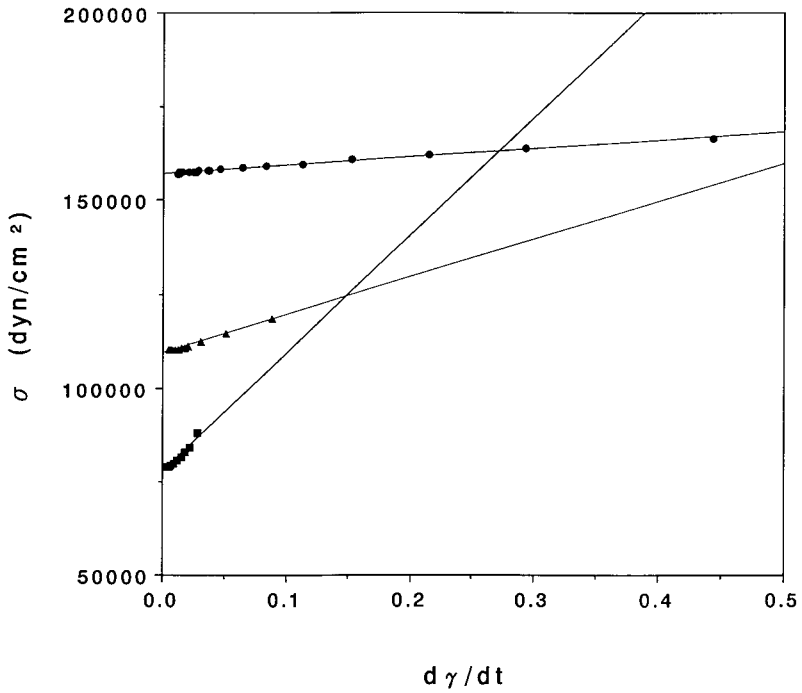

Figure 10 Relationship between shear stress γ and shear rate $d\gamma/dt$ for the PBA/P(VDF-HFA) (90/10) blend. Dead load (kg): (■) 0.5, (▲) 0.7, and (●) 1.

We explain why the calculated $\gamma \sim t$ curves deviate from the measured γ *versus* t plots. One reason is the contribution of other factors to shear adhesion behavior. As shown in Figure 7, the friction coefficient μ between the adhesive and adherend may strongly influence the shear adhesion when the cohesive failure of adhesive layer occurred. In other words, the μ influences the shift

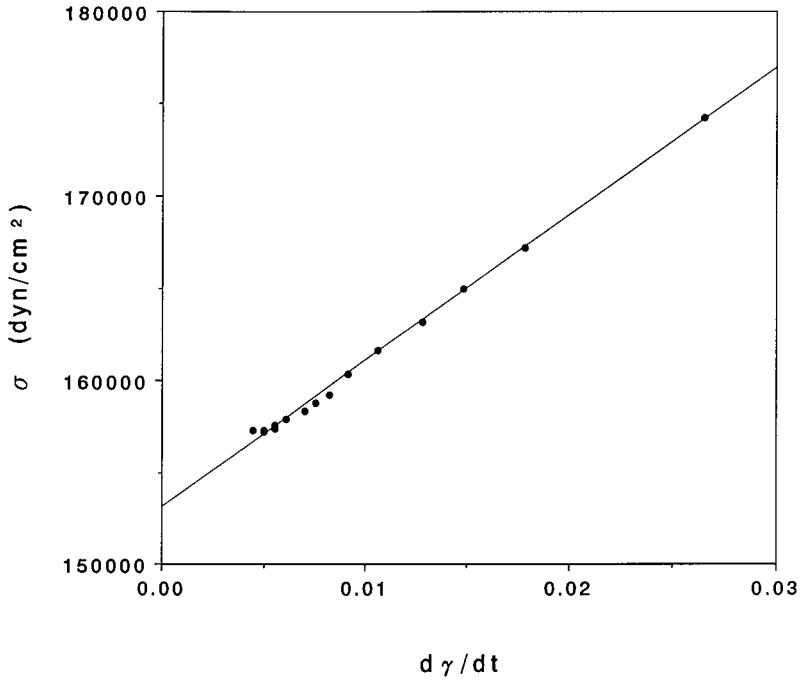

Figure 11 Relationship between shear stress σ and shear rate $d\gamma/dt$ for the PBA/P(VDF-HFA) (80/20) blend. Dead load (kg): (●) 1.

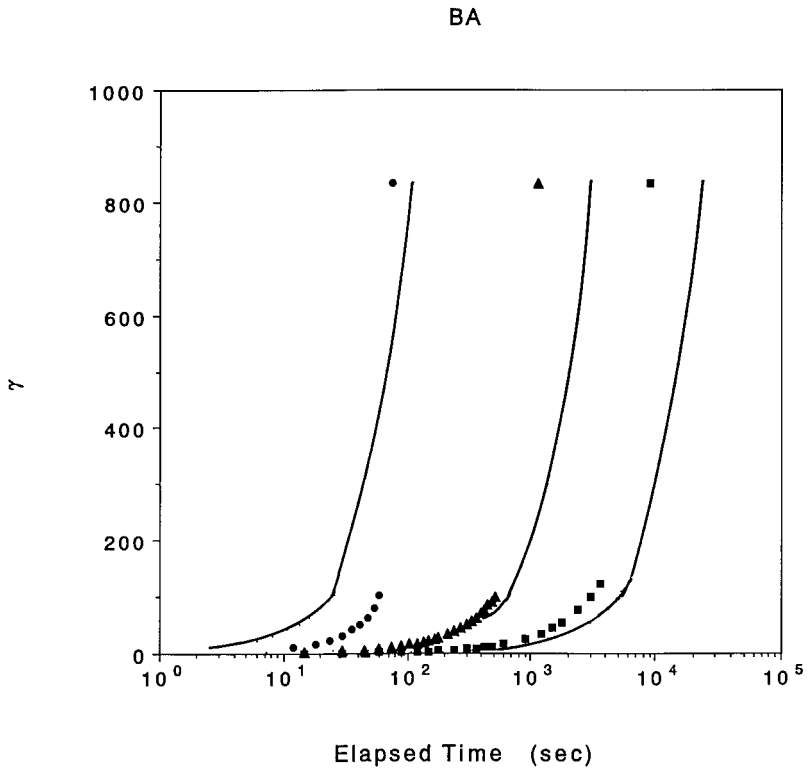

Figure 12 Comparison of measured and calculated shear strain γ and elapsed time for PBA. Dead load (kg): (■) 1, (▲) 0.5, and (●) 0.2. Closed symbols are measured value, and solid line is calculated curve. BA, butyl acrylate.

to short elapsed time side of the calculated $\gamma \sim t$ curve. Another reason is the range of the shear creep deformation in adhesive polymer. In this study, it was assumed that the shear creep deformation occurred in the $0 < \gamma \leqq 1$ region. Therefore, to determine the range of shear creep deformation, we should investigate the strain-stress curve for adhesive polymer. On the contrary, we considered that the discrepancy between $t_{c,\mathrm{cal}}$ and $t_{c,\mathrm{exp}}$ was caused by the balance of cohesive strength of adhesive and shear stress σ. For the adhesive polymer, the cohesive strength is proportional to tensile strength or modulus. As described previously, σ increases with increasing shear deformation Δl because of decreasing test area A. On the other hand, cohesive strength of the adhesive decreases with increasing Δl. Thus, cohesive failure occurred as the elapsed time at which cohesive strength of the adhesive was lower than σ. As the results, it is presumed that the $t_{c,\mathrm{cal}}$ is longer than $t_{c,\mathrm{exp}}$.

In this study, the experimental shear adhesion of the PBA/P(VDF-HFA) blend was evaluated with viscoelastic characteristics, such as dynamic viscosity, σ *versus* $d\gamma/dt$ plots and shear creep deformation. However, the measured γ *versus* t plots cannot be fitted to the calculated shear strain. In general, holding power or shear adhesion was qualitatively correlated with the mechanical properties.[7,8,11–14,16,17] In fact, shear adhesion for PBA/P(VDF-HFA) blends could not be evaluated by the mechanical properties. Consequently, to elucidate the shear adhesion of a PSA tape, it is necessary that another factor, (e.g., the friction coefficient μ and the cohesive strength of adhesive polymer) has to be introduced for the analysis of shear adhesion or holding power.

CONCLUSIONS

Holding power for PBA/P(VDF-HFA) blends improved with increasing P(VDF-HFA) content because the storage modulus G' and loss modulus G'' of P(VDF-HFA) is higher than that of PBA. The shear adhesion of PBA/P(VDF-HFA) blends was characterized with dynamic viscosity, shear stress *versus* shear plot and the generalized viscoelastic model. However, measured shear adhesion did not fit to the calculated one obtained with these viscoelastic properties. We pointed out that shear adhesion is influenced by viscoelastic prop-

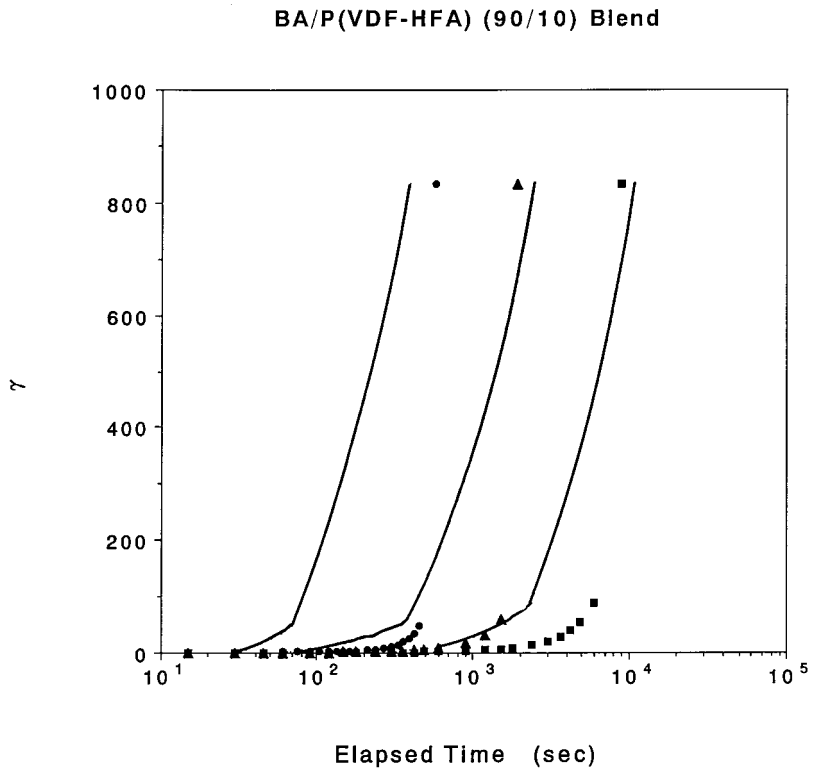

Figure 13 Comparison of measured and calculated shear strain γ and elapsed time for the PBA/P(VDF-HFA) (90/10) blend. Dead load (kg): (■) 1, (▲) 0.7, and (●) 0.5. Closed symbols are measured value, and solid line is calculated curve. BA, butyl acrylate.

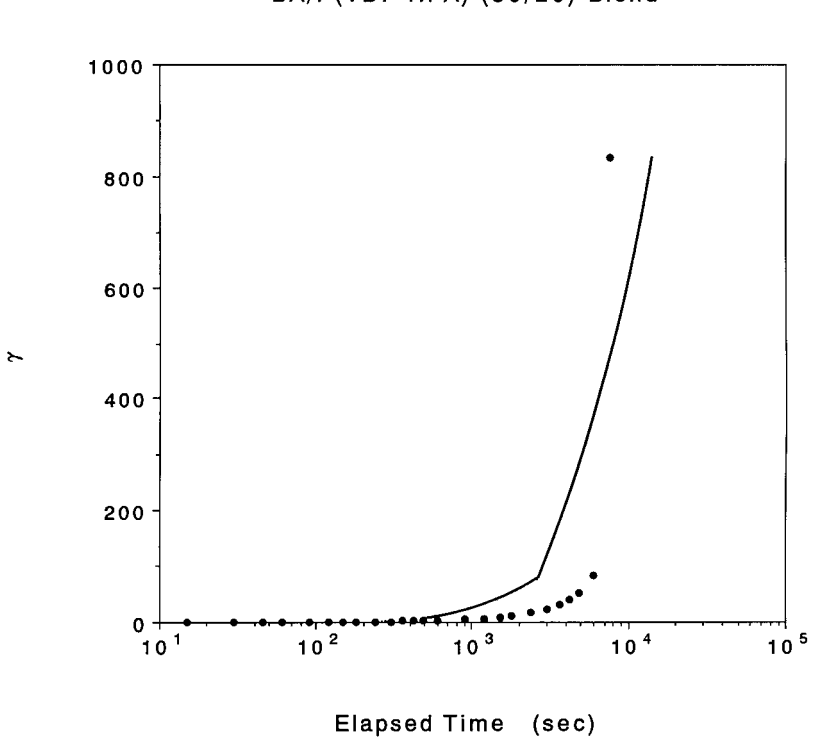

Figure 14 Comparison of measured and calculated shear strain γ and elapsed time for the PBA/P(VDF-HFA) (80/20) blend. Closed circle is measured value at 1 kg of dead load, and solid line is calculated curve.

erties in adhesive bulk and other factors, such as friction coefficient and cohesive strength of adhesive.

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