Studies on Tack of Pressure-Sensitive Adhesive Tapes: On the Relationship between Pressure-Sensitive Adhesion and Surface Energy of Adherends

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Synopsis

The relationship between wetting and pressure-sensitive adhesion was studied using an adhesive composed of poly(butyl acrylate) and various adherends of different surface tension. The amount of adhesive deposit was determined quantitatively by tracer technique although the unbonding process was apparently observed as interface failure. The adhesive force and amount of deposit were both dependent on the critical surface tension of the adherends. Maximum tack value and contamination were observed with adherends whose critical surface tension was close to that but a little higher than that of the adhesive. The adhesive force obtained was lower than cohesive strength of adhesive. From this evidence, a mechanism for pressure-sensitive adhesion was discussed: the bond breaks in the addesive mass around the very minute spots where interaction is at work between adhesive and adherend. Inasmuch as the density of the minute spots per unit area depends on the surface tension, the adhesive force also depends on the surface tension.

INTRODUCTION

In the preceding papers,[1,2] it has been reported that the tack[1] and the amount of adhesive deposit[2] of pressure-sensitive adhesives depend on the critical surface tension of the adherend, and a mechanism for bond breaking has been proposed.

The present paper deals with the quantitative examination of the locus of failure of pressure-sensitive adhesion using carbon 14-labeled poly(butyl acrylate) adhesive. The proposed mechanism on pressure-sensitive adhesion is discussed on the basis of the experimental results.

EXPERIMENTAL

Preparation of ^{14}C-Labeled Adhesive

n-Butanol-1-^{14}C (250 μCi) was diluted with 7.4 g inactive n-butanol and esterified with 10.9 g acrylyl chloride in 46 ml ethyl ether in the presence

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of 17.6 g N,N'-dimethylaniline under nitrogen atmsophere. After the reaction, the mixture was washed with water, followed by diluted sulfuric acid and neutralization by saturated sodium bicarbonate solution. The oil layer was separated and dried over anhydrous sodium sulfate overnight. The dried solution was distilled under reduced pressure. Yield was 9.9 g (77%), bp 40°C (11–12 mmHg), specific activity 19 μCi/g, and radiochemical yield 75%.

The labeled monomer obtained was diluted with 10 g inactive butyl acrylate and polymerized in 30 g ethyl acetate at 70°C for 7.5 hr under nitrogen atmosphere in the presence of 2 mg benzoyl peroxide. The polymer was precipitated with excess methanol and purified by reprecipitation. Yield was 6.4 g (32% polymerized), specific activity 9.7 μCi/g, radiochemical yield 33%.

The adhesive was prepared by mixing 6.4 g active polymer with 1.6 g inactive poly(butyl acrylate) ($[\eta] = 2.0$ at 25°C in acetone). Specific activity of the adhesive was 7.7 μCi/g. The apparent viscosity of adhesive was measured to be *ca.* 10^7 poises by shear creep method[3].

Preparation of Low Molecular Weight Poly(butyl Acrylate)

Low molecular weight polymer of butyl acrylate was prepared by telomerization in benzaldehyde. Butyl acrylate, 32 g, was polymerized in 53 g benzaldehyde in the presence of 0.22 g benzoyl peroxide at 60°C for 8 hr. Oligomer was precipitated by adding the mixture to an excess of methanol containing water and purified by reprecipitation. Yield was 21 g (66%) and number-average molecular weight by end determination was 2.24×10^4. The apparent viscosity of the oligomer was measured to be *ca.* 10^3 poises by shear creep method.[3]

Preparation of Adhesive Specimen for Measurement

The adhesive solution (8% in ethyl acetate) was coated on biaxially drawn poly(ethylene terephthalate) film (Toray's Lumirror No. 25) and then dried. The thickness of dry adhesive layer was controlled within 0.02 ± 0.001 mm.

Adherend Materials

Adherends used for measurement of peel force, contact angle, and adhesive deposit after peeling were test panels of $50 \times 125 \times 3$ mm, which were stainless steel (SUS 27, mirror faced), poly(tetrafluoroethylene), high- and low-density polyethylene, polystyrene, poly(hexamethylene capramide), polypropylene, poly(ethylene terephthalate), and poly(methyl methacrylate). Probes for tack measurement were prepared from the materials as described above.

Measurements of Peel Force, Probe Tack, and Radioactivity

The 180° peel force was measured using a Shopper-type tensile tester in accordance with PSTC test method. Thickness of adhesive layer of test

samples was controlled within 0.02 ± 0.001 mm. The Polyken probe tack tester was also used for measurement of tack: contact pressure 100 g/cm², contact time 1 sec, rate of separation 1 cm/sec. Tack measurements were carried out at 20 ± 2°C. For counting of radioactivity, a liquid scintillation counter (Packard Tri-Carb Scintillation Spectrometer, Model 3320) was used at the Tokyo Metropolitan Isotope Research Center. The counting specimen was the adherend sample from which adhesive specimen had been peeled off by the same manner as the peel force measurement. Total area of each test sample was 16.5 × 80 mm. The test sample was immersed in scintillating solution and then counted. The scintillator was based on toluene, and its composition was 4 g PPO and 0.1 g POPOP in 1 liter of toluene. Activity measurement was 10 minutes of counting repeated more than 10 times. The number of disintegrations was obtained by the correction of external standard method.

Contact Angle of Adhesive on Adherend

A droplet of low molecular weight poly(butyl acrylate) was put on the surface of the adherend, and the contact angle was measured after four to six days when equilibrium was attained, using a contact angle goniometer (made by Erma Optical Works) at 20 ± 2°C and 65 ± 5% R.H.

Critical Surface Tension of Adherends and Adhesive

Zisman's critical surface tension, γ_c, was used as the surface energy of adherends in this work. The values in the literature[4] were used, since the experimental values of γ_c showed good agreement with the values in the literature as reported in the preceding papers.[1,2] Surface tension of poly-(butyl acrylate) was reported as $\gamma_L = 28$ dynes/cm by Yamauchi and others.[5] On the other hand, γ_c for poly(butyl acrylate) was found to be 31 dynes/cm from the plot of cosine of contact angle versus surface tension of a mixture of water and propylene glycol.

RESULTS AND DISCUSSION

The experimental results are shown in Table I. Peel force and probe tack both varied, depending on γ_c of the adherend. The unbonding process was apparently interface failure, but adhesive deposit was found on the surface of every adherend after peeling. The quantity of adhesive deposit was also dependent on γ_c of the adherend. If the adhesive deposit is uniformly distributed on the surface of the adherend, 0.1 g/cm² of deposit will correspond to 10 Å of thickness, with the assumption that the density of the adhesive equals 1.0 g/cm³. The deposit will be scattered on the surface as a random aggregate of very minute spots of the adhesive mass because of microroughness of adherend and adhesive. That the adhesive deposit was observed even at the surface of poly(tetrafluoroethylene) is due to the particular effect of scintillation counting. By direct counting using a

TABLE I
Contact Angle, Tack Values, and Adhesive Deposit of Poly(butyl Acrylate)
Adhesive on the Surface of Various Adherends

Adherends		Cosine of contact angle of oligo-butyl acrylate	Amount of ad-hesive deposit, $\mu g/cm^2$	Peel forced[4], g/1.5 cm width	Probe tack,[d] g/0.5 cm diam. probe
Material	γ_c,[a] dynes/cm				
Poly(tetrafluoroethylene)	18.5	0.485	0.11	7	0
Polypropylene	29	0.883	0.03	144	96
Low-density polyethylene	26[b]	0.946	0.03	69	84
High-density polyethylene	31	0.951	0.07	123	not measured
Polystyrene	33	0.994	0.38	505	130
Poly(methyl methacrylate)	39	0.994	0.27	550	260
Poly(hexamethylene capramide)	42[c]	0.917	0.07	495	not measured
Poly(ethylene terephthalate)	43	0.968	0.08	399	160
Stainless steel	—	0.746	0.02	137	130

[a] γ_c Values in ref. 4.
[b] γ_c Value in ref. 11.
[c] γ_c Value in ref. 12.
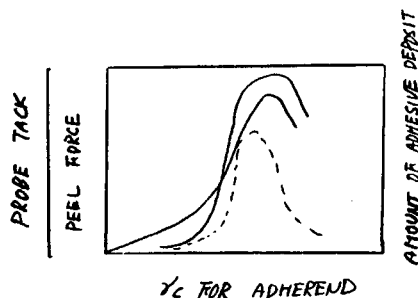[d] Thickness of adhesive layer, 0.02 ± 0.001 mm.

Fig. 1. Dependence of peel force, probe tack, and amount of adhesive deposite on γ, for adherend, measured at 20°C, 65% R.H., adhesive thickness 0.02 ± 0.001 mm. (O) peel force, rate of peeling, 30 cm/min; (□) probe tack, contract pressure, 100 g/cm²; contact time, 1 sec; rate of separation, 1 cm/sec; (●) amount of adhesive deposit determined from the radio activity at the surface of adherend after peeling off; rate of peeling, 30 cm/min.

G.M. tube[2] and measurement of contact angle,[6] the adhesive deposit could not be detected with poly(tetrafluoroethylene).

The variations of peel force, probe tack, and adhesive deposit versus critical surface tension are illustrated in Figure 1. Maximum values of peel force and tack were observed at 33 to 39 dynes/cm of γ_c; these were a little higher than the surface tension of the adhesive ($\gamma_c = 28$ dynes/cm and $\gamma_c = 31$ dynes/cm). On the other hand, the amount of adhesive deposit also varied with γ_c of the adherend, and a maximum deposit was observed near but somewhat below γ_c where maximum tack was observed.
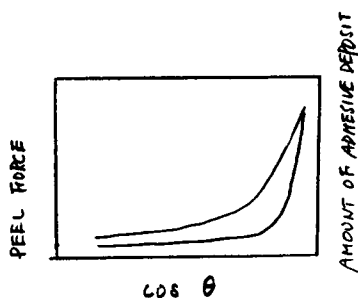
Fig. 2. Dependence of peel force and amount of adhesive deposit on cos θ of adhesive. (low molecular weight PBA):   (O) peel force;   (●) amount of adhesive deposit.
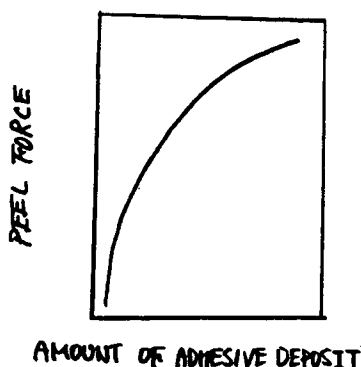

Fig. 3. Relationship between wettability and peel force.

The wettability, given by the cosine of the contact angle in Table I, was correlated with both the amount of adhesive deposit and the adhesive forces measured, as shown in Figure 2.   These facts imply that pressure-sensitive adhesion is mainly dependent on the wettability of the adhesive on the surface.   The significance of wettability is also shown by Figure 3, in which peel force is plotted versus amount of adhesive deposit.   A similar relationship was found in the case of rubber-based adhesive.[7]

Table II shows a comparison between work of adhesion, ideal adhesive force, and measured tack values.   The ideal adhesive force was calculated using the equation derived by Good[8]:

$$\sigma_{LS}{}^a = 2.05\Phi\sqrt{\gamma_L\gamma_S/z_{0,LS}}$$

where Φ is the interaction parameter introduced by Good and Girifalco,[9] γ_L and γ_S are surface tension of liquid (adhesive) and solid (adherend), respectively; and $z_{0,LS}$ is the distance where the intermolecular forces between two substances react, and is equal to $z_{0,LS} = \frac{1}{2}(z_{0,L} + z_{0,S})$.   We postulated $z_{0,LS}$ to be 4.5 Å, assuming that the dispersion force between two polymer molecules will be predominant.[8]   The ideal adhesive force at the interface was calculated to be *ca.* 10^9 dynes/cm². On the other hand, the cohesive strength of the adhesive was found to be 3×10^6 dynes/cm² at the

TABLE II
Comparison of Ideal and Measured Adhesive Forces[f]

Adherend Material	γ_c, dynes/cm	W_A[a] erg/cm²	Φ[b]	σ_{LS}[a,c], dynes/cm²	Peel force,[c] dynes/cm²	Probe tack,[c] dynes/cm²
Poly(tetrafluoroethylene)	18.5	41.6	0.91	9.44×10^8	4.6×10^3	0
Polypropylene	29	52.7	0.93	1.21×10^9	9.4×10^4	4.8×10^5
Low-density polyethylene	26	54.5	1.01	1.24×10^9	4.5×10^4	4.2×10^5
High-density polyethylene	31	54.6	0.93	1.25×10^9	8.0×10^4	not measd.
Polystyrene	33	55.8	0.92	1.27×10^9	3.3×10^5	6.5×10^5
Poly(methyl methacrylate)	39	55.8	0.85	1.28×10^9	3.6×10^5	1.3×10^6
Poly(hexamethylene capramide)	42	53.7	0.78	1.22×10^9	3.2×10^5	not measd.
Poly(ethylene terephthalate)	43	55.1	0.79	1.25×10^9	2.6×10^5	8.0×10^5
Stainless steel	—	48.9	0.21[d]	1.13×10^9	9.0×10^4	6.5×10^6

[a] $W_A = \gamma_L(1 + \cos \theta)$; where θ was the contact angle of oligo-BA on the adherend.

[b] $\Phi = \sqrt{\gamma_L(1 + \cos \theta)}/2\sqrt{\gamma_S}$.

[c] σ_{LS}[a] $= 2.05\Phi\sqrt{\gamma_L\gamma_S}/z_{0,LS}$, where $z_{0,LS}$ was assumed to be 4.5 Å.

[d] γ_c of stainless steel was assumed to be 500 dynes/cm.

[e] Thickness of adhesive layer, 0.02 ± 0.001 mm.

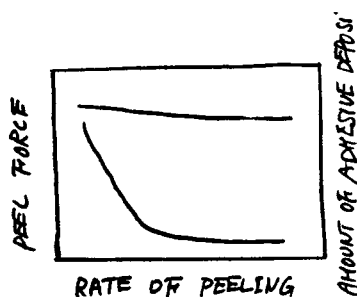[f] Cohesive strength of adhesive was measured to be 3×10^6 dynes/cm² by butt joint method.

Fig. 4. Dependence of peel force and amount of adhesive deposit on rate of peeling in the case of polystyrene as adherend: (O) peel force; (●) amount of adhesive deposit.

butt joint. Therefore, the adhesive bond should not break at the interface but break in the adhesive layer. If wetting by the adhesive is completely spread over the surface of the adherend, bond breaking will be due to the apparently cohesive failure; the measured force of adhesion will be nearly the same as its cohesive strength. As described above, the amount of adhesive deposit was very limited in most adherends, and the tack values were found to be 5×10^4 to 1×10^6 dynes/cm², which were somewhat lower than the cohesive strength of the adhesive.

From this evidence, it can be concluded that the wetting by the adhesive is incomplete and is scattered on the surface as very minute spots.[1,2] When bond breaking occurs, the adhesive joint should not separate at the interface, but the breaking should occur by cohesive failure in the adhesive mass near the interface. The breaking will be due to the viscous flow of adhesive mass around the very minute spots on the surface. The density of the spots will be dependent primarily on the surface chemical conditions and secondarily on the viscoelastic property of the adhesive. The measured values of adhesive force and amount of adhesive deposit were, therefore, dependent on the γ_c of the adherends.

The relationship between peeling rate and adhesive deposit was studied using polystyrene as an adherend, on which adhesive deposit was remarkable high after peeling off. The result is shown in Figure 4. Peel force was independent of rate from 10 cm/min to 60 cm/min. However, the amount of adhesive deposit was very remarkable at 10 cm/min of peeling rate, but suddenly dropped at 20 cm/min and then decreased only slightly with the rate. The failure was unstable and partially cohesive at 10 cm/min; e.g., Aubrey et al.[10] reported the phenomenon of "slip stick" peeling at a medium peeling rate at 10–20 cm/min. Therefore, from the relationship between peel force and amount of adhesive deposit, it will be concluded that, except for unstable peeling region, the wetting is dependent on the bonding process of adhesion but independent of the unbonding process.

These facts also indicate that pressure-sensitive adhesion is mainly controlled by wetting at the bonding process, although the force of adhesion

is measured as the mechanical force necessary for breaking the adhesive mass.

CONCLUSIONS

In pressure-sensitive adhesion, wettability has a great deal of effect. Adhesive deposit was confirmed quantitatively for the various adherends by using a tracer technique, although unbonding is apparently the result of interface failure. The amount of adhesive deposit varied from about 0.05 $\mu g/cm^2$ to 0.4 $\mu g/cm^2$ depending on the critical surface tension of the adherend. Assuming that the adhesive deposit is spread uniformly on the surface of the adherend, the thickness is calculated to be only 10 Å when the amount of deposit is 0.1 $\mu g/cm^2$. However, the deposit will be scattered as the aggregate of very minute wetting spots on the surface.

Peel force and probe tack were also dependent on the critical surface tension of the adherend. These values of adhesive force were lower than the cohesive strength of the adhesive or the ideal adhesive force calculated. It is concluded that reduction of adhesive force will be due to the stress concentration in the adhesive mass at the very minute wetting spots on the surface. If the density of the minute spots per unit area is dependent on surface tension, the adhesive force is also dependent on it. The relationship between rate of peeling and adhesive deposit was also studied.

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