Studies on Tack of Pressure–Sensitive Adhesive Tapes

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Synopsis

It has been found that tack values of pressure-sensitive adhesives are dependent on the surface energies for adherends. The parabolic curves with maxima are obtained from the plots of tack values versus critical surface tensions for the substrates. The maximum occurs at the region where the two surface tensions are almost similar. On the other hand, tack is measured as a dynamic value indicated as the force necessary to deform the adhesive mass. To explain why the tack values is controlled by the surface character of the adherend, a mechanism is proposed for adhesive bond breaking. Primarily, bonding occurs by wetting the surface with adhesive. When the adhesive bond breaks by external force, unbonding proceeds from the viscoelastic deformation of the adhesive mass around the wetted spots on the surface of the adherend. As the total area of wetted spots is determined by surface energy, the tack value is dependent on the critical surface tension of the adherend.

INTRODUCTION

Recently, it has been reported that the adhesive bonding force is dependent on the surface chemical properties of adhesive and adherend.[1–5] The adhesive specificity is explained by the difference of wettability of adhesive to substrates differing in their surface free energies.[6]

This paper attempts to clarify the relationship between the surface chemical characters of substrates and tack of pressure-sensitive adhesives.

EXPERIMENTAL

Adhesives

Three kinds of pressure-sensitive adhesives are used for this study: Type 1, an adhesive composed of natural rubber and of tackifier, which is a mixture of pentaerythritol ester (Hercules's Pentalyn H, A. V. = 12, softening point = 92°C) and triethylene glycol ester (Hercules's Staybelite Ester No. 3, A. V. = 7.8, softening point = 2°C) with hydrogenated rosin; Type 2, an acrylic adhesive, which is a copolymer of ethyl acrylate (64%) and 2-ethylhexyl acrylate (36%), $[\eta]$ (at 20°C in benzene) = 0.94; Type 3, poly(ethyl vinyl ether), which is a mixture of polymer of high molecular

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weight; η_r (at 20°C in benzene) = 4.0 (63%), and polymer of low molecular weight, η_r (at 20°C in benzene) = 0.3 (37%).

A solution of an adhesive is coated on the biaxially drawn poly(ethylene terephthalate) film with 0.025 mm thickness (Torey's Lumirror No. 25). The thickness of the dry adhesive layer is controlled within 0.020 ± 0.001 mm.

Tack Measurements

The Polyken tack tester[7] is used for measurement of adhesive bond strength. The tester provides for a probe holder, bringing together the probes of various materials and the structure for contact with adhesives at controlled rate, pressure, and time, and subsequently breaking the tack bond thus formed at a controlled rate.

Tack measurements were carried out in an air-conditioned room at 20°C or in a small cabinet circulated by air at constant temperature above 20°C. The tip of the probe was cleaned by washing the surface with distilled n-hexane (in the case of stainless steel probes) or by polishing with 1000-mesh emery paper and subsequently by washing with distilled n-hexane (in the case of plastic probes).

The 180° peel forces were also measured as the tack measurement after prolonged time of contact with various substrates. The apparatus used was a Shopper-type tensile tester.

Material of Adherends

Plastic probes were prepared by lathing plastic rods, which were poly-tetrafluoroethylene (Teflon) (manufactured by Mitsui Fluoro Chemicals Co.), high-density polyethylene (PE) (Showa Denko's Showrex), poly-styrene (PST) (Asahi Dow's Styron), poly(methyl methacrylate) (PMMA) (polymerized commercial methyl methacrylate in the presence of radical initiator), and poly(hexamethylene capramide) (Torey's Nylon 6). The compositions of these materials were confirmed using infrared spectra. The critical surface tensions γ_c for these materials were determined graphically from the plot of cosine of contact angle θ versus surface tension of aqueous solutions of dipropylene glycol.

The contact angle measurements were made by direct observation of the drops using a contact angle goniometer made by Erma Optical Works, and the surface tensions of liquids were determined by the Wilhelmy slide method using Simazu Surface Tensometer ST-1.

The plastic plates for peel force measurements were obtained commercially, and composition and γ_c were confirmed by the same manner as described above.

These measurements were carried out in an air-conditioned room at 45% RH, 20°C.

Apparent Viscosity

The apparent viscosities of adhesives, η^*, were determined by the shear creep method.[8]

RESULTS AND DISCUSSION

γ_c for Plastic Probes and Plates

Figures 1 and 2 show the plots of cos θ versus surface tension of the liquids toward plastic probes and plates, respectively.   The γ_c values obtained are tabulated in Table I, and these values are in good agreement with those in the literature.
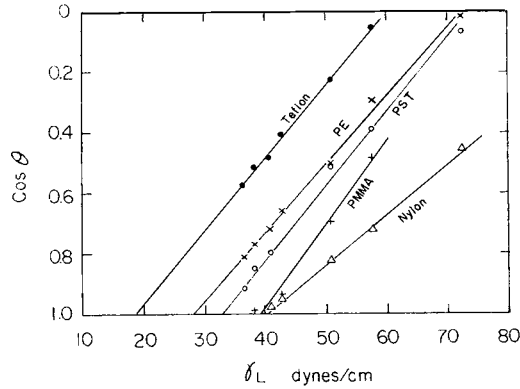

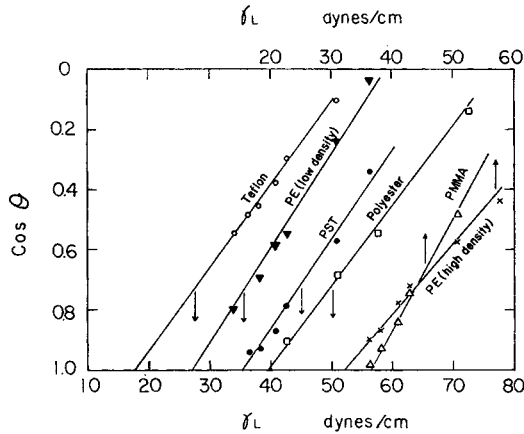Fig. 1. γ_c Plots for various plastic probes.

Figure 2. γ_c Plots for various plastic plates.

Effect of Contact Time and Rate of Separation

Figure 3 shows the effects of contact time and of rate of separation on the tack value for stainless steel probes.   The tack value increases with increasing contact time, rate of separation, and viscosity of adhesive.   The effect of contact time is due to the increase of real contact area by wetting because of the deformation of the viscoelastic adhesive mass by the com-

TABLE I
Critical Surface Tension for Various Plastic Probes and Plates

Plastics	γ_c, dynes/cm at 20°C		
	Probe	Plate	Literature
Polytetrafluoroethylene (Teflon)	19	18	18[6]
Polyethylene (low density)		27	26[1]
Polyethylene (high density)	28	32	31[6]
Polystyrene	33	35[a]	33[6]
Poly(methyl methacrylate) (PMMA)	39	37	39[6]
Poly(hexamethylene capramide) (Nylon 6)	41		42[13]
Poly(ethylene terephthalate)		40	43[6]

[a] Contains $CaCO_3$ as filler.

pression.   The wetting of adhesive on stainless steel is rapid, and tack values increase very quickly up to 0.5 sec of contact.   The effect of pressure is of course important to control the rate of wetting.   For example, Dahlquist showed that the room temperature compliance at 1 sec is typically about 1×10^{-6} cm^2/dyne.[9]

As the stress increases with shear rate, the tack value is dependent on the rate of separation.   The rate dependence is mainly attributable to the elasticity of adhesive.   It has also been shown that the dependence of dynamic modulus and the dependence of tack value on rate of separation can be plotted on the same coordinates.[9]   Values for Young's modulus for
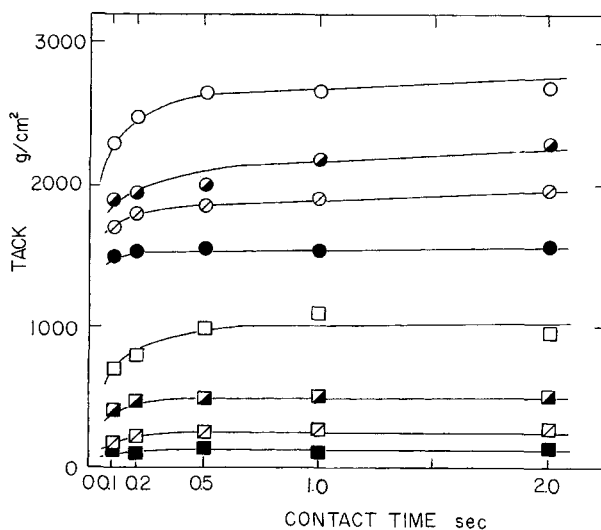

Fig. 3.   Effects of contact time and rate of separation on probe tack value, at 20°C. Rubber-based adhesive, NR:tackifier ratio, 60:40.   Tackifier: Pentalyn H, indicated by circles, log $\eta^*_{60°C}$ for adhesive is 7.99; Staybelite Ester No. 3, indicated by squares, log $\eta^*_{60°C}$ for adhesive is 5.71.   Rate of separation: (O, □) 5.0 cm/sec; (◑, ◪) 1.0 cm/- sec; (⊘, ◨) 0.2 cm/sec; (●, ■) 0.005 cm/sec.   Contact pressure = 100 g/cm.

pressure-sensitive adhesives within 10^6–10^8 dynes/cm² have been reported in the literature.[8,9,18]

The tack value is also dependent on the viscosity of adhesives; e.g., the tack value for a blend of natural rubber with Pentalyn H ($\eta^* = 9.8 \times 10^7$ poises) is much higher than that for the blend with Staybelite Ester No. 3 ($\eta^* = 5.1 \times 10^5$ poises).

The effects of viscosity are also shown in Table II. The contribution of viscosity is very important to the tack value as well as to the elasticity. This implies that the tack value is related to the force necessary to deform the pressure-sensitive adhesive mass until it breaks by viscous flow.

These experimental facts indicate that the tack measurement is related to the unbonding process, and the bonding process is controlled by wetting.

TABLE II
Apparent Activation Energies for Viscosity and
Tack Values of Adhesives[a]

Ratio of Pentalyn H/ Staybelite Ester No. 3	$\log \eta^*_{60°C}$	E_{vis}, kcal/mol	$Tack_{60°C}$, g/cm²	E_{tack}, kcal/mol
100/0	7.99	7.3	305	3.7
80/20	7.98	5.5	100	4.9
60/40	7.46	4.2	72	6.0
40/60	7.36	3.5	—	6.9
0/100	5.71	—	—	—

[a] Adhesives are composed of natural rubber and mixture of Pentalyn H and Staybelite Ester No. 3. The probe tack values were determined at 1 sec of contact time, 1 cm/sec rate of separation, and 100 g/cm² contact pressure.

Adhesion Specificity

In order to estimate the effect of wetting, the tack values were measured for various plastic probes. Figures 4 to 6 indicate the relationship between the tack values and γ_c for various plastic probes under different contact times and contact pressures. The maximum work of adhesion is observed at the surface having γ_c values between 33 dynes/cm for polystyrene and 39 dynes/cm for poly(methyl methacrylate). These parabolic curves with a maximum have been found for any adhesives used, such as rubber-based, acrylic, and vinyl ether adhesives.

It is very difficult to determine the surface tensions for pressure-sensitive adhesives because they are sticky viscoelastic materials and composed of many heterogeneous components with different surface energies.

However, it is possible to estimate the surface tensions for adhesives to be 33–39 dynes/cm, as follows: (1) Kitazaki, Watanabe, and Toyama[1] have found γ_c to be 36 dynes/cm for adhesive composed of natural rubber and rosin. Since γ_c for poly(cis-1,4-isoprene) has been determined to be 31 dynes/cm,[10] the adhesive composed of natural rubber and of hydrogenated
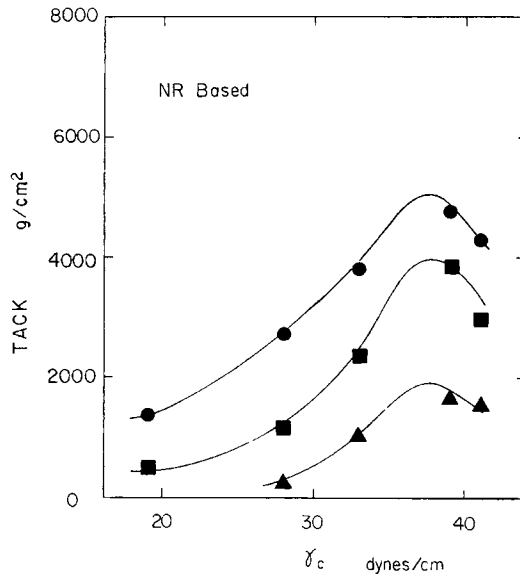
Fig. 4. Relationship between tack value and surface energy, at 20°C. Rubber-based adhesive, NR:tackifier (Pentalyn H) ratio, 60:40. (●) Contact time = 100 sec, rate of separation = 1.0 cm/sec, contact pressure = 500 g/cm^2; (■) contact time = 1.0 sec, rate of separation = 1.0 cm/sec, contact pressure = 100 g/cm^2; (▲) contact time = 0.1 sec, rate of separation = 1.0 cm/sec, contact pressure = 10 g/cm^2.
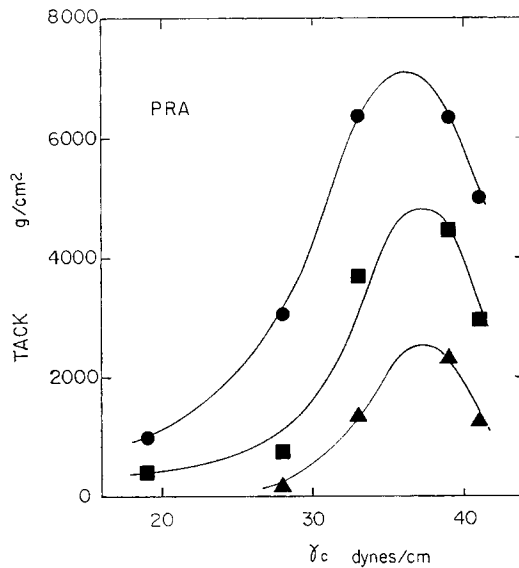

Fig. 5. Relationship between tack value and surface energy, at 20°C. Acrylic adhesive: ● contact time = 100 sec, rate of separation = 1.0 cm/sec, contact pressure = 500 g/cm^2; (■) contact time = 1.0 sec, rate of separation = 1.0 cm/sec, contact pressure = 100 g/cm^2; (▲) contact time = 0.1 sec, rate of separation = 1.0 cm/sec, contact pressure = 10 g/cm^2.
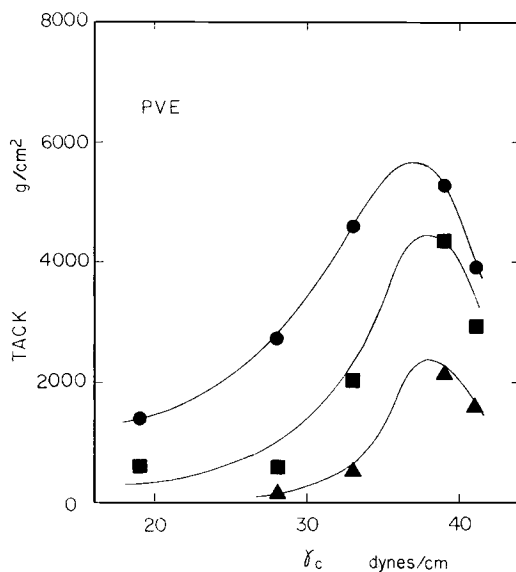
Fig. 6. Relationship between tack value and surface energy, at 20°C. Vinyl ether adhesive: (●) contact time = 100 sec, rate of separation = 1.0 cm/sec, contact pressure = 500 g/cm^2; (■) contact time = 1.0 sec, rate of separation = 1.0 cm/sec; contact pressure = 100 g/cm^2; (▲) contact time = 0.1 sec rate of separation = 1.0 cm/sec, contact pressure = 10 g/cm^2.

rosin ester of which γ_c should be fairly high as well as rosin has γ_c near to 36 dynes/cm. (2) The γ_c value of poly(ethyl acrylate) was determined as 35 dynes/cm[11]; therefore, the copolymer of ethyl acrylate with 2-ethyl-hexyl acrylate (less than 36%) should have a γ_c value almost equal to that of poly(ethyl acrylate). (3) For poly(ethyl vinyl ether), Kitazaki and his co-workers[1] determined γ_c to be 36 dynes/cm.

From these results, it can be possible to conclude that the maximum work of adhesion attains at the substrate having a γ_c near to those of adhesives.

Similar results were found by Kitazaki and co-workers;[1] Uffener,[2] and also Iyengar and Erickson[3] who used the solubility parameters of adhesives instead of γ_c for adhesion of polyester.

On the other hand, some works do not fit these results. Dahlquist[4] indicated that the peel force of pressure-sensitive adhesive tapes increases with increasing γ_c without maximum; but the experimental data are rather scattered. Levine, Ilkka, and Weiss[5] showed similar results using epoxy adhesive; however, the surface tension of the adhesive is too high (50 dynes/cm) compared with γ_c for substrates (up to 43 dynes/cm).

Recently, Dahlquist discussed the significance of surface energy in adhesion.[17]

The tack value increases with increasing contact time and contact pressure, as shown in Figures 4, 5, and 6, indicating that the real contact area increases by the deformation of pressure-sensitive adhesive. The surface
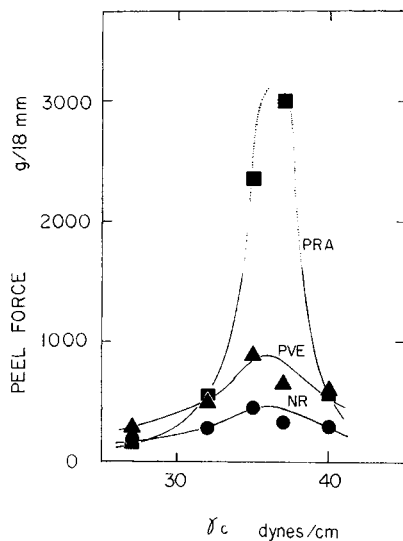
Fig. 7.   Relationship between peel force and surface energy, at 20°C.   Contact time = 168 hr, rate of peeling = 300 mm/min.

chemical influence is still important even under heavier contact pressure and prolonged contact time, as is indicated by the upper curves with a maximum.   It is, therefore, very interesting to know the force of adhesion after very long contact time.   The mechanical flow of adhesive will be attained at equilibrium, and the tack value should be affected more strongly by the wetting if the surface chemical factor is predominant.   The result is found to have a maximum, as is shown in Figure 7.   In the figure, poly-acrylate adhesive apparently showed cohesive failure and is indicated by a dotted line in order to distinguish it from the others because they were found to break the adhesive bond apparently by intersurface failure.

Zisman[6] pointed out that the maximum work of adhesion occurs at γ_c, expressed by the following equation, which is derived from Young-Dupre's equation and his straight-line relationship between γ_L and $\cos \theta$:

$$\gamma_c = \frac{1}{b} + \frac{1}{2} \cdot \gamma_L \tag{1}$$

where γ_L is the surface tension of the adhesive and b is the slope of the plot for γ_L versus $\cos \theta$.   In general, it leads to a considerably higher γ_L at the maximum.   However, this theory does not agree with many experimental studies; e.g., Sharpe and Schonhorn[20] indicated that the wetting is incomplete and an imperfect adhesive bond is formed when the surface energy of the adhesive is greater than that of the adherend.

According to Fowkes,[21] the surface energy is the sum of the contributions from the different intermolecular forces such as dispersion force, dipole-hydrogen bonding, etc.   At higher surface energy, the polar contributions will be predominant.   In such cases, no interaction or repulsion can be

possible to work between different components.[1] Considering the concept above, it will be possible to understand the presence of the maximum work of adhesion at a region where γ_c for adhesive and substrate are nearly the same, as is shown in Figures 4 to 7.

Effect of Temperature

Table II shows the relationship between the apparent activation energies for tack values and for viscosities of adhesives. Each activation energy agrees within experimental error. These values are also in the range of dissociation energy for van der Waals bonds. It implies that the tack value is related to the viscous resistance of the adhesive mass until the bond breaks.[12]

Proposed Mechanism of Adhesive Bond Breaking

As described above, the tack value is dependent on the surface chemical character of the substrate, in spite of the fact that the mechanical work of adhesion is much greater than the thermodynamic work of adhesion.

As the primary stage, the bonding begins by the wetting of the surface by the adhesive. When the bond breaking occurs, the adhesive joint should not separate at the intersurface between the substrate and adhesive, but the break should occur by cohesive failure in the adhesive mass near the boundary layer although the observed unbonding is apparently intersurface failure. However, it is difficult to find residual fragments of adhesive on the surface because the amount of pickoff is very limited. The bond breaking will be due to the viscous flow of adhesive mass around the very minute spots on the surface where the interaction works between substrate and adhesive. The strength for breaking the bond is the force necessary for deforming the adhesive mass until the bond will break. Although the number of spots in the unit area will be dependent on contact time and contact pressure, primarily the formation of the spots will be controlled by the critical surface tension of the substrate. The tack value is considerably high because of the viscoelastic deformation of adhesive mass at the boundary layer.[19] Thus, it is possible to understand that the tack value of pressure-sensitive adhesive is dependent on both the surface chemical and rheological properties.

In order to prove the points discussed above, it is necessary to show the presence of pickoff on the adherend as proof of cohesive failure. Although it is possible to find a number of reports describing cohesive bond breaking,[14] we confirmed the presence of pick-off using a tracer technique. The results will be published in the near future.

References

1. Y. Kitazaki, A. Watanabe, and M. Toyama, *Preprints of the Fourth Conference on Adhesion*, Osaka, Japan, June 1966, p. 31.
2. M. W. Uffener, *Adhesives Age*, **10** (12), 30 (1967).
3. Y. Iyengar and D. E. Erickson, *J. Appl. Polym. Sci.*, **11**, 2311 (1967).
4. C. A. Dahlquist, *ASTM Special Technical Publication No. 360*, 46 (1963).

5. M. Levine, G. Ilkka, and P. Weiss, *Polymer Letters*, **2**, 915 (1964).

6. W. A. Zisman, *Ind. Eng. Chem.*, **55** (10), 19 (1963); *ibid.*, in *Contact Angle, Wettability and Adhesion*, Advanced Chemistry Series No. 43, American Chemical Society, Washington, D.C., 1964, p. 1.

7. F. H. Hammond, Jr., *ASTM Special Technical Publication No. 360*, 123 (1963).

8. W. M. Bright, in *Adhesion and Adhesives, Fundamentals and Practice*, Society of Chemical Industry, Mackay and Co., Ltd., London, 1954, p. 130.

9. C. A. Dahlquist, in *Adhesion, Fundamentals and Practice*, The Ministry of Technology, Maclaren and Sons Ltd., London, 1966, p. 143.

10. L.-H. Lee, *J. Polym. Sci. A-2*, **5**, 1103 (1967).

11. H. D. Feltman, and J. R. McPhee, *Text. Res. J.*, **34**, 634 (1964).

12. H. Kambe and K. Kamagata, *J. Appl. Polym. Sci.*, **13**, 493 (1969).

13. T. Fort, Jr., in *Contact Angle, Wettability and Adhesion*, Advanced Chemistry Series No. 43, American Chemical Society, Washington, D.C., 1964, p. 302.

14. C. W. Hock, *Hercules Chemist*, **47**, 16 (1963).

15. J. J. Bikerman, *The Science of Adhesive Joints*, Academic Press, New York, 1968.

16. G. J. Crocker, *Rubber Chem. Technol.*, **42** (1), 30 (1969).

17. C. A. Dahlquist, in *Aspects of Adhesion*, Vol. 5, D. J. Alner, ed., University of London Press, London, 1969, p. 183.

18. D. H. Kaelble, *J. Adhesion*, **1**, 102 (1969).

19. D. H. Kaelble, *Trans. Soc. Rheol.*, **9**, Part 2, 135 (1965).

20. L. H. Sharpe, and H. Schonhorn, in *Contact Angle, Wettability and Adhesion*, Advanced Chemistry Series No. 43, American Chemical Society, Washington, D.C., 1964, p. 189.

21. F. M. Fowkes, *Ind. Eng. Chem.*, **56**, 40 (1964).