Studies in the Nature of Adhesive Tack

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Synopsis

By measuring tack energy using a modified probe tack testing procedure, the interrelation of bulk energy and surface energy effects in pressure-sensitive adhesives was studied. Tack energy was strongly influenced by the solvent used in the preparation of the adhesive film. A procedure was empirically derived which reduced the number of variables to a single variable, yielding a single master curve in which the independent variable was the speed of probe withdrawal expressed on a logarithmic scale. The form of the curve was a simple exponential function, $y = A \exp(mx)$, where A and m are constants and y and x are the dependent and independent variables, respectively. The constant m was found to be a unique function of the type of adhesive used. A theoretical interpretation of the devised procedure was based on bulk viscoelastic effects and a combined activation energy–free volume concept of adhesive bonding. The wider implications of this are briefly discussed.

INTRODUCTION

The phenomenon of tack is a complex combination of properties and is exhibited by a diverse range of substances, for example, syrup, tar, printing ink, natural rubber, etc., and is more commonly described by the layman as stickiness. In adhesion science, the term more specifically refers to the spontaneous adhesion of an adhesive surface to another surface under light contact pressure which may or may not be chemically identical; and in the case of chemically dissimilar materials, this is termed pressure-sensitive adhesion. This paper is concerned with pressure-sensitive tack which for convenience may be described as in ASTM D1878-61T as "the property of a material which enables it to form a bond of measurable strength immediately upon contact with another surface."

Previous methods of measuring tack[1–13] have measured tack force, that is, the force required to mechanically debond the adhesive from the substrate surface. However, Wake[14] and Salomon[15] have indicated that the energy dissipated during this process is a more fundamental parameter than force, and Gent and Kinloch[16] proposed an energy criterion for adhesive debonding.

This criterion is considered with the adhesion of viscoelastic adhesives to rigid substrates and stipulates that, regardless of test specimen geometry, there is a characteristic failure energy per unit area of interface, which is a function of the rate of debonding. In other words, the total energy dissipated on adhesive debonding, θ, has two components: the reversible work of adsorption, θ_0, and the irreversible work of deformation of the adhesive during debonding, H:

$$\theta = \theta_0 H \tag{1}$$

At infinitely slow rates, $H \rightarrow 1$ and $\theta \rightarrow \theta_0$. Andrews and Kinloch[17] have evaluated θ_0 by varying substrate surface free energy characteristics and have found close agreement between θ_0 and the thermodynamic work of adhesion, W_A, for each substrate/adhesive assembly.

These experiments were carried out on test specimens which had been prepared in such a way that the observed effect could be linked unambiguously with the debonding stage. In the tack test, however, debonding occurs a comparatively short time after bonding has commenced such that bonding and debonding effects are operating concurrently. In addition, the rate of tack testing refers to the strain rate imposed on the whole adhesive/substrate assembly rather than the constant rate of interfacial separation. The resulting situation is, therefore, considerably more complex, and it is the purpose of this paper to study this complex situation using tack energy measurements and simplify experimentally the procedure and also propose a theoretical interpretation.

EXPERIMENTAL

Materials

An adhesive based on poly(isobutyl vinyl ether) was used which was a mixture of high, intermediate, and low molecular weight as follows: poly(isobutyl vinyl ether) $(K = 30)$, 33 parts; poly(isobutyl vinyl ether) $(K = 60)$, 16.8 parts; poly(isobutyl vinyl ether) $(K = 125)$, 12.3 parts. This mixture was chosen because it has a useful balance of physical properties. The polymers were dissolved in toluene such that the total solids content was 30 mass per cent.

Preparation of Adhesive Films

The film of adhesive of the required thickness was isolated from the solvent by spreading a layer of solution of uniform wet film thickness onto a roll of silicone-coated release paper (type 00/15/17, supplied by Stirling Coated Materials Ltd., London) and evaporating the solvent at ambient temperature and pressure for 24 hr. Generally, the wet film thickness was in the range of 0.1 to 1.5 mm. The dry film was further dried for 72 hr at 5-mm mercury

TABLE I
Liquids Used to Determine Critical Surface Tension

Liquid	Surface tension, mN/m	
	Measured (23°C)[a]	Literature value (20°C)[b]
Tritolyl phosphate	44.3	40.9
Formamide	58.6	58.4
Glycerol	68.0	64.3

[a] By Searle Balance
[b] Fowkes.

pressure at 20°C, then laminated to a clean rigid glass plate, taking care to avoid the inclusion of air bubbles. The silicone release paper was removed and discarded and the film stored at 5-mm mercury pressure at 20°C until ready for use.

Apparatus and Procedure

The principle of the probe method used here was outlined by Hammond[4] and Wetzel.[2] In this case, a Type E Tensometer (made by Monsanto-Tensometer Ltd., Swindon) was used as the tensile testing machine and the results indicated as a force–distance curve on an electronic pen recorder (Speedomax G, Leeds and Northup Ltd., Birmingham) which was an integral part of the Tensometer Type E. The energy of tack was computed by a digital x–y integrator which converted the instantaneous force and the corresponding chart movement into electronic pulses which were counted. These pulses were then converted into energy units (joules). The principle of operation of the integrator was to break down the area under the force–distance curves into a number of rectangles, at the same time computing their areas and summing to give the total area. Manual checking indicated that the area under a typical curve obtained during tack measurement was accurate to within ±3%.

The Tensometer permitted the variables in the tack test such as dwell time, probe speed, and probe load to be varied over a wide range, both at ambient temperatures and at other temperatures, by the use of an environmental chamber (made by Sondes Place Research Institute, Dorking, Surrey) in which probe and adhesive were contained.

The probe geometry used in the work consisted of a solid cylinder of material 10 mm in diameter and of total length 25 mm. One end of the cylinder was shaped to a hemisphere of radius 4.5 mm. At the other end was a circular collar thickness 3 mm and radius 6.25 mm, which was an integral part of the probe and retained the probe in a probe holder. The probe was retained in a low-friction guide such that when in contact with the adhesive film, the applied load was the weight of the probe material alone.

Various types of probe material were used and the critical surface tension γ_c of the probe materials was determined by the Zisman sessile drop technique (Tables I and II).

Stereoscan electron micrographs of the probe surfaces were determined in order to ascertain the variation of surface roughness of the probe surfaces. The order of surface roughness was polyethylene > poly(tetrafluoroethylene) = poly(hexamethylene adipamide) > poly(methyl methacrylate).

TABLE II
Critical Surface Tension of Various Probe Materials and the Adhesive

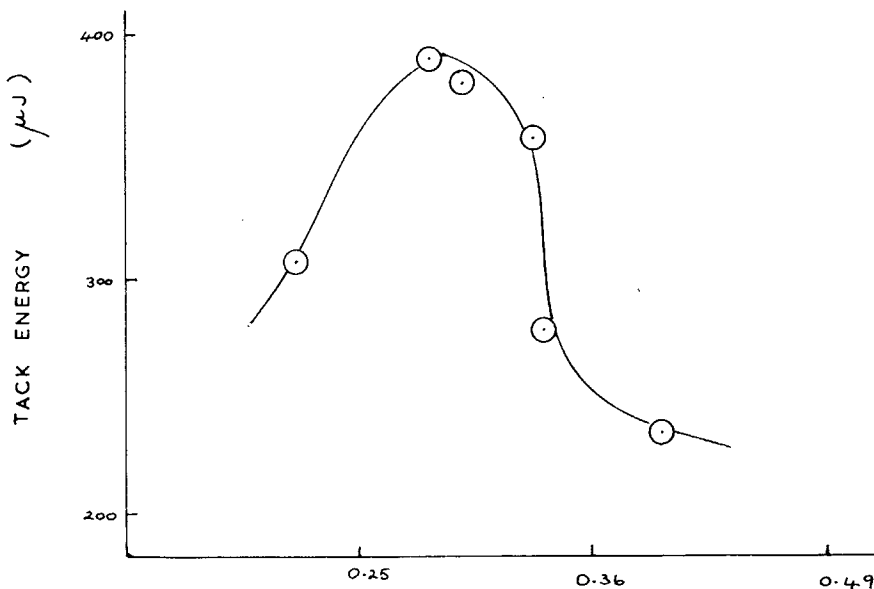| Material	Critical surface tension γ_c, mN/m	
	Measured (23°C)	Literature value (20°C)
Adhesive	29 ± 2	—
Poly(tetrafluoroethylene)	18.5	18.5
Polyethylene	34.0	31.0
Poly(methyl methacrylate)	42.0	39.0
Poly(hexamethylene adipamide)	43.5	46.0

Fig. 1. Variation of tack energy with solvent: Temp. = 294°K; Probe load = 2.5 g; probe speed = 0.966 mm/sec; dwell time = 10 sec; film thickness = 1.45 mm; probe γ_c = 43 mN/m.

RESULTS AND DISCUSSION

The adhesive was cast from a solution in toluene for the purposes of tack measurement. However, by casting the adhesive from solutions in various solvents, a variation in tack energy was observed, even though care was taken to eliminate residual solvent by prolonged storage at reduced pressure. Expressing the results as the variation of tack energy with solvent cohesive energy density δ^2 (defined as $\Delta E_{vap}/V_M$, where ΔE_{vap} is the molar energy of vaporization and V_M is the molar volume), a bell-shaped curve is obtained and is indicated in Figure 1. The peak in tack energy observed corresponds to the cohesive energy density of the adhesive by analogy with solvent swelling experiments.[19]

Attempts to detect residual solvent by gas chromatography of pyrolized samples did not succeed.

The tack energy was greatest where the solvent used was methyl isobutyl ketone or cyclohexane and least in the case of ethyl acetate or methylene dichloride.

Variation of tack energy was studied by maintaining four parameters constant and by varying probe withdrawal speed in conjunction with the remaining parameter. Expressing the results as a graph of tack energy versus the logarithm of probe withdrawal speed, a series of smooth curves was obtained which could be shifted horizontally of the abcissa to form a single continuous curve.

Figure 2 indicates the single continuous curve obtained by varying of adhesive film thickness concurrently with $\log_{10}$ (probe withdrawal speed). This procedure is part of the Williams-Landel-Ferry shift procedure used in adhesion science to indicate rate effects on the behavior of viscoelastic adhesives. In this case, it is observed that decreasing film thickness is equivalent to de-
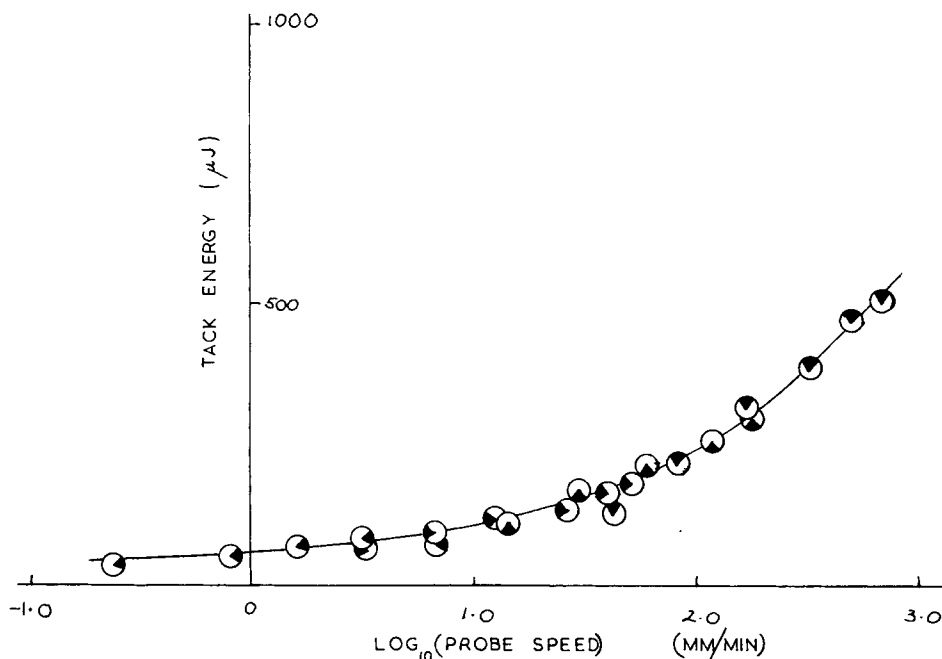
Fig. 2. Variation of tack energy with film thickness: (◓) 0.471 mm; (◒) 0.571 mm; (◑) 0.866 mm; (◐) 1.490 mm; dwell time = 10 sec; probe load = 4.41 g; probe γ_c = 43 mN/m; temp. = 295°K.

creasing rate, which is entirely opposite to the expected effect since rate is expressed as the ratio of speed to film thickness. However, by postulating that at low film thicknesses the contact area between adhesive and probe is reduced due to limiting of penetration of the probe into the adhesive, it is clear that tack energy will also be reduced and this effect clearly overrides the real increase in straining rate.

The shift factors necessary to construct Figure 2 are indicated in Table III.

Figures 3 and 4 indicate the effect of variation of tack energy with $\log_{10}$ (probe speed) at two values of adhesive film thickness at the same time varying the dwell time of the probe on the adhesive surface prior to debonding. The shift factors used to construct these curves are indicated in Tables IV and V, respectively.

Empirically, therefore, variation in dwell time during bonding is equivalent to variation in probe withdrawal speed. The basis for this equivalence is the time-dependent compliance of the adhesive during bonding which increases as the dwell time increases. At the instant debonding commences, this value of compliance has a direct influence on the storage modulus during debond-

TABLE III
Relative Shift Factors Used to Construct Figure 2[a]

Film thickness	1.49 mm	0.866 mm	0.571 mm	0.471 mm
$\Delta \log_{10}$ (probe speed), mm/min	0	—0.55	—1.10	—1.40

[a] The negative signs indicate that the shift was from right to left.
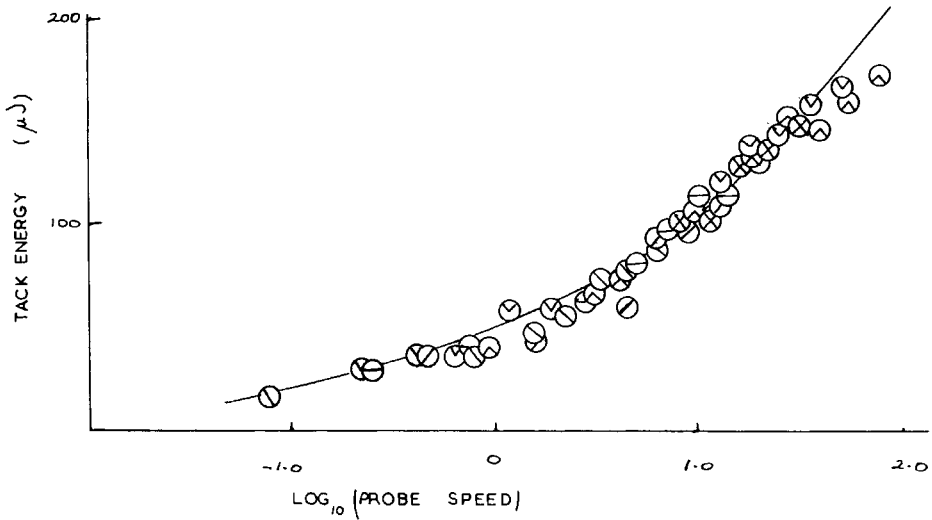
Fig. 3. Variation of tack energy with dwell time: (◑) 2 sec; (◒) 5 sec; (◓) 10 sec; (◔) 20 sec; (◉) 40 sec; (○) 60 sec; film thickness = 0.95 mm; probe load = 2.5 g; probe γ_c = 43 mN/m; temp. = 295°K.
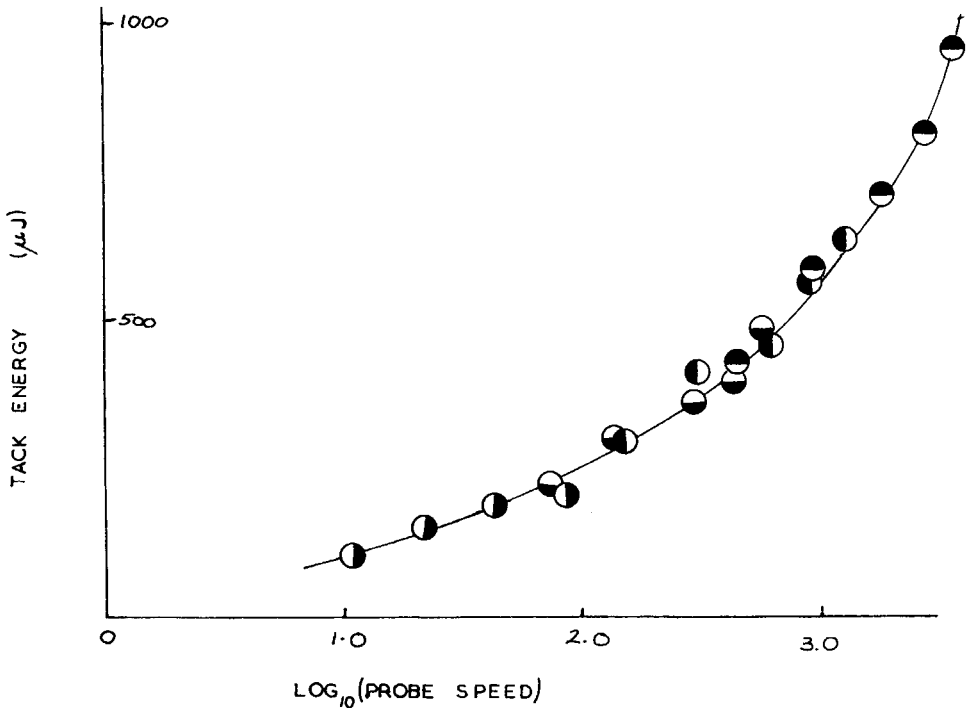

Fig. 4. Variation of tack energy with dwell time: (◐) 2 sec; (◑) 10 sec; (◒) 20 sec; (●) 60 sec; film thickness = 1.50 mm; probe load = 4.41 g; probe γ_c = 43 mN/m; temp. = 295°K.

ing and hence tack energy. The variation of tack energy with probe with-drawal speed and probe load is indicated in Figure 5, and the shift factors used to construct Figure 5 are indicated in Table VI.

The probe load strongly influences the compliance of the adhesive during

bonding which in turn determines the tack energy observed on debonding hence variation of probe load is empirically equivalent to a variation in probe withdrawal speed.

The effect of temperature on tack energy is indicated in Figure 6 and the appropriate shift factors, in Table VII. The equivalence of temperature and time is a well-established principle and accounts for the observed behavior.

Figure 7 indicates the variation of tack energy with $\log_{10}$ (probe speed). By varying the probe material, a series of curves is obtained which, by empirically shifting on the abscissa, yield a single continuous curve (Figure 8) using shift factors indicated in Table VIII. There is no theoretical justification or precedent for this procedure in the literature on tack. A theoretical justification is derived later.

The superposition of dwell time with rate, probe load with rate, adhesive film thickness with rate, and temperature with rate has been interpreted in terms of the bulk modulus properties of the adhesive which are rate sensitive. A considerable simplification in the presentation of tack energy data has resulted. The superposition of probe surface tension effects is clearly linked to interfacial properties of substrate and adhesive during bonding and debonding.

Empirically, however, the superposition of tack data can be taken a step further. If the curves derived in Figures 8, 6, 5, 4, 3, and 2 are shifted horizontally, it is possible to construct a single, continuous curve covering all the data, and this is shown in Figure 9.

The curve obtained is of the form

$$y = A \exp (mx) \tag{2}$$

where A and m are constants, $y =$ tack energy, and $x = \log_{10}$ (probe withdrawal speed).

To construct Figure 9, it was arbitrarily decided to give the constant A the value of 100 μJ, whence it is found that the value of m is 0.90. The significance of Figure 9 is that all the variables in the tack test are reduced to a single variable. A considerable simplification in the presentation of tack energy data results, which also raises several important theoretical points.

On a practical level, the constant m is identical over a very wide range of parameters, suggesting that it is a unique function of the adhesive used. To test this, master curves similar to Figure 9 were constructed using different adhesives. In each case, a constant value of m was found which was unique

TABLE IV
Relative Shift Factors Used to Derive Figure 3

Dwell time	2 sec	5 sec	10 sec	20 sec	40 sec	60 sec
$\Delta \log_{10}$ (speed), mm/min	−1.05	−0.78	−0.57	−0.37	−0.16	0

TABLE V
Relative Shift Factors Used to Derive Figure 4

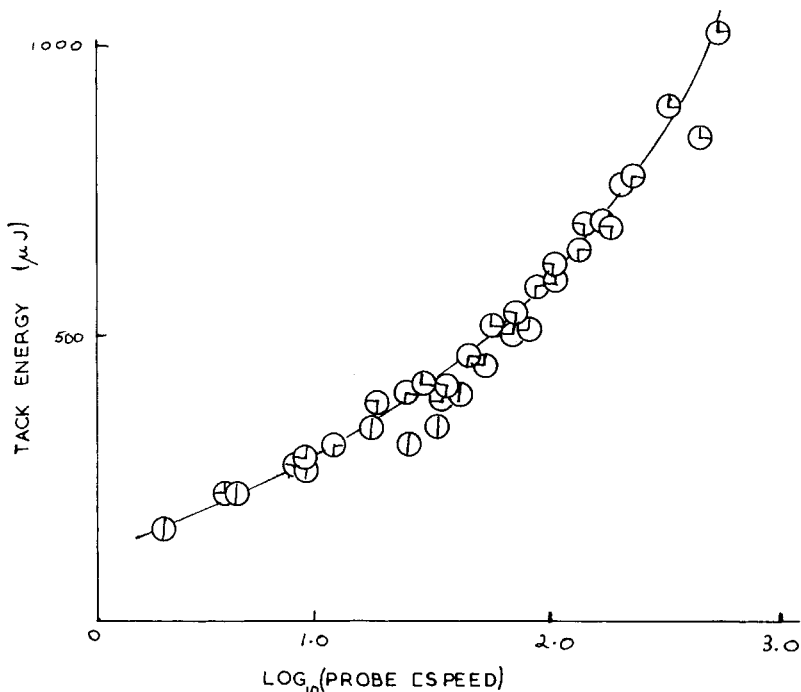| Dwell time	3 sec	10 sec	20 sec	60 sec
$\Delta \log_{10}$ (speed), mm/min	−1.35	−0.88	−0.55	0

Fig. 5. Variation of tack energy with probe load: (⊙) 2.45 g; (⊚) 4.45 g; (⊙) 7.45 g; (○) 9.45 g; (⊚) 12.45 g; film thickness = 1.45 mm; probe γ_c = 43 mN/m; dwell time = 10 sec; temp. = 295°K.

for the particular adhesive used (see Table IX). The precise structure of the acrylic polymers was not known since they are commercially available and subject to trade secrecy.

From the known physical characteristics of the adhesives, a high value of m indicated high energy dissipation. It is well known that energy dissipation in viscoelastic materials is related to the loss factor δ, which is the ratio of dissipated energy to stored energy. As such, it is a measure of the liquid-like behavior of the material. This energy dissipative and storage process occurs at the bonding and debonding stage, hence it is related in some way to the value of δ at the bonding and debonding step. The loss factor during debonding, δ_2, is strongly influenced by the loss factor δ_1 during bonding, and consequently

$$m = F(\delta_1, \delta_2) \qquad (3)$$

where F represents a function.

Further investigation showed that on varying the radius of curvature of the probe tip, a variation in the magnitude of tack energy occurred. In the extreme case, the radius of curvature is infinite (i.e., a flat probe). This did not

TABLE VI
Relative Shift Factors Used to Derive Figure 5

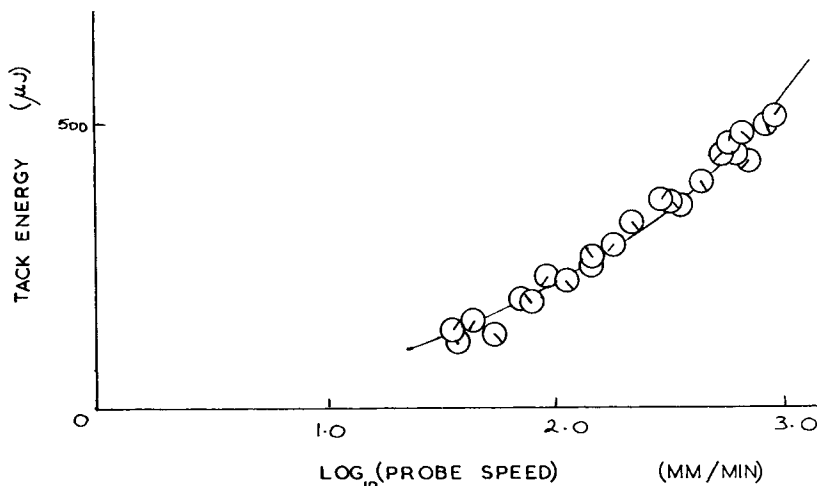| Probe load	2.45 g	4.45 g	7.45 g	9.45 g	12.45 g
$\Delta \log_{10}$ (speed), mm/min	−1.12	−0.79	−0.50	−0.39	0

Fig. 6. Variation of tack energy with temperature: (Φ) 297°K; (⊘) 282°K; (⊙) 304°K; (⊙) 309°K; film thickness = 1.39 mm; dwell time - 10 sec; probe load = 4.41 g; probe γ_c = 43 mN/m.

alter the shape of the curve, but merely gave a parallel curve at higher values of tack energy, suggesting that the constant A is related to the radius of curvature of the probe tip.

Theoretical Considerations

Apart from surface free energy effects, tack parameters such as dwell time, temperature, film thickness, probe load, and probe withdrawal speed have been linked with modulus or compliance effects either at the debonding or bonding stage. Since the modulus of viscoelastic materials can be linked to time effects, the reduction of the number of variables by superimposing on a rate-related parameter can be justified by invoking time–temperature superposition principles well established by previous work in adhesion science.

In the case of surface energy effects, however, no such reduction has any practical or theoretical precedent. At the debonding stage, fracture mechanical considerations by Williams[20] have shown that interfacial separation is related to the energy expended in applying a stress. This is termed the energy balance criterion. The adhesive fracture energy θ_a is a time-dependent function in viscoelastic adhesives,[16] and it has been further shown[17] that as the rate of debonding decreases, θ_a approaches the value of the reversible thermodynamic work of adhesion W_a. These considerations apply similarly to the debonding stage in the tack test and partly explain why tack energy is closely related to the surface energy considerations in addition to bulk modulus effects.

TABLE VII
Relative Shift Factors Used to Derive Figure 6

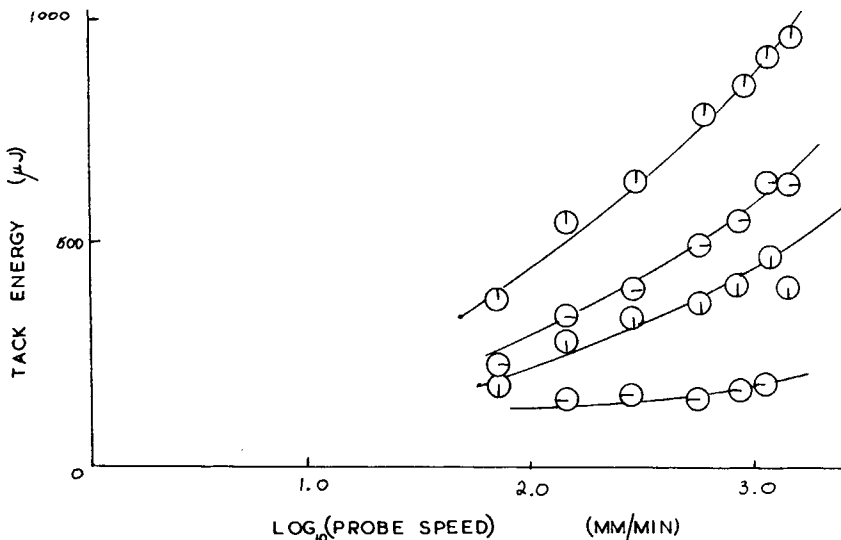| Temperature	292°K	297°K	304°K	309°K
$\Delta \log_{10}$ (speed), mm/min	0	—0.11	—0.22	—0.30

Fig. 7. Variation of tack energy with probe type: (⊖) poly(tetrafluoroethylene); (⊙) polyethylene; (⊝) poly(methyl methacrylate); (◍) poly(hexamethylene adipamide); temp. = 295°K; probe load = 4.41 g; dwell time = 10 sec; film thickness = 1.45 mm.

However, the tack test involves a bonding stage which occurs a relatively short time prior to debonding, and surface effects during bonding consequently influence the observed tack energy.

Comparatively little information on the mechanisms involved in the bonding stage for viscoelastic adhesives has been reported in the literature. Schonhorn[21] and Cherry[22] have studied the wetting process of polymeric liquids on various substrates using a contact angle technique. They have shown that the wetting process is time dependent and that a shift factor (a_T) may be defined which is a function of adhesive viscosity, adhesive surface tension, and a reciprocal length which is a function of the nature of the substrate/adhesive interface. This evidence points to a viscous flow process of wetting, and Cherry proposed a theory based on Eyring's theory of viscosity[23] and related this to the observed contact angle.

Eyring's theory of viscosity relates the viscosity in simple liquids to the activation energy of vaporization, ΔE_{vap}, of the molecule

$$\eta = K \exp \frac{\Delta E_{vap}}{zkT} \tag{4}$$

where K and z are constants, k = Boltzmann's constant, η = viscosity, and T = temperature. At a solid–liquid interface, assume that the adhesive surface layer viscosity η_s is related to the energy of adsorption ΔE_{ads} of the substrate by an analogous equation to eq. (4).

Ferry[24] has shown that in the adhesive bulk, the viscosity η_B is related to the available free volume f by the Doolittle equation.[25]

Combining these two considerations, we obtain eq. (5):

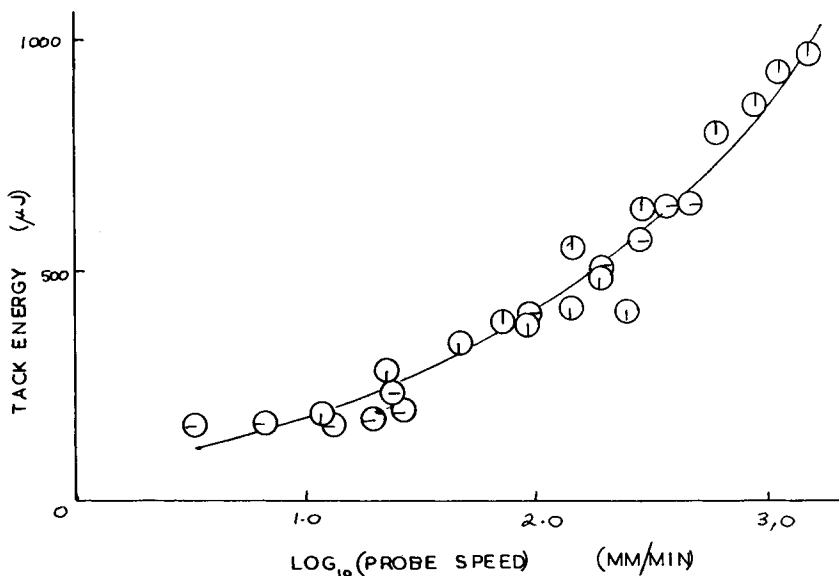$$\eta_s/\eta_B = \exp \left(\frac{\Delta E_{ads}}{zkT} - \frac{1}{f} \right) \tag{5}$$

Fig. 8. Variation of tack energy with probe type. Conditions as in Fig. 7.

A constant applied load will cause surface flow and bulk flow in the viscoelastic adhesive. This situation may be crudely represented by a Voigt model containing two dashpots.

The first dashpot represents the bulk flow component and the second dashpot, the surface flow component. The equation of the element is then

$$\sigma = E\epsilon + \eta_B \frac{d\epsilon}{dt} + \eta_s \frac{d\epsilon}{dt} \tag{6}$$

where σ = stress, ϵ = strain, and t = time. This may be reexpressed using eq. (5) as

$$\sigma = \eta_B \frac{d\epsilon}{dt} \left[1 + \exp\left\{ \left(\frac{\Delta E_{ads}}{zkT}\right) - \frac{1}{f} \right\} \right] + E\epsilon \tag{7}$$

The solution of this equation is

$$\epsilon = \sigma_0 J \left[1 - \exp\frac{-t}{(1+A)\tau} \right] \tag{8}$$

where σ_0 is the constant applied load, J is the compliance of the model, $\tau = \eta_B/E$ is called the retardation time, and $A = \exp\{(\Delta E_{ads}/kTz) - (1/f)\}$.

For an infinite number of elements, a more realistic representation of vis-

TABLE VIII
Relative Shift Factors Used to Derive Figure 8 from Figure 7

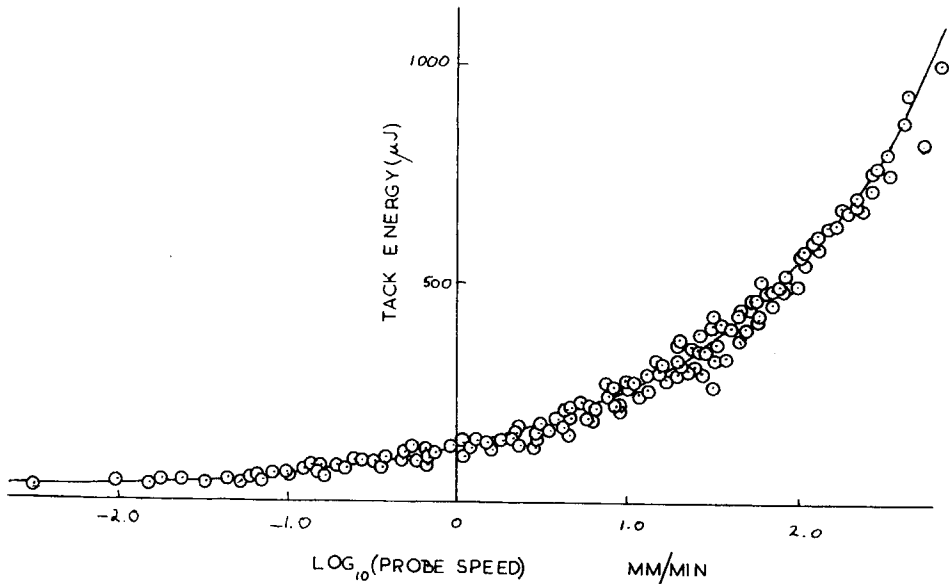| Probe material	γ_c, mN/m	Shift factor
Poly(hexamethylene adipamide)	43.5	0
Poly(methyl methacrylate)	42.0	−0.51
Polyethylene	34.0	−0.81
Poly(tetrafluoroethylene)	18.5	−1.65

Fig. 9. Tack energy master curve.

coelastic behavior is obtained, and eq. (8) becomes eq. (9):

$$\epsilon = \sigma_0 \int_0^\infty J_t \left[1 - \exp\left\{ \frac{-t}{(1+A)} \right\} \right] d\tau \tag{9}$$

Comparing this with the standard Voigt element (one dashpot), the only difference is that all the retardation times τ_i have been altered by a constant factor

$$1 + \exp\left\{ \frac{\Delta E_{ads}}{zkT} - \frac{1}{f} \right\}$$

Consider the case where the same adhesive is applied (separately) to two different substrates of absorption energies $\Delta E'_{ads}$ and $\Delta E''_{ads}$. Then the observed retardation times τ_1 and τ_2 will have the following relationship:

$$\frac{\tau_1}{\tau_2} = \frac{1 + \exp\left\{ \frac{\Delta E'_{ads}}{zkT} - \frac{1}{f} \right\}}{1 + \exp\left\{ \frac{\Delta E''_{ads}}{zkT} - \frac{1}{f} \right\}} \tag{10}$$

The ratio τ_1/τ_2, termed the shift factor, is a particular form of the superposition principal due to Williams, Landel, and Ferry.[26] In this case, however, the shift factor is due entirely to surface energy variation during a bonding stage. We may, therefore, define a shift factor a_γ, where $\log_{10} a_\gamma = \tau_1/\tau_2$ and state that the variation of surface energy during an experiment involving bonding of a viscoelastic adhesive to a substrate is to multiply the time scale of that experiment by a constant factor which is dependent on that surface energy.

In particular, the energy of adsorption governs the bonding process in tack

tests, and the superposition of the tack energy data may be justified by the interrelationship of surface energy and bulk free volume effects.

The inherent limitations of the Voigt model or its modifications are well known. At present, however, a more realistic representation (e.g., the response of individual polymer chains in the material and then the response of entanglements or functions) has not yet been fully worked out, but in any case would be formidably complex. The value of the model is to circumvent these difficulties until a quantitative model has been worked out and at the same time give a reasonable representation of experimental observations.

Eyring's theory of viscosity relating viscosity to energy of vaporization (or adsorption) is supported by rather tenuous experimental evidence. It works reasonably well considering the simplifications made in the case of simple liquids, but fails in the case of high polymers.

The theory presented here has postulated that in the bonding process of a viscoelastic adhesive, the energy of adsorption is of more fundamental significance in the adhesion process than are other parameters such as contact angles. It is well known that the energy of adsorption is not a constant over the entire surface of the substrate, but varies on a molecular scale from one site to another. In certain places, the local energy of adsorption may be so high as to prevent interfacial separation on debonding. The result of this is that a submicroscopic quantity of adhesive is retained on the surface. In other sites, lower values of adsorption energy would permit true interfacial separation. This type of behavior has been observed with pressure-sensitive adhesives[9,10,13] on various substrates.

CONCLUSIONS

A method of measuring tack energy has been devised and measures the energy dissipated during debonding (at constant strain rate) of a substrate from a pressure-sensitive adhesive. The accuracy of the method was ±3%. The variation of tack energy with adhesive solvent cohesive energy density was a bell-shaped curve, the maximum occurring at the cohesive energy density of the adhesive.

Tack energy was determined under various conditions, and it was found convenient to express the results in terms of the probe withdrawal speed using a logarithmic scale. On a purely empirical basis, the data were horizontally shifted along the abscissa and a single continuous master curve was constructed which represented all the data. This effectively reduced the number of variables to a single variable. A theoretical interpretation of this empirical procedure was based on the time-dependent bulk properties of the adhesive or, in the case of surface energy effects, on a combined activation energy/free volume concept of surface wetting.

TABLE IX
Values of Constant m for Different Polymeric Adhesives

Polymer	Value of m
Poly(isobutyl vinyl ether)	0.90
Poly(alkyl acrylate)	0.727
Poly(vinyl acetate-co-alkyl acrylate)	0.516

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