Surface Energetics, Adhesion, and Adhesive Joints

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Certain aspects of the adsorption theory of adhesion are developed more fully than has been done previously. The consequences of nonreciprocity of spreading are pointed out, and are used to develop a more general practical point of view with respect to the adhesive bonding of materials of low-surface free energy. The system epoxy adhesive-(nonsurface-treated) polyethylene, normally considered nonadherent, is investigated experimentally in some detail. It is shown how this system, without material modification, can be made adherent. An area of study for possible adhesives for materials of low-surface free energy is suggested.

At present three theories of adhesion exist—the adsorption theory [9], the diffusion theory [24, 25, 26], and the electrostatic theory [10, 23]. The majority of those who have concerned themselves with the subject of adhesion lean toward the adsorption theory, if for no other reason than a recognition that the phenomenon of wetting is intimately related to adhesion. The word "adhesion" (unmodified) here means strictly an interfacial phenomenon, while "practical adhesion" means the strength with which two materials stick together—that is, the force required to separate them, or joint strength.

We develop certain aspects of the adsorption theory of adhesion more fully than has been done previously, based solely on (free) surface energetics, and show how they can be applied to real or practical systems. As a consequence, it is shown that the deBruyne adhesion rule [7] is incorrect in part. Our concern is mainly with what we believe to be the most important problem in the making of adhesive bonds—that is, the achievement of extensive and proper (no intermediate phase) interfacial contact. We discuss also the breaking strength of certain adhesive joints where this is necessary to the development of our thesis. However, the processes of making and breaking adhesive joints bear no

direct fundamental relation to each other, although the breaking strength of an adhesive joint is, in general, a consequence of how it is made.

The adhesion and practical adhesion of combinations of (organic) low-surface free energy materials ($<$ 100 ergs per sq. cm.) mainly are discussed, since these, in general, present the most difficulty in bonding, and there exists the most confusion concerning them. High-surface free energy materials (metals, metal oxides, glasses, etc.) are not discussed in detail, since the principles discussed can be directly extended to include these materials.

Theoretical

Thermodynamics. Consider an equilibrium closed system of a liquid, L_2, in contact with a plane surface of an isotropic solid, S_1 (which is not soluble in L_2), and saturated vapor, V_2°, of liquid L_2. The Young-Dupré equation is

$$\gamma_{S_1V_2^\circ} - \gamma_{S_1L_2} = \gamma_{L_2V_2^\circ} \cos \theta \qquad (1)$$

where the γ's are surface tensions and θ is the usually defined contact angle. Let us further consider the surface of the solid to be an equilibrium surface. Under these circumstances the surface tension and surface free energy of the solid are the same and we can write

$$F_{S_1V_2^\circ} - F_{S_1L_2} = F_{L_2V_2^\circ} \cos \theta \qquad (2)$$

where the F's are now surface free energies.

The maximum reversible work of adhesion of L_2 to S_1 is

$$W_{adh} = F_{S_1}^\circ + F_{L_2V_2^\circ} - F_{S_1L_2} \qquad (3)$$

where $F_{S_1}^\circ$ is the surface free energy of the solid, S_1, in vacuum. Upon substituting in Equation 3 the value of $F_{S_1L_2}$ from Equation 2, we obtain

$$W_{adh} = \left(F_{S_1}^\circ - F_{S_1V_2^\circ} \right) + F_{L_2V_2^\circ} (1 + \cos \theta) \qquad (4)$$

As has been pointed out by Bangham and Razouk [3], this is the work required to strip the liquid from the solid so as to leave a surface on the solid which is identically the equilibrium surface on the solid in a vacuum. This work of adhesion is different from the work of adhesion required to strip the liquid from the solid so as to leave the equilibrium adsorbed film of vapor V_2 on the solid surface. This latter work of adhesion is

$$W_{adh}' = F_{L_2V_2^\circ} (1 + \cos \theta)$$

and differs from W_{adh} by the term $\left(F_{S_1}^\circ - F_{S_1V_2^\circ} \right)$. Now $F_{S_1}^\circ$ must always be greater than $F_{S_1V_2^\circ}$; hence the term $\left(F_{S_1}^\circ - F_{S_1V_2^\circ} \right)$ is always positive [3]. This means that the work required to strip the liquid from the solid completely is greater than that required to strip the liquid

from the solid so as to leave an equilibrium film of adsorbed vapor of the liquid.

Since the work of cohesion of L_2 is given by

$$W_{coh} = 2F_{L_2V_2^\circ} \tag{6}$$

Equation 4 tells us that if $\theta = 0$—that is, if liquid L_2 spreads on solid S_1—the maximum reversible work of adhesion is always in excess of the work of cohesion by an amount at least $\left(F_{S_1^\circ} - F_{S_1V_2^\circ}\right)$; we say at least because Equation 4 is valid only for $\theta > 0$.

Now assume that by some means we cause liquid L_2 to solidfy on solid S_1 in such a manner that we again have an equilibrium system, this time of solid S_1 in contact with solid S_2 in the presence of saturated vapor of S_2. The Young-Dupré equation for this system is

$$\gamma_{S_1V_2^\circ\prime} - \gamma_{S_1S_2} = \gamma_{S_2V_2^\circ\prime} \cos \theta \tag{7}$$

where the γ's are again surface tensions and the prime on the subscript indicates that the saturation vapor pressure of S_2 is different from that of L_2. We again assume that S_1 and S_2 are equilibrium surfaces, so that we may write

$$F_{S_1V_2^\circ\prime} - F_{S_1S_2} = F_{S_2V_2^\circ\prime} \cos \theta \tag{8}$$

where the F's are again surface free energies.

The maximum reversible work of adhesion of S_2 to S_1 is

$$W_{adh} = F_{S_1^\circ} + F_{S_2V_2^\circ\prime} - F_{S_1S_2} \tag{9}$$

Substituting in Equation 9 the value of $F_{S_1S_2}$ from Equation 8 we get

$$W_{adh} = \left(F_{S_1^\circ} - F_{S_1V_2^\circ\prime}\right) + F_{S_2V_2^\circ\prime} (1 + \cos \theta) \tag{10}$$

This is the equation for the maximum reversible work of adhesion for two solids in contact and is the counterpart of Equation 4 for the case of a liquid in contact with a solid. Our definition of the final solid-solid state as an equilibrium state implies that there are no residual stresses in either solid produced by the solidification of L_2.

Equation 10 could just as well have been derived on the basis of bringing into contact with each other an equilibrium planar surface of solid S_2 and a similarly defined surface of solid S_1 and then separating them in the appropriate fashion.

We showed that if L_2 spreads on S_1, the maximum reversible work of adhesion of L_2 to S_1 is greater than the work of cohesion of L_2. Conversely, if the maximum reversible work of adhesion of L_2 to S_1 is greater than the work of cohesion of L_2, then L_2 must spread (initially) on S_1. We can write, then, from Equations 3 and 6,

$$W_{adh} - W_{coh} = F_{S_1^\circ} - F_{L_2V_2^\circ} - F_{S_1L_2} = Sp \tag{11}$$

where Sp is the initial spreading coefficient [6, 16, 17].

We said, however, that if $W_{adh} - W_{coh} > 0$, L_2 must (initially) spread on S_1—that is, for spreading to occur

$$F_{S_1^\circ} - F_{L_2V_2^\circ} - F_{S_1L_2} > 0$$

or

$$F_{S_1^\circ} > F_{L_2V_2^\circ} + F_{S_1L_2} \qquad (12)$$

This relationship says that for spreading of liquid L_2 on solid S_1 to occur, the surface free energy of S_1 must exceed the sum of the surface free energies of the liquid (in contact with its saturated vapor) and of the solid-liquid interface.

Formation of Interface. Two materials probably adhere, at least initially, because of van der Waals attractive forces acting between the atoms in the two surfaces. Now interfacial strengths, based on van der Waals forces alone, far exceed the real strengths of one or other of the adhering materials. This means that interfacial separation probably never occurs to any sensible extent when mechanical forces are used to separate a pair of materials which have achieved complete interfacial contact (probably a highly unlikely situation), or a number of separate regions of interfacial contact. It follows, then, that breaking a joint mechanically, in general, tells nothing directly about interfacial forces.

Van der Waals forces are operative over very small distances. Hence, in order that materials adhere, the atoms in the two surfaces must be brought close enough together for these forces to become operative. If we had a piece of A (solid) and B (solid) and each had an absolutely smooth (on an atomic scale) planar surface which we then brought together in a perfect vacuum, all attempts to get them apart mechanically would result in failure in the bulk of either A or B. But real surfaces differ from these ideal surfaces in that they are rough and contaminated and both of these imperfections contribute to a greatly decreased real area of contact between the surfaces of A and B. In general, however, where they have achieved contact—that is, where they have been brought close enough for van der Waals forces to become operative—they have adhered, and when they are separated mechanically a little of A remains on B, and B on A, depending on the geometry in the neighborhood of each area of contact. The general reaction based on visual examination is that the solids did not adhere or the failure was in adhesion. The first statement, we believe, is incorrect, because surely some areas of A and B achieved interfacial contact, and the second is incorrect because where the surfaces were not in contact there was no adhesion and it makes no sense to talk about the failure of something that did not exist.

This point of view leads to the conclusion that to get A and B to make a stronger joint we need to increase their real area of contact. This means that one or both of the materials must be made to conform better to the surface roughness of the other. This implies, in a practical sense, that one of the materials should be fluid when placed in contact with the other. However, that one of the materials be liquid is a necessary, but may not be a sufficient, condition for if the liquid makes a

nonzero contact angle with the solid, its tendency to create a large interfacial area of contact is relatively small. The result is that the liquid may do a great deal of bridging, trap a great deal of air, and achieve little penetration into the surface roughness of the solid, and stress concentrations due to a nonzero contact angle become important. However, if the liquid member spontaneously spreads on the solid, the interfacial area of contact increases, because the liquid can now flow more completely into the micro or submicro pores and crevices in the surface of the solid and can displace adsorbed gases and other contamination. In addition, the zero contact angle tends to minimize stress concentrations. The effect of creating a spontaneous spreading situation, then, is twofold—the real area of contact is increased and stress concentration is minimized [11].

It becomes important now to point up the fact that spreading is a nonreciprocal phenomenon—that is, for two liquids, the fact that pure A spreads on pure B means that pure B positively will not spread on pure A (see, for example, Harkins [14]) and the same appears to be true of adhesion in a practical sense. In a practical sense, if A adheres strongly to B, then B will not adhere strongly to A. What, of course, we really mean is that if we can make a strong joint between A and B when A is the liquid member (subsequently solidified) and B the solid, then it appears that we cannot, in general, make a strong joint when B is the liquid member and A the solid, for reasons mentioned above. It may be possible to make a strong joint if both are fluid simultaneously.

It may appear that we have said that spreading of the liquid member is the *sine qua non* of adhesion and, also, of practical adhesion. In a sense we have, but this requires qualification. From a purely thermodynamic point of view, it makes no difference for an ideal system A-B, in the final state, whether the final state was achieved by making A fluid, or B fluid, or both fluid, or both solid, if we define the final state as being that of complete interfacial contact of A and B. But, in a real or practical sense, the achievement of adhesion and practical adhesion is time-dependent and, in general, it may make a difference how—that is, from which side—we attempt to approach the equilibrium state. If we work from the side of the low-surface free energy solid and the high-surface free energy liquid the rate of approach to equilibrium may be intolerably slow, or in the case of a liquid which sets to a solid (as by cross linking) in a relatively short time span, the rate may become essentially zero. This is the case in the epoxy adhesive–polyethylene joint, to be discussed shortly. If, however, the low surface free energy solid can be made fluid, the rate of approach to equilibrium may be greatly accelerated. The rate of approach to equilibrium may (and, in general, should) be rapid if both phases are fluid simultaneously. Stresses induced by differential shrinkage have been neglected in this discussion. However, we are mainly concerned with the conditions for creation of extensive and proper interfacial contact, and the subject of shrinkage-induced stress concentrations is treated extensively elsewhere [9, 11].

We have specifically mentioned only van der Waals forces in connection with the preceding treatment. This is not to be construed as meaning that other molecular forces may be excluded from participation in adhesion. In the initial process involving the establishment of interfacial contact, all those molecular forces involved in wetting

phenomena can be considered to be important. Chemisorption is not excluded, but if it is to occur molecular contact must have already been established—that is, van der Waals forces must already be operative. Therefore, any such chemical reaction as does occur, occurs after adhesion is a *fait accompli*. Further, since we believe that sensible interfacial separation does not occur under mechanical influences even when only van der Waals forces are operative, it follows that we do not believe that chemisorption has any positive influence on the mechanical strength of an adhesive joint. It may have negative influence on strength if weak boundary layers [5] are formed. However, chemisorption may increase the permanence of an adhesive joint by retarding or preventing destruction of the interface as by dewetting by moisture, low surface tension liquids, etc.

In order to be able to use Expression 12 it is necessary to determine $F_{S_1}^o$, $F_{L_2V_2}^o$, and $F_{S_1L_2}$. There exists a good method only for the determination of $F_{L_2V_2}^o$, the surface free energy (surface tension) of the liquid, but no satisfactory method for determining directly either $F_{S_1}^o$ or $F_{S_1L_2}$. Zisman's [27] work on wetting and his concept of γ_c, the critical surface tension of wetting, provide us with some characterization of $F_{S_1}^o$ or $F_{S_1V_2}^o$. However, if we are willing to accept the empirical relationship which Zisman has established between γ_c and $F_{L_2V_2}^o$ (or $\gamma_{L_2V_2}^o$), it is unnecessary to concern ourselves with either $F_{S_1}^o$ or $F_{S_1L_2}$. If we admit that γ_{cS_1}, the critical surface tension of wetting, is the surface tension which a liquid, L_2, would have to possess in order just to spread on S_1, then the criterion for spreading, Expression 12, may be replaced by the criterion [13,27].

$$\gamma_{cS_1} > \gamma_{L_2V_2}^o \qquad (13)$$

the terms of which are experimentally much more accessible than the thermodynamic quantities which we have been discussing. Expression 13 provides a useful working relationship. It may be possible to decide, *a priori*, whether A will adhere strongly to B—that is, form a strong joint—or will not, from a knowledge of the parameters γ_{cS_1} and $\gamma_{L_2V_2}^o$ at the temperature at which the bond is to be made.

Table I gives representative values of γ_{cS_1} and $\gamma_{L_2V_2}$ for a number of polymers. The values of γ_c given have been determined at 20°C. At present, there exist no data concerning the value of γ_c for various substrates at elevated temperatures. Strictly speaking, therefore, predictions based on the above relationship are limited to 20°C. However, since the temperature coefficient of surface tension for a large number of organic materials, as given by Harkins [15], appears to be approximately 0.1 dyne per cm. per °C., the same relative surface tension relationship between liquid and solid will probably exist at somewhat elevated temperature as exists at 20°C.

One further note of caution with respect to the use of the critical surface tension in this context is necessary. The precise value of γ_c

Table I. Critical Surface Tension (γ_c) and Surface Tension
(γ_{Lv}) of Selected Systems

System	γ_c, Dynes/Cm., 20°C.	γ_{Lv}, Dynes/Cm., 25°C.
Teflon FEP	16[a]	–
Teflon TFE	18.5[a]	–
Polyethylene	31[a]	–
Polystyrene	33[a]	–
DER332LC epoxy resin	–	47.2
DER332LC epoxy resin, 100 pbw[b] +DEAPA[c], 7pbw	–	32.9
Fluorinated epoxy resin	–	40.3
Fluorinated epoxy resin, 100 pbw +DEAPA, 7 pbw	–	38.8
DEAPA	–	23.6

[a] Values from [27].
[b] Parts by weight.
[c] Diethylaminopropylamine.

obtained for a surface is dependent, in general, upon the particular series of liquids used to determine it. A series of liquids which inter-acts more strongly with a surface will, in general, give a higher γ_c than another series which interacts less strongly with the same surface. One should, therefore, use for prediction the γ_c value obtained by use of a series of liquids which is, in general, characteristic of the liquid material in the system for which the prediction is being made. This is necessary in light of the findings of Fowkes [12], that a low-energy liq-uid will spread on a high-energy solid only if the intermolecular forces in the solid and the liquid can interact with each other. For example, if a liquid exhibiting only a dispersion force contribution to its surface tension is placed on a solid which exhibits both dispersion and hydrogen bonding forces, then, in general, the only interaction between the two phases will be a dispersion force interaction, and the simple spreading criterion must be modified to take this into account.

Experimental

Experiments concerning the practical adhesion between a conven-tional epoxy adhesive and a conventional polyethylene illustrate some of the principles which we have been discussing.

Materials. Epoxy resin DER332LC (Dow Chemical Co., Midland, Mich.) is a very pure diglycidyl ether of bisphenol A, having an epoxy equivalent weight of 179 maximum (the pure material would have an epoxy equivalent weight of 170), a total chloride content less than 0.1% by weight, and a viscosity of 6400 centipoises maximum at 25°C.

Diethylaminopropylamine (Miller-Stephenson Chemical Co., Inc., Philadelphia) was distilled under nitrogen through a 6-inch Vigreux column and the first fraction discarded. The product, distilling at 68°C. and 26-mm. pressure, was stored in the dark in tightly stoppered glass containers prior to use.

The epoxy adhesive consisted of 100 parts by weight of the above resin and 7 parts by weight of the diethylaminopropylamine, thoroughly mixed and used immediately.

Polyethylene (Marlex 5003, Phillips Petroleum Co., Bartlesville, Okla.) was formed from powder into 0.009-inch-thick sheets between specularly smooth Mylar sheets in a metal mold at a temperature of 150°C. and pressure of 1000 p.s.i. for approximately 5 minutes. The polymer has a density of 0.95 and a melt index of 0.3.

The above polyethylene was irradiated in 0.009-inch-thick sheet at 21° to 23°C. in a nitrogen atmosphere with 1-m.e.v. electrons to a total dose of 20 megarads to give the material which is termed irradiated or cross-linked polyethylene.

The metal tensile-shear adherends were of 2024-T3 aluminum (Aluminum Co. of America). Their dimensions were 5 by 1 by 1/16 inch. The surface of the aluminum was prepared by first vapor-degreasing in trichloroethylene and then etching for 7 minutes at 65°C. in the following solution:

Sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$)	1 part by weight
Water	30 parts by weight
Sulfuric acid (95%)	10 parts by weight

After etching, the specimens were rinsed for 5 minutes in running tap water and for 1 minute in running distilled water, and then dried in a forced air oven at 60°C. Specimens were stored in desiccators over Ascarite and removed just prior to use.

Procedures. For the measurement of tensile-shear strengths, standard composite test pieces consisting of aluminum—epoxy adhesive—polyethylene sheet—epoxy adhesive—aluminum were prepared for bonding in a special device designed to maintain a half-inch overlap. The thickness of the epoxy adhesive was maintained constant by insertion of a piece of 0.003-inch-diameter gold wire in each glue line between the aluminum and the polyethylene. Clean gloves and tweezers were used in all specimen preparations to avoid possible contamination. Bonding was accomplished, at approximately 20-p.s.i. pressure, by placing stacks of composites in forced air ovens at specified temperatures for 16 hours. The bonded specimens were tested in tensile shear in accordance with ASTM D 1002-53T, except that the strain rate was 0.1 inch per minute.

A DuNouy tensiometer was used to measure the surface tension of the epoxy resin and curing agent. The instrument was calibrated with water and benzene. Prior to each determination, the surface tension of water was measured. Mixtures of the epoxy resin and curing agent were equilibrated for a few minutes after mixing before the surface tension was determined. Since the mixtures had high viscosities, the DuNouy ring was equilibrated in the surface of the liquid for a few minutes at a stress several tenths of a dyne below the point of maximum stress, to permit the material to relax. The break point was approached slowly until rupture occurred. Three readings were taken for each mixture. Deviations of the order of ±0.2 dyne per cm. or less were obtainable by this procedure. The surface tensions were calculated using the appropriate correction parameter of Harkins and Jordan [18].

Results. Figure 1 shows the effect of the ultimate temperature of bond formation on the tensile-shear strength of the aluminum-epoxy-polyethylene composite structure described previously. It is rather obvious that at temperatures close to 100°C. the epoxy, even though its viscosity is low, has not formed a strong bond with the polyethylene, for the reason, we believe, that it has not achieved extensive interfacial contact with the polyethylene before solidification occurs. If, however, one first solidifies the epoxy at some temperature below 100°C. and then raises the temperature close to, or above, the melting point of the
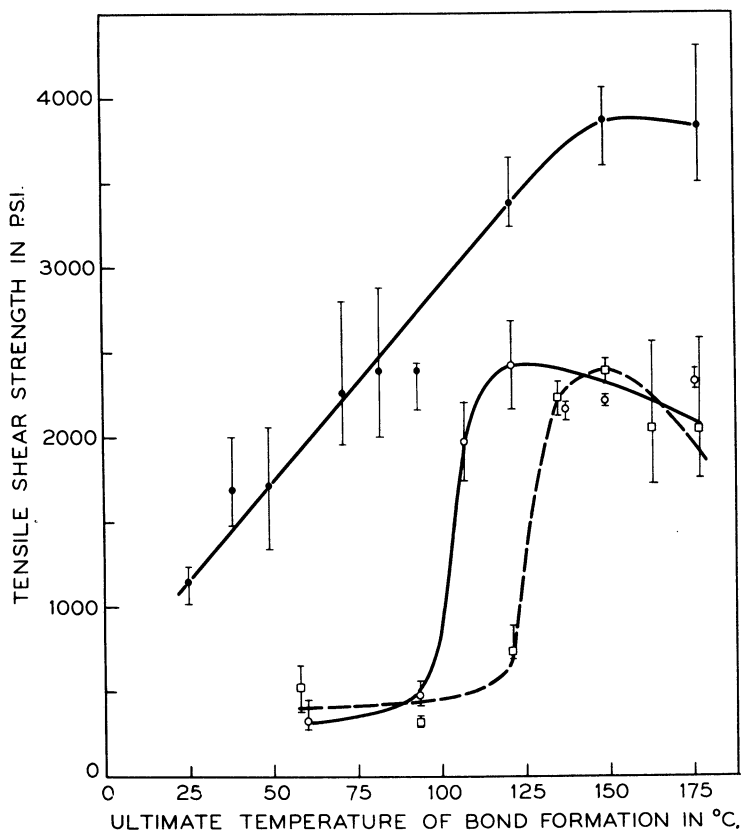

*Figure 1. Dependence of bond strength on temperature
of bond formation*

● Aluminum–epoxy–aluminum composite
□ Aluminum–epoxy–polyethylene–epoxy–aluminum composite
O Aluminum–epoxy–cross-linked polyethylene–epoxy–aluminum
composite

Ranges indicated. Results based on five
replicates, each point

polyethylene, a striking increase in the bond strength results. This, in fact, occurs (and the bond strengths are a function of the ultimate temperature only) regardless of whether the temperature is immediately raised to the neighborhood of the melting point of the polyethylene while the epoxy is still liquid, or whether the epoxy is first solidified at some temperature below 100°C. and the temperature is then raised. We believe that in these instances the surface energetics are now favorable for spreading of the polyethylene to occur and sufficient time is allowed for extensive and proper interfacial contact to take place. The viscosity of the polyethylene at 145°C. is approximately 10^6 centipoises (determined by stress relaxation method [22]), whereas the viscosity of the epoxy, when it is the liquid member, at 25°C. is approximately 10^3 centipoises. It is interesting to note, therefore, that viscosity of the liquid member apparently is of no real importance in this instance, because sufficient time can be allowed for good wetting by the polyethylene to take place.

The behavior of the cross-linked polyethylene is also particularly interesting. The temperature at which the bond strength of the composite bearing this material begins to rise markedly is some 20°C. below the comparable temperature for the identical un-cross-linked polyethylene, and not above it, as might generally be believed. The explanation for this, we believe, is simple. The crystalline melting point of polyethylene is lowered by irradiation, not raised, as Mandelkern, et al. [20] and Marker, Early, and Aggarival [21] have pointed out. The irradiated polyethylene, therefore, spreads at a lower temperature than the unirradiated polymer because its melting point is lower.

The bend strength of the composite bond containing the irradiated polyethylene is remarkable. The aluminum adherends must be bent through an angle of about 110° before failure of the bond occurs. On a number of occasions, bending the specimen has resulted in fracture of one of the aluminum adherends, rather than failure of the bond.

The present generally accepted procedure for structurally bonding polyethylene with an adhesive is to oxidize the polyethylene surface; this raises its surface free energy and improves the wettability of the polyethylene by the adhesive [2]. An improvement in bond strength is thus obtained. We are not, however, aware of any previous work in which the strength levels reported were comparable to those which we have obtained.

Discussion

The deBruyne adhesion rule states [7]: "Provided we use pure or simple substances as adhesives then there is a good deal of evidence that strong joints can never be made by polar adherends with nonpolar adhesives or to nonpolar adherends with polar adhesives." It is possible to support the portion of the rule which deals with nonpolar adherends and polar adhesives on the basis that polar adhesives generally have higher surface free energies than nonpolar adherends, and therefore will wet them very poorly [27]. It is not possible, however, to support the other portion of the rule which deals with polar adherends and nonpolar adhesives, since the surface energetics are favorable in this instance and spreading should result. This portion of deBruyne's adhesion rule must, therefore, be incorrect. That it is incorrect is further

attested by the fact that we have obtained strong bonds between a cured epoxy adhesive and a number of nonpolar thermoplastics—e.g., polyethylene, polypropylene, Teflon FEP, and polystyrene—also between the above-mentioned thermoplastics and metals such as aluminum, copper, and stainless steel, by the melt technique. DeBruyne has recently stated that he now also believes this portion of his rule to be incorrect [8], and that the rule was simply an expression of the facts as they were known at the time the rule was formulated.

It might be instructive now to develop a more general but practical point of view based on the consequences of nonreciprocity of spreading, and our experiments. Examples of materials which are at present difficult to bond with conventional adhesives without surface modification are: polyethylene, polypropylene, Teflon TFE, Teflon FEP, polystyrene, etc.—that is, the class of nonpolar thermoplastics. They are difficult to bond because they are materials of low-surface free energy, much lower than conventional adhesives. However, because they are of low-surface free energy and because they can be rendered fluid (mobile), as by raising the temperature, they can be made to form strong joints with a large number of suitable materials of higher surface free energy. So far as we have been able to determine, this particular aspect of adhesive bonding has not previously been pointed out, and it is rather startling when one first comes to the realization that materials which are generally believed to be impossible to bond conventionally without surface modification are precisely those materials which, when used as adhesives, form strong joints with a large number of substrates. Recently Korolev *et al.* [19] have discussed practical adhesion between poly (tetrafluoroethylene) and metals in these same terms.

Future Work. The spreadability-adhesion criterion, as we have discussed it, immediately draws attention to low surface tension polymers as potential adhesives for low-surface free energy solids. It is known that low surface tension is associated with the substitution of fluorine for hydrogen in organic materials. This knowledge suggests that useful adhesive materials may result from the appropriate substitution of fluorine or fluorinated side chains for hydrogen in hydrogen-containing polymers. Certain such fluorinated materials might be capable of forming strong joints with such polymers as polyethylene, polypropylene, and Teflon TFE, which cannot now be structurally bonded by conventional adhesives without prior surface modification.

One class of such materials is the fluorinated alkyl esters of acrylic and methacrylic acid, a number of which have been prepared [1]. One of these esters, poly(1,1-dihydropentadecafluoro-octyl methacrylate), has a $\gamma_c \approx 11$ dynes per cm.—less than Teflon TFE or even FEP [4]. Such materials, and others within the general class of unsaturated, appropriately fluorinated, polyesters warrant investigation for use either as thermoplastic hot-melt adhesives, or for cross linking *in situ* to form rigid thermoset adhesives. The saturated, appropriately fluorinated polyesters also warrant investigation as thermoplastic hot-melt adhesives.

Several very interesting classes of materials may also result from proper fluorination of conventional monomeric or polymeric diepoxides. The conventional diepoxides or "epoxies" are extremely useful adhesive materials. The epoxy resin which we have examined in this study has a surface tension of 47.2 dynes per cm. Appropriate fluorination of this

and similar materials would markedly reduce their surface tensions. We have prepared a diglycidyl ether of bisphenol A (obtained from the Research Laboratories of Allied Chemical, Morris Township, N. J.) in which the pendant methyl groups on the bridge carbon atom were replaced by perfluoromethyl groups. Neither the surface tension nor some other properties were markedly affected by this substitution. This might have been predicted on the basis of the relatively small volume substitution of fluorine in the molecule. Longer fluorinated chains would proportionately affect physical and mechanical properties. It is tempting to speculate that adhesive systems useful for the polyolefins and polystyrene might lie among such polymers.

Acknowledgment

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