

# Mechanisms Assisting or Impeding Adhesion in Biological Systems

R. E. BAIER, E. G. SHAFRIN, AND W. A. ZISMAN

*Surface Chemistry Branch  
Chemistry Division*

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**NAVAL RESEARCH LABORATORY**  
**Washington, D.C.**



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## ABSTRACT

Intimate molecular contact at joint interfaces is essential for the extremely localized surface forces to result in adhesion exceeding the cohesive strength of the joined materials. Liquids, however viscous, are perhaps a more important class of adhesives in biology than in any other field. Attention is focused on the spreading of well-defined liquids over rigid or coherent phases of potential biological interest. The contact angle ( $\theta$ ) of liquids on solids provides an inverse measure of liquid spreading. Rectilinear plots of  $\cos \theta$  vs liquid surface tension ( $\gamma_{LV}$ ) define the critical surface tension of wetting ( $\gamma_c$ ) for each solid. Direct, simple correlations exist between  $\gamma_c$  and solid surface composition. Wetting and adhesion can be completely changed by adsorbed films, even monolayers; adsorbed water, for example, can markedly decrease  $\gamma_c$ . Thus, adsorbed proteins, water, and trace surface-active agents are major influences in biological environments. Hydrogen-bonding and bound water are significant factors in the wettability of many pure polyamides, while configuration changes are especially important for polypeptides and proteins like polymethylglutamate, gelatin, and collagen. Wettability properties and the  $\gamma_c$  concept are pertinent to current adhesional and biomedical problems. Coupling agents have a potential role in bioadhesion. Further research is needed on the surface properties of biomaterials.

## PROBLEM STATUS

This is an interim report. Work is continuing on the problem.

## AUTHORIZATION

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## MECHANISMS ASSISTING OR IMPEDING ADHESION IN BIOLOGICAL SYSTEMS

### INTRODUCTION

Although much attention has been given to the formation, structure, and properties of biological interfaces, an especially unsettled aspect of the subject is biological adhesion, without which organized tissue would not exist. Adhesive behavior in biological environments has received increased attention recently in research on surgical adhesives, marine fouling, dental restoratives, extracorporeal circuits, and prosthetic implants.

Our report will cover the following topics: (a) the adhesion between dry solids, (b) the role of liquid spreading and wetting in making adhesive joints, (c) recent advances concerning the relationship of wetting to solid surface constitution, (d) surface chemical interferences and aids in adhesion, and (e) examples of the relevance of the preceding knowledge to some current problems of bioadhesion.

### THE ADHESION BETWEEN DRY SOLIDS

Adhesion between dry solids in contact is caused by a strong, but extremely localized, field of attractive force emanating from each solid surface. There is much evidence that this field of force varies as the inverse seventh power of the distance from each atom in the solid surface. In the absence of ions or strong permanent dipoles in (or near) each solid surface, the total force of attraction is generally negligible when two plane solids are separated by distances variously estimated from tens to hundreds of angstroms. Only when there is a large area of intimate (or real) contact between the dry solids can they be made to adhere significantly (Fig. 1). When two hard solids are pressed together, the effort required to pull them apart is usually insignificant; this results because the real area of contact is generally a very small fraction of the apparent area (1,2). But if one or both solids is sufficiently soft, the real area of contact and the adhesion developed under modest loads can be large (3,4). Reports that strong adhesion had occurred between carefully polished, contacting, hard flats have been shown to result from a surface tension effect (see next section) caused by the presence of a thin adsorbed layer of liquid between them. It is also well established that, because of the extreme localization of the attractive force field, a very thin adsorbed film of oxide or as little as one condensed monolayer of organic contamination can decrease greatly the adhesion of solids (3,5-8).

Bowden and Tabor (2) have investigated the loss of adhesion following elastic recovery, or release of elastic strains, on removing the load applied to press the two hard solids together. In Fig. 1 the location of areas of elastic deformation behind contacting asperities is indicated by the arrows. Upon removing the applied load ( $W$ ), the elastic strains which had developed at the base of each compressed asperity are decreased, and the released internal stresses help to break the adhering junctions. If these elastic stresses can be removed by annealing the two solids while  $W$  is maintained, strong adhesive junctions will persist even after removing the load (4).

A wealth of experimental evidence that contacting, clean, dry solids adhere significantly has come from research on the nature of their dry (or boundary) friction. Many

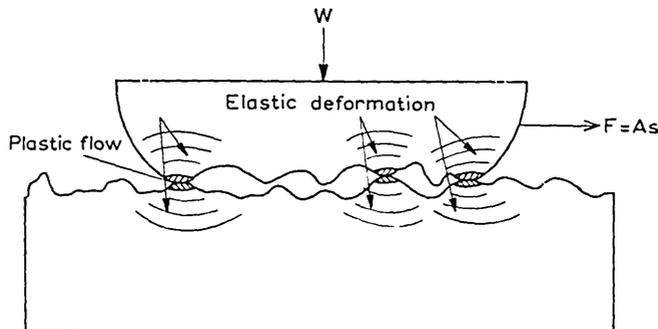


Fig. 1 - Contact of two solids at asperities

well-controlled experiments (2) have demonstrated that the boundary friction is caused by the adhesion of the two rubbing solids at the areas of real contact. In Fig. 1 the region of the plastically deformed contacting asperities is indicated by the shaded areas. Such adhesion, or cold welding, makes it necessary to apply a force ( $F$ ) to overcome friction. To a first approximation  $F$  is equal to the true (or real) area ( $A$ ) of all the contacting asperities multiplied by the average shear strength ( $s$ ) of the junctions; that is, to a first approximation

$$F = As. \quad (1)$$

The principal cause of wear is the breaking of these junctions, usually by a shearing of the weaker of the two contacting asperities. Adhesion between contacting solids is made evident more readily by sliding one over the other than by pulling them apart, because in measuring the frictional force there is no necessity of removing the internal stresses caused by the applied load in order to detect the existence of the effect (4).

A massive and reliable literature exists on the friction-lowering properties of thin adsorbed films of oxides, water, or organic compounds. Indeed, if it were not for the adsorption of a monolayer or more of such compounds, it would be impossible to avoid serious adhesion, or cold welding, and wear on rubbing most solids together.

In rubbing together clean, dry, solid polymers, high friction and wear (and even cold welding) are common. The effect of varying the chemical composition of the polymer is exemplified by the data in Table 1 on the coefficient of static friction ( $\mu$ ) for an interesting analogous series of polymers. This value of  $\mu = 0.33$  for polyethylene on polyethylene is compared with the value of  $\mu$  for structurally similar polymer pairs formed by the substitution of a portion of the covalent hydrogen atoms in the polyethylene with either fluorine or chlorine atoms (9). Whereas fluorine substitution in polyethylene lowered  $\mu$  until it decreased to only 0.04 when fully fluorinated, an analogous progressive chlorination of polyethylene increased  $\mu$  so that it was 0.9 with 50% chlorination (as in poly(vinylidene chloride)). These results are of biological and medical interest in view of the many potential uses of such polymers in prosthetic implants as well as biological research.

#### ROLE OF LIQUID SPREADING AND WETTING IN MAKING ADHESIVE JOINTS

When two, flat, smooth, solid surfaces are separated by a thin layer of a liquid having a zero contact angle, strong adhesion can result. This property is evident from

Table 1  
Effect of Constitution on Friction and Wettability of  
Halogenated Polyethylenes

Polymer	Structural Formula	Static Coefficient of Friction	Critical Surface Tension (dynes/cm)
Poly(vinylidene chloride)	$\begin{array}{c} \text{H} \quad \text{Cl} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{Cl} \end{array} \quad \begin{array}{c} \text{H} \quad \text{Cl} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{Cl} \end{array} \quad \begin{array}{c} \text{H} \quad \text{Cl} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{Cl} \end{array} \quad   \quad \text{n}$	0.90	40
Poly(vinyl chloride)	$\begin{array}{c} \text{H} \quad \text{Cl} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array} \quad \begin{array}{c} \text{H} \quad \text{Cl} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array} \quad \begin{array}{c} \text{H} \quad \text{Cl} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array} \quad   \quad \text{n}$	0.50	39
Polyethylene	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array} \quad \begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array} \quad \begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array} \quad   \quad \text{n}$	0.33	31
Poly(vinyl fluoride)	$\begin{array}{c} \text{H} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array} \quad \begin{array}{c} \text{H} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array} \quad \begin{array}{c} \text{H} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array} \quad   \quad \text{n}$	0.30	28
Poly(vinylidene fluoride)	$\begin{array}{c} \text{H} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{F} \end{array} \quad \begin{array}{c} \text{H} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{F} \end{array} \quad \begin{array}{c} \text{H} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{F} \end{array} \quad   \quad \text{n}$	0.30	25
Polytrifluoroethylene	$\begin{array}{c} \text{F} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{F} \end{array} \quad \begin{array}{c} \text{F} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{F} \end{array} \quad \begin{array}{c} \text{F} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{F} \end{array} \quad   \quad \text{n}$	0.30	22
Polytetrafluoroethylene (Teflon)	$\begin{array}{c} \text{F} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{F} \quad \text{F} \end{array} \quad \begin{array}{c} \text{F} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{F} \quad \text{F} \end{array} \quad \begin{array}{c} \text{F} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{F} \quad \text{F} \end{array} \quad   \quad \text{n}$	0.04	18

the idealized diagram of Fig. 2 and an application of the classic Laplace-Kelvin equation of capillarity (10,11), since

$$p_L - p_A = \gamma_{LV} \left( \frac{1}{R} - \frac{1}{r} \right). \quad (2)$$

Here  $R$  is the radius and  $r$  is one-half the thickness of a thin, circular layer of liquid in contact with the solid. If  $r \ll R$ , then  $p_L - p_A$  will be a greater negative quantity, and there will be a greater pressure  $p_A$  in the air outside the liquid than the value  $p_L$  inside; hence, the two plates will be forced together under the pressure difference  $p_A - p_L$ . From equation (2) it follows that many common liquids which wet two such solid surfaces completely will hold them together. Budgett (12) found that when two, highly polished steel flats (4.5 cm in diameter) were completely wetted by a paraffin oil having a surface tension ( $\gamma_{LV}$ ) of 28 to 30 dynes/cm, a total force of about 20 kg was needed to pull the plates apart. The force calculated from Eq. (2) was 30 kg.

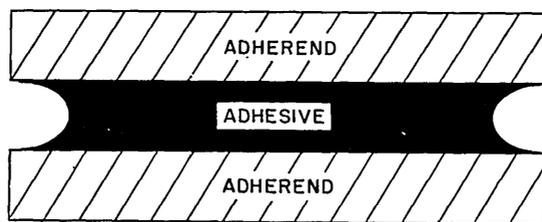


Fig. 2 - Idealized adhesive joint

Such a method of forming an adhesional joint has several obvious limitations:

1. The resistance of the joint to shear stresses is determined solely by the viscosity of the liquid film; hence, only if the viscosity is very great could the joint long withstand an external shearing stress.
2. It would be necessary to prepare extremely closely fitted, smooth, solid adherends to bring the solid surfaces together closely enough to form a joint having high tensile strength.
3. Freedom of the solid surfaces and the liquid from dust or other particles could be critically important in forming a strong joint.

However, a stronger and much more useful joint would be formed if the viscosity of the intervening thin liquid layer were increased greatly through any of various mechanisms such as (a) solvent permeation or evaporation, (b) polymerization, and (c) cooling until the liquid solidifies.

Whereas joints with great resistance to tensile stress but low resistance to shearing stress are of little utility in forming most adhesive joints, they may be important in the many relatively mobile, conformable systems found widely in biology. The limited shear strength required in such biological joints may be satisfied if the liquid is very viscous. It should be remembered that proteinaceous viscous glues obtained from fish and animal sources were among the earliest adhesives known to man. Various naturally occurring polymerizable liquids or even weakly crosslinked polymers probably could serve as biological adhesives in many situations. It is obvious that any crosslinking of the liquid adhesive would strengthen the joint, and any depolymerization or thinning through dilution or as the result of enzymatic action would weaken it. Since many biological membranes or

other biological systems are sufficiently nonrigid to conform to the requirement for coplanarity and/or efficient mating of contours of the opposed surfaces, it is very probable that intervening liquid films cause many biological surfaces to adhere adequately for Nature's purpose.

McBain and coworkers (13,14) first established the following three requirements for the formation of a useful, strong, adhesive joint: (a) good wetting, (b) solidification, and (c) sufficient deformability to reduce the buildup of elastic stresses in the formation of the joint. For example, these conditions were found necessary to obtain good glass-to-metal joints (15). The second and third requirements have been fully investigated, but the first requirement was not given adequate attention until much later (16,17-19). In effect, McBain's three requirements had well-summarized much of what was known until recently about the technology or "art" of making strong adhesive joints.

Of course, real, solid, flat surfaces are not planar; too little attention had been given to the disturbing effects of surface roughness on adhesion. The innumerable small hills, valleys, and crevices in the surface of practically any real solid create problems which must not be neglected if strong, durable adhesive joints are desired. A viscous liquid can appear to spread well over a solid surface and yet have trapped many gas pockets or voids in small surface pores and crevices where the liquid adhesive has formed a mantle over neighboring peaks without fully penetrating into the valleys. Even if the liquid adhesive spreads spontaneously over the solid, it is not certain that intimate contact of liquid and solid interface will have occurred everywhere. This problem is magnified when the liquid rapidly polymerizes or hardens soon after being applied. To what extent voids or gas pockets remain at the solid/adhesive interface is a question which can only be answered by using appropriate methods of examining the joint.

When a liquid adhesive solidifies, the loss in joint strength caused by the interfacial voids is much greater than would be expected from the ratio of the interfacial area occupied by voids to that of the entire joint interface. This result arises from the action of both internal and external stress concentrations, each of which has been given increasing attention in the past several decades. In his classic investigation of the strength of solids, Griffith (20) showed that adhesive joints may fail at relatively low applied stresses if there are present cracks, air bubbles, voids, inclusions, or other surface defects. On application of an external load to the joint, stress concentrations arise that can be much higher than the mean applied stress. Real joints are better represented by Fig. 3 than Fig. 2. If the gas pockets or voids in the surface depressions of the adherend are all nearly in the same plane and are not far apart (as is shown for the upper adherend of Fig. 3), cracks can readily propagate from one void to the next, and the joint can break easily as if it had a built-in zipper. This situation occurs in molding rubber and plastics when a release agent coats the surface of the mold (21). Therefore, if roughening the surface does not increase the number of voids too much, the kind of roughness shown on the lower adherend would be preferable, because crack propagation in the resin would have to follow a much longer nonrectilinear path to connect neighboring voids.

Internal stresses and stress concentrations usually develop during solidification of the adhesive, the most common cause being the difference in the thermal expansion coefficients of adhesive and adherend. In many applications of adhesives this matching process is difficult to do. In general, the theoretical strength of the adhesive joint is considerably decreased by the development of internal stress concentrations, and the effect is especially serious in joining adherends with an adhesive such that neither has significant ability to shrink during the cooling or curing of the joint.

Finally, in a lap joint (Fig. 4), poor wetting of the adherend tends to produce a greater stress concentration at the free surface of the adhesive, where failure is most likely to be initiated. As the contact angle ( $\theta$ ) of the adhesive becomes large, the maximum stress concentration increases and moves toward the lineal boundary, where the adhesive and atmosphere make contact with the adherend (22).

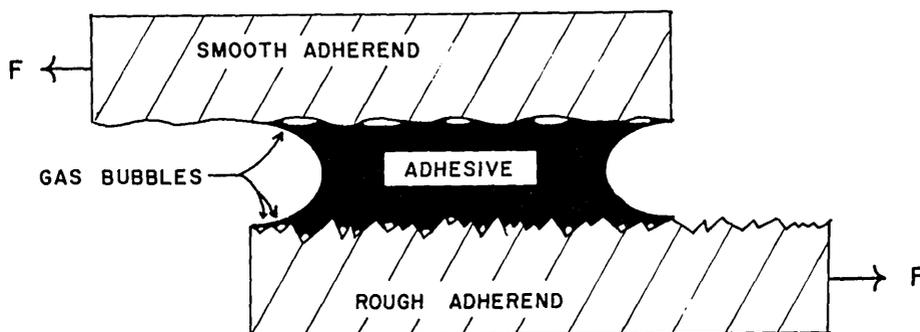


Fig. 3 - Effect of surface roughness on coplanarity of gas bubbles

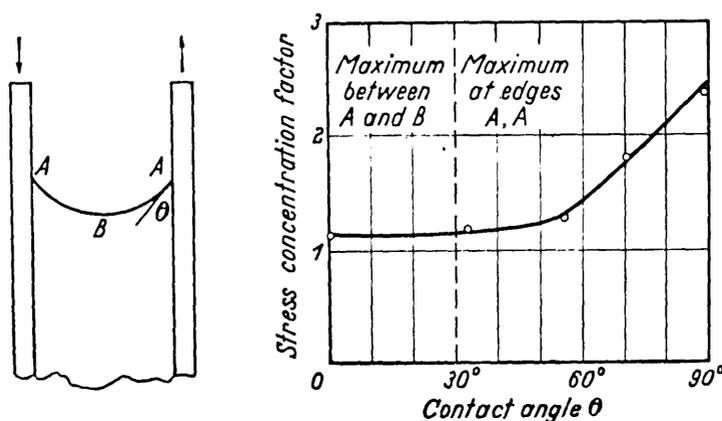


Fig. 4 - Variation of stress concentration maxima in lap joint adhesive with angle of contact

#### RECENT ADVANCES CONCERNING THE RELATIONSHIP OF WETTING TO SOLID SURFACE CONSTITUTION

In considering the wetting properties of solid surfaces, a useful distinction into two broad classes of solids can be made according to the specific free surface energy ( $\gamma_{S0}$ ) of the solid (23), even though reliable determinations of the latter quantity cannot yet be made for most solids. As indicated in Table 2, solids having strong intermolecular forces always have specific surface free energies at ordinary temperatures which range from around 200 to 10,000 ergs/cm<sup>2</sup>; the higher values correspond to the hardest materials with very high melting points. The much weaker intermolecular forces in soft, low melting, organic solids are reflected by their lower specific surface free energies which range from 10 to <100 ergs/cm<sup>2</sup>. We have classified the former as having "high-energy surfaces" and the latter as having "low-energy surfaces" (23). For a liquid, however, the specific free surface energy is its surface tension ( $\gamma_{LV}$ ), and this is easily measured. The specific surface free energies of organic liquids, as well as of most inorganic liquids (excluding the liquid metals), at ordinary temperatures are comparatively very low; hence, one would expect these liquids to spread spontaneously on contact with solids of high surface energy, since there would result a large decrease in the surface free energy of the system. As the surface free energies of such liquids are comparable to those of low-energy solids, among the organic liquids should be found those which exhibit nonspreading on low-energy solids (17,19).

Table 2  
Classification of Solid Surfaces

High-Energy Surfaces	Low-Energy Surfaces
Strong intermolecular force	Weak intermolecular force
Hard	Soft
High-melting	Low-melting
Crystalline	Poorly cryst.
Est. $\gamma_s \approx 200$ to 10,000 ergs/cm <sup>2</sup>	Est. $\gamma_s < 100$ ergs/cm <sup>2</sup>
Inorganic (metals, oxides, etc.)	Organic (waxes, polymers, etc.)

By wetting we mean the adhesion of liquids to solids and the extent to which the liquid spreads. Thomas Young (24) first discussed the contact angle of a liquid and the equilibrium of a drop resting on a plane solid surface under the action of the three surface tensions shown in Fig. 5. Here  $\gamma_{LV}$  is the surface tension at the interface of the liquid and vapor phases,  $\gamma_{SL}$  that at the interface of the solid and the liquid, and  $\gamma_{SV}$  that at the interface of the solid and vapor. Hence,

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta. \quad (3)$$

In effect, Young provided the first good approach for describing the wettability and spreading of a liquid on a solid and its relation to the equilibrium contact angle.

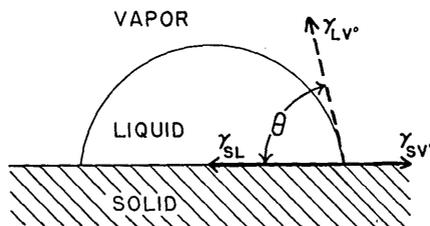


Fig. 5 - Schematic diagram of a finite contact angle formed by a sessile drop resting on a solid surface

First, consider that the liquid/solid interface is a plane. When  $\theta = 0$ , the liquid is said to spread spontaneously or completely on the surface of the solid; when  $\theta \neq 0$ , the liquid is said to be nonspreading. However, because we always find some liquid-to-solid adhesion, we can say that every liquid can wet every solid to some extent. On a sufficiently smooth and homogeneous solid surface,  $\theta$  is independent of the volume of the liquid drop. Since the tendency for a given mass of liquid to spread (and adhere) increases as  $\theta$  decreases, the contact angle is a useful inverse measure of wettability;  $\cos \theta$  is an obvious direct measure. As  $\theta$  decreases, a liquid drop will spread and contact a larger area of the surface; as  $\theta$  vanishes the area covered by the liquid drop becomes increasingly great; therefore, when  $\theta = 0$ , spontaneous spreading will occur.

The oldest experimental problem in measuring contact angles is the difference between the advancing contact angle ( $\theta_A$ ), which is observed when a liquid boundary advances over a clean, dry, solid surface, and the receding contact angle ( $\theta_R$ ), which is

observed when the liquid boundary recedes from a previously wetted surface. The major question has been which value is more significant,  $\theta_A$  or  $\theta_R$ , and many proposals have been made for using some function of  $\theta_A$  and  $\theta_R$ . The most common cause of the difference observed is the entrapment of liquid in the valleys, crevices, and pores of the solid surface as the liquid flows over it. When the liquid recedes, the surface uncovered usually includes wet areas; hence,  $\theta_R$  is always lower than  $\theta_A$ . When care is exercised to prepare solids with sufficiently smooth, clean, homogeneous surfaces, no significant differences are found between the slowly advancing and slowly receding contact angles of pure liquids (17,19).

Wenzel (25) investigated how the gross or macroscopic roughness of a solid surface was related to the apparent (or measured) contact angle ( $\theta'$ ) between the liquid and the envelope to the surface of the solid and to the true contact angle ( $\theta$ ) between the liquid and the surface at the air/liquid/solid contact boundary. Using as the measure of the roughness ( $r$ ) the ratio of the true area of the solid to the apparent or envelope area, he found the simple relation

$$r = \frac{\cos \theta'}{\cos \theta} . \quad (4)$$

Wenzel's equation is important because  $r$  varies widely in practice; instances where  $r = 1.00$  are rare, indeed. Perhaps the nearest to such a smooth surface is that of freshly fire-polished glass or a very carefully cleaved single crystal of mica. Even carefully machined and ground metal surfaces usually range from over 3.0 to rarely less than 1.5. Several consequences of Wenzel's equation are especially important. When  $\theta < 90^\circ$ , equation (4) indicates that  $\theta' < \theta$ . Since most organic liquids exhibit contact angles of less than  $90^\circ$  on clean polished metals, the effect of randomly roughening the metals is to make the apparent contact angle  $\theta'$  between the drop and the envelope to the metal surface less than the true contact angle  $\theta$ . In other words, each liquid will appear to spread more after the metal surface has been roughened. When  $\theta > 90^\circ$ , Eq. (4) indicates that  $\theta' > \theta$ . Since pure water makes a contact angle of from  $105^\circ$  to  $110^\circ$  with a smooth paraffin surface, the effect of roughening the paraffin makes  $\theta'$  greater; values of  $140^\circ$  have been observed. Various investigators have discussed the effect of roughness on  $\theta$  in more detail (26-29); their work is especially interesting in describing contact angle hysteresis on surfaces having an orderly roughness such as in woven textiles.

Surface roughness increases the difficulty of accurately measuring  $\theta$ . The experimental methods used to measure the contact angle generally measure  $\theta'$ , and all too often it is assumed that  $\theta' = \theta$ . Analysis of Eq. (4) reveals that the smaller the contact angle to be measured, the smoother must be the solid surface to obtain a given precision of measurement. When the contact angle is large, a high surface finish is not so essential.

In 1946 because of the astonishing dearth of reliable experimental data and the intractability of available theoretical relationships, we commenced a series of investigations to learn how solid and liquid constitution affected the equilibrium contact angle. A variety of pure liquids and solids were examined under controlled experimental conditions. We relied frequently on the use of various homologous series of liquid compounds. In the early work the solid surfaces used were chemically well-defined, solid polymers pressed into the form of smooth polished plates. Guided by the results of such experiments, we turned to polished solid surfaces of glass or metals each coated with an adsorbed, condensed, organic monolayer. Using such solids and liquids carefully freed of surface-active impurities, these systems exhibited reproducible contact angles; furthermore, the advancing and receding contact angles of each solid/liquid pair were identical so long as the liquid drop was advancing or receding sufficiently slowly to be reasonably close to equilibrium conditions.

A rectilinear relation was established empirically between the cosine of the contact angle ( $\theta$ ) and the surface tension ( $\gamma_{LV^\circ}$ ) for each homologous series of organic liquids

(17,19,30). Figure 6 illustrates the results observed with the n-alkanes on polytetrafluoroethylene (Teflon) (23). We defined as the critical surface tension ( $\gamma_c$ ) for wetting by a homologous series of liquids the intercept of the horizontal line  $\cos \theta = 1$  with the extrapolated straight-line plot of  $\cos \theta$  vs  $\gamma_{LV}$ . Even when  $\cos \theta$  is plotted against  $\gamma_{LV}$  for a variety of nonhomologous liquids, the graphical points fall close to a straight line or collect around it in a narrow rectilinear band. Certain surfaces, such as polytetrafluoroethylene, exhibit curvature of the plot for values of  $\gamma_{LV}$  above 50 dynes/cm (Fig. 7). But in these cases the curvature results because weak hydrogen bonds form between the molecules of liquid and those in the solid surface (19). This happens primarily with liquids of high surface tension, because many of them are able to donate hydrogen bonds and the fluorine atoms in the polytetrafluoroethylene surface are acceptors of a weak hydrogen bond. In the absence of hydrogen-bonding with the atoms in the solid surface, as is true of polyethylene or of poly(vinyl chloride), the  $\cos \theta$ -vs- $\gamma_{LV}$  graph for any low-energy surface is always a straight line or a narrow rectilinear band.

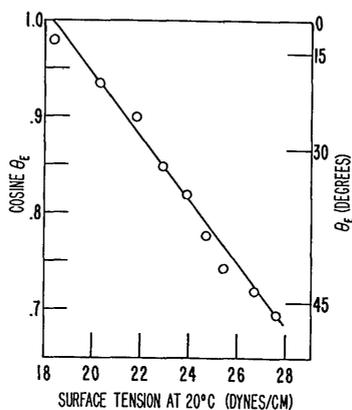


Fig. 6 - Wettability of polytetrafluoroethylene by the n-alkanes

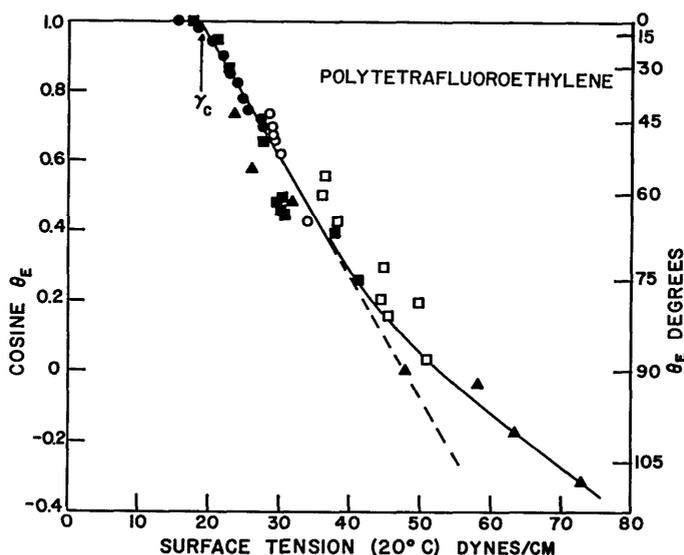


Fig. 7 - Wettability of polytetrafluoroethylene by water and a variety of organic liquids

Whenever rectilinear bands are obtained in this type of graph, the intercept of the lower limb of the band at  $\cos \theta = 1$  is chosen as the critical surface tension ( $\gamma_c$ ) of the solid. Although this intercept is less precisely defined than the critical surface tension of a homologous series of liquids, nevertheless it is an even more useful parameter because it is a characteristic of the solid surface alone; it has proved a useful empirical surface parameter.

By comparing values of  $\gamma_c$  of structurally "homologous" or "analogous" solids, such as an unbranched polyethylene compared with its various chlorinated or fluorinated analogs (Table 1, last column), and by making the reasonable assumption that the surface composition of the solid polymer is the same as that of the extended polymer molecule oriented parallel to the surface, it is possible to investigate the effect of the surface constitution of such polymeric solids on their critical surface tensions. Striking differences are evident from the plot of Fig. 8 for  $\gamma_c$  against the atom percent chlorine or fluorine replacement of the hydrogen in polyethylene. We see that whereas fluorination of polyethylene decreases  $\gamma_c$ , chlorination raises it.

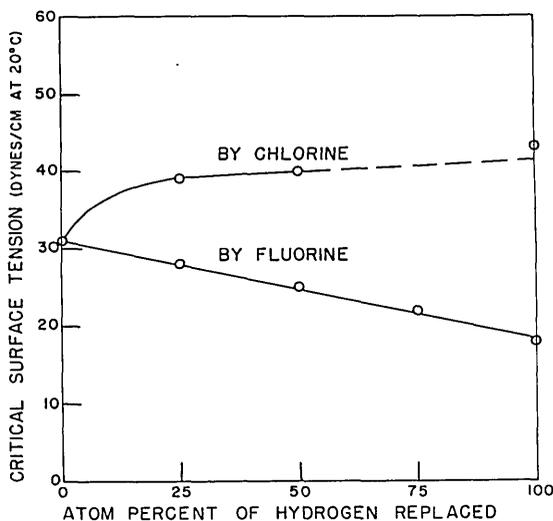


Fig. 8 - The effect of progressive halogen substitution on the wettability of polyethylene-type surfaces

Results of our investigations of clean, smooth, plasticizer-free, polymeric solids of general interest are summarized in Table 3. Values of  $\gamma_c$  for a series of hydroxyl-rich surfaces of the starch polymer type and of cellulose, like dry clean wood, range from 40 to 45 dynes/cm (31). These values of  $\gamma_c$  are reasonably close to that of 43 dynes/cm reported for the oxygen-rich surface of Dacron or Mylar, i.e., poly(ethylene terephthalate). Nylon 66, with its many exposed amide groups, has the highest  $\gamma_c$  value (46 dynes/cm) of the common plastics reported. Since  $\gamma_c$  values for all of these polymers are well below the surface tension of water (72.8 dynes/cm), all are hydrophobic to some extent.

The results of a wide variety of similar measurements of  $\cos \theta$  vs  $\gamma_{LV}$  proved that the value of  $\gamma_c$  of low-energy organic surfaces, as well as of high-energy surfaces coated by condensed organic monolayers, was determined essentially by the nature and packing of the outermost or exposed surface atoms of the solid; it was independent of the chemical nature and arrangements of the atoms and molecules beneath that solid surface or surface coating (30). Moreover, a uniform, condensed monolayer of stearic acid, or of primary octadecyl amine, or of octadecyl alcohol (approximately 24 Å thick) is sufficient to

Table 3  
Critical Surface Tension ( $\gamma_c$ ) of Various Polymeric Solids

Polymeric Solid	$\gamma_c$ at 20°C (dynes/cm)
Poly(1,1-dihydroperfluorooctyl methacrylate)	10.6
Polyhexafluoropropylene	16.2
Polytetrafluoroethylene	18.5
Polytrifluoroethylene	22
Poly(vinylidene fluoride)	25
Poly(vinyl fluoride)	28
Polyethylene	31
Polytrifluorochloroethylene	31
Polystyrene	33
Poly(vinyl alcohol)	37
Starch	39
Poly(methylmethacrylate)	39
Poly(vinyl chloride)	39
Poly(vinylidene chloride)	40
Poly(ethylene terephthalate)	43
Cellulose	45
Poly(hexamethylene adipamide)	46

completely change the wetting properties to the same characteristic value of  $\gamma_c$ , regardless of the nature of the solid substrate. This result provides very strong evidence that the attractive forces emanating from the metallic or nonmetallic solid substrate are minor at a distance of only 24 Å. These findings exemplify the extreme localization of the attractive field of force emanating from these solid surfaces. Hence, the field of force becomes unimportant at a distance of very few atom diameters, and there is little contribution to the liquid adhesion by atoms not in the first few surface layers of the solid. When the constitution of the solid, or of the adsorbed monolayer, was such that either ions or large, uncompensated, permanent dipoles were located in the outermost portion of the surface monolayer, we found good evidence that the residual field of force of the surface was much less localized (32,33).

Table 4 summarizes our results on wetting vs surface constitution for low-energy solid surfaces. In the first column is given the constitution of the atoms or organic radicals in the solid surface arranged in the order of the increasing values of  $\gamma_c$  (given in the second column). These data have also been grouped under the subheadings fluorocarbons, hydrocarbons, and chlorocarbons.

Some results of major interest in surface and polymer chemistry can be deduced readily from Table 4, and they deserve attention. The surface of lowest  $\gamma_c$  ever found (and hence the one having the lowest surface energy  $\gamma_{so}$ ) is that comprised of close-packed perfluoromethyl ( $-\text{CF}_3$ ) groups. Replacement of a single fluorine atom by a hydrogen atom in a terminal  $-\text{CF}_3$  group more than doubles  $\gamma_c$ . A parallel and regular

Table 4  
Critical Surface Tensions ( $\gamma_c$ ) of Low-Energy Surfaces

Surface Constitution	$\gamma_c$ at 20°C (dynes/cm)
Fluorocarbon Surfaces	
- CF <sub>3</sub>	6
- CF <sub>2</sub> H	15
- CF <sub>3</sub> and - CF <sub>2</sub> -	17
- CF <sub>2</sub> -CF <sub>2</sub> -	18
- CF <sub>2</sub> -CFH-	22
- CF <sub>2</sub> -CH <sub>2</sub> -	25
- CFH-CH <sub>2</sub> -	28
Hydrocarbon Surfaces	
- CH <sub>3</sub> (crystal)	20 - 22
- CH <sub>3</sub> (monolayer)	22 - 24
- CH <sub>2</sub> -CH <sub>2</sub> -	31
↔ CH ↔ (phenyl ring edge)	35
Chlorocarbon Surfaces	
- CClH-CH <sub>2</sub> -	39
- CCl <sub>2</sub> -CH <sub>2</sub> -	40
= CCl <sub>2</sub>	43

increase of 3 to 4 dynes/cm in  $\gamma_c$  has been observed with progressive replacement of fluorine by hydrogen atoms in the surfaces of bulk polymers (Fig. 8). Even more effective is the replacement of fluorine by chlorine, as shown by the 12.5 dynes/cm increase in  $\gamma_c$  in going from polytetrafluoroethylene to polytrifluorochloroethylene (Table 3).

Among the hydrocarbons the lowest values of  $\gamma_c$  are found in surfaces comprising close-packed, oriented, methyl groups. The lowest value obtained (22 dynes/cm) results when the methyl groups are in the close-packed array found in the easiest cleavage plane of a single crystal of a higher paraffin (such as n-hexatriacontane). The less closely packed arrangement found in a condensed monolayer of a high-molecular-weight fatty acid adsorbed on glass or certain metals leads to a value of  $\gamma_c$  equal to 24 dynes/cm. The great sensitivity of the contact angle (and hence of  $\gamma_c$ ) to such subtle changes in the packing of the methyl groups comprising the surface of the solid is remarkable, and it has been shown to be highly significant in many technological aspects of wetting, boundary lubrication, and adhesion. The transition from a surface composed of methyl (-CH<sub>3</sub>) groups to one of methylene (-CH<sub>2</sub>-) groups results in an increase in  $\gamma_c$  of some 10 dynes/cm; this is to be compared with the increase of 12 dynes/cm observed in going from a surface of perfluoromethyl (-CF<sub>3</sub>) groups to one of perfluoromethylene (-CF<sub>2</sub>-) groups.

The presence of aromatic carbon atoms in the hydrocarbon surface also increases  $\gamma_c$ . Thus, the introduction of a significant proportion of phenyl groups in the surface in going from polyethylene to polystyrene raises  $\gamma_c$  from 31 to 33 dynes/cm. A further increase to 35 dynes/cm results when the surface is composed solely of phenyl groups, arranged in the surface edge on, as in the cleavage surface of naphthalene.

In general, the observed effectiveness of atomic substituents tending to increase  $\gamma_c$  can be expressed by the inequality series below:

$$F < H < Cl < (Br) < (I) < O < N .$$

#### SURFACE CHEMICAL INTERFERENCES AND AIDS IN ADHESION

An adequate knowledge of adhesive action should be able to explain poor as well as good adhesion; hence, it should be able to explain the properties of "abhesives," which are materials commonly applied as thin coatings to one solid to prevent – or greatly decrease – the adhesion to another solid after having been brought into intimate contact with it. Abhesives are employed in molding, casting, or rolling operations; therefore, it is common in industry and the arts to refer to them as "parting," "mold-release," or "antistick" agents.

Table 5 gives the values of  $\gamma_c$  of each of the types of films or coatings much used as release agents. Evidently, each adhesive coating converts the solid into a low-energy surface, and any liquid placed on such a coated surface will exhibit an equilibrium contact angle which will be larger the more  $\gamma_{LV}$  exceeds  $\gamma_c$ . As  $\theta$  becomes larger, more interfacial voids develop, and such poor adhesion results that after the liquid has solidified in the mold, the application of a modest external stress suffices for effective separation from the wall of the mold (18,19). Therefore, the basis of adhesive action is in the surface energy decrease induced in the high-energy surface by the adsorption of a monolayer of a polar amphipathic compound having an outermost terminal group such as  $-\text{CH}_3$  or  $-\text{CF}_3$  (cf. Table 4).

Table 5  
Critical Surface Tensions of Wetting of Surfaces  
Coated with Abhesive Films

Coating Material	$\gamma_c$ at 20°C (dynes/cm)
Polymethylsiloxane film	24
Fatty acid monolayer	24
Polytetrafluoroethylene film	18
$\psi'$ -Fatty acid monolayer	15
Polymethacrylic ester of $\phi'$ -octanol	10
Perfluorolauric acid monolayer	6

The preceding analysis of adhesion makes it evident that to obtain optimum adhesive strength in a joint, it is essential to keep the interface of each adherend as free as possible from low-energy organic films in order to decrease the incidence and size of interfacial voids. This conclusion may be of importance in biological systems, for it means that an apparently subtle change in the surface composition of a biological membrane can greatly decrease (or increase) its wettability and also its adhesion. An outermost substituent which decreases  $\gamma_c$  (such as  $-\text{CH}_3$  or  $-\text{CH}_2-$ ) would decrease adhesiveness, whereas one which increases  $\gamma_c$  (such as phenyl,  $-\text{OH}$ ,  $-\text{SH}$ ,  $-\text{COOH}$ , or  $-\text{NH}_2$ ) would increase adhesiveness.

Many high-energy solids, such as glass, silica, alumina, metals, metal oxides, and a great variety of organic polymeric solids like cellulose, polysaccharides, and proteins readily adsorb water. When a polymolecular or "duplex" film of water is present on such

surfaces, all but the most firmly adsorbed portion (often only a monolayer) can be removed by gentle heating, by drying in a vacuum, or by using a water-displacing agent at ordinary temperatures (34,35). Removing the last traces of water, however, can be difficult.

Our recent investigations have demonstrated that adsorbed water greatly decreases the surface energy of glasses, silica, alumina, and metals (36-38). At room temperature only one condensed monolayer of adsorbed water will convert these high-energy solid surfaces into low-energy surfaces. As more water is adsorbed than a monolayer, the critical surface tension ( $\gamma_c$ ) decreases somewhat and approaches that of a bulk water surface (about 22 dynes/cm at 20°C). Therefore, if any liquid devoid of hydrophilic groups (such as a hydrocarbon, chloro-, bromo-, or iodocarbon) contacts such a moist surface, it will not spread and will exhibit an appreciable contact angle. But liquids containing accessible hydrophilic groups will tend to spread more readily upon such moist surfaces. If the organic liquid is sufficiently hydrophilic, it may spread so vigorously as to displace the bulk adsorbed water, and in the most extreme situation it may even displace or desorb all but the last monolayer of water.

The essential mechanism by which certain liquid polar-nonpolar compounds displace water from the surface of hydrophilic solids such as glass and metal has been described (34,35). Good examples of this large group of compounds are found among the liquid alcohols, ketones, acetates, acetoacetates, ether alcohols, Freons, and the lower methyl silicone polymers (trimer and tetramer). Because there are so many water-displacing agents among the lower boiling, polar-nonpolar, hydrophilic organic compounds, it is probable that in the applications of some liquid resin systems to make adhesive joints, an addition agent, impurity, or diluent can function as a water-displacing agent. When such an agent is used, it may be possible to obtain good wetting and adhesion by the resin even if the relative humidity is high. However, if any hydrophilic groups are added to the resin molecules to give the resin a positive spreading coefficient on water and some water-displacing ability, the substitution should not be carried too far because then the resin will become more susceptible to water permeation and to the effect of water in displacing it after it has been adsorbed on the adherend.

Since a polymolecular adsorbed film of water offers little resistance to shearing stresses, the presence of such a layer of water on the adherend surface will normally greatly decrease the strength of the adhesive joint formed. An exception is the special case where the adhesive is a gradually thickening aqueous solution, such as a viscous aqueous silicate solution (e.g., a cement), or a polymer-thickened aqueous solution. But, if an organic liquid adhesive, while polymerizing, is not able to react with, dissolve, or displace all of the adsorbed water on the adherend, a weak joint will result after the joint has "set." Such problems are frequent where joints must be made under very humid conditions or under water. In biological systems such problems are commonplace.

Still another problem after a good adhesive joint has formed is the gradual deterioration resulting from prolonged immersion in water or in a very humid atmosphere. This problem is all too often encountered in the failure of protective coatings on wood, brick, or concrete. The same problem is found in the deterioration of a composite plastic reinforced with a hydrophilic solid fiber such as glass. A similar dental problem is the gradual deterioration of dental fillings made from cements or from many organic composite materials. It is a challenge to understand how barnacles and other marine organisms can maintain such strong adhesion to foreign surfaces under these adverse circumstances.

A general solution to such problems does not exist; however, several approaches are known. Obviously, long exposure to moisture requires that the adhesive used to make the joint be chemically resistant to decomposition by water. The use of an appropriate coupling agent in forming the joint is also beneficial, and since their applications are now expanding rapidly, they will be discussed below.

A coupling agent is a special type of adhesion promoter; it functions by altering the surface of the solid to facilitate its interaction with the liquid adhesive by either chemical or physical processes. A number of materials already in use as coupling agents were designed to react chemically with both the adherend and adhesive. But high strength can be achieved in a joint if there is a sufficiently intimate molecular contact between adhesive and adherend; following this line of reasoning Zisman has pointed out that surface-active coupling agents can be designed which do not require chemical interaction with both phases (39). Several new classes of such compounds have been synthesized and investigated at our Laboratory (40-42). These molecules are sufficiently surface active to adsorb strongly on the solid, high-energy adherend; then the adsorbed monolayer presents an outermost surface on which the liquid adhesive can spread spontaneously without chemically combining with that film-coated surface.

Since many organic adhesives are applied as solutions or dispersions which are thinned with solvents having low surface tensions, it might be supposed that they would invariably spread spontaneously on those adherends having high-energy surfaces; and it would be presumed that the use of a coupling agent to improve wetting would be unnecessary. In practice, however, such adhesives do not always spread readily or evenly over many kinds of metals, or inorganic surfaces, because such high-energy surfaces are the most susceptible to the adsorption of interfering low-energy films of the type discussed earlier. An unrecognized (but important) function of the adsorbed film of adhesion promoter is to prevent such contamination by serving as a preliminary protective coating for the high-energy solid during the period prior to application of the liquid adhesive. A second function is to prevent the adsorption of an undesirable contaminant which has migrated toward the high-energy adherend surface from the liquid adhesive. In either case, the adsorbed monolayer of coupling agent should prevent surface contamination by organic substances, or by water, which could (a) interfere with spontaneous spreading by the liquid adhesive, (b) interpose a weakly bound layer at the interface, or (c) introduce a plane of easy parting after solidification of the adhesive (39,41).

Figure 9 presents schematically the role of a surface-active coupling agent in an adhesive joint. The desired wetting properties are obtained by incorporating an appropriate atomic group (or radical) at the outer end of the oriented adsorbed molecule. The opposite end of the molecule can comprise one or more polar groups each of which is able to adsorb, as independently as possible, on the adherend surface by strong physical or chemical adsorption. The coupling agent would thus be highly resistant to displacement by solvents or by surface-active components in the liquid adhesive. Since the small size of the water vapor molecule makes moisture permeation of organic coatings a constant threat to the integrity and longevity of adhesive joints, the outer surface of the film of coupling agent should be more hydrophobic in constitution than hydrophilic. Finally, where there is a chemical reaction between coupling agent and adherend, the product should have optimum water-immersion resistance by being insoluble in water and by being hydrolytically stable.

For example, highly adsorptive chlorine-containing compounds can be chosen which when adsorbed have covalent chlorine atoms in the outermost film surface, form a very hydrophobic coating, are resistant to chlorine hydrolysis, and yet have critical surface tensions of wetting of 40 dynes/cm or more at 20°C (19,30,43). Obviously, the choice of the adsorbing group to be used for coupling the agent to the solid surface will depend on the nature of that solid and on whether or not any chemical interaction with the adherend surface can impart high resistance to water-degradation of the joint. Thus, for oxygen-rich surfaces, a variety of substituted silanes and many types of coordination complexes with chromium have been used; variations in structures of such compounds are still appearing. Similarly, substituted amines have been proposed for use on glasses, paper, and cellulose. Chlorophenyl-substituted mono- and dicarboxylic acids are already being applied by us to metal surfaces and have been proposed for surfaces of metal oxides and the hydroxyapatite constituent of teeth (41). The specific types of surface-active coupling

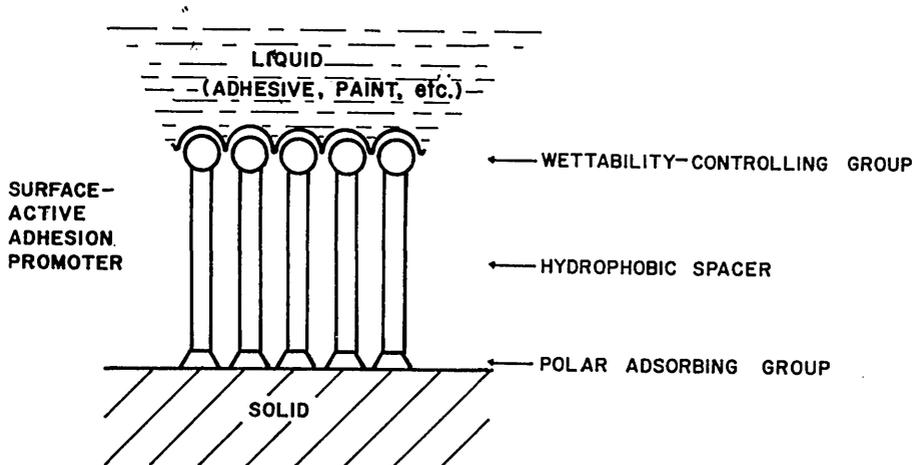


Fig. 9 - Schematic representation of a surface-active coupling agent

agents discussed above were designed to be added to an adhesive joint of current interest. However, effective coupling agents may already be present in biological systems in the form of the naturally occurring amino acids, carboxylic acids and salts, amines, and even the lower molecular weight proteins or polypeptides. Manifestly, synthetic materials chosen for such use would have to be free from toxic or irritant properties.

#### DISCUSSION OF ADDITIONAL PROBLEMS OF BIOADHESION

##### The Correlation of $\gamma_c$ with Biological Interactions

The correlation of  $\gamma_c$  with biological interactions can be illustrated by three brief examples:

- (1) The contact interaction of blood with foreign surfaces.
- (2) The interaction of isolated cells with foreign surfaces.
- (3) The selective behavior of highly developed organisms on solids.

When blood contacts foreign solid surfaces, there are specific adsorptive interactions which can initiate important events, such as the formation of a thrombus and blood coagulation. Two well-recognized processes may occur: first, the adsorption of proteins leading to coagulation; second, the adhesion of platelets at first to the solid and then to each other. The growing mass of platelets forms a thrombus which adheres to the solid surface.

The surface attraction of the solid is involved in three ways: in the adsorption of proteins, in the initial adhesion of the platelets, and in some control of the adhesional lifetime of the formed thrombus. The lifetime (and therefore the aggregate size) of the formed thrombus should decrease with decreasing  $\gamma_c$  of the foreign surface because of the poorer adhesion to lower energy surfaces. Consequently, the smaller size of the thrombus upon detachment from such a surface should result in a decreased likelihood of embolism downstream. Lyman and coworkers (44), studying the relation of blood coagulation induction times to  $\gamma_c$ , reported an encouraging inverse correlation. Since thrombus formation involving cell adhesion is a parallel process *in vivo*, very likely there is also a correlation of platelet adhesion with  $\gamma_c$ .

Concerning the foreign-surface interaction of isolated cells from a variety of tissues, there seems to be general agreement that adhesion and spreading of cells can be a direct function of the solid surface energy. For example, experiments of Taylor (45,46) and of Weiss and Blumenson (47) using serum-free media have demonstrated that cells attach and spread more readily on high- $\gamma_c$  materials like glass and less readily on low- $\gamma_c$  materials like Teflon and silicone-coated surfaces. Taylor's results on cellulose acetate and various proteins are difficult to interpret without determining the value of  $\gamma_c$  for each by methods other than the comparison of hydrophobic contact angles.

Since it has been observed that dead cells can exhibit as much variety in their adhesion behavior as living cells (45,46,48), the initial stages of adhesion must be much influenced by the simple surface-chemical mechanisms discussed earlier. This is important to note since cell aggregation studies have shown that the initial contact of cells with each other is essentially a random process with any cell potentially adherent to any other cell (48). Subsequently, however, metabolic activity and cell movements may play the dominant role in determining the persistence of individual adhesive joints and the relative competition among adhesive joints in an aggregating cell mass.

Although the above correlations with surface constitution seem promising, they hold only for serum-free media; recent work demonstrates that these simple relations disappear in the presence of proteins adsorbed on the solids (47). For example, cells will adhere well on both Teflon and glass surfaces in the presence of horse serum (47). We can understand such interferences because our work has established that an adsorbed monolayer will completely change the wetting and adhesion of the solid substrate.

Since single cells respond to differences in the surface properties of various solid substrates, it is not surprising that small organisms do likewise. Marine larvae, for instance, exhibit varied behavior in their settling and ultimate adhesion to solid surfaces and are known to respond specifically to the presence of different adsorbed films (49) and particularly to proteins (50).

While the above examples are encouraging and well-documented, they pertain to laboratory simulations of biological systems. Since the presence of proteins plays a major role in even such model systems, in real biological systems where numerous proteins, as well as other surface-active materials, are present, the difficulties are compounded. Thus, if surface energy considerations are to be useful, it will be in the sense that they define properties of the underlying substrate which may influence the conformation of the adsorbed species making up the new outermost molecular layer.

#### Influence of Surface Properties on Cell Adhesion

There is the real possibility that changes in the surface properties of cells mediate the various stages of cell adhesiveness. For example, any of the numerous surface-chemical interferences to adhesion, which we discussed earlier, might diminish the strength of cell-to-cell joints and lead to the increased invasiveness characterizing malignant cells.

It is also possible that the blood vessels change their internal surface properties with aging, perhaps suffering surface chemical alterations leading to increased critical surface tensions and thus increased adhesion to the walls of material circulating in the blood. A related current difficulty is the present debate regarding the "wettability" of the vascular endothelium and its relation to blood flow. Perel'man (51) maintains that the vessel endothelial lining is "nonwetable" in agreement with Moolten et al. (52), while

Zubairov and coworkers (53) and Copley (54) reject this thesis on the basis of essentially similar experiments, all involving the creation of a polar/nonpolar interface in the blood vessel. We believe that the rapid and spontaneous adsorption of proteins and other blood surfactants at such an interface will surely alter the estimated value of  $\gamma_c$  and the wettability from that of the unmodified vessel wall.

We can anticipate major influences in biological environments, not only from the water and from the numerous hydrogen-bonding and surface-active molecules present, but also from the variety of configurational changes known to occur with biopolymers. For example, although hydrogen-bonding ability is a general feature of the surface of a membrane of such a simple polyamide as a nylon (55), both polypeptides and proteins will either exhibit or mask their hydrogen-bonding abilities depending on the conformation of the polyamide chain, the location of the side groups, and the nature of the adjacent liquid phase. Variation in the wetting by hydrogen-bonding liquids with conformational changes has been demonstrated in the alpha-to-beta transition of the model polypeptide, polymethylglutamate (55), and in the collagen-to-gelatin transition (55). If one could manage to induce or modify specific configurations of proteins at the site of interest, adhesion could be either hindered or assisted.

The knowledge we have gained from studies of simple systems may well provide a useful starting point for the better understanding of biological adhesion, which is the necessary prerequisite for our beneficial interference with living systems.

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13. ABSTRACT <p>Intimate molecular contact at joint interfaces is essential for the extremely localized surface forces to result in adhesion exceeding the cohesive strength of the joined materials. Liquids, however viscous, are perhaps a more important class of adhesives in biology than in any other field. Attention is focused on the spreading of well-defined liquids over rigid or coherent phases of potential biological interest. The contact angle (<math>\theta</math>) of liquids on solids provides an inverse measure of liquid spreading. Rectilinear plots of <math>\cos \theta</math> vs liquid surface tension (<math>\gamma_{LV}</math>) define the critical surface tension of wetting (<math>\gamma_c</math>) for each solid. Direct, simple correlations exist between <math>\gamma_c</math> and solid surface composition. Wetting and adhesion can be completely changed by adsorbed films, even monolayers; adsorbed water, for example, can markedly decrease <math>\gamma_c</math>. Thus, adsorbed proteins, water, and trace surface-active agents are major influences in biological environments. Hydrogen-bonding and bound water are significant factors in the wettability of many pure polyamides, while configuration changes are especially important for polypeptides and proteins like polymethylglutamate, gelatin, and collagen. Wettability properties and the <math>\gamma_c</math> concept are pertinent to current adhesional and biomedical problems. Coupling agents have a potential role in bioadhesion. Further research is needed on the surface properties of biomaterials.</p>			

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KEY WORDS

LINK A

LINK B

LINK C

ROLE

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Adhesion  
 Adhesive joints  
 Adhesives  
 Abhesives  
 Abhesion  
 Biological systems  
 Biological interfaces  
 Bioadhesion  
 Blood coagulation  
 Cell adhesion  
 Contact angle  
 Liquid adhesives  
 Liquid spreading  
 Protein configuration  
 Polymers  
 Solid surfaces  
 Stress concentration  
 Surface chemical interference  
 Surface chemistry  
 Thrombus  
 Wettability  
 Wetting