Adhesion Characteristics of Gold Surfaces

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Measurement of the contact area between a gold coated glass ball and a polyurethane surface during a pull-off test at constant load allows one to show that the energy of adhesion corresponds to that of a low energy surface. These results, which seem equally valid for other elastomers, rubber-based adhesives and even epoxy adhesives, throw doubt on our understanding of the adhesion process. If the cause of the low surface energy measured over inorganic surfaces is an adsorbed layer, the latter is not displaced by the adhesive.

Surface energy is a determining factor in adhesion. If the surface energy of a substrate is low, its ability to form strong adhesive bonds (the adhesive strength) is also low, and the converse.

In a recent review article published in this journal (1), it was shown that gold has a low surface energy, involving essentially dispersive, rather than polar, interactions. This low surface energy could not be increased in spite of a variety of cleaning methods being used.

However, from the nature of metals their surface energies should be high, as is the case for molten gold.

When a metal or inorganic solid has a low surface energy, this is usually attributed to the adsorption of substances which lower the surface energy. As the observed adhesive strength of metals is usually high, it indicates that the adhesives displace the adsorbed layer.

Polyurethane has been used in the study presented below to determine the energy of adhesion, and, by inference, gold's surface properties. As polyurethane has surface properties similar to other rubber-like materials, its adhesive strength to gold should be the same as that of all rubber or rubber-based adhesives.

From the kinetics of the breaking of adhesion between an elastomer and a gold surface, it can be shown that either gold has a low surface energy, or the adsorbed surface layers are not readily displaced by adhesives.

Furthermore, as similar results were obtained for a drop of epoxy adhesive on gold, this argument is probably valid for other adhesives in contact with gold.

Calculation of the Energy of Adhesion from an Adherence Test

In the following discussion, only the calculations relevant to determining the adhesion characteristics of gold surfaces are shown. For a comprehensive analysis of the theory used in these experiments, the reader is referred to a recent paper by one of the authors (Barquins, *Int. J. Adhesion and Adhesives*, 1983, 3, (2), 71–84).

If a rigid sphere, of radius R , is pressed under a load P against a flat and smooth surface of an elastomeric solid, the area of contact is greater than the value which can be deduced from the classical Hertz elastic theory (2).

This phenomenon is due to the existence of molecular attraction forces of van der Waal's type, which produce infinite stresses at the edge of the contact. These tend to increase the contact zone and the elastic penetration of the sphere, as shown in Figure 1. The profile of the surface near the contact edge is similar to the fracture geometry for mode I propagation (opening mode). Therefore, this contact edge may be seen as a crack tip that advances or recedes as the applied load P is decreased or increased (3).

The edge of the contact area, like any three-dimensional crack, is subjected locally to a plane strain state so that the strain energy release rate G is given by:

$$G = (a^3 K/R - P')^2 / 6 \pi a^3 K \quad 1$$

in which a is the radius of the contact area; R is the radius of the sphere; P' is a fixed force applied to the sphere; and K is an elasticity constant of the material linked to the Young modulus E and the Poisson ratio ν by $K = 4E/3(1 - \nu^2)$. In the case of a rubber-like material $\nu = 0.5$, so that $K = 16E/9$.

At equilibrium under the load P (ie $P' = P$), one has $G = w$ (Griffith's criterion), w being the thermodynamic work of adhesion (or Dupré's work of adhesion), determined from surface (γ_A, γ_B) and interaction (γ_{AB}) energies of solids A and B in contact (Figure 2) by:

$$w = \gamma_A + \gamma_B - \gamma_{AB} \quad 2$$

When the equilibrium is disrupted by application of a tensile force P' ($P' < 0$) G immediately becomes greater than w and the two solids begin to separate, with a slow decrease in contact area. The difference ($G - w$) represents the crack extension force, and under this force the crack (i.e. the edge of the contact area) takes a limiting speed $v = da/dt$ so that the corresponding viscoelastic losses exactly equilibrate the 'motive power' ($G - w$). If it is assumed that viscoelastic losses are proportional to w (4) and are localised at the crack tip, i.e. gross displacements are purely elastic, one can write (3) the general equation of the kinetics of the adherence of elastomers:

$$G - w = wF(a_T v) \quad 3$$

where the second term corresponds to the viscous drag resulting from the losses at the crack tip. $F(a_T v)$ is a dimensionless function only dependent on the temperature T through the shift factor a_T in the Williams-Landel-Ferry transformation and on the crack speed $v = da/dt$. This function is characteristic of the viscoelastic material for the crack propagation in opening mode and is directly linked to the frequency dependence of the imaginary component of the Young's modulus. So, $F(a_T v)$ varies in a large range of speeds and temperatures as a power function of the parameter $a_T v$:

$$F(a_T v) = (a_T v)^n \quad 4$$

At constant temperature T :

$$F(a_T v) = \alpha(T)v^n$$

If the crack propagation speed is not too low, one has $w \ll G$, and consequently, equation 3 can be expressed as the approximation:

$$G \approx wF(a_T v)$$

$$\text{or } G \approx w\alpha(T)v^n$$

The experimental determination of the relation between the strain energy release rate G and the associated crack propagation speed v allows one to deduce, from equation 3, the value of the energy of adhesion w .

For example, open symbols in Figure 3 represent, in Log-Log coordinates, the kinetics of the adherence of a hemispherical glass lens (radius = 2.19 mm) in adhesive contact on a polyurethane surface (Young's modulus $E = 5.6$ MPa) when three different fixed tensile forces P' (-10, -30 and -40 mN) are imposed in order to disrupt the equilibrium observed after a 10 min contact time under the load $P = 50$ mN in the room atmosphere (temperature = 293 K, relative humidity = 50 per cent). These unloading experiments were carried out using an apparatus already described (3), consisting essentially of a precision balance supporting, at the end of its arm, the hemispherical glass lens. The contact area, illuminated by reflection of monochromatic light, is observed through the lens with a microscope. During the separation of the two bodies, a 16 mm camera (25 frames per second) located at the top of the microscope records contact areas. The frames are then enlarged and measured. Knowledge of the evolution of the radius and contact with time allows one to determine, at any time, the crack speed and the associated strain energy release rate, which is calculated from equation 1.

Fig. 2 The work required to separate two adhering bodies A and B, in a reversible and isothermal process, is equal to the difference between the energies of the system in its final and initial states

From experimental data (open symbols) in Figure 3, one can deduce that the function $F(a_r v)$ varies, as expected (3), as the 0.6th power of the crack speed v and then calculate the energy of adhesion from equation 3 as $w = 60 \text{ mJ/m}^2$.

The same set of experiments were carried out using a similar hemispherical glass lens covered with evaporated gold (450 Å chromium, 2000 Å gold evaporated at 10^{-9} bars). Results are given in Figure 3 (full symbols). As can be seen, again variation of the function $F(a_r v)$ with the 0.6th power of the crack speed is found, the gold coating causing only a slight increase in the energy of adhesion $w' = 70 \text{ mJ/m}^2$.

Surface Energy and Energy of Adhesion

For a reversible and isothermal transformation, the work done to perform the separation of two solids A and B in intimate contact is w , defined by equation 2. If the body B is a liquid, the Young-Dupré equation applies:

$$\gamma_B \cos \theta = \gamma_A - \gamma_{AB} \quad 5$$

where θ is the contact angle (Figure 4), so that the equation 2 can be expressed as:

$$w = \gamma_B (1 + \cos \theta) \quad 6$$

If only dispersive forces are operative, the Berthelot principle (5) then reads:

$$w = 2(\gamma_A \cdot \gamma_B)^{1/2} \quad 7$$

Equations 2, 5, 6 and 7 therefore allow us to relate the energy of adhesion to the surface energy.

In the following, the elastomer will be treated as the liquid phase B, of surface energy γ_B . For that reason, its surface energy has to be determined.

Table I
Surface Energy γ_s of Various Rubbers.

γ_s^d is the part of γ_s due to Dispersive Interactions, and $\gamma_s^p = \gamma_s - \gamma_s^d$ is the part due to Polar Interactions

Rubber Type	γ_s (mJ/m ²)	γ_s^d (mJ/m ²)	γ_s^p (mJ/m ²)	Reference
Styrene-Butadiene	30	29.5	0.5	J. Schultz and A. Carré (7)
Rubber-Butadiene (40/60)	29.3	27.8	1.30	M. Michel (8)
Neoprene	31.02	31±9	0.02	Y. Tamai (9)
Synthetic Rubber X	52.5	40.7	12	This work
Nitrile Rubber (66/34)	36	26.5	9.5	J. Schultz and A. Carré (7)
Blend of X and Natural Rubber	46.0	45.8	0.2	This work
Natural Rubber	27±3	32*	0	This work
Natural Rubber	35	—	—	Kendall (10)
Polyurethane	55±5	40**	20	This work
Polyurethane	46	32.6	13.4	B. Linberg (11)
Polyurethane	50.4	31.2	19.2	A Toussaint and R. Poisson (12)

* From the contact angle with CH₂I₂ which gives a higher value for the surface energy of rubber than other liquids

** From the contact angle with bromonaphthalene

Surface Energy of Elastomers

The surface energy of polyurethane and other rubber-like materials is not very easy to measure. Indeed, during contact angle measurements many solvents stain or diffuse into the solids. Nevertheless, we have measured the contact angles of water, methylene iodide or bromonaphthalene over sheets of polyurethane, synthetic and natural rubbers.

From experimental data and known values of the test liquids-surface tension, we can read, in the Neumann table (6), the surface energies of polyurethane and rubber substrates (Table 1). Methylene iodide could not be used with polyurethane because it diffuses into it very rapidly; as for the bromonaphthalene, it stains the surface and the accuracy of measured values is probably not very good, but the order of magnitude is correct and comparable with literature values presented in Table 1

This table gives, for several rubber-like materials, surface energies and parts due to dispersive and polar interactions respectively. It can be seen that dispersive components of surface energies are mostly in the range $\gamma_s^d = 35 \pm 5$ mJ/m².

This supports the prediction that other elastomers will behave in the same way as far as their adhesive properties are concerned. From results of Table 1, we will treat the polyurethane as a surface with essentially dispersive energy with the value $\gamma_s^d = 40$ mJ/m².

Behaviour of Gold with Polyurethane

From the data of Figure 3, we have deduced that the energy of adhesion for the gold-polyurethane contact is $w' = 70$ mJ/m².

As the polyurethane gives essentially dispersive surface interactions with $\gamma_s^d = 40$ mJ/m², equation 7 allows one to assess the surface energy of gold: $\gamma_s^d = 31$ mJ/m². This result confirms measurements of the gold surface energy by the liquid wettability method, and therefore indicates that adhesion to a gold surface is an adhesion to a surface of low energy.

Whatever the explanation, this has important consequences in the practical application of rubber adhesives: as we have seen, the various rubber-like materials have similar surface energies, thus, the energy of adhesion of rubber based adhesives (whether on tapes or in solution) to gold is 70 mJ/m². These results seem to be applicable also to epoxy adhesives as discussed below.

Behaviour of an Epoxy Resin Drop Over Gold Surfaces

The epoxy resin studied had a surface energy of some 40 ± 10 mJ/m² and the hardener's surface energy was in the same range. Thus the mixture had also a surface energy around 40 mJ/m². When a typical diglycidyl ether of bisphenol A resin, 828 EL (Shell Epon 828 electronic grade), was desposited on a gold surface, the experimental value of the contact angle θ was initially equal to 46.5°.

This is exactly the expected value which is calculated using both equations 6 and 7, linking θ and w , from the energy of adhesion of a liquid with a surface energy equal to 40 mJ/m² in dispersive interactions with a gold surface ($\gamma = 31$ mJ/m²).

If we make an adhesive by mixing this resin with a hardener of nearly the same surface energy, we expect that, initially, the liquid adhesive mixture will make a contact angle in the same

range. Actually we found, for a mixture of the resin 828 EL with triethylenetriamine as hardener, a contact angle of 37°...

If we leave the mixture at the ambient, it will gel and harden, and during the whole process we did not observe any important change in contact angle, as shown in Table II. This fact means that the term ($\gamma_A - \gamma_{AB}$) in equation 5 remains constant and that there is little or no rearrangement of the layer underlying the adhesives. Thus when epoxy adhesives adhere to a solid gold surface, they leave its energy at a low level, as is the case with elastomers which we considered above.

Conclusion

It is known, from studies of their wettability by liquids, that the energy of gold surfaces exposed to the atmosphere is low (1). The present study has revealed that this characteristic of gold surfaces is not materially affected if they are in contact with a polyurethane elastomer.

The adhesion between polyurethane and gold is therefore essentially the result of low energy dispersive interactions. This indicated that adsorbed surface films on the gold surface are not disturbed by the polyurethane. The same appears to be true in respect of the adhesion to gold of other rubber-like materials and adhesives, including epoxy resins.

These findings throw some doubt on our understanding of adhesion process, since it would appear as if adhesion to gold is indirect, in that it takes place through the medium of a low energy superficial layer on the metal.

The adhesion of polyurethane to glass is shown to be very similar to that of polyurethane to gold, and we suggest that adhesion to most inorganic solids may, like adhesion to gold, take place primarily through a low energy superficial layer. □

Table II

Evolution with Time of the Contact Angle and its Cosine for an Epoxy Resin (DGEBA 828 EL), a Hardener (triethylenetriamine) and their Mixtures

Time (min)	Mixture	Resin	Hardener
0	46.5 (0.69)	42.5 (0.74)	38 (0.79)
0.5	37.3 (0.79)	—	—
2	—	37.3 (0.79)	—
5	—	36 (0.8)	35.9 (0.81)
15	—	36.6 (0.8)	35 (0.8)
20	27.7 (0.88)		
25	27 (0.89)		
40	27.2 (0.89)		
60	25 (0.9)		
90	26 (0.9)		

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