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Polymer-Aluminium Adhesion. I. The Surface Energy of Aluminium in Relation to its Surface Treatment

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The influence of different surface treatments (degreasing, phosphatization, sealed and non-sealed anodization) on the surface energy of an aluminium substrate has been examined. The surface energy has been determined by wettability measurements using the two liquid phase method and taking into account the roughness and porosity of the treated substrate. The comparison of the interfacial interaction energies Al/polymer and Al/water shows that the treatment leading to the highest γ_s^D value and the lowest surface polarity, *i.e.* phosphatization, gives the highest adhesion strength and the best moisture resistance of the metal/polymer assembly.

INTRODUCTION

The association of solids of high surface energy (minerals, metals, glasses, carbon . . .) and solids of low energy (polymers) is often used in materials such as bonded joints, coated metals, composites. The performances of these materials depend, to a large extent, on the quality of the interface formed between the two types of solids, hence on their adhesion. The improvement of these multiphase-materials properties and a better understanding of the mechanism of adhesion request a suitable characterization of the high surface energy solid.

To tackle this problem, an aluminium surface has been chosen as a model and the surface characteristics of the metal have been modified by different

treatments. From the number of recent publications concerning the adhesion of aluminium, one can judge its present importance.¹⁻⁶

The first part of this study concerns the surface energy measurement of differently treated aluminium substrates.

The method used is based on the study of liquid/solid interactions by contact angles in a three-phase solid/liquid/liquid system.

MATERIALS

Aluminium is usually covered with a layer of natural oxide, contaminated by many compounds difficult to extract, resulting essentially from the laminating oils. This contaminated oxide layer, which confers to the material poor adhesive qualities, is removed or modified by surface treatment.

Among the most commonly used treatments, the following have been considered:

- solvent degreasing,
- conversion by phosphatization,
- anodization both sealed and non-sealed.

The solvent degreasing treatments have been performed on a highly smooth aluminium (1007) used as an optical reflector. For the other treatments a 5052 laminated aluminium has been employed.

Degreasing

The solvent degreasing allows one to eliminate, more or less, any impurities attached to the natural oxide layer.

Two different solvents have been used: hexane and dimethylformamide (DMF). The degreasing is performed in a Soxhlet extractor for 24 hours.

Conversion by phosphatization

The conversion treatment considered is an amorphous phosphatization. The aluminium is treated with a solution containing phosphoric acid, chromic acid, and fluorides. The blue-green film formed on the surface is assumed to have the following overall chemical composition: $\text{Al}_2\text{O}_3, 2\text{CrPO}_4, 8\text{H}_2\text{O}$.⁷

The coating, when dry, is essentially Cr^{III} and Al phosphates.⁸

This conversion treatment constitutes a particularly efficient and economic surface preparation.

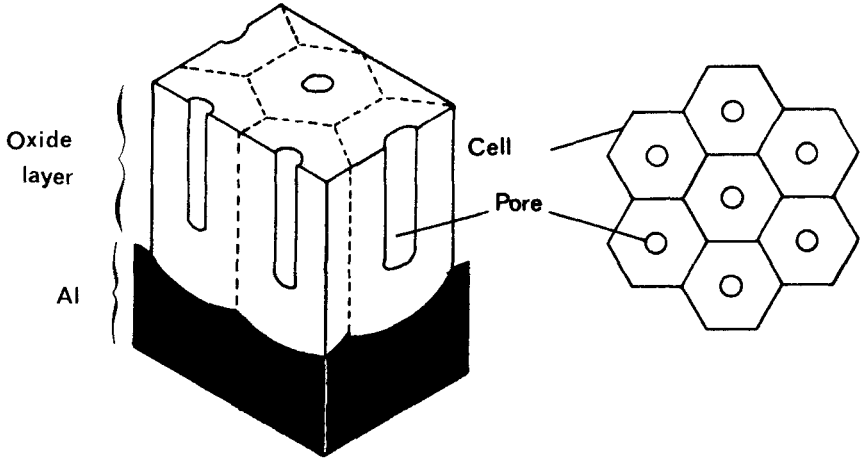


FIGURE 1 Model of anodic oxide structure.

Anodization

The surface layer, formed by anodic oxidation in a sulphuric acid medium, constitutes a compact system of hexagonal cells, each containing a pore⁹ (Figure 1).

About 10^{10} pores per cm^2 are formed. These have a diameter ranging from 100 to 300 Å⁹ depending on experimental conditions (electrolyte composition, temperature, current density . . .).

The thickness of the oxide layer, varying with the time of treatment, is equal to 20 μm in the case studied, the pore radius being of the order of 100 Å.

The pores can be clogged by a subsequent sealing in boiling water, the transformation of the anhydrous alumina into hydrated alumina (boehmite) being accompanied by an increase in volume.¹⁰

Sealing was effected by immersion in boiling water in the presence of salts (acetates).

In order to reduce the experimental scatter, it was found necessary to dry the samples of treated aluminium at 110°C for 48 hours. This drying modifies both the water content of the surface layer⁸ and also the degree of atmospheric pollution. These effects in turn necessarily modify the surface energy of the substrate.

Nevertheless, since a similar treatment is generally observed in practice before aluminium/polymer contact (*e.g.* in the coating of strip metal), it was concluded that the above procedure allowed a compromise to be met between real industrial conditions and those necessary in the laboratory in order to obtain meaningful results.

PRINCIPLE OF THE METHOD

For a solid displaying a low surface energy, such as a polymer, the surface energy can be obtained by a classical method considering contact angles of a series of liquids.¹¹ But solids having a high surface energy such as minerals, glasses or metals are generally completely wetted by the liquids used in the classical method. This is the reason why we have used a method, developed in our laboratory,¹² which measures the contact angles $\theta_{SW/H}$ of water, W , on the solid, S , in the presence of a non-polar liquid medium H (generally a normal alkane), non-miscible with water.

At equilibrium, Young's relationship¹³ is written:

$$\gamma_{SH} = \gamma_{SW} + \gamma_{HW} \cos \theta_{SW/H} \quad (1)$$

where γ_{SH} , γ_{SW} and γ_{HW} are the interfacial energies between the different phases.

According to Fowkes,¹⁴ the solid/liquid interfacial energies may be expressed as:

$$\gamma_{SH} = \gamma_S + \gamma_H - 2(\gamma_S^D \gamma_H^D)^{1/2} \quad (2)$$

$$\gamma_{SW} = \gamma_S + \gamma_W - 2(\gamma_S^D \gamma_W^D)^{1/2} - I_{SW}^P \quad (3)$$

The terms γ and γ^D stand respectively for the surface energy and its dispersive component, and I_{SW}^P represents the polar interaction solid/water.

Although there is no generally accepted theoretical relationship describing I_{SW}^P as a function of the polar components, γ_S^P and γ_W^P , we shall consider that the polar interaction energy is given by:^{11,12,15}

$$I_{SW}^P = 2(\gamma_S^P \gamma_W^P)^{1/2} \quad (4)$$

From relationships (1), (2) and (3), it can be established that the surface properties of the solid are determined by the following equation:

$$\gamma_W - \gamma_H + \gamma_{HW} \cos \theta_{SW/H} = 2(\gamma_S^D)^{1/2} [(\gamma_W^D)^{1/2} - (\gamma_H^D)^{1/2}] + I_{SW}^P \quad (5)$$

By using a series of alkanes, γ_S^D and I_{SW}^P can be calculated from the slope and the intercept at the origin of the line obtained by plotting $(\gamma_W - \gamma_H + \gamma_{HW} \cos \theta_{SW/H})$ versus $(\gamma_W^D)^{1/2} - (\gamma_H^D)^{1/2}$. The polar component, γ_S^P , can then be calculated from Eq. (4).

The surface and interfacial energies of the liquids are given in Table I.

It should be noticed that the above analysis depends implicitly on the assumption that water is capable of displacing a hydrocarbon on the solid surface. The criterion for displacement of one liquid by another has previously

TABLE I
Surface and interfacial energies of
liquids in $\text{mJ} \cdot \text{m}^{-2}$ (Ref. 12)

Alkanes	γ_H	γ_{HW}	Water:
Hexane	18.4	51.1	$\gamma_W = 72.6 \text{ mJ} \cdot \text{m}^{-2}$
Octane	21.3	51	$\gamma_W^D = 21.6 \text{ mJ} \cdot \text{m}^{-2}$
Hexadecane	27.1	51.3	$\gamma_W^P = 51 \text{ mJ} \cdot \text{m}^{-2}$

been established.¹⁶ In the present case, the necessary condition can be written :

$$\gamma_{SW} - \gamma_{SH} - \gamma_{HW} < 0$$

All the cases treated here fulfil this requirement.

CONTACT ANGLE CALCULATIONS

The principle of the method of surface energy determination is described above. However, the surface treatments may also affect the roughness by increasing or decreasing the number of surface defects. Whereas the surface energy characterizes intrinsic nature and energy of interactions at the surface, roughness and porosity play a multiplicative role by increasing the contact area at the solid/liquid interfaces.

Contact angle on a rough surface

The effect of roughness on wettability has been demonstrated by Wenzel,¹⁷ who showed that the real contact angle, θ_r , of a liquid on a rough surface and the theoretical contact angle, θ_0 , which would be displayed by the liquid on the same, but perfectly smooth surface, are related by the following relationship:

$$r = \frac{\cos \theta_r}{\cos \theta_0} \quad (6)$$

The term r represents, furthermore, the ratio of the real solid/liquid contact area to the apparent area of this interface.

A novel method has been used to determine this coefficient on solid surfaces. It involves contact angle measurement of a liquid on the rough surface coated with a thin gold film and the contact angle of the same liquid on a perfectly flat gold surface prepared by metallizing a clean and smooth glass plate. Metal plating is achieved by high-vacuum metal depositing. Wenzel's coefficient is then calculated from the values of the contact angles of a liquid (formamide, for instance) on the gold-plated substrate and on the reference surface.

TABLE II

Surface roughness of aluminium with reference to a glass surface (Ref. 18)

Solid surface	r
Microscope glass slide (reference)	1
Anodized aluminium	1.47
Sealed anodized aluminium	1.08
Phosphatized aluminium	1.01

Table II shows the coefficients of roughness obtained on aluminium, subjected to the various surface treatments.

To our knowledge, no other methods make it possible to take roughness into account in wettability phenomena. The parameters normally defining roughness are of little use in this type of problem.

It should be noticed that pores of anodized aluminium have a diameter much smaller than the thickness of the gold coating ($\approx 0.2 \mu\text{m}$) which implies that the metallized anodized aluminium surface is rough but probably not porous.

Contact angle on a porous surface

In a study of the aluminium surface wettability, the effects of porosity on contact angle cannot be neglected, pores being able to be filled by liquids due to capillary phenomena. According to Arslanov and Ogarev¹⁹ the capillary pressure, P_c , developed in a pore of an anodic oxide is equal to:

$$P_c = \frac{2\gamma_L \cos \theta}{R} \quad (7)$$

where γ_L is the surface energy of the liquid, θ the contact angle, and R the pore radius. Relationship [7] is easily derived from Laplace's equation.

When $\theta < \Pi/2$, P_c is positive so that the liquid in contact tends to penetrate into the porous medium spontaneously. Given that alkanes completely wet anodized aluminium, we must consider that they enter the pores. Afterwards, when the water droplet is placed on the surface, we suppose that a water/solid and water/alkane mixed interface forms under the droplet (Figure 2).

For such a system, the contact angle θ , can be described by Cassie-Baxter's relationship:²⁰

$$\cos \theta = x_1 \cos \theta_1 + x_2 \cos \theta_2 \quad (8)$$

with $x_1 + x_2 = 1$.

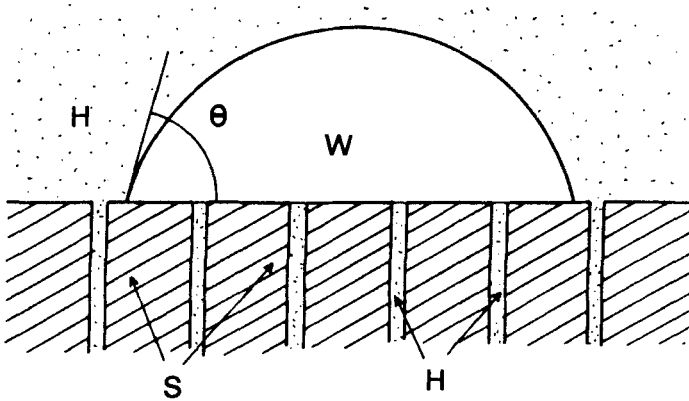


FIGURE 2 Schematic representation of the water (*W*) contact angle on a porous medium in a hydrocarbon (*H*) environment.

The terms x_1 and x_2 represent the surface fractions of constituents S_1 and S_2 ; θ_1 and θ_2 being the contact angles obtained respectively on S_1 and S_2 .

Taking into account Eq. (8), it will be considered that the contact angle of water on anodized aluminium in an alkane medium follows the equation:

$$\cos \theta = s \cos \theta_s + h \cos \theta_h \quad (s + h = 1) \quad (9)$$

s being the solid surface fraction and h the surface fraction occupied by pores. The angle θ_s corresponding to a non-porous solid, is the only angle representing the solid/water interactions. The angle θ_h is that which would be observed on a hypothetical surface entirely occupied by the alkane. In this case it is easy to show that $\theta_h = \Pi$, so that relation (9) becomes:

$$\cos \theta = (1 - h) \cos \theta_s - h \quad (10)$$

We still have to take into account the macroscopic roughness characterized by Wenzel's coefficient, r , and finally θ_s will be calculated from the following relationship:

$$\cos \theta_s = \frac{\frac{\cos \theta_r}{r} + h}{1 - h} \quad (11)$$

The term h has been computed from Scanning Electron Microscopy data.¹⁸ Equation (12) gives h where N is the number of pores per cm^2 , and R is their radius.

$$h = N\pi R^2 \quad (12)$$

TABLE III

Contact angles of water in hydrocarbons as a function of surface treatment (s = standard error in degrees)

Alkanes	1	2	3		4		5	
	Hexane	D.M.F.	Phosphatization		Anodization		Sealed anodization	
	degreasing	degreasing	$s = \pm 0.4$		$s = \pm 0.5$		$s = \pm 0.5$	
	$s = \pm 0.4$	$s = \pm 0.7$	(6)		(11)		(6)	
			θ_{exp}	$\rightarrow \theta_{\text{calc}}$	θ_{exp}	$\rightarrow \theta_{\text{calc}}$	θ_{exp}	$\rightarrow \theta_{\text{calc}}$
Hexane	102.4	72.2	121.5	121.5	28.5	22.5	84.5	84.9
Octane	104.4	74.2	131	131	30	24	82.5	83
Hexadecane	106.1	86.3	142	142	52.5	45.3	87.5	87.7

1, 2: 1007, highly smooth aluminium.

3, 4, 5: 5052, laminated aluminium.

θ_{exp} : experimental value.

θ_{calc} : calculated value (taking into account roughness and porosity effects).

Experimentally, it has been verified that the measured contact angles of water in alkanes increase with porosity. For example, the water contact angle in hexane is equal to 28.5° for an anodized substrate having 5.5×10^{10} pores per cm^2 . It is reduced to 20° for 4.2×10^{10} pores per cm^2 . The porosity has been reduced by increasing the current density in the electrochemical treatment.

EXPERIMENTAL RESULTS

Water advancing contact angles at equilibrium on the five aluminium surfaces have been measured in alkanes by using a RAME-HART A-100 apparatus allowing direct measurements to be made.

TABLE IV

Surface characteristics of aluminium in $\text{mJ} \cdot \text{m}^{-2}$. Average error: $\pm 10\%$

Surface treatment	γ_s^D	I_{sw}^D	γ_s^P
Hexane extraction	42	38.7	7.5
DMF extraction	135	62.5	19
Phosphatization	150	18	1.5
Anodization	125	95	44
Sealed anodization	41	55.5	15

These results clearly show to what extent the surface energy of aluminium can be affected by the surface preparation.

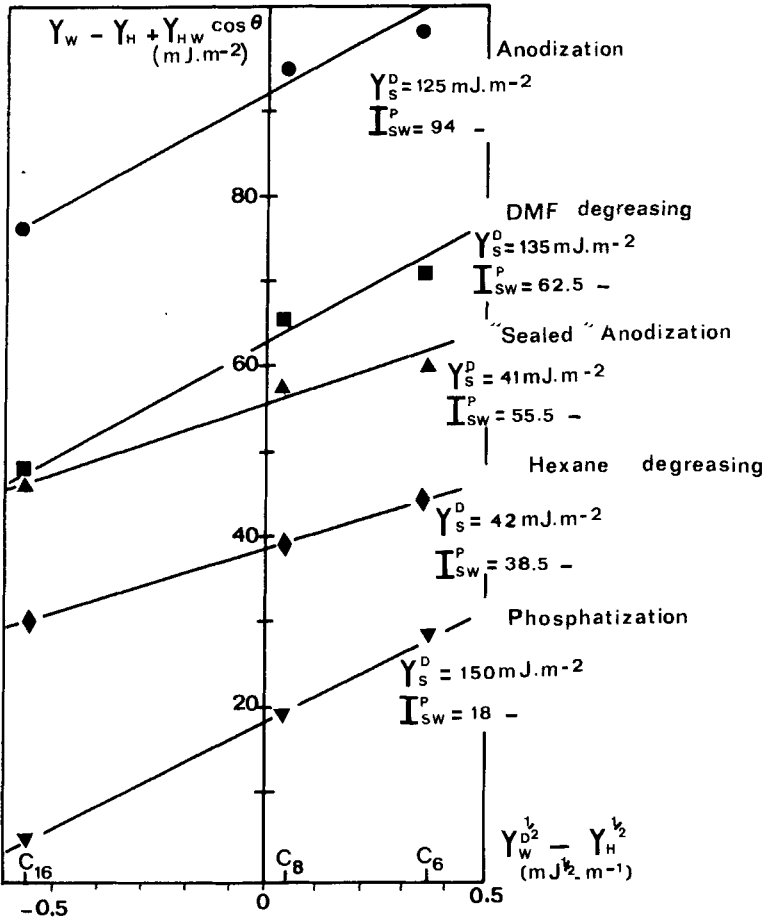


FIGURE 3 Determination of the surface energy of the treated aluminium substrate.

Experimental and theoretical values calculated by taking into account roughness and porosity are given in Table III. Each value is the mean of more than 100 measurements.

Figure 3 represents the lines of linear regression obtained from relationship (5) for each surface treatment. Table IV summarizes the surface characteristics of the aluminium substrates.

These results clearly show to what extent the surface energy of aluminium can be affected by the surface preparation.

TABLE V

Reversible energy of adhesion of aluminium to an epoxy-phenolic coating and water ($\text{mJ} \cdot \text{m}^{-2}$)

Surface treatment	W_0 Al/coating	W_0 Al/water
Phosphatization	169	131
Anodization	176	198
"Sealed" anodization	101	115
DMF extraction	182	170
Hexane extraction	103	99

APPLICATIONS

Knowing the surface energies of the substrates, we are now able to calculate the reversible energies of adhesion of aluminium to a polymer by using simple relationships similar to those used for calculating solid/liquid adhesion energies.²¹ For instance, in Table V, we give the reversible energies of adhesion, W_0 Al/coating, between different aluminium surfaces and an epoxy-phenolic resin. The surface energy components of this epoxy-phenolic resin have been determined by classical contact angle measurements, *i.e.* $\gamma_S^D = 50 \text{ mJ} \cdot \text{m}^{-2}$ and $\gamma_S^P = 4 \text{ mJ} \cdot \text{m}^{-2}$ (Ref. 22).

Also given in this table are the reversible energies of adhesion between aluminium and water, W_0 Al/water; this quantity represents the affinity of aluminium for water.

The affinity of the aluminium surface for water plays an important role in the behavior of the assembly aluminium/resin when submitted either to a test in an autoclave or a test of durability. Let us compare the values obtained for a system consisting of aluminium after phosphatization with those for a system of anodized aluminium. The intrinsic energy of the aluminium/polymer bond is similar for the two cases (169 and 176 $\text{mJ} \cdot \text{m}^{-2}$) but because of its polarity, the anodized aluminium presents a great affinity for water (W_0 Al/water = 198 $\text{mJ} \cdot \text{m}^{-2}$). In practice, we notice that the system anodized aluminium/coating is not very resistant to corrosive solutions, whereas the system phosphatized Al/coating resists very well.

Thus it can be deduced that simultaneous good "dry" adhesion and high water resistance are obtained when the dispersive component, γ_S^D , is high and the polar component, γ_S^P , is low.

In a second part of this study, we shall go more into the quantitative interpretation of the variations, in liquid media, of the failure energy of model assemblies consisting of treated aluminium and elastomers SBR and NBR of different polarities.

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