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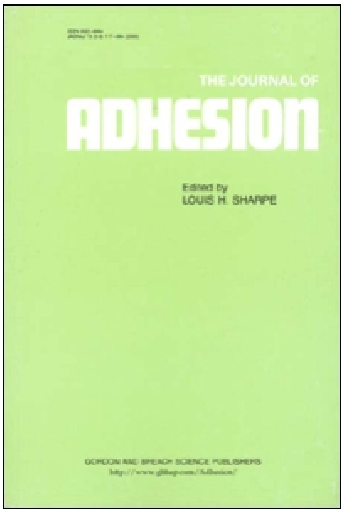

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A Review of Adhesion Mechanisms Using the Peel Test in Air and Liquid Media

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A Review of Adhesion Mechanisms Using the Peel Test in Air and Liquid Media*

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This paper deals with the analysis of peel energy of assemblies measured in different environments, *i.e.* in air and in the presence of liquids, and constitutes a brief review of the work of Professor Schultz' team in this domain. It is shown how such measurements can lead to a better knowledge of the nature as well as of the magnitude of fundamental interactions established at the interface between two solids. Earlier experiments have shown that peel energy can be expressed as a product of three terms corresponding, respectively, to the reversible energy of interfacial adhesion, the hysteretic losses of the bulk materials and the molecular dissipation near the crack front during peeling. This approach is well-verified when only physical interactions (van der Waals) are involved at the interface. However, more complex cases correspond to systems where specific interactions are also established between both materials, in particular acid-base interactions and creation of chemical bonds. In both cases, peel measurements in liquid media can lead to the determination of fundamental parameters, such as the interfacial density of specific interactions at the interface and the acid-base or chemical components of the work of adhesion. Finally, the effect of interdiffusion phenomena on peel energies can also be investigated in the case of elastomer/elastomer assemblies.

KEY WORDS: interfacial interactions; acid-base interactions; dispersion interactions; chemical interactions; peel energy; energy of adhesion; surface free energy; work of adhesion; adhesion mechanisms; environmental effects

1 INTRODUCTION

The energy of adhesion corresponds to the energy of the intermolecular forces which are acting across the interface between two substrates. However, it is known that the work of separation is always much higher than that predicted from the knowledge of those forces due to the dissipation phenomenon occuring during the separation.

Using a peel test, Gent and Schultz[1] have found the following relationship:

$$\frac{G_L}{G} = \frac{W_{0L}}{W_0}$$

where G and W_0 are, respectively, the measured energy of adhesion and the reversible energy of adhesion in air, whereas the subscript L indicates the presence of the liquid medium.

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* One of a Collection of papers honoring Jacques Schultz, the recipient in February 1995 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

Therefore, it was proposed that the measured adhesion strength, G, must be factorizable into two terms, one representing the reversible energy of adhesion, W_0, and the other one related to dissipation effects due to irreversible deformation processes within the adhesive. It was assumed that the interfacial interactions are of the physical type and that they can be calculated from the surface free—energies of the contacting materials. However, even when the dissipation effect due to the viscoelastic properties of the materials can be neglected, it was shown that molecular dissipation can intervene. Moreover, other mechanisms of adhesion such as anchoring, interdiffusion, weak boundary layers, for instance, can be involved and the interpretation of the measured adhesive strength be more complex.

Nevertheless, the knowledge of the nature of the interactions is an important parameter in the understanding of the behavior of adhesive joints. Spectroscopic analyses are mostly devoted to this study: by deposition of a thin film (a few angströms for XPS and less than 200 nm for FTIR in the reflection-absorption mode, for example), it is possible to establish the nature of the interactions.

As a complementary technique, Schultz and Carré[2] have used the variation of the peel energy as a function of the properties of the liquid medium to separate physical and chemical contributions to the measured energy of adhesion. The purpose of this paper is to show how the peel test in different environments helps to define the nature of the interactions established between two materials and also to give the limitations of the method by using results from our Laboratory.

In honour of the continuous work Professor Schultz is performing in adhesion science, we present a review paper based on different, representative, studies of his team in this area.

2 PRINCIPLE OF THE METHOD

Bond strength is often evaluated by a peel test in the case where at least one of the two parts of the assembly is flexible. The main advantage of this test is to measure the energy of separation, G, at a constant rate of propagation of the crack so that the value can be interpreted in terms of fracture mechanics. The adhesive fracture energy, or energy of separation, is given by:

$$G = \frac{F}{b}(1 - \cos\alpha) \tag{1}$$

where F/b is the peel force per unit width, and α the peel angle.

The measured energy depends upon the rate and the temperature of separation. A major contribution is due to the energy dissipated irreversibly during the fracture. In the case of viscoelastic materials, the original relationship proposed by Gent and Schultz[1] and completed by Carré and Schultz[3] is the following:

$$G = W_0 \times g(M_c) \times f(R, T) \tag{2}$$

W_0 is the reversible energy of adhesion. $f(R, T)$ is a factor of viscoelastic dissipation which depends, at constant test geometry, only on the rheological properties of the viscoelastic material, and thus on the propagation rate, R, of the failure front and the temperature T. $g(M_c)$ is a molecular dissipation factor which takes into account the fact that, even when the viscoelastic dissipation is negligible, the measured energy stays higher than the calculated reversible energy of adhesion.

The peel strength in the presence of a liquid which does not modify the bulk properties of the elastomer by swelling or reaction and, consequently, does not change the viscoelastic properties, can be written as:

$$G_L = W_{0L} \times g(M_c) \times f(R, T) \tag{3}$$

When the locus of the failure is identical in both media, the ratio of Equations (2) and (3) leads to:

$$\frac{G_L}{G} = \frac{W_{0L}}{W_0} \tag{4}$$

The variation of the reversible energy of adhesion due to the liquid is equal to:

$$\Delta W_0 = W_{0L} - W_0 \tag{5}$$

It is also possible to calculate the effect of the liquid on the energy of separation:

$$\Delta G = G_L - G \tag{6}$$

This variation can be determined experimentally over a large domain of peel rates in order to be sure that the liquid is present at the peel front. Thus, Equation (4) can be modified as follows:

$$\frac{\Delta W_0}{W_0} = \frac{\Delta G}{G} \tag{7}$$

If Equation (7) is verified, it can be assumed that only physical interactions are present at the interface. When the experimental ratio is different from the calculated one, it can be assumed that not only physical interactions are present at the interface but that other interactions such as acid-base interactions, covalent bonding or other adhesion mechanisms can be involved. In the case of chemical bonding, a chemical contribution, φ_{chem}, to the measured energy has to be taken into account and can be evaluated.

The total interfacial energy, W_0, is equal to the sum of the physical interactions, W_ϕ, and the chemical contribution, W_{chem}. Assuming that the liquid is not affecting the chemical interfacial bonds, it can be shown that:

$$\Delta W_0 = \Delta W_\phi \tag{8}$$

and the physical and chemical contributions can be evaluated:

$$\left.\begin{aligned} \varphi_\phi &= \frac{\Delta G}{G} \Big/ \frac{\Delta W_0}{W_\phi} \\ \varphi_{\mathrm{chem}} &= \frac{W_{\mathrm{chem}}}{W_0} = 1 - \frac{\Delta G}{G} \Big/ \frac{\Delta W_0}{W_\phi} \end{aligned}\right\} \tag{9}$$

$\Delta G/G$ is the experimental variation determined in the peel test and the necessary requirements to apply the method are:

- the liquid affects only the physical interactions,
- the liquid does not modify the bulk properties of the polymer by swelling or dissolution,
- the failure occurs in both media (air and liquid) at the same place,
- the liquid is present at the crack tip during the separation.

This last requirement has been studied in detail by Carré and Schultz.[4] The approach is based on work done by Shanahan and Schultz[5] on environmental stress cracking. The penetration rate of a liquid in a crack of about 1 μm opening is mainly affected by three parameters:

- the viscosity of the liquid,
- its surface energy,
- the solid/liquid interactions.

For a good wetting liquid such as silicone oil, Figure 1 shows the effect of the viscosity on the separation energy of aluminum/elastomer assemblies as a function of the peel rate. Three domains can be considered. First, for low peel rates and low viscosity liquid, the reduction in peel energy is maximum and the liquid is present at the crack tip. At the opposite, for high peel rates and whatever the liquid viscosity, the peel energy is identical to that observed in air. This means that the penetration rate of the liquid in the crack is lower than the peel rate and the liquid is no longer in contact with the fracture front. Between these two domains, there is a partial effect of the liquid depending on these two parameters. The rate at which the liquid is no more in direct contact with the crack front can be calculated by Equation (10):

$$R_d > \frac{2\gamma_L \cos(\theta - \alpha)}{K\eta} \tag{10}$$

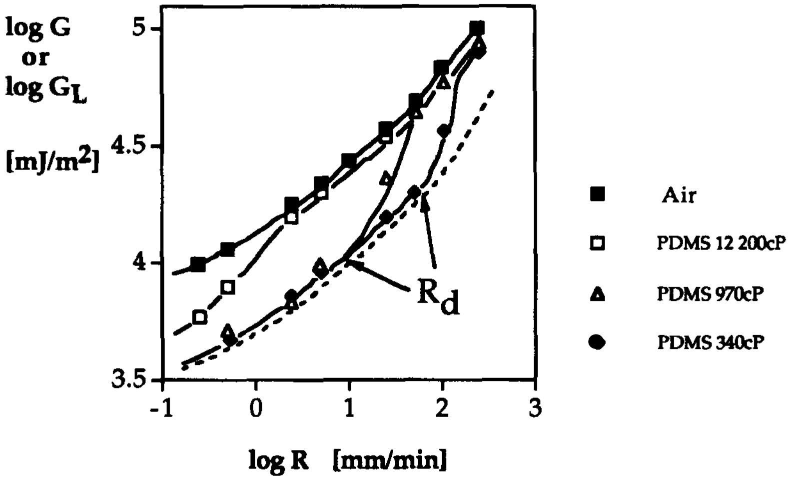

FIGURE 1 Failure energy *vs* peel rate in air and in PDMS oils of different viscosities.

where γ_L is the surface energy of the liquid, η its viscosity, and K is a dimensionless factor depending on the geometry of the crack. θ and α are, respectively, the liquid/solid contact angle and the half angle of the wedge-shaped crack.

Optimum conditions of separation are obtained with low viscosity liquids which present low liquid/solid contact angles. Moreover, it is better to perform the measurements over a sufficiently large range of peel rates and with at least two liquids.

Practically, the peel test is performed first in air and in a second step, on the same sample, in the liquid environment. The whole assembly is immersed in a liquid tank during the separation as shown on Figure 2.[1-2] However, it is also possible to inject the liquid continuously onto the peel crack with a syringe. For good wetting liquids and reasonnable peel rates, both experiments lead to the same reduction in peel energy.

The following examples are chosen to illustrate the application of the method. First, the simplest case in which only physical interactions are intervening is considered. Then, more complex cases are presented:

- acid-base interactions which are widely studied nowadays and can be approached by the peel test in liquid medium,
- chemical bonding and weak boundary layer,
- modification of the cohesion near an interface,
- interdiffusion effect as an additional adhesion mechanism.

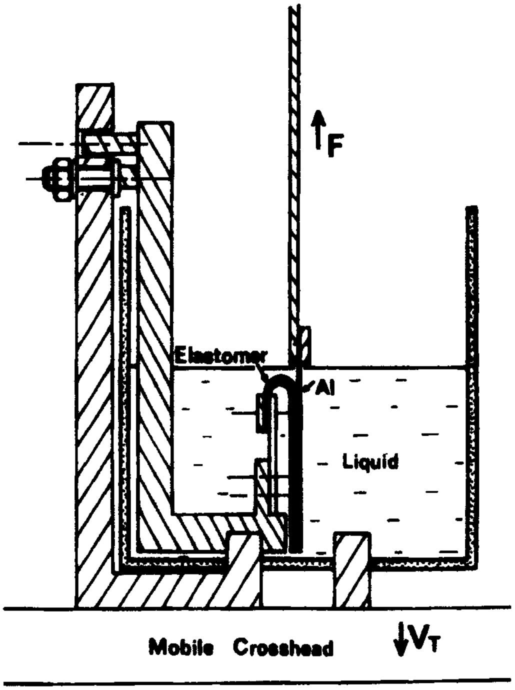

FIGURE 2 Experimental set-up used in References 1 and 2.

Although there is no direct correlation between these examples, the complexity of adhesion mechanisms appears and shows that it is necessary to approach the understanding of these phenomena from different points of view.

3 PHYSICAL INTERACTIONS

The proposed method is especially well suited to demonstrate that physical interactions ensure the strength of the interface. The locus of failure is considered as interfacial, or at least very close to the original interface.

In sealed anodized aluminum/elastomer assemblies,[2] the locus of failure is clearly interfacial and the variation of the peel energy in the presence of alcohols has been predicted from the knowledge of the surface free energies of the different materials in contact. The reversible energy of adhesion in air and in a liquid medium can be evaluated using Dupré's relationship[6] when the failure is interfacial:

$$\left.\begin{aligned} W_0 &= \gamma_{S_1} + \gamma_{S_2} - \gamma_{S_1S_2} \\ W_{0L} &= \gamma_{S_1L} + \gamma_{S_2L} - \gamma_{S_1S_2} \end{aligned}\right\} \tag{11}$$

where γ_{S_1} and γ_{S_2} are the surface free energies of the two solids, $\gamma_{S_1S_2}$, γ_{S_1L} and γ_{S_2L} are the interfacial free energies between the two solids, on the one hand, and the solid (S_1 or S_2) and the liquid (L) on the other hand.

It can be shown that:

$$\left.\begin{aligned} W_{0L} &= W_0 + \Delta W_0 \\ \text{with}\quad \Delta W_0 &= 2\gamma_L - W_{S_1L} - W_{S_2L} \end{aligned}\right\} \tag{12}$$

W_{SL} represents the liquid/solid adhesion energy and is given by a relationship similar to that first proposed by Kaelble and Uy[7] and then by Owens and Wendt:[8]

$$W_{SL} = 2(\gamma_S^D \gamma_L^D)^{1/2} + 2(\gamma_S^P \gamma_L^P)^{1/2} \tag{13}$$

where γ^D corresponds to the dispersive component of the surface free energy of the solid (S) and the liquid (L). In the present case, the polar component γ^P may be due to both hydrogen bonding and dipole interactions since it is difficult to distinguish experimentally between both contributions.

Knowing the surface free energies for both contacting solids and the liquid, it is possible to evaluate W_0 and ΔW_0. It should be noticed that all γ values used in this paper were inferred from contact angle measurements of the usual liquids in either the one[9] or the two-liquid phase method.[10]

The surface free energies of the elastomers (a 40/60 styrene-butadiene copolymer, SBR, and a 34/66 acrylonitrile/butadiene rubber, NBR) and the aluminum[11] are given in Table I. The liquids used for the peel experiment are different alcohols.

Figure 3 shows the example of the behavior of the SBR-based assembly; the separation is performed in air and in methanol. Both curves are parallel, which means that, to a first approximation, the variation of the dissipated energy with the peel rate is identical in air and methanol. The dotted line corresponds to the theoretical variation and it agrees very closely with the experimental one. It is, therefore, possible to say that, in this case, only physical interactions of the van der Waals type are taking place at the

TABLE I
Surface properties of solids and liquids used

Surface	γ[mJ/m^2]	γ^D[mJ/m^2]	γ^P[mJ/m^2]
SBR	30	29.5	0.5
NBR	36	26.5	9.5
Sealed anodized aluminum	56	41	15
Methanol	22.6	15.2	7.4
Ethanol	22.8	17	5.8
Butanol	24.6	23.8	1

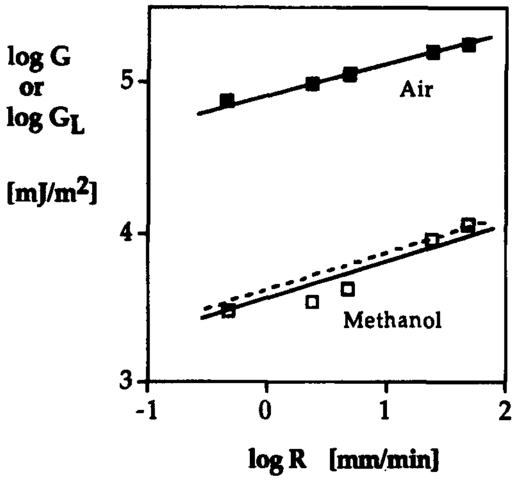

FIGURE 3 Influence of a liquid medium on the failure of sealed anodized aluminum/SBR assembly. Experimental and theoretical (-----) results.

elastomer-aluminum interface. Identical results are obtained for the NBR-based assembly and the other liquids.

The situation is much more complex when the expected variation is lower than the experimental one and the interpretation needs to be based on a good knowledge of the adhesion mechanisms.

4 MORE THAN PHYSICAL INTERACTIONS

When other interactions in addition to physical interactions ensure the strength of an interface, it is interesting to know more about the nature of these interactions. We have shown in the preceding section that the peel test in a liquid medium can affect, when the liquid is properly chosen, the physical interactions. Other interactions, however, can take place: covalent or ionic bonds and acid-base interactions. The difficulty is then to evaluate those interfacial interactions, especially acid-base interactions. Moreover, other adhesion mechanisms can also intervene. In the following part, we will illustrate how peel testing in liquid medium can be helpful.

4.1 Effect of Acid-base Interactions: Polymer Blends/Aluminum Assemblies

Adhesion mechanisms to an aluminum substrate (A4, 99.4% purity) of binary blends and models of hot-melt adhesives, have been recently analysed.[12] These blends consisted of EVA copolymer (vinylacetate content of 28% by weight) and terpene-phenol resins. Three terpene-phenol resins, TPR 1, 2 and 3, with different degrees of functionality d_{OH} were used (Fig. 4). d_{OH} is defined as the average number of hydroxyl groups per molecule of resin. The d_{OH} values were equal to 0.7, 1.1 and 1.4 for TPR 1, 2 and 3, respectively. Blends, with EVA contents ranging from 30 to 70% by weight, were prepared by mixing EVA and TPR under nitrogen at a constant temperature.

The nature of the interactions established between the blends and the aluminum surface (in fact, natural aluminum oxide) were first analysed by means of Fourier transform infrared spectroscopy in the reflection-adsorption mode (IRAS). A film ($\approx 50\,\mu m$ thick) was molded onto the substrate, then gradually dissolved by dipping into chloroform until its thickness reached about 30 nm, as determined by weight measurements. The interfacial region was then studied by IRAS at an angle of incidence of 86°.

When EVA/TPR blends are brought into contact with the substrate, preferential interactions between TPR and aluminum are clearly evidenced by IRAS. Effectively, a new contribution for the absorption band of the phenolic ring of the resin at $1515\,cm^{-1}$, corresponding to the interactions between π-electrons and the hydroxyl function, shows that electron acceptor-donor interactions ($n\cdot\pi^*$-type acid-base interactions according to the generalized Lewis' concept), are directly established between the phenolic ring of TPR resins and the oxygen atom of the aluminol groups present on the aluminum surface (Fig. 5). According to Murphy and Rao,[13] this leads to an estimated value of the variation of enthalpy, $-\Delta H^{AB}$, for the establishment of such interactions, close to 30 kJ/mol. This value is about twice that for EVA carbonyl function/aluminol

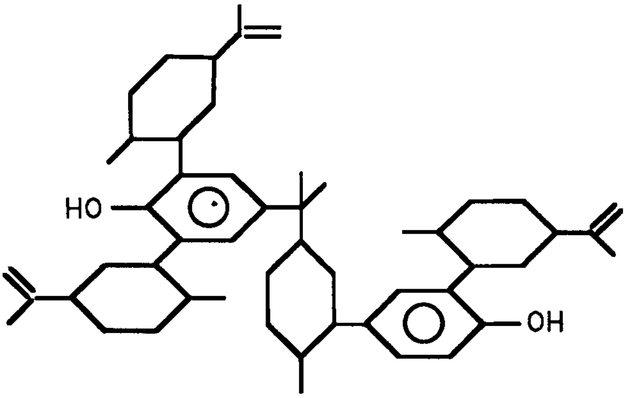

FIGURE 4 Chemical formula of terpene-phenol resin with $d_{OH} = 2$.

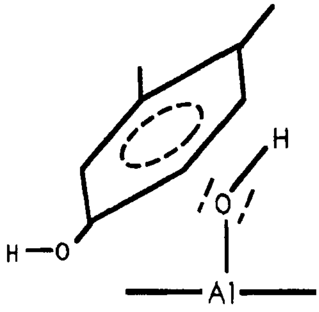

FIGURE 5 Acid-base interactions ($n\cdot\pi^*$-type) between TPR and aluminols at EVA-TPR blends/aluminum interfaces.

group interactions and it explains why preferential interactions between TPR resin and aluminum are favored at the interface.

Secondly, the peel energy, in air and in presence of ethanol, between flexible aluminum substrates (100 μm thick) and various EVA/TPR blends (100 μm thick) molded on thick metallic sheets, was measured by 180° peeling experiments at different peeling rates ranging from 0.5 to 500 mm/min. For all the systems studied, it appears that the experimental values of $\Delta G/G$ are smaller than the theoretical ones, *i.e.* $\Delta W_0/W_0$. This indicates that strong interactions, such as covalent bonds or acid-base interactions, which are not sensitive to the presence of ethanol, are established at blend/substrate interfaces. On the one hand, no covalent bonds have been evidenced by IRAS spectroscopy. On the other hand, acid-base interactions of the $n\cdot\pi^*$-type between the phenolic ring and aluminol are not destroyed by ethanol, since the formation of acid-base pairs between ethanol and the adhesive or the substrate corresponds to lower absolute values of ΔH^{AB}.[14]

Therefore, the discrepancy between experimental results and theoretical predictions can be essentially attributed to acid-base interactions at the blend/substrate interfaces. Considering that the reversible work of adhesion is the sum of two components, W^D and W^{AB}, corresponding, respectively, to van der Waals and acid-base interactions, the term W^{AB} can be estimated from the experimental value of $\Delta G/G$. Moreover, Fowkes and Mostafa[15] have proposed for W^{AB} the following expression:

$$W^{AB} = f \times n^{AB} \times (-\Delta H^{AB}) \qquad (14)$$

where n^{AB} is the number of acid-base pairs per unit interfacial area and f is a correction factor to transform enthalpy values into free energy values and taken equal to unity, to a first approximation. Since the value of $-\Delta H^{AB}(\approx 30\,\text{kJ/mol})$ has been previously determined by IRAS, an estimation of n^{AB} can then be proposed. Typical values of W^{AB} and n^{AB} for EVA/TPR 1, 2 and 3 at different blending ratios in contact with aluminum are gathered in Table II. These values are in good agreement with those available in the literature for other systems.[14] It appears, in particular, that the number of acid-base interactions, n^{AB}, at the interface increases with the functionality, d_{OH} of the resin.

TABLE II
Acid-base component, W^{AB}, of the work of adhesion and number of acid-base pairs per unit interfacial area, n^{AB}, of different EVA-TPR blends/aluminum interfaces

Type of TPR in the blend	d_{OH}	%TPR (by weight)	W^{AB} (mJ/m^2)	n^{AB}(μmol/m^2)
TPR 1	0.7	50	14	0.5
		62.5	17	0.6
TPR 2	1.1	50	30	1.0
		62.5	55	1.9
TPR 3	1.4	50	118	4.0

Finally, the correlation between, on the one hand, the interfacial spectroscopic data and, and on the other hand, adhesive strength measurements in air and in liquid environment, allows us to calculate fundamental parameters of adhesion, in particular, the acid-base component of the work of adhesion as well as the interfacial density of acid-base pairs.

The effect on peeling behavior of different assemblies of the existence at the interface of covalent bonds, which are generally much stiffer than acid-base interactions, is considered in the next sections.

4.2 Effect of Chemical Bonds: Polymer/Aluminum Assemblies

Adhesion of polyolefins to aluminum surfaces is generally very poor and can be improved by introducing functional groups at the polymer surface. Besides surface treatments such as flaming, plasma treatment, for instance, it has been shown that grafting of small quantities of polar groups (acrylic acid, maleic anhydride, etc.) on the polymer chain leads to improved adhesive behavior. The direct evidence of the formation of a chemical bond at the interface between the polymer functions and the aluminols of the metal surface is generally not possible due to the small number of bonds. However, the existence of such bonds has been demonstrated in several cases by using infra-red spectroscopy on model interfaces. Indeed, when the aluminum foil is replaced by γ-alumina and by using a high concentration of grafted species, the presence of a peak at around 1570–1580 cm^{-1} corresponding to an aluminum carboxylate is observed.

On the real assemblies, the chemical contribution can be deduced from the variation of the peel energy in air and in liquid medium. As an example, the behavior of ethylene-vinyl acetate copolymer (EVA)/aluminum assemblies is given here. Spontaneous delamination occurs between these two materials when the polymer is non-grafted although the non-dispersive component of its surface free energy is not negligible. To improve its adhesive behavior, two modifications are made. First, maleic anhydride is introduced during the polymerization (0.39% by weight) leading to a sample called EVAM and, on a second step, the grafting of acrylic acid is realized (sample EVAM-AA). The surface properties of the polymers and the aluminum foil are given in Table III.

Orientation phenomena as evidenced by wettability measurements indicate that the surface properties of both grafted polymers are comparable. The polymer-water

TABLE III
Surface properties of grafted EVAs and the aluminum foil

Surface	γ [mJ/m^2]	γ^D [mJ/m^2]	γ^P [mJ/m^2]
EVAM	42	40	2
EVAM-AA	39	38	1
Aluminum	68	55	13

interaction energy is equal to about 73 mJ/m^2 after 300 hours of contact on water, whereas the value for the non-modified polymer stays around 20 mJ/m^2.

According to Schultz *et al.*,[16] the polar component of the surface free energy of the polymer is proportional to that of the substrate and then one can write:

$$\gamma^P_{\mathrm{EVA}_{\mathrm{Al}}} = \gamma^P_{\mathrm{EVA}_{\mathrm{W}}} \frac{\gamma^P_{\mathrm{Al}}}{\gamma^P_{\mathrm{W}}} \tag{15}$$

where $\gamma^P_{\mathrm{EVA}_{\mathrm{Al}}}$ represents the value in contact with the aluminum and $\gamma^P_{\mathrm{EVA}_{\mathrm{W}}}$ that in contact with water. In the present case, 7 mJ/m^2 will be considered for both EVAM and EVAM-AA.

It is then possible to evaluate the physical interactions between the polymer and the aluminum substrate and their variation in the presence of ethanol, as given in Table IV.

A 180° peel test performed in air and in ethanol measures the strength of the interface. The peel energy is reported (Table IV) for a low peel rate (0.5 mm/min) at room temperature and the decrease in presence of ethanol. It has to be noticed that similar results are obtained for PDMS oil. The locus of failure is mainly interfacial as shown by scanning electron microscopy and wetting measurements after separation. The chemical contributions can be evaluated from the experimental results and the calculated variation of the physical interactions in the presence of the liquid, was done as previously. It can be seen that φ_{chem} increases with the addition of acrylic acid on the polymer chain.

The same approach has been applied to polypropylene/aluminum assemblies. Addition to the polymer matrix of grafted polypropylene chains leads to improved adhesive properties. However, due to the fact that the grafting step induces chain scission, the molecular weight of the grafted species decreases. Consequently, although chemical bonds are formed at the interface between the two materials, the peel energy passes through a maximum when the concentration of maleic anhydride in the blend

TABLE IV
Calculated ($\Delta W_\phi/W_\phi$) and measured ($\Delta G/G$) variations in peel energies of two grafted EVAs/aluminum assemblies

	G [J/m^2]	$\frac{\Delta G}{G}$ [%]	W_ϕ [mJ/m^2]	$\frac{\Delta W_\phi}{W_\phi}$ [%]	φ_{chem} [%]
EVAM	1400	−53	186	−87	39
EVAM-AA	1600	−42	231	−87	52

increases. This effect has been attributed to the decrease of the cohesive strength of the interfacial layer rich in polymer chains of lower molecular weight.

This shows that, even though covalent bonding favors interfacial strength, it does not constitute a guarantee of high performance. The next example shows also that the intrinsic properties of the polymer can be modified locally by the presence of the interface and that the variation of peel energy can be understood by the modifications of the energy of cohesion of the interfacial layer.

4.3 Effect of Cohesive Rupture: Elastomer/Aluminum Assemblies

In the first example (Section 3), adhesion of sealed anodized aluminum to elastomer was due solely to interfacial van der Waals interactions and the locus of failure was interfacial. If the surface treatment of the aluminum substrate is a conversion treatment by phosphatization (called phosphated Al), the failure does not occur at the interface. Contact angles on the metal surface after separation clearly indicates the presence of an elastomer layer. The failure occurs in the elastomer near the interface. However, the energy of failure is always much lower than the energy of peeling of an elastomer assembly in which the aluminum substrate has been replaced by a cotton cloth strip. Therefore, the large difference between these values has been interpreted in terms of length of the molecular chains between crosslinks in the bulk and near the interface.

In Equation (2), W_0 is replaced by the reversible energy of cohesion W_0^c which is given by:

$$W_0^c = 2\gamma_s + W_{\text{chem}}^c \tag{15}$$

When the liquid modifies only the physical interaction, Equation (15) is written as:

$$W_{0L}^c = 2\gamma_{sL} + W_{\text{chem}}^c \tag{16}$$

Equation (4) still applies and leads to:

$$\left.\begin{aligned} W_0^c &= \frac{\Delta W_0^c}{\dfrac{G_L}{G} - 1} \\ \text{with } \Delta W_0^c &= 2\gamma_L - 2W_{sL} \end{aligned}\right\} \tag{17}$$

γ_L and W_{sL} are, respectively, the surface free energy of the liquid and the elastomer/liquid adhesion energy. G and G_L are the measured energies of separation of the assembly in air and liquid.

The results for the SBR/phosphated Al assembly in air and in ethanol are reported in Table V. The physical and chemical contributions to the reversible energy of cohesion of SBR are both important.

The threshold energy of cohesion of the elastomer in the interfacial area can also be evaluated from the peel experiments. According to Lake and Thomas,[17] when the viscoelastic dissipation can be neglected, the threshold energy of failure in the bulk, G_0, can be written as:

$$G_0 = W_{\text{chem}}^c \times g(M_c) \tag{18}$$

TABLE V
Determination of the reversible energy of cohesion of SBR in the fracture zone in SBR/phosphated aluminum assembly

G_L/G in ethanol	ΔW_0^c [mJ/m^2]	W_0^c[mJ/m^2]	$W_{0\phi}^c = 2\gamma_s$ [mJ/m^2]	$W_{0\text{chem}}^c$ [mJ/m^2]
0.44	-52	93	60	33

with $g(M_c) = n$ the number of C—C bonds in the chain between two crosslinks. Because W_{chem}^c is of the same order of magnitude as W_ϕ^c, Carré and Schultz[3] propose to write G_0 as:

$$\left.\begin{aligned} G_0 &= W_0^c \times g(M_c) \\ \text{with } W_0^c &= W_\phi^c + W_{\text{chem}}^c \end{aligned}\right\} \tag{19}$$

This value depends on the degree of crosslinking and has been obtained by a tear test in conditions near equilibrium (low rate of failure and high temperature). The threshold energy of cohesion of the bulk elastomer is taken as a reference ($G_{0_{\text{ref}}}$) and is equal to 100 J/m^2.

If one considers that the tearing (using a geometry of the specimen close to that used in the peel experiment) can be taken as the reference energy of peeling, G_{ref}^c, it is possible to evaluate the energy of cohesion of the interfacial layer of elastomer, $G_{0_{il}}$, knowing that:

$$\frac{G^c}{G_{\text{ref}}^c} = \frac{G_{0_{il}}}{G_{0_{ref}}} \tag{20}$$

where G^c is the energy of peeling of the assembly under the same test conditions (rate and temperature) used to determine G_{ref}^c. The calculation leads to a $G_{0_{il}}$ value of 2.5 J/m^2 in this case. Hence, the elastomer near the aluminum surface is much more crosslinked than in the bulk and the drastic decrease of the energy of peeling of the assembly can be explained by the low cohesion of the interphase.

The overcrosslinking of the elastomer near the interface can be due to a catalytic effect or a migration phenomenon of the curing agent. This example shows that the indirect characterization of this layer is possible.

4.4 Effect of Interdiffusion: Elastomer/Elastomer Assemblies

The autohesion of a styrene-butadiene copolymer (SBR) obtained by a solution process and containing about 26% of styrene, on the one hand, and a polyisoprene rubber (PI) with a high amount of cis 1–4 units, on the other hand, has been studied. Both elastomers contain 50 phr of carbon black and are crosslinked by sulfur.

The same procedure as first proposed by Chang and Gent[18] has been used to study these joints. Before bonding, the elastomer sheets are partially and separately crosslinked to various extents. Two sheets of the same elastomer and with the same degree of crosslinking are brought into contact in a heated press until completion of the reaction of vulcanization. Therefore, symmetrical and homogeneous joints are obtained and the interfacial stresses are minimal. The peel energies can be compared because the final properties of the elastomers are identical whatever the degree of crosslinking before contact. Moreover, Chang and Gent have shown that the strength of self-adhesion of unfilled and peroxide-cured elastomers is proportional to the number of crosslinks formed during the contact. Joints with no interfacial covalent bonds for fully precured sheets up to joints for which the cohesion of the interface is equal to that in the bulk for uncured sheets can be obtained.

Due to the fact that filled elastomers are considered in our case, the state of cure has been estimated from swelling measurements in cyclohexane. The degree of conversion of the vulcanization reaction, α, has been defined as the swelling ratio at the precure time divided by the value corresponding to optimum curing.

On both sides of the interface, the material is identical so that the interfacial energy of adhesion in air and in the liquid can be written as:

$$\left.\begin{aligned} W_0 &= 2\gamma_s + W_{\text{chem}} \\ W_{0L} &= 2\gamma_{sL} + W_{\text{chem}} \end{aligned}\right\} \qquad (21)$$

As previously, the peel test is made at different peel rates and in different media (ethanol, polydimethylsiloxane oil (1.7 cP) and isopropanol). Table VI shows the surface properties of the elastomers and the liquids.

The chemical contribution, φ_{chem}, is calculated according to Equation (9). Figure 6 shows φ_{chem} values for SBR joints as a function of the degree of crosslinking before

TABLE VI
Surface properties of the elastomers and the liquid media

Surface	γ[mJ/m^2]	γ^D[mJ/m^2]	γ^P[mJ/m^2]
SBR	30.6	30	0.6
PI	33.6	33	0.6
Ethanol	22.8	17	5.8
Isopropanol	22.0	16.5	5.5
PDMS 1.7 cP	18.7	18.7	0

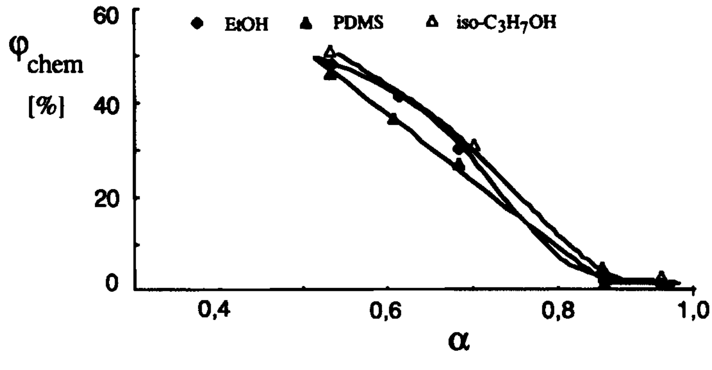

FIGURE 6 Chemical contribution, φ_{chem}, as a function of the degree of precrosslinking, α, of SBR assemblies.

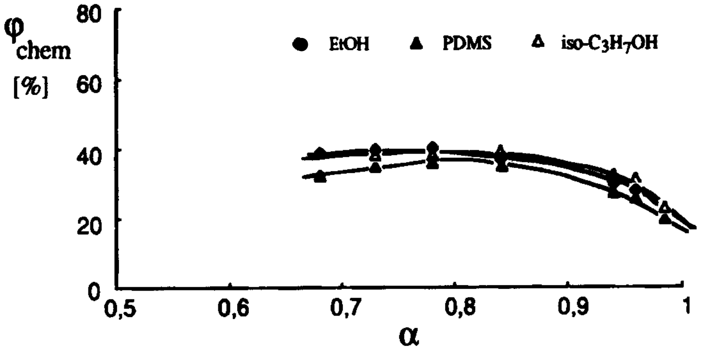

FIGURE 7 Chemical contribution, φ_{chem}, as a function of the degree of precrosslinking, α, of PI assemblies.

assembly. As expected, the chemical contribution is negligible when the degree of precure is close to the optimum of curing; no crosslinking agent is left during the assembly stage for the formation of covalent bonds at the interface. However, φ_{chem} increases progressively only for α values lower than about 0.85. The good agreement seen for the different liquids also indicates that the hypothesis of van der Waals interactions holds for essentially non-polar elastomers such as SBR.

The behavior of PI joints is quite different, as can be seen on Figure 7. For α values close to 1, the chemical contribution is as high as about 20%. As previously, the absence of crosslinking agent does not allow the formation of sulfidic links. Moreover, the maturation effect of the polysulfidic links should not intervene.[19] Therefore, only chain interdiffusion phenomenon can be responsible for the observed behavior at α values close to 1. When the degree of precure decreases (α decreases), φ_{chem} values increase and then level off rapidly, contrarily to what happens for SBR joints. This variation can be attributed to strain-induced crystallization occuring during separation when the interfacial strength becomes higher. The viscoelastic properties are modified and the fracture mechanism changes. Strain-induced crystallization has already been proposed to explain the tear behavior of natural rubber, whereas it is known that SBR is not sensitive to this phenomenon.

This last example shows that the calculated chemical contribution includes the effect of the interdiffused chains and it is not possible to know if:

- the chains are extracted,
- the failure occurs along the chains which have interdiffused,
- a chemical bond formed at the interface is broken.

5 DISCUSSION AND CONCLUSION

The application of the peel test in air and liquid media to different studies of adhesive joints shows that this procedure helps one to understand the adhesion mechanisms in numerous cases. It has to be noticed that the principle of reducing the interfacial energy can be applied to other separation measurements. For instance, it has been successfully used in the study of the adhesive behavior by ultrasonic vibrations[20] of thin metal films evaporated on polyethylene terephthalate. Other results[21] could have been described showing the interest of this approach. However, it is clear that some questions remain:

- The validity of Equation (4) rests on the assumption of identical dissipation factor $f(R, T) \times g(M_c)$ in both air and liquid. The parallelism of the variation of the energy of separation as a function of the peel rate in log-log scales in both media is used as a criterion. However, this criterion may not be sensitive enough to be sure that the simplification is possible. Moreover, Equation (4) applies to viscoelastic dissipation and strictly not to plastic dissipation. Some examples in the present paper definitely do not deal with materials exhibiting purely viscoelastic behavior.
- The evaluation of the physical interactions, W_ϕ, is quite difficult in many cases. It supposes that the surface properties of both contacting materials are known and that the room temperature properties are representative of those in the assembling conditions. If one is confident about the van der Waals components of the surface free energy, the non-dispersive components are questionable. The polar component of the surface free energy is still often used although it has been shown that the acid-base interactions are generally predominant. However, the acid-base characteristics of flat surfaces are not easily assessed. Inverse gas chromatography is adapted to powders such as silica or carbon black but more difficult to apply to polymers.[22] Also, different semi-empirical acid-base approaches are available: Gutmann,[23] Drago,[24] Pearson.[25] Each one has been successfully employed but no consensus develops for one or the other.
- The same questions can be asked for the liquids. For instance, water has been considered as a highly polar liquid for a long time. But water can be considered as an amphoteric liquid with electron acceptor and donor numbers according to Gutmann, for instance. It is clear that the prediction of the variation of the reversible energy of adhesion in the presence of the liquid depends on the characteristics chosen.
- When other adhesion mechanisms intervene, such as mechanical anchoring, interdiffusion, for instance, the principle of the method can still be used but the interpretation is even more complex.
- The presence of low molecular weight materials (polymer chains or additives) and dissolution phenomena at the interface may also play a role.
- The determination of the locus of failure (cohesive or interfacial) is important for the prediction of the reversible energy of adhesion and its variation in the presence of the liquid.

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