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Effect of Orientation and Organization of Polymers at Interfaces on Adhesive Strength

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To gain a better understanding of polymer adhesion, one must take into account the phenomena of orientation and organization of macromolecules at interfaces which can lead to the creation of interphases. The formation of such interphases involves chemical, physicochemical and physical mechanisms which are illustrated by examples taken from our recent work dealing mainly with adhesive assemblies and composite materials.

INTRODUCTION

During the past years, most of our studies were devoted to the understanding of the fundamental mechanisms of adhesion in order to establish quantitative relationships between the intrinsic properties of the solids in contact, the properties of the interface and the final performance of multicomponent materials such as adhesive joints, coatings and paints, polymer blends, filled polymers and composite materials.

Many theories or theoretical models have been proposed to explain the multidisciplinary aspects of adhesion. However, it appears that the phenomena of orientation and restructuring of polymers at interfaces together with the formation of interphases exhibiting properties different from the bulk polymer are of great importance for a better understanding of adhesion phenomena.^{1,2}

This will give us an opportunity to briefly review recent work performed in our Laboratory on this subject.

ORIENTATION OF POLYMER CHAINS AT INTERFACES— POTENTIAL SURFACE ENERGY

Surface energy cannot be considered as being an intrinsic property of a polymer since it can drastically change, depending on the nature of the medium in contact

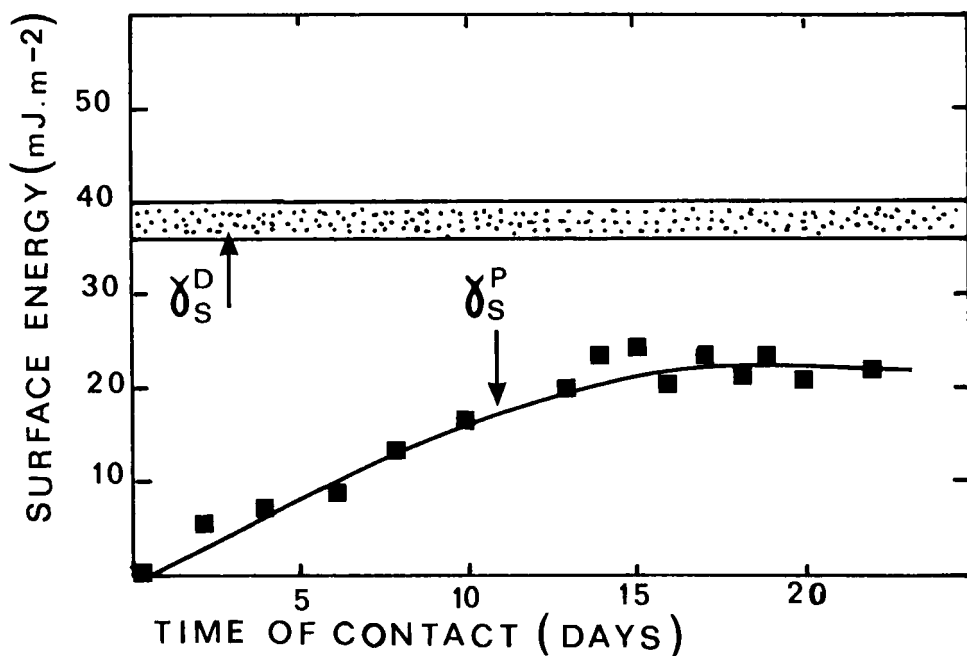


FIGURE 1 Evolution with time of contact on water of the surface energy components of acrylic acid grafted polyethylene.

and the polarity and mobility of the polymer chains. This phenomenon results from an orientation or organization or packing of the macromolecules in order to minimize the interfacial energy between the polymer and the orienting medium. It is, therefore, proposed to replace the static concept of surface energy by the more dynamic concept of potential surface energy.³

An illustration of this concept may be found in the next example concerning grafted polyethylene (PE)/aluminium (Al) adhesion.³

The adhesive strength of a PE/Al assembly is very low. When PE is replaced with a 1% by weight acrylic acid grafted PE, the adhesive strength as measured by a peel test, increases by a factor of roughly 100. However, unexpectedly the surface properties of both polymers are identical, i.e. a dispersive component on the order of 35 mJ m^{-2} and a surface polarity equal to zero. This is explained by potential surface energy; in contact with air (non polar), the lowest possible surface energy is exhibited. It is only when in contact with the polar aluminium that the carboxylic groups of the grafted polymer will orient themselves towards the metal to form strong bonds.

This system has been modelled by following "in-situ" the evolution of the surface energy of the polymers when put into contact with a model highly polar medium such as water. Figure 1 shows the considerable increase of surface polarity of the grafted PE as a function of time of contact. This increase is explained by the orientation to water of the acrylic grafts initially buried in the bulk of the polymer.

A complete thermodynamic analysis of these orientation phenomena which has led to the concept of potential surface energy, has been published.⁴⁻⁶

ORGANIZATION AT INTERFACES—FORMATION OF INTERPHASES

The orientation of the macromolecular chains through interaction with the substrate could constitute the first step in the organization of the polymer affecting several layers and leading to the formation of an interphase. The following examples taken from our recent work show the potential influence of such boundary layers on the adhesive strength of assemblies.

For the sake of clarity, these interphases will be classified rather arbitrarily according to their chemical, physicochemical or physical origin.

Interphase of Chemical Origin

It is generally believed that the adhesive strength of an assembly does not depend on the nature of the substrate when the failure is cohesive within the polymer. We have recently shown that a metallic substrate is capable of modifying drastically the polymerization reaction near the interface.⁷ A DGEBA based epoxy resin has been polymerized in contact with steel and steel metallized with gold, nickel or aluminium. The polymerization reaction is followed, thermodynamically and kinetically, by differential scanning calorimetry and rheological measurements. The chemistry and kinetics of curing are dependent on the nature of the metal and the area of metal/resin contact. The enthalpy and rate of polymerization are very different when the epoxy resin is in contact with one metal or the other as seen from the total enthalpy of reaction ΔH or the time of inhibition of cure at 200°C shown in Table I. Moreover, some substrates such as nickel induce new reactions evidenced by the supplementary peaks in the thermal diagram.

It is, therefore, understandable that for given polymerization conditions, the degree of crosslinking of epoxy near the interface can differ considerably from one substrate to the other. We have verified that the mechanical properties and the durability of assemblies are strongly dependent on the nature of the metal. As shown in Table I the strength of assemblies measured in shear is increased by 80% when going from gold to aluminium although the failure is purely cohesive within the epoxy resin.

Such results obtained on model systems are of considerable importance in practical applications.

This example is concerned with an interphase which could be called of chemical

TABLE I
Enthalpy and inhibition time of curing of an epoxy resin in contact with metallic surfaces—
Shear strength of the assemblies

System	ΔH Curing (kJ g ⁻¹)	Inhibition time of curing at 200°C (min)	Shear strength (MPa)
Epoxy	Gold	0.47	10
	Steel	0.40	14.5
	Aluminium	0.33	18
	Nickel	0.27	12

TABLE II
Threshold value of adhesion T_0 and average molecular weight
between crosslinks M_c of SBR/Al assemblies

	T_0 ($J m^{-2}$)	M_c ($g mole^{-1}$)
SBR (Tearing)	100	12,000
SBR/Anodized Al	63	7,500
SBR/Sealed Al	6	700
SBR/Phosphatized Al	2.5	240

origin since the chemical curing reaction at the interface leads to the formation of the interphase.

Another example of an interphase of chemical origin is given by our work done on elastomer/aluminium adhesion.^{8,9} A styrene-butadiene elastomer (SBR) is adhered on aluminium having received different surface treatments (anodization, sealing, phosphatization) conferring very different surface energies to the metal. Since the failure in peeling is always cohesive within the elastomer, one would expect a unique value of the adhesive strength whatever the surface treatment. As seen in Table II showing the threshold value of adhesion, i.e. measured at zero rate of separation, the adhesion energy depends strongly on the nature of the surface treatment of aluminium.

Although the failure is cohesive within the elastomeric adherent, the energy of cohesion of the elastomer near the phosphatized surface is about 40 times lower than the cohesion energy of the bulk elastomer as measured by tearing. As shown from the calculated values of the average molecular weight between crosslinks M_c , this phenomenon is due to a higher crosslinking density near the treated metal. It is supposed that the aluminium surface directly intervenes on the crosslinking kinetics (catalysis, preferential adsorption of peroxide. . .). In this case, in agreement with Lake and Thomas theory,¹⁰ the interphase results from an over-crosslinking of the elastomer near the metal; for instance, in the case of phosphatized aluminium, the elastomer is 50 times more crosslinked than in the bulk leading to a cohesive strength near the interface 40 times lower.

Interphases of Physicochemical Origin

Interphases of physicochemical origin can also be found as shown in the next examples. The phenomena responsible for the formation of such interphases are, for instance, the migration to the interface of the low molecular weight fraction leading to a mechanically weak boundary layer in polypropylene-aluminium assemblies¹¹ or the immobilization of polymer chains through strong adsorption leading to a glassy behaviour of the polymer near the interface in elastomer matrix-carbon fiber composites.¹²

Polypropylene (PP) exhibits poor adhesion properties to aluminium due to its low surface polarity. An original way to modify the properties of PP is to add to the polymer a small quantity of the same polymer grafted with a polar species such as

maleic anhydride (MA). Since the two polymers are compatible, good dispersion is obtained and the polymer mixture may behave like a bulk grafted polymer with good adhesive properties.

Maleic anhydride is grafted on the homo or copolymer (5% ethylene) in order to get a 4.5% grafting ratio. This grafted product is then diluted into the virgin polymer leading to MA concentrations ranging from 100 to 10,000 ppms.

Through wettability measurements, XPS and IR analysis, peeling experiments in liquid media, it could be demonstrated that the higher the MA content of the mixture, the higher the potential surface polarity and the higher the contribution of chemical bonds to the interfacial adhesion energy. According to these results, the expected adhesive strength of the polymer/aluminium assembly should increase continuously with MA content until a plateau value is reached corresponding to the saturation of all the hydroxyl groups available on the surface of alumina covering the metal. This is not the case as shown in Figure 2; at a given peel rate, the adhesive strength goes through a maximum when the MA content is increased.

During the grafting reaction through the peroxide radical, a chain scission occurs. Therefore, each grafted polypropylene chain will present a molecular weight lower than that of the non-grafted polymer chains in which it is incorporated. Because of the driving force resulting from interfacial attraction, the grafted chains of lower molecular weight will migrate easier and faster and enrich the surface in low molecular weight fraction thus provoking the formation of an interphase of low cohesion.

The experimental curves of Figure 2 giving the energy of adhesion W versus the

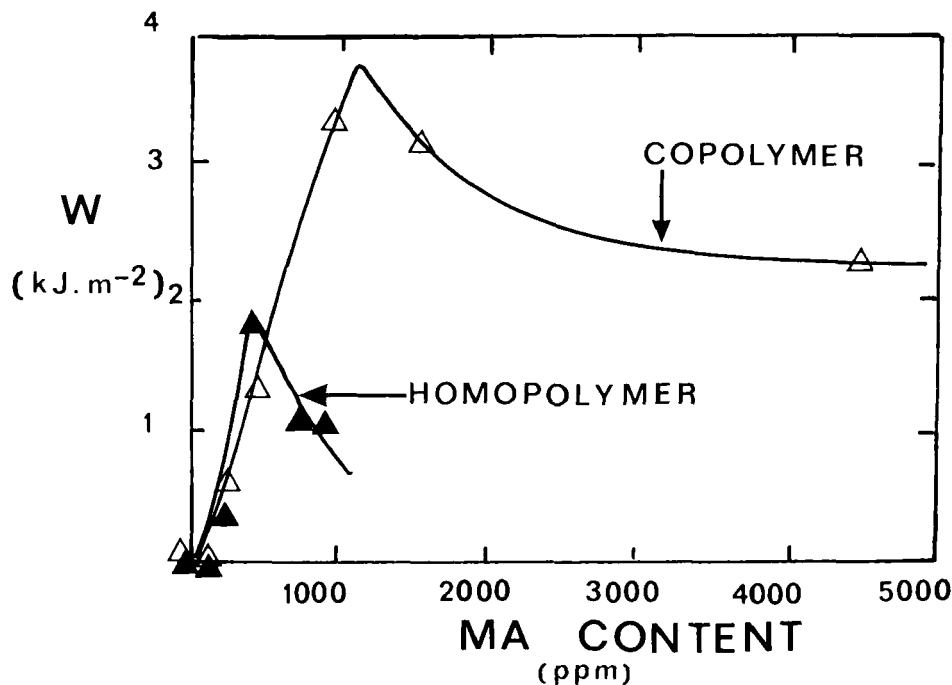


FIGURE 2 Variation of peel energy with maleic anhydride content for polypropylene and ethylene-propylene copolymer (peel rate: 5 mm min⁻¹).

MA content of the polymer can therefore be explained by the existence of two simultaneous mechanisms:

- adhesion increased with MA content due to chemical bond formation
- cohesion of the polymer near the interface decreases as the low molecular weight fraction accumulates.

This dual mechanism implies that the locus of failure should be at the interface for low MA content, whereas, it should be cohesive in the polymer for higher MA content. This was verified by examining the surface composition of the aluminium substrate after separation from the polymer using XPS analysis. For low MA contents (before the maximum), XPS peaks corresponding to pure alumina are observed; for high MA contents (after the maximum), these peaks have totally disappeared leaving only the carbon peak corresponding to the polymer.

This method of adding small quantities of a polyolefin grafted with polar species to the same non-grafted polymer could constitute an interesting way for the improvement of the adhesion of such polyolefins, if the problem of the weak interphase created through migration can be controlled.

The second example of an interphase of physicochemical origin is concerned with carbon fibre-ethylene vinyl acetate copolymer (EVA) composites.¹²

By testing dynamically unidirectional composites containing varying amounts of untreated and oxidized carbon fibres, one observes a drastic change in the viscoelastic behaviour of the EVA matrix in the presence of the highly reactive oxidized fibre, i.e. the relaxation times of the EVA chains are much lower than in the pure matrix or in the presence of the untreated fibre. This is attributed to the formation of an interphase resulting from chains of reduced mobility similar to what is called immobilized rubber in carbon black reinforced elastomers. Strong interactions at the interface with the oxidized carbon fibre leads to less mobile chains and in turn to a glassy or pseudo-glassy behaviour of the polymer layer near the interface.

The adhesive strength of the fibre-matrix interface, or more precisely the capacity of the interface to transfer the stress from the matrix to the fibre is determined by means of the well known fragmentation test on single fibre composites using an acoustic emission measuring device.¹² On Figure 3 it is seen that at temperatures lower than the glass transition temperature of EVA, i.e. -36°C , the fragmentation results agree well with the classical analysis of Cox^{13,12} relating the critical size I_c of the fibre fragment to the elastic modulus E_m of the matrix:

$$I_c/d = K (E_f/E_m)^{1/2}$$

where d is the fibre diameter

E_f , the elastic modulus of the fibre

and K , a constant.

At temperatures higher than T_g , this law is not obeyed anymore. However, by replacing the elastic modulus E_m of the bulk matrix by the equivalent modulus E_m^* corresponding to the glassy state of the polymer, all data obtained at higher temperatures are shifted and verify the analytical model of Cox.

This demonstrates that through strong physicochemical interactions, an interphase of immobilized macromolecules can be created which influences drastically

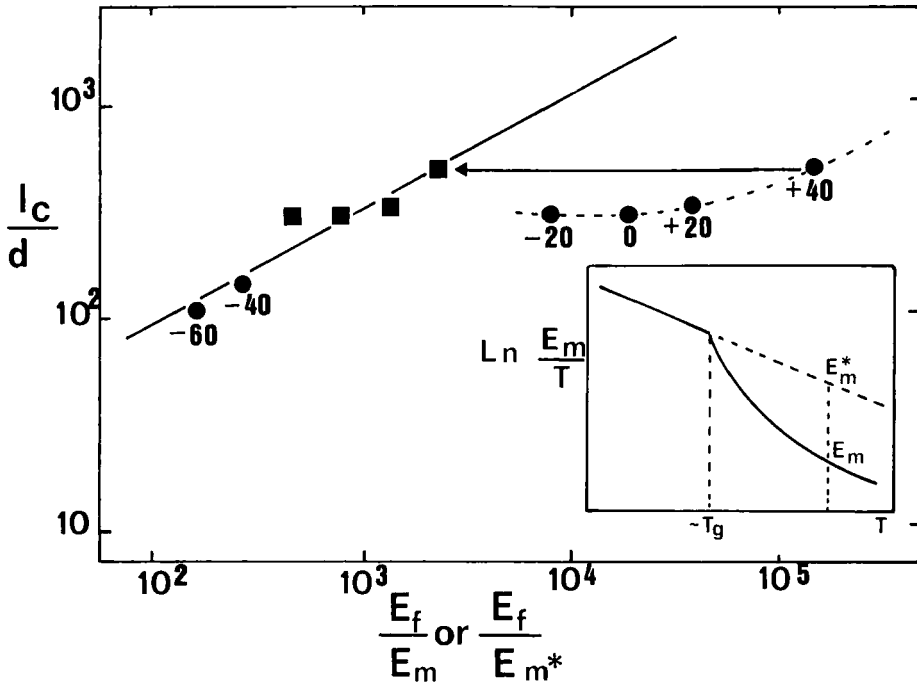


FIGURE 3 Variation of the critical aspect ratio I_c/d with the ratio of fibre to matrix elastic moduli E_f/E_m (on the right: determination of the equivalent elastic modulus E_m^* of the matrix in its glassy state).

the adhesive strength of the fibre-matrix interface and hence the final performance of composite materials.

This type of interphase has also been observed in the case of a styrene butadiene rubber matrix.¹⁴

Interphases of Physical Origin

This last example dealing with an interphase of physical origin also shows that the formation of interphases is largely governed by the level of interfacial interactions. It is well known that an interphase of transcrystalline structure can be created when semi-crystalline polymers are in contact with a solid surface. This phenomenon has been widely described in the literature and is attributed either to crystalline parameters matching or thermal conductivity mismatching or high flow field developed during processing.

An illustration of the importance of such transcrystalline interphases on the micro-mechanical properties of composite materials is given by our recent study of composites made of a polyetheretherketone (PEEK) matrix reinforced with carbon fibres having received different surface treatments.^{15,16}

The thickness and structure of the transcrystalline layer can be modified by the moulding conditions such as isothermal crystallisation at temperatures ranging from 200 to 300°C and in turn can alter the stress transfer capacity of the fibre-matrix interface measured by fragmentation as already seen in the previous example. As

expected the shear strength of the interface depends strongly on these isothermal crystallisation conditions and goes through a minimum value at 240°C which corresponds to the highest rate of crystallisation. More interesting is the fact that the thickness and properties of this transcrystalline interphase are also strongly affected by the level of physical interactions with the carbon fibre. As an example, Figure 4 shows the nucleating ability of the high surface energy oxidized carbon fibre. Under the same experimental conditions, the untreated carbon fibre induces no crystallisation.

It has also been shown that, whatever the conditions, the elastic modulus of these interphases is always lower than the modulus of the bulk matrix leading to a lower stress transfer capacity from the matrix to the fibre.^{15,16}

Such data demonstrate that the formation and characteristics of transcrystalline interphases can be controlled not only by the processing conditions but also by the level of interactions at the solid-polymer interface.

CONCLUSION

Several examples of interphases have been described. Different mechanisms of formation are involved such as:

- orientation of macromolecules at interfaces
- under or overcrosslinking reactions
- migration of low molecular weight species
- strong adsorption followed by reduced mobility of the macromolecules
- transcrystallisation.

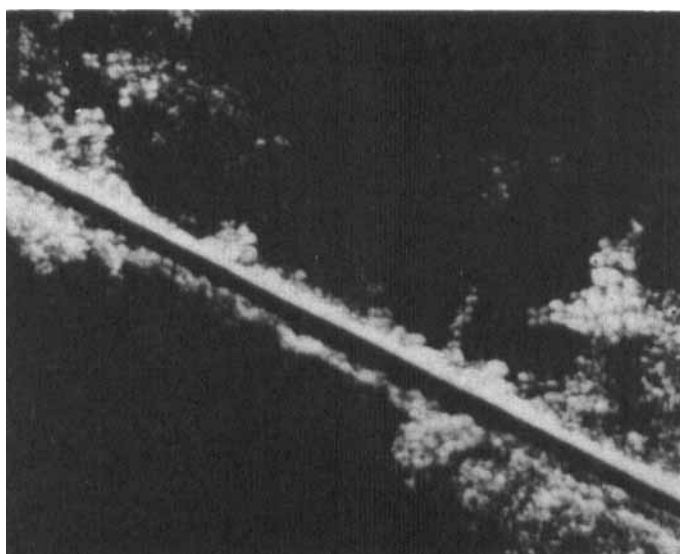


FIGURE 4 Optical micrograph of an oxidized carbon fibre-PEEK interphase (isothermal crystallisation at 240°C during 5 min).

They all greatly alter the adhesive strength of multicomponent materials. Therefore a complete understanding of polymer adhesion allowing performance prediction must take into account the potential formation of these boundary layers.

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