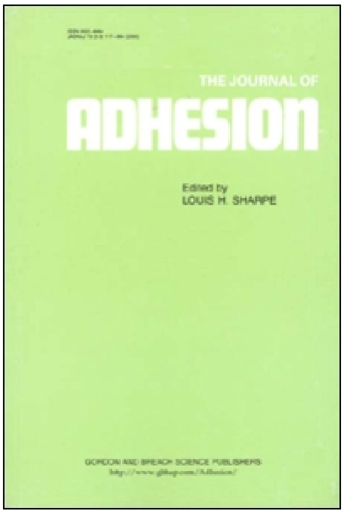

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Some Fundamental Issues in Adhesion: A Conceptual View*

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The role of interfacial interactions in determining the global response of joint systems is discussed in relation to the question of true interfacial failure and the ubiquitous occurrence of interphases. The discussion is from the point of view of systems involving adhesives, coatings and composites rather than, *e.g.*, particle-particle or particle-substrate systems and is strictly conceptual in nature. It is proposed that interfacial interactions, rather than *directly* exerting an effect on the global response of joint systems, are instead the driving force for the many and varied processes that create interphases. It is such interphases, or transition zones between phases, which affect the global mechanical response of joint systems.

Keywords: Interfacial interactions; interfacial failure; directed failure; global mechanical response of joints; interphases; concepts; adhesion; phase transformation

INTRODUCTION

There are many unresolved issues in adhesion. This is understandable because the subject is highly interdisciplinary and this often leads to different interpretations of the same phenomenon (or phenomena – there may be several involved, depending on the particular systems in question) by workers from different disciplines. One of the most fundamental of these issues is the simple matter of what one means when one uses the term "adhesion". This is beyond being purely about

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semantics. It is about (inadvertently) misleading or confusing one's self and one's colleagues by using the term "adhesion" to mean either of two things:

(1) The forces at the interface which cause materials to attract one another. These are not, in most "real world" circumstances, capable of being precisely quantified (unless one knows the actual (real) area of contact and is dealing with simple compounds, precisely characterized, which do not in any physical or chemical sense modify each other by their contact) or
(2) The breaking stress or energy or some other *mechanical* quantitation of the resistance to separation – in the simplest case, of a pair of materials (usually solid objects) which have been joined.

The first relates to the question, "Why do materials brought into contact (in the gross sense) with each other resist separation?", a *qualitative*, equilibrium or quasi-equilibrium issue and the second to the question, "What is the *level* of resistance to separation of a joined pair of materials?", a *quantitative*, non-equilibrium issue.

Therefore, using the same term to refer to these two different phenomena, the first of which relates to the *formation* of joints and the second to the *destruction* of joints is almost guaranteed to confuse. This is not a trivial matter. Such misuse creates problems, which mainly have to do with the confusion of *interfacial* phenomena, called "adhesion", with the breaking strength or failure energy of a joined system of materials, also called "adhesion", which involves mechanical and other processes taking place in the *volume* of the materials, and treating the two as if they are *directly* related, which they are not. It is, therefore, incumbent on workers to say exactly what they mean when they use the term "adhesion".

It is well known that materials in contact with each other influence the structure and/or the composition and/or the properties of one or both materials in the near-interface region – most often called the interphase [1]. The mechanisms that produce interphases are many and varied and it is probably true that interphases are almost always present where two materials join. Therefore, it is generally misleading to speak about such parameters as the "*interfacial* shear strength" of a composite material or a structure such as an adhesive joint. The term to be used should probably be "*interphasial* shear strength", relating to the properties of the transitional phases that exist in the interfacial region.

This, again, is not a trivial matter, as already mentioned in connection with the term "adhesion", because language influences perception. In this case, it leads to the perpetuation of the concept of true and pervasive "interfacial failure" which is thought to result from weak interfacial forces – weak, that is, relative to the cohesive forces of one or other of the adhering materials. In the opinion of the author, and others [2], true interfacial failure is a highly uncommon occurrence (see the following section). The notion of true interfacial failure also leads to the concept of "interfacial *strength*", as if the interface possessed such a *measurable* strength parameter related to the surface energetics of a material combination, independent of the geometry (macro as well as micro) of the joint, of the mechanical properties of the materials in the combination and of the interphase – which it does not.

INTERFACIAL FAILURE

One of the most serious questions relating to adhesion phenomena is, "Does true interfacial failure actually occur when joints are forced to fail solely by (internal and/or external) mechanical influences?" One can argue that interfacial failure has to be a rather uncommon occurrence because the surfaces of "real" adherends are in general irregular, three-dimensional contours (relative to atomic dimensions). On probability grounds, therefore, one should not expect failure to occur exactly along this predetermined, irregular, three-dimensional path (the original interface) in response to some mechanical loading – whether direct or induced [2]. Furthermore, because the surface is three-dimensionally irregular, a simple external mode of loading (*e.g.*, tension, shear) is transformed into complex, mixed, and varying modes of loading from point to point and region to region along the interface. In addition, it is extremely difficult to prove conclusively, in any given actual case, that true interfacial failure occurs for the reasons that:

(1) Most commonly-used surface analytical techniques essentially provide (at their most sensitive level) an average composition of a (usually) relatively small region of a failure surface which may not truly represent the variability of the composition (or the spatial

distribution of residual material) over the entire failure surface. In addition, in many instances, the scale of observation of such techniques is gross enough to miss rather small structures which may be significant in determining the locus of failure in a joint. As Cruzet, Ryschenkow and Arribart [3] have pointed out from the results of their studies of "adhesive" failure in a glass-polyurethane elastomer system using Atomic Force Microscopy (AFM), "...the apparent structures at the surface may be organized at a very small scale, and heterogeneities whose dimensions (typically less than 1000 Å) are much smaller than the spatial resolution of the spectroscopic technique have not been detected yet". They then proceed to show that AFM reveals aspects of the scale and distribution of remaining material (in this case, the polyurethane elastomer) generally undetectable by other means. Their results have very important implications with regard to the location and mechanism(s) of failure in joint systems.

(2) In order to say, unequivocally, that a true interfacial failure had occurred in an experimentally-investigated system, one must establish that there had, in fact, been contact between the two phases in the area that appears bare of one phase; otherwise, it makes no sense to talk about "interfacial" or "adhesion" failure if one does not actually know whether "adhesion" (in the sense of contact) actually did exist in the bare area prior to failure;

(3) All material initially present in a joint does not necessarily remain in the joint upon failure. That is, bulk or interphase material (adhesive, coating, metal oxide, etc., in addition to electrons and other charged particles and various forms of radiation) may be ejected from the joint system as a result of the failure process. A discussion of this is given in Ref. [4]. Such behavior casts serious doubts on the correctness of assuming that fractographic analysis (see (1), above) can unequivocally pinpoint the locus of failure unless appropriate steps are taken to verify that material is not ejected from the system during failure;

(4) In the case of polymer-polymer adhesion, the potential for interdiffusion exists (even though, in certain cases, it may occur over only a small distance); therefore, an *interphase*, rather than an *interface*, is likely to form. Therefore, strictly speaking, there is no interface at which failure can occur;

(5) It is now well-known that the solidification of a liquid in contact with a solid (or even with another liquid or air [5], almost always has compositional and/or structural consequences on the previously-liquid material in the vicinity of the interface. That is, inter*phases*, rather than simply inter*faces*, are formed. This occurs by a number of mechanisms, both chemical and physical, for example, bound polymer (changed, *i.e.*, restricted, segmental mobility), selective adsorption of a component active in producing solidification (changed curing), transcrystallinity (changed morphology), etc.;

(6) When "surface" treatments are performed on materials, the resulting compositional and structural changes produced by the treatment are not usually confined strictly to the surface of the material. That is, these changes occur to some depth, thus producing a region with changed properties (an interphase) which can substantially alter, if not dominate, mechanical response in the vicinity of an interface (see for example, Schonhorn *et al.*, Ref. [6]).

(7) Molecular dynamic modeling studies of the interaction of micrometer-sized two-dimensional particles by Quesnel *et al.* [7] have shown that when the particles are separated under displacement control, atoms are transferred both ways, *i.e.*, cohesive separation occurs, rather than interfacial separation. In addition, the study showed that there is a hysteresis associated with the processes of approach and separation of the particles, *i.e.*, that the apparent surface stress as a function of centroid distance was not the same on approach as on separation. This result suggests that the processes involved in the approach and contact ("interfacial adhesion") of the particles are different from those involved in the separation ("joint failure") of the particles; this reinforces the notion that the processes involved in the making and breaking of joints are fundamentally different – thus, not *directly* relatable.

INTERFACIAL FORCES AND GLOBAL MECHANICAL RESPONSE

The question, "What, precisely, is the role of interfacial forces in determining the ultimate (macro) mechanical response (*e.g.*, strength) of bonded structures such as adhesive joints, composites, coatingsubstate systems, etc.?", is a very fundamental one in adhesion science and it has not been fully, nor finally, answered. Do interfacial forces *per se* determine, by their "weakness" or "strength", the "weakness" or "strength" of joint systems? And do they, by their "weakness" or "strength", directly determine whether the system will fail "interfacially" (determined by means varying from the naked eye to various microscopies and spectroscopies) or cohesively? The simple answer is "No". This is based on a number of factors: (1) what we know to be the highly complex nature of the (micro or sub-micro) mechanical response in even "simple" joint systems (*e.g.*, butt or lap joints); (2) our rather well-developed knowledge concerning the existence of a wide variety of interphases, sometimes even a hierarchy of physcial structures in the interfacial region, with mechanical (and other) properties different from the bulk materials of the joint system. These (and other factors, *e.g.*, local geometries, interfacial microroughness) combine to intervene, as it were, between the interfacial forces and the macroscopic response of a joint. This intervention makes it very problematic to say with certainty that a particular interfacial interaction resulted directly in a specific macroscopic mechanical response.

However, it does seem, from the results of a very large body of work, that the types (read, "strengths" or "energetics") of interfacial forces existing in given joint situations do many times correlate, in a rough and general way, with the macro response of given joints (see, for example, Schultz *et al.* [8]). What, then, is really the connection (the "bridge") between this micro or sub-micro cause and the macro effect? Can a logical, more believable conncetion be found between interfacial forces and joint mechanical response? The search for this connection is made more complicated by the fact that if one is dealing with curing resin systems, which are more or less complex formulations of several materials and not simple compounds, the questions is: "Interfacial forces involving what component(s)?"

Equally complicating, in the case of already polymerized system (*e.g.*, hot-melt, heat reactivated, pressure-sensitive, solvent-borne adhesives), is the fact that they are also more or less complex formulations. Even "single-polymer" materials {*e.g.*, poly(ethylene) PEEK, thermoplastic poly(urethanes)} are not single compounds because, at the very least, the main polymers have a distribution of molecular weights and, in some cases, even a hierarchy of physical structure(s) which further complicates the issue.

In the face of all of this complexity, what then can we say about how interfacial forces affect macroscopic joint response? What is the role of interfacial structure and interactions or, more broadly, is there a credible model that permits us to understand how strcitly surface interactions between contacting phases in a joint affect (global) mechanical behavior of the macroscopic joint system? To answer these questions, let us consider the following conceptual view.

It is reasonable to invoke the concept of interphases (discussed below) rather than the concept of "strength" (presumed leading to cohesive failure) or "weakness" (presumed leading to interfacial failure) of interfacial forces to explain or understand global response of joint systems and apparent modes of failure. The concept of interphases is fruitful in this respect for at least two reasons: (1) interphases are known to exist and (2) they are amenable to treatment (at least in concept) by known principles of mechanics. What is more, the concept of interphases essentially reconciles, or bridges, two "extreme" views of adhesion phenomena: (1) that of chemists – who favor the interface-intensive approach, in which molecular structures *at* the interface which change the interactions energies between the materials of the joint are postulated to act directly to change the mechanical response of the joint; (2) that of mechanical engineers and applied mechanicians – who essentially usually ignore the details of the interface (*i.e.*, it is either weak or strong) and attempt to understand system response in terms of the bulk response of the two joined materials and a geometry.

It would be expected that a mobile (*i.e.*, deformable) polymer or prepolymer brought into contact with a given (solid) substrate will be influenced by contact with that solid in a number of ways. It is also to be expected that interfacial forces will determine the fundamental nature of that influence. However, that influence cannot be the creation of a simple "link" between the two contacting phases, because we know that interphases are essentially always created by *various* chemical and physical processes in the interfacial region. But we know that there is a reasonable (but not complete) correlation between interfacial forces and global mechanical response. Accordingly, it must be that the interfacial interactions are the driving force for the many and varied processes that create interphases. This could occur through, for example, selective adsorption of mobile components (active or passive) in the fluid phase, with compositional consequences as well as determination of conformation and orientation – any or all of which may have long-range (*e.g.*, 50 – 1000 Å) structural and other consequences that are preserved when the system solidifies. In other words, interfacial interactions, rather than being *per se* or directly the cause of global mechanical performance, *indirectly* affect performance by creating, or participating in the creation of, mechanically-mediating interphases, *i.e.*, regions rather than two-dimensional interfaces which, most likely, vary in structure and properties across the region. This, presumably, is the connection between interfacial interactions and global mechanical response. It is a rather important connection, because it bears directly on the matter of interfacial interactions, interphases and global mechanical response and directly impacts the conventional assumptions in this area of work. We present a brief discussion of interphases in the following section.

INTERPHASES

There are many studies which highlight the fact that substrates or fillers of various kinds create interphases by affecting the curing of thermosetting polymers, *e.g.*, epoxy resins, or the structure of thermoplastic polymers in the vicinity of the substrate or filler. Among the earliest studies were those of Kumins and Roteman [9], who showed that the glass transition temperature (T_g) of a PVAc/PVC copolymer was raised by several degrees in the presence of a TiO_2 filler. Kwei [10] proposed a model to describe the effect of filler on polymer segment mobility in filled polymer systems. Droste and DiBenedetto [11] found that the T_g of a thermoplastic epoxy polymer filled with glass beads and a clay was raised by incorporation of this filler. The explanation given by all of these authors ascribed the increase in T_g to "bound" polymer, that is polymer with reduced mobility due to adsorption on a solid.

In more recent work, Dillingham *et al.* [12] showed spectroscopically that the molecular structure in the interfacial region of an epoxy/

aluminium joint varied with the curing agent and the curing temperature and was different from the bulk cured resin. Subsequently, Ondrus *et al.* reported similar findings with epoxy/steel and epoxy/aluminium joints primed with an aminosilane. Garton *et al.* [13] showed that the acidic surface of carbon fiber selectively adsorbed amine curing agent and catalyzed the reaction between the amine and an epoxy resin. Zukas *et al.* [14] discovered, in a model system of an amine-cured epoxy and an activated alumina, that the alumina modified the rate of the crosslinking reaction and produced material in the interphase that was structurally different from the bulk. These studies illustrate that contact with certain solids can alter polymerization reactions and produce interphases with structures different from the bulk polymer. Using NMR imaging and FT-IR microscopy, Mavrich *et al.* [15] showed an accelerated curing rate for an epoxy resin in the presence of both Kevlar-49^{TM} and D-glass fibers and a preferential segregation of the epoxy resin to the Kevlar-49 fiber. These are all examples of production of interphases by *chemical* modification of bulk material.

Interphases produced by purely *physical* processes are also well-known. An example is the remarkable change in the morphology of the surface region of crystallizable polymers, *e.g.*, polyethylene, nylon 6, FEP Teflon, etc., which can be induced by solidifying the polymer from the melt in contact with a nucleating substrate. Such a process produces the so-called transcrystalline region. This region has properties (particularly mechanical properties and wettability) that are different from the bulk (see Kwei *et al.* [16]) and these properties influence the mechanical behavior of joint systems of materials which contain them (see Schonhorn *et al.* [17]).

These examples illustrate the concept that interfacial forces act to determine the composition or structure of the interfacial region. These forces do so by determining, or influencing, the processes that will occur in that region – processes that produce interphases which are themselves the actual agents that influence the global mechanical properties of joined systems.

The following example rather well illustrates the danger in assuming that interfacial forces have a *direct* role in determining global joint response.

A REVEALING EXPERIMENT ABOUT "INTERFACIAL" FAILURE

Thompson [18] at the Naval Research Laboratory in Orlando, Florida, described the following experiment to the author and said that he did not understand the results:

He prepared 90-degree peel test specimens using a cured nitrile rubber (39% acrylonitrile content) approximately 6.4 mm (1/4 inch) thick and steel of sufficient thickness so that it did deform significantly during the peel test.

The nitrile rubber was prepared for bonding by first scraping its surface to remove gross amounts of wax and mold release agent and then solvent-wiping it. It was then chlorinated by wiping the surface with a filter paper soaked with a 5% solution of trichloroisocyanuric acid (TCICA) in ethyl acetate and allowing it to dry.

The treated rubber was bonded to the steel, in a press, using an unsupported epoxy film adhesive. These specimens were then tested in a 90-degree peel test. They gave peel strength of about 4.4 KN/m (25 pli) with failure in the interfacial region (what would commonly be called "interfacial failure").

Thompson then did a second test. He took a fresh specimen made with chlorinated rubber and then, bending back the rubber, made a shallow cut in it, with a sharp razor blade, parallel to the steel surface near the interface and measured the 90-degree peel strength of this specimen. He found that this gave a very high peel strength of about 22KN/m (125 pli), with failure completely cohesive in the rubber. Failure did not propagate in the interfacial region, at a lower peel strength, as it did for the original chlorinated specimen. Rather, it failed cohesively in the rubber at a high peel strength despite the fact that, in all other respects except for the razor cut, this specimen was identical to the original chlorinated specimen.

This is a very important result, which illustrates that a joint system which initially exhibits mechanically "weak" behavior – with failure in the interfacial region – can be made to give "strong" behavior simply by essentially changing the *local* geometry in the interfacial region. This change has nothing at all to do with interfacial interactions. For a more complete discussion see Ref. [19].

EXPLANATION OF THE OBSERVED BEHAVIOR

A reasonable explanation for this observed behavior is as follows:

The razor cut leads to a stress concentration which, during testing, "directs" the failure away from the interfacial region and into the bulk rubber. That is, the razor cut determines that the stress concentration in the interfacial region of the "non-cut" specimen, which caused failure initiation (and propagation) in the interfacial region, is directed away from the interfacial region and relocated to the *bulk rubber* near the interface (really, inter*phase*). So, failure initiates in the bulk rubber and, because the stress concentration is now located in the bulk rubber and not in the interfacial region, it propagates in the bulk rubber and this leads to a high peel strength.

CONCLUSIONS

1. One should be careful to specify what one means when one uses the term "adhesion", which has at least two common meanings among workers in the field. Used carelessly, it can mislead or confuse.
2. True interfacial failure in most joint systems involving real materials in real situations is uncommon or, at the very least, not unequivocally confirmable on several grounds, *e.g.*, probability, interdiffusion, loss of material in the joint by ejection during failure, the presence of interphases and the limitations of analytical (detection) methods.
3. Interfacial interactions, rather than directly influencing the global mechanical behavior of joints, are the driving force for the many and varied processes that create interphases. It is these interphases, rather than the interfacial interactions *per se*, that directly influence the global mechanical behavior of joint systems. However, interfacial forces initiate and influence the processes that produce such interphases.
4. The experiment involving directed failure of the adhesively-bonded nitrile rubber-steel joint reinforces the notion that failure initiates and propagates where *local* stress exceeds *local* strength. This is most likely to occur in a local region where the stress concentration

is high. And what determines the local stress? Presumably, that is determined by the mechanical properties of the materials in the joint (including interphases) and the joint geometry, in addition, of course, to the test parameters – all of these – in *a systems way*. This implies that the local stress is not determined *per se* by the interfacial properties of the materials in the joint. In particular, the behavior of the joint is not, in general, determined by whether those interfacial forces or that boundary layer are "weak" or "strong". One might also generalize to say that the basis of the mechanical behavior of any real joint system is far too complex to permit one to draw simple connections between interfacial forces and mechanical response.

5. A joint that exhibits failure in the interfacial region at some relatively low failure stress does not necessarily have an inherently "weak" interface or "weak" boundary layer. That is, it does not necessarily have an interface that can only be improved, *e.g.*, by surface treating one or both adherends to increase interfacial forces. What one may need to do, in fact, is to decrease, remove or relocate a stress concentration in the interfacial region, thereby causing the failure to go elsewhere in the joint. While surface treatment of one or both adherends may accomplish this, it is clearly not the only way to do it, as the experiment with the razor cut shows. The razor cut may not be a very practical or a very convenient way to increase the failure stress of a joint. However, the result of the experiment surely makes a strong fundamental point about the importance of understanding the matters of stress concentration and directed failure in joints and their influences on joint performance.

The summary conclusion to be drawn is that failures that occur in joints in the interfacial region should not be succinctly characterized as being due to "weak interfacial forces" or a "weak boundary layer". Those kinds of ("interfacial") failures may, in fact, be driven by mechanical and geometric factors.

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