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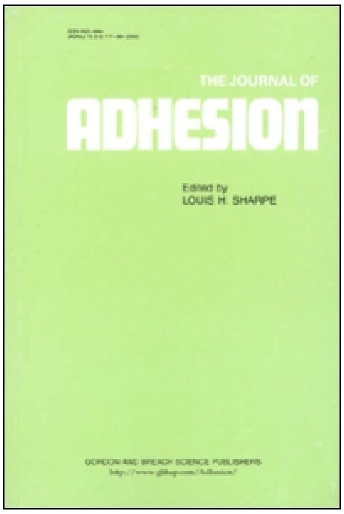

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Keynote Address

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KEYNOTE ADDRESS†

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INTRODUCTION

I thought that what I'd do for this talk would be simply to present some personal points of view on what I considered to be some important (and unresolved, at least in my mind) problems in the science and technology of adhesion and also to say something about what I think we ought to be doing about them.

I thought I'd talk about:

1) Certain aspects of adhesion theory
2) Boundary layers ("interphases")
3) The interphase vs the interface
4) Conservation of material in a joint during failure
5) Problems in determining locus of failure
6) Fracto-emission during joint failure
7) Structure in thermoset materials
8) Non-destructive evaluation

THEORIES OF ADHESION

I'd like to remind you that all major theories of interfacial adhesion, to varying degrees, point to the 2-dimensional interface as the sole source of strength or weakness . . . performance . . . in an adhesive joint. That is, that interaction energies between atoms or molecules at the interface determines joint performance—through polar groups, strong interfacial interactions, etc. . . . which is generally the point of view of the chemist. Implicit in this is the notion that you

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can identify, isolate and assign direct, simple cause and effect relationships between 2-dimensional interfacial structure and macroscopic mechanical response of an adhesive joint.

The mechanical engineers, the stress analysts and the fracture mechanics people have another point of view—different from the chemist. They don't usually consider the interface but attempt to understand joint response in terms of the bulk response of the materials comprising the joint and a geometry.

I think that it makes sense to try to develop ways to modify interfacial adhesion as chemists seem to like to do, particularly since modification of an interfacial *region* plays a role in the matter of durability in adverse environments. However, I believe that we get into trouble when we try to interpret what we think we have done to the interface (microscopically) by making mechanical measurements of gross macroscopic *systems*—that is, joints—without having good models with which to connect the two; that is, having models which connect the micro-cause with the macro-effect. I feel that there is room for a potential "middle ground" which can bridge these two extreme points of view. This "middle ground" needs much more study than it's been given. It involves the consideration of boundary layers or, as I like to call them, *interphases*.

BOUNDARY LAYERS ("INTERPHASES")

We get into difficulty when we consider that an adhesive joint consists solely of two adherends and an adhesive. We have this difficulty because solids, such as metals and polymers, generally are themselves composite structures. This can modify their mechanical response, particularly when a layer as, for example, a surface layer (an interphase) which has a response different from the bulk is an integral part of a joint made with such a solid.

Boundary layers on *metals* are generally oxides. The mechanical (and, of course, other) properties of an oxide on a particular piece of metal depend on the history of that particular piece of metal, so interphase properties are determined by the conditions that generated them.

The matter of interphases in *polymeric materials* is much more complex and subtle than it is in metals. This is so because of the great variety in behavior among polymeric materials due to the interplay of functional, structural and morphological factors. In addition, polymers are always a mixture of compounds because they always have a molecular weight distribution. Finally, we usually have to work with polymers which are compounded with fillers, plasticizers, extenders, mold release agents, etc., and this makes the problem even more complex.

THE INTERPHASE VS THE INTERFACE

We certainly know that interphases exist and that they must influence the mechanical behavior of adhesive joints. Given this, we have to find ways to measure their appropriate properties and then to develop methodologies to calculate joint mechanical response which include these properties. The question is, how do you do it?

It's clear that interphases which are, in general, quite thin relative to the joints in which they are present, will not have much effect on small deformation properties of the joint. However, they can have remarkable effects on the ultimate properties, e.g., breaking stress, of the joint. This is particularly important if they are sensitive to various environments—such as temperature and moisture. It is also highly probable that interphases are not homogeneous, in the sense that their composition, structure and, therefore, properties vary across their depth.

If you believe what I've said about interphases having important effects on joint behavior is true, then several questions immediately arise:

a) How do you model the joint to include interphases?

b) What are appropriate properties of the interphase to measure?

c) How do you measure these properties?

I believe this is an area on which some effort needs to be focussed. Certainly the composites people are doing that. Despite its inherent complexities, what I have said provides a conceptual way in which one can go about the job of analyzing joint behavior in a realistic way. At the very least, the inerphase model has the virtue of being demonstrably close to reality.

On the other hand, if one believes that the inter*face,* rather than the inter*phase,* plays the major role in determining ultimate properties of a joint and its behavior in hot/wet environments, then one should substitute *face* for *phase* in the questions which I just asked and consider how, even in concept, one rationally goes about working the inter*face* into a mechanical model of the joint. I mean, one can at least talk conceptually about the "conventional" mechanical properties of an inter*phase,* which has a large enough assembly of atoms or molecules to have a (shear or tensile) modulus or a Poisson's ratio or, if you define it carefully, a strength (or breaking stress), or a strain energy release rate, useful for modelling. On the other hand, I don't see, even in concept, how one could measure (or even rationally assign) mechanical properties to an essentially two-dimensional array of atoms or molecules, which is what an inter*face* is, except perhaps in an oriented monolayer on a liquid hypophase. Furthermore, I'm not sure about concepts of tensile and shear strength in such a two-dimensional array except, perhaps, in an oriented monolayer on a liquid hypophase. Finally, I certainly would not consider it likely that failure will occur along a highly-irregularly-contoured, three-dimensional path (the original inter*face*), based usually on arguments involving liquid/solid interfacial models which say that the interface is "weak" (weak in what way? relative to what?) when, on probability arguments alone, I would expect such a failure path to be a highly unlikely one.

"POLAR" GROUPS AND JOINT STRENGTH

As I said before, it is really difficult to assign, with any real degree of confidence, direct, simple, cause and effect relationships in the study of mechanical behavior of joints (for example, breaking strength). I'm sure that all of you are familiar with many studies in which workers have added carboxyl or "polar" groups to polyethylene with a resulting increase in the strength of joints made by melt bonding to aluminum. They have then claimed that the reason for higher joint strength is the stronger interactions between the carboxyl groups and the metal (or metal oxide) at the interface. That is, the explanation involves directly the notion of a "stronger interface". However, there are alternative, and perhaps more logical, explanations for this improvement.

One of them is this. A (mobile) polymer in contact with a given substrate will develop a particular interfacial structure and composition. This interfacial structure will be characteristic of the composition and structure of both the polymer and the substrate, as well as the ambient conditions. It is most reasonable to expect that this interfacial structure acts as a "template", determining the organization of the polymer to a depth of at least tens but perhaps hundreds and, in some cases, even thousands of Angstroms away from the original interface. Solidification preserves this organization to create, in effect, an interphase with unique properties which becomes a permanent part of the joint, influencing its mechanical response.

So . . . the alternative view becomes that the interface, rather than being *directly* the cause of enhanced joint performance ("stronger interface"), is *indirectly* the case of enhanced joint performance through its creation of a mechanically-mediating interphase, a *region* rather than a two-dimensional interface. Carboxyl groups in polyethylene would be expected to cause molecules containing them to be preferentially adsorbed over molecules not having carboxyl functionality, resulting in a different conformation (and, perhaps, even composition) of the polymer at the interface and creation of an interphase which is different from that of the unmodified polymer.

Further, it is well known that in semi-crystalline polymers such as polyethylene, when we solidify them from the melt in contact with a solid substrate, we can produce a (microscopically) visibly different structure in the polymer near the interface—the so-called transcrystalline structure—which has mechanical properties different from the ordinary bulk structure of the polyethylene from which it came. This, at the very least, puts on shaky ground the postulate of a simple cause and effect relationship between the failure load of a joint and polar groups at the interface.

The point again is that considerable attention should be given to the origin, structure and properties of the interphase—because we know that interphases are a part of joints and do influence their behavior.

CONSERVATION OF MATERIAL IN JOINTS DURING FAILURE

We very often use fractography of adhesive joints to determine locus of failure and to diagnose problems in a joint. So far as I know, it's always tacitly assumed that all joint material is conserved during the failure process.

Conclusions which we reach about the locus of failure, and about the failure process itself, from fractographic examination may be flawed if we make the assumption that material is conserved. That is, those conclusions may be flawed unless we do collateral studies to prove that material is not ejected from the joint during failure. The work that I'm going to talk about was done many years ago during an internship assignment in my laboratory . . . but it was never published.[1]

Single-lap joints were made from transparent polycarbonate adherends using a simple UV-curable adhesive. They were then loaded in tension and the initiation and propagation of failure was photographed with a movie camera, using a mirror to look at the joint simultaneously from the front and side.

I show below two photographs of such a joint, with the center 1/8-inch bonded,

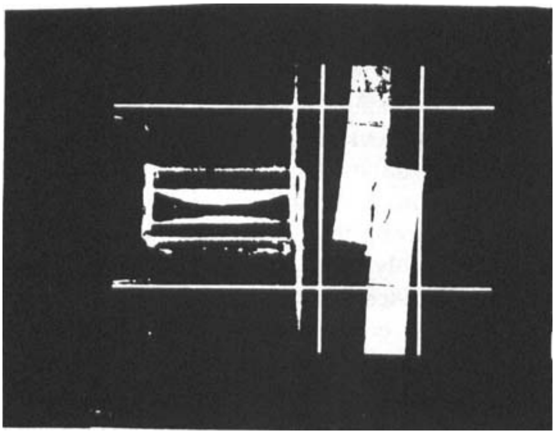
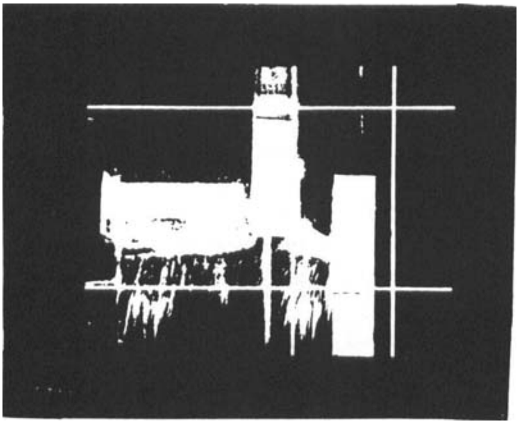


FIGURE 1

A

Configuration of impending failure



B

Final separation

as it is about to fail (a), and as it finally separates (b). You can clearly see that considerable material, apparently particulate, is ejected from the joint at failure. Therefore, material was *not* conserved in this joint during failure. If one also observes the fracture surfaces of the adhesive on the two adherends from that failed joint one sees that they are very hackled and rough. That indicates that a large amount of energy was stored and then rapidly dissipated in the adhesive at failure. The material almost "explodes" at fracture because it is quite brittle. This explains the relatively large amount of material ejected at failure.

However, the major point that I want to make is that the *potential* always exists, even in joints which don't have relatively brittle adhesives, for material ejection to occur, particularly if the joints are fractured at high strain rates. It's simply a matter of the degree to which this occurs and, therefore, the degree to which the interpretation of fractographic evidence is made more complicated and questionable. I believe that this is an extremely important matter to which we should pay some attention, because it raises the question of whether or not interpretations of fractographic evidence are always sound and, in fact, whether conclusions drawn from the usual evidence is always credible. Remember that the production of particulates may, in fact, result from an entirely different mechanism or mechanisms from that (or those) which initially produced the failure of the bonded assembly, *e.g.*, reflection of a release wave from the traction points in a tension-induced failure.

As Tom Dickinson and his coworkers at Washington State University have pointed out from their recent studies of fracture-inducted material ejecta, the aggregate surface area of the ejected material particles may be greater than the cross-sectional area of the fractured sample; therefore, ejecta should be considered in any description of fracture for most materials. As they also point out, high strength materials yield the most finely-divided ejecta with high surface areas. This is, of course, because those are the materials which usually store the highest strain energy prior to fracture, therefore the ones which produce the more violent "explosions" at break.

LOCUS OF FAILURE

As I've just said, a very important part of the study of the failure of bonded joints is determination of the locus of failure. From that information you can draw a number of important and useful conclusions regarding the properties of the joint components such as: the goodness or poorness of "adhesion", *i.e.*, the strength or weakness of the interphase, the suitability of the surface preparation of the substrates, etc.

The most popular methods for determination of the locus of failure are the various surface sepectroscopies—Auger, XPS, SIMS and variations thereof, etc., which identify the surface composition—and SEM, which visualizes the surface topography and, if operated in a certain mode, the surface distribution of certain elements. The virtue of all of these is their sensitivity, which increases with the further development of the instrumentation, to detect smaller and smaller amounts of various atoms.

However, as sensitivity gets greater and greater, you might want to ask the question, "Does the information which we get from these instruments of every-increasing sensitivity and selectivity truly teach us more about the failure process or are we merely learning more and more about less and less?" By this I mean that we are looking at progressively smaller and smaller aggregates of atoms, or of structure, or of topography . . . and then using the information from these smaller and smaller ensembles to reach conclusions about macroscopic mechanical behavior (*failure*) of a bonded assembly. A follow-up question might be . . . "Can you treat these smaller and smaller pieces of information as if they are truly representative of the *macroscopic* failure process?"

In our complicated systems, we really don't understand in much detail why or where the failure initiates at the molecular level and how in detail it produces the failure of a joined system at the macroscopic level. That is, we don't know either what series of events or what causes of that series of events produces what we see by surface analytical measurements. In fact, we don't even know, in most cases, if what we are looking at is related to a cause of failure or is a result of failure or what!

For example, we fail a hypothetical joint between adhesive, A, and two metal adherends, B1 and B2, each of which has a similar oxide layer. Assume that the joint actually fails in the oxide layer of B1. However, because the breaking load is large and the stored energy prior to failure is high, the release wave produces a shock which causes a secondary failure, at least in part, in the adhesive layer remaining on B2, and *that* material is partly expelled from the joint, taking with it the "split" oxide from B1. The true or primary failure was actually in an oxide layer, but surface analysis would show that one adherend had oxide on it and one had primarily adhesive. The conclusion would be that the joint had failed primarily "in adhesion". That would be incorrect, because the surface on B2 was produced as a result of a secondary process which occurred after the primary cohesive failure in the oxide.

The point is that we need to know much more about the details of the failure process before we can be sure that we aren't drawing false conclusions from the results of analysis of the surfaces of a failed joint.

FRACTO-EMISSION

This brings me to another related subject on which the Dickinson team is doing work. This is the matter of particulate and radiation emission from fracturing systems, which Dickinson calls "fracto-emission". These emissions include electrons, ions, neutral atoms, photons and radiowaves.

One striking conclusion from the work of this group is that when adhesive joints as, for example, between polymers and other materials such as glass, metals or dissimilar polymers, are fractured in what they call an "interfacial" or "adhesive" failure mode, the emission intensities, quote ". . . often exceed cohesive failure signals by orders of magnitude, the energy distributions are considerably higher, and the durations of the emission after fracture are often many hundreds of seconds as compared with only a few seconds for the cohesive cases. As previously discussed, the key physical phenomenon that is responsible for these unique emission characteristics is the separation of charge when interfaces between dissimilar materials fail."[2]

The work of this group has been aimed, up to the present, at understanding the physical phenomena involved, and not necessarily how these phenomena may be used to gain an understanding of the failure mechanisms of adhesive joints. It is my feeling that work should be started within the adhesion community aimed at seeing how Dickinson's studies could be used to broaden our knowledge of fracture in adhesive joints at the fundamental level. I am sure that some of you are familiar with Dickinson's work but I urge that some positive steps be taken to explore the application of his work to the area of failure in bonded systems.

Further in this regard, DeVries' group at the University of Utah has done considerable work using a combination of electron spin resonance (to measure the generation of free radicals resulting from bond breakage), FTIR (to measure the presence of end groups) and molecular weight determination of material taken from specimens of materials pulled to various stages up to failure (to measure how molecules get chopped up), to get at what happens at the molecular level during the failure of materials.

I think it would be very worthwhile for those of us interested in the failure behavior of bonded systems at the molecular level to become more familiar with these sorts of techniques which measure things that happen at the molecular level during failure. Furthermore, we should be developing methodologies for connecting this sort of fundamental information with what happens at the macroscopic level, in ways which will be useful *specifically* to adhesion scientists or technologists.

What I'm saying is that adhesion scientists should be working hard on the problem of the relationship between the microscopic events in materials failure and the macroscopic response of systems of joined materials. Furthermore, that there are techniques out there which other workers are using, which may be appropriately applied to the problem, and we should be investigating them and developing them to suit our own purposes.

STRUCTURE IN THERMOSET MATERIALS

A potentially important area for consideration is the matter of structure or morphology in thermoset polymers. Much has been done in the area of crystallizable thermoplastic polymers—most notably, polyethylene, where it was shown that the properties of the materials were, as is to be expected, highly dependent on the morphology induced in the material by processing. However, very little has been done with thermosets except for a few studies by Koutsky[3] and Drzal[4] and some others, which produced evidence of a nodular structure in cured epoxies. Nothing, to my knowledge, has been done on a more fundamental level except for Wu's work at NBS . . . but that relates mainly to segmental structure. The work is preliminary and I'm not sure whether its aimed at discovering whether a heirarchy of structure exists in thermosets.

Significant structures in thermoset polymers would be expected to influence properties. So, if we knew how to visualize these structures and, eventually, how to manipulate them (as we do with the crystalline structure in crystallizable thermoplastics) we would understand a great deal more about how to manipulate properties. The big questions, of course, are:

a) Is there likely to be significant structure and what is its basis?
b) How do we visualize it?
c) How do we manipulate it?
d) What are its effects on properties?

This is a difficult challenge, because it is possible that microscopic structure in many thermosets may be no more than random fluctuations in cross-link density. That is, there would be no structure—but we need to know that. However, it is more likely to be something like islands of high cross-link density material in a sea of lower cross-link density material. The question then becomes "Are the sizes of the islands such, and are the differences in cross-link densities between the islands and the sea such that we can perceive structure?". I don't know the answer to that but I think that this is an important enough question that we ought to get some studies going to find the answer.

NON-DESTRUCTIVE EVALUATION

One of the most cost-saving quality control procedures for bonded structures is non-destructive evaluation, the Holy Grail of which has been a method providing a clear *a priori* assessment or outright measurement of the strength of a bonded assembly. Methods for NDE have used ultrasonic radiation (many techniques in this area), X-radiation and, most recently, nuclear magnetic resonance imaging which is in early stages of development. The most common of these methods uses ultrasonics, at least in the aircraft industry. All of the techniques attempt to detect flaws in bonded structures—with flaws of certain size or frequency of occurrence generally being the criterion for rejection of a bonded assembly. None of the techniques is *a priori* capable of determining the probable strength of a bonded structure, except by a long history of correlative testing of parts of identical geometry and association of strength with flaw size and geometry.

No technique, so far as I am presently aware short of destructively testing a bonded structure, can measure its strength. One can assess probable strength by the ultrasonic technique which I mentioned a moment ago and one can uncover flaws, but one can't measure strength non-destructively. One reason is that there is no fundamental correlation between small deformation properties which, *e.g.*, ultrasonic techniques generally measure, and failure properties, even in joints of the simplest geometry. Failure initiates where *local* stress exceeds *local* strength. Local stress cannot usually be determined except by birefringence and perhaps interferometric methods and then usually only in optically-transparent materials. Another reason is that the mode and rate of loading which ultrasonic transducers apply to a bonded system may be, and usually is, quite different from what the part, or even a test specimen, will actually experience in a realistic loading to failure. There is also the problem of scale. It is usually the microscopic, rather than macroscopic, stress concentration which is important in failure initiation and I am not aware of the development of microscopic birefringence and interferometric methods which are applicable, at the moment, to solid films. Were such methods to be available, they would essentially point the finger at a likely area for failure initiation—certainly a useful piece of information—but not provide a measurement of the likely breaking stress of the bonded assembly.

In my opinion, it is not likely that we will have an ideal NDE method, one which provides a measurement of bonded assembly strength, in the near future unless some new fundamental knowledge about materials behavior becomes available.

SUMMARY

1. We know that interphases are a part of joints and that they can influence their mechanical behavior. We need to know more about them, for example:

   a) How do you model the joint to include interphases?
   b) What are the appropriate properties of the interphase to measure?
   c) How do you measure these properties?

2. There are alternative ways to explain joint behavior other than by strong and weak interfacial forces. Interphases can be created by conversion of surface-influenced conformational structures into unique structures extending into the bulk of a polymer and joint behavior can be mediated by these created structures. We need to look into this.

3. All material comprising a joint is not necessarily conserved during failure of a joint. This fact can lead to erroneous conclusions based on data from surface analysis about the mode and the locus of failure in a joint. We need to know much more about the details of the failure process and about its relationship to the ejection of microscopic and macroscopic fragments from failing joints to be sure of our interpretations.

4. The phenomenon of fracto-emission, which involves submicroscopic particles such as electrons, ions, neutrals, and various forms of radiation, is another aspect of conservation of material in joints. It is, therefore, related to the loss of microscopic and macroscopic fragments which I have just mentioned. As for the micro and macro cases, we need to know much more about the failure processes

which lead to these submicro emissions from a joint. We need to tailor our work to the needs of adhesion scientists and technologists.

5. There are experimental techniques such as ESR, FTIR and molecular weight determination which, in combination, can help us to understand the molecular basis of failure. We need to be paying more attention to them and to adapting the experimental protocols to our own needs.

6. We do not know for sure whether thermoset polymers have microscopic or submicroscopic structure. Such structure, if present, could influence mechanical and other properties of thermosets, in a way similar to how variations in crystalline structure affect the properties of thermoplastics. It seems, therefore, that it is important for us to look into whether or not some significant structure exists in thermoset polymers.

7. The Holy Grail of NDE—assessing *a priori* the probable failure behavior of a bonded structure—is not within our reach at present for good theoretical reasons.

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