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## **The Interphase in Adhesion**

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# The Interphase in Adhesion†

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The role of weak boundary layers (WBL) in determining the breaking stress of adhesive joints has been proposed to be that of a discrete surface layer of material with strength properties inferior to the bulk material from which it originated. The breaking strength behavior of various polyethylene-epoxy adhesive lap joints has been used as *prima facie* evidence for the presence or absence of WBL. So-called WBL in PE appear not to be removable by extraction, by abrasion or by fractionation but they seem to disappear when one uses PE as a hot-metal adhesive. We shall attempt to place the WBL matter in better perspective by discussing boundary layers in a general way; that is, evidence for their existence, what they might be where we can isolate and identify them, how they develop and how we can control their properties and, finally, how they influence joint behavior. We conclude that the WBL postulated to explain the behavior of unmodified PE is probably a fiction and that the mechanics of the composite system alone, independent of any material property change in the vicinity of the interface, can determine that the joint shall fail in a thin layer of PE (with properties no different from the bulk) near the interface. Modification of PE mechanical properties in a thin layer near the interface, as by crosslinking or the presence of a transcrystalline structure, can markedly change the mode and locus of failure. The basis for these changes may be as "simple" as a decrease in stress concentration at the joint edges associated with the rise in toughness of the PE produced by cross-linking or transcrystallinity in the surface region.

## INTRODUCTION

Too often, adhesive joints are considered to consist of only three parts—two adherends and an adhesive—when, in reality, many adherends and adhesives may exist as layer structures in a joint. That is, such materials may have upon them surface layers with characteristics different from the bulk. The nature of such surface layers and their effects on adhesive joint behavior have been discussed by Bikerman in the context of "weak boundary layers."<sup>1</sup>

† This paper was presented at the *Symposium on Recent Advances in Adhesion* during the 162nd National American Chemical Society Meeting, September, 1971.

His ideas have not received an acceptance in proportion to their usefulness in developing an understanding of the mechanical behavior of adhesive joints.

Accordingly, we would like here to discuss boundary layers ("interphases") in a more general way; that is, evidence for their existence, what they are, how they develop and how we can control their properties and, finally, how they influence joint behavior. Additionally, we will discuss, in introductory fashion, what we will call, for now, "virtual" boundary layers.

## THEORIES OF ADHESIVE JOINT STRENGTH

The current view on what causes materials to stick together are these:

(1) The *chemical reaction theory* which states that the adhering materials undergo chemical reaction with each other to form primary valence bonds at the interface. The creation of primary valence bonds supposedly strengthens the interface so that interfacial or "adhesional" failures do not occur. While it may be true that chemical reaction does sometimes occur at the interface, there is no proof that such reaction contributes to the mechanical strength of an adhesive joint.

(2) *Mechanical adhesion* or "*hooking*," is sometimes looked upon as an essential part of two materials sticking together. The fact that very high joint strengths can be obtained when very smooth adherends are used, for example glass, tends to weaken any widespread applicability of such a concept. It probably has some validity in the case of porous adherends such as wood, cloth and paper.

(3) The *electrostatic theory* treats the adhesive-adherend system as a capacitor which is charged due to the contact of two different substances. The strength of the joint is presumed due to the existence of an electrical double layer.

Derjaguin<sup>2</sup> proposed the electrostatic theory based in part upon the fact that fracture of a joint can sometimes lead to electrification of the fracture surfaces and even to electrical discharge and electron emission. He says that separation of the parts of the capacitor, as occurs during breaking of the joint, leads to separation of charge and to development of a potential difference which increases until a discharge occurs.

There is no *a priori* reason to believe that the phenomena resulting from the *breaking* of an adhesive-adherend system have any connection whatsoever with the phenomena involved in the *making* of an adhesive-adherend joint. Furthermore, there has not been any credible evidence which has shown that the two electrically charged fracture surfaces are identically the

same two electrically neutral surfaces which were placed in contact initially to form the system.

4) The *diffusion theory*, by Voyutskii,<sup>3</sup> maintains that diffusion of polymers across the interface determines joint strength, and that surface contact alone is not sufficient. The requirement of diffusion alone is sufficient to restrict the applicability of this theory to those systems in which diffusion can occur. This means, essentially, that it is restricted to systems of polymeric materials. It cannot apply to systems involving one or more hard solids, e.g., glass or metals (really metal oxides), since sensible diffusion cannot occur in these systems during the times and at the usual temperatures employed in the adhesive joining process.

Mutual diffusion of certain combinations of polymeric materials does, of course, occur. That it can be the basis for a broad understanding of adhesion phenomena is seriously open to question.

5) We come, finally, to the view of adhesion and joint strength phenomena which is, in our opinion, the most general and widely applicable of all the present views. This is the so-called *mechanical deformation theory* or the *rheological theory of adhesive joints*.<sup>1</sup> This theory, in substance, says that whatever the cause of interfacial adhesion, the strength of adhesive joints is determined by the mechanical properties of the materials making up the joint and by the local stresses in the joint. It is not determined by interfacial forces because clean failure "in adhesion" is a highly uncommon occurrence. Failure is essentially always cohesive, in the adhesive or adherends or both, or in some boundary layer.

Note, particularly, that this theory does not concern itself with interfacial forces (Van der Waals, valence, electrostatic) or "hooking" but it does consider boundary layer phenomena.

It is our opinion that the simple hypotheses of this theory, and the notion of boundary layers, constitute potentially the most powerful approach to understanding the mechanical behavior of adhesive joints which we have today. The theory need not (and should not) be interpreted so narrowly as to apply only to breaking strength. It should be regarded more generally as a theory of mechanical behavior of adhesive joints. Joints are viewed as composite structures whose mechanical behavior (deformation and failure) can be described by applying the principles of analytical mechanics. The difficulty in this approach is basically the difficulty in setting up and solving exactly the system of equations describing the joint. Even the simple lap joint has not been described satisfactorily, analytically. All the theories of lap joint behavior, as de Bruyne points out,<sup>4</sup> "... find a maximum shear stress on the very edge of the adhesive layer at each end of the overlap and

yet this edge, being a free boundary, can develop only tangential tension or compression but no shear, which should be zero at this very place." That is, the theories provide an inadequate analysis. The point to be made here is that the mechanical deformation theory of adhesive joint behavior is potentially capable of describing the mechanical response of adhesive joints. Assuming this capability, the theory can be used to make predictions, *a priori*, of the mechanical behavior of joints.

## BOUNDARY LAYERS

There are problems which arise from considering adhesive joints to be "simple" composite structures of adherend 1, adherend 2 and adhesive—that is, considering them to consist solely of three bulk solid phases, each characterized by its own single set of material constants. The principal problem is that, in general, solids may have upon them surface layers which have characteristics different from the bulk. That is, many solids are themselves composite layer structures and this can modify their mechanical response when the surface layer (the boundary layer) is an integral part of a structure containing the solid in question. Thus, any analysis of mechanical behavior of adhesive joints must take account of the possible presence and influence of boundary layers.

There cannot be any dispute that certain kinds of boundary layers exist and that they do influence adhesive joint mechanical behavior. We know that a joint made with oily cold-rolled steel will be relatively weak compared to one made with thoroughly degreased steel, unless we use an adhesive able to absorb or disperse the oil. This oil is a simple boundary layer. Waxed paper has on it a boundary layer, wax, which gives this material release properties. Poly(vinyl chloride) is frequently formulated with plasticizers to give it flexibility. Many of these plasticizers migrate to the surface of the PVC to form a liquid, oily layer. This is a boundary layer.

All of the above are examples of boundary layers with properties obviously different from the base bulk material. Most important, as far as we are concerned, is that the mechanical properties of the layers are different from the mechanical properties of the bulk and that they, therefore, influence mechanical properties of joints that we make with them. All of the above are examples of potential weak boundary layers.

## Metals

What about boundary layers on metals? Intrinsic boundary layers on metals are, of course, usually oxides. The mechanical (and other) properties of an

oxide on a particular piece of metal depend on the history of that particular piece of metal. These properties may be different from the properties of an oxide on a piece of metal of originally identical composition but which had a somewhat different history. In other words, boundary layer properties may be dependent upon the conditions used to generate them. For example, oxide layer thickness can have a marked effect on the strength behavior of a particular adhesive joint. If one examines single-lap joints made with identical aluminum pieces which have been anodized for different lengths of time, one finds that joint strength decreases with anodizing time (see Table I). Since

TABLE I  
Effect of Anodizing Time on lap joint strength<sup>a</sup>

Adherends	Joint strength (psi)	
	5 min. Anodize	30 min. Anodize
$\frac{1}{8}$ "-2024T3 Aluminum	3900	2150
$\frac{1}{8}$ "-6061T6 Aluminum	3575	875

*Adhesive:* Poly(vinyl butyral)-phenolic, cured 165°C, 30 mins., 1100 psi pressure.

*Anodizing Conditions:* 15% (aqueous) H<sub>2</sub>SO<sub>4</sub>, 10 amp/ft<sup>2</sup>, 23°C, unsealed.

<sup>a</sup> Data of F. A. Keimel, private communication.

oxide thickness increases with anodizing time, one draws the conclusion that the thicker oxide results in lower joint strength. This should not be surprising since stress distribution in a joint is a function of the thickness (and some other properties) of the various members making up the joint and the oxide layer (a boundary layer) is a part of that joint. The point is that the strength of the joint may be changed by changing some geometrical or mechanical property of a boundary layer and this fact is most often neglected in attempts to understand adhesive joint behavior.

### Polymers

The matter of boundary layers in organic polymeric materials is considerably more complex and subtle than in metals. The complexity of the problem arises from the tremendous variety in behavior among polymeric materials because of the interplay of functional, structural and morphological factors. Added to this is the fact that an organic polymer is literally never a single component material, because it is never of a single molecular weight. Further,

the materials with which we deal are usually compounded (with fillers, extenders, plasticizers, etc.) and this adds yet another order of complexity to the problem. Finally, composite structures containing certain materials exhibit characteristic (weak) boundary layer behavior when, in fact, the existence of a (weak) boundary layer has never been demonstrated but only inferred, solely on the basis of joint strength measurements.<sup>5</sup> In such cases, it is possible that the mechanics of the loaded structure alone, independent of the existence of any boundary layer, can account for such behavior. We will return to this particular subtlety later.

### THE ADHESIVE JOINING OF POLYETHYLENE

Perhaps we can use the results of some studies on the adhesive joining of polyethylene to illustrate the matter of boundary layers in polymeric materials. It is difficult to join, in what is loosely called a structural manner, any of the myriad varieties of polyethylene using conventional adhesives (epoxies, polyesters, etc.) without prebond treating the polyethylene. The reason usually cited for this difficulty is that the material is waxy and nonwetttable and what one needs to do to improve its joinability is to improve its wettability. To accomplish this, the material may be flamed, subjected to a corona discharge or immersed in conventional laboratory glassware cleaning solution (sodium dichromate in concentrated  $H_2SO_4$ ) or some other oxidizing solution. All of these treatments alter the chemical functionality of the surface as evidenced by a reduced water contact angle. It is this improved wettability which is usually cited to be the reason for improved joint strengths through oxidation, polar groups, stronger surface interactions with the adhesive, etc. In other words, the improvement is considered to be strictly a surface effect. However, recent work has shown that wettability changes are probably secondary or side effects of the conventional treatments, and that the primary effect to be desired is a change in the mechanical properties of a thin surface layer in the polyethylene, in the order of 1000 Å or so.

The primary evidence in this regard comes from Schonborn and Hansen<sup>6</sup> and from Morris.<sup>7</sup> The first authors exposed polyethylene to an R.F. excited glow discharge in noble gasses, a process they called CASING. They found that a piece of CASED polyethylene heated above its normal melt temperature will retain its shape. This is because the treatment produces a thin, tough, crosslinked surface region on the polymer. The crosslinked region forms a container for the molten polymer, as Figure 1 shows. They obtained the "skin" for examination, by extracting the soluble interior in a suitable solvent, and found it to be quite thin. Figure 2 shows a plot of thickness vs time of bombardment for a high-density polyethylene. We see that the "skin"

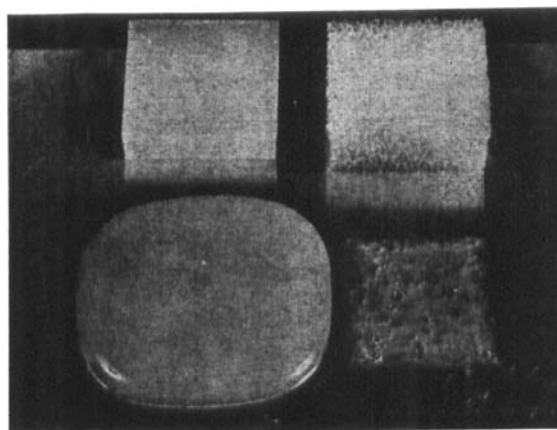


FIGURE 1 Effect of heating above normal melting temperature on polyethylene CASING-treated (top row) and untreated (bottom row). Material on right is foamed polyethylene. (Photo courtesy R. H. Hansen).

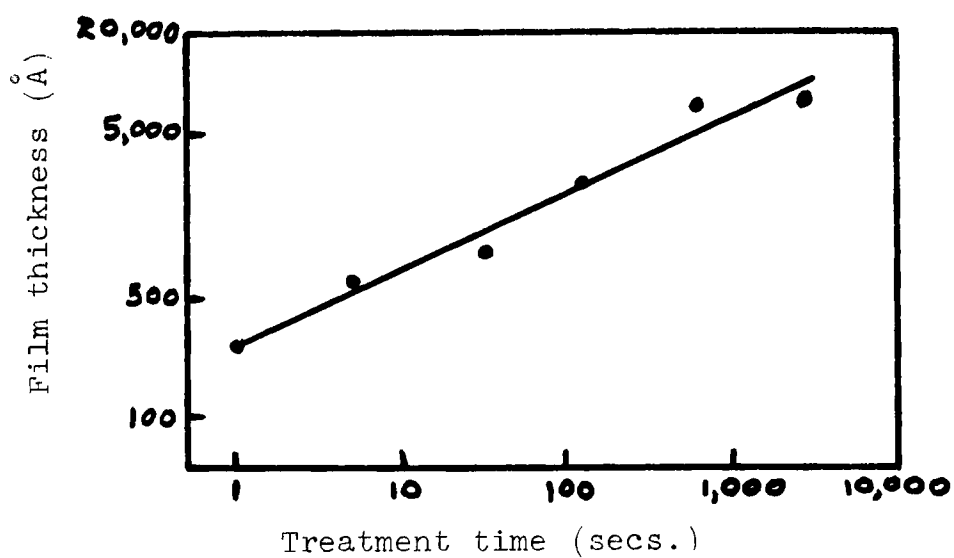


FIGURE 2 Estimated "skin" thickness on polyethylene resulting from CASING. CASING gas is helium at 1 mm. pressure. Adapted from Schonhorn and Hansen, *J. Appl. Polymer Sci.* 11, 1461 (1967).



thickness varies from about 300 Å at 1 second to about 10,000 Å at 10,000 seconds. Since they also found that a 5 second exposure was sufficient to maximize its joinability, with a conventional epoxy adhesive in an aluminum single-lap joint, it appears that, in this instance, a layer only 500–1000 Å or so thick governs this behavior. Here, then, is an example of a boundary layer which has been fabricated in a polymeric material—a boundary layer which dramatically increases the strength of joints made with the material.

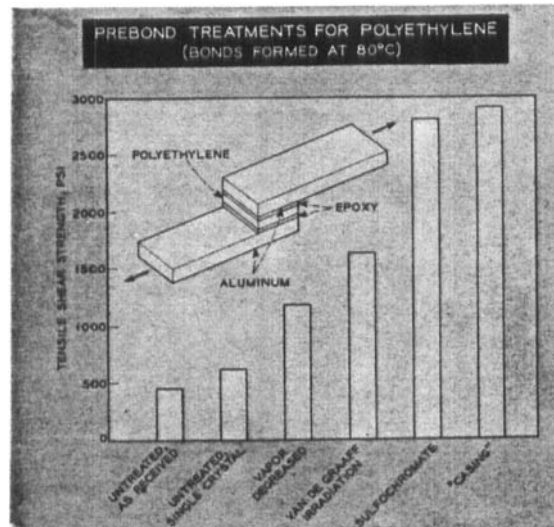
These authors also found that the water contact angle was virtually unchanged from that on the unexposed material provided treatment times were short (5 seconds or less).

Morris<sup>7</sup> treated various polyethylenes in aqueous ammonium persulfate for various times and measured their joinability with a conventional epoxy adhesive using an aluminum double-lap joint. He found marked increases in joint strength with treatment time. He also found, despite the fact that ammonium persulfate is a strong oxidizing agent, very little evidence of polymer oxidation either by ATR or contact angle measurements. ATR spectra of untreated and treated material were substantially the same and in all cases the treated material showed a  $\gamma_c$  no more than 5 dyne/cm greater than the untreated. He did determine, by solvent extraction, that the treated material contained about 1% by weight of insoluble material. This was the only substantial change produced in the material by the treatment. He concluded that crosslinking of the surface region of the polyethylene was the primary effect of the treatment.

Figure 3 is a bar chart comparing the strengths of aluminum single-lap joints made with a conventional epoxy adhesive and variously treated high-density polyethylene. Joints made with polyethylene treated with glass cleaning solution, by CASING and with elemental fluorine<sup>8</sup> (not shown) at ambient conditions all give equivalent strengths. This despite the fact that their  $\gamma_c$  are widely different. The fluorinated material has a  $\gamma_c$  of about 20 dynes/cm and, in addition, exhibits a gel skin as does the glass cleaning solution treated material.

According to these studies, then, the only common property produced in these polyethylenes by the various treatments which give high joint strength is a thin crosslinked or gel surface layer. Although the mechanical properties of these "skins" have not been measured, because of their extreme thinness, we can probably assume, on the basis of the properties of bulk crosslinked polyethylene, that they will be considerably tougher than uncrosslinked material. It may well be the increased *toughness* (meaning here increased resistance to crack propagation) of these surface regions which is directly responsible for increased joint strength.

Let us turn now to a final item in the interphase or boundary layer behavior of, particularly, polyethylene.



**FIGURE 3** Breaking strength of joint shown as a function of various treatments of polyethylene (high-density).

Polyethylene and other crystallizable thermoplastics, under certain conditions, exhibit the phenomenon of transcrystallinity. Transcrystallinity refers to the morphological condition induced in such materials by solidifying them from the melt, in contact with a substrate. The surface region next to the substrate develops a columnar structure obviously different from the normal spherulitic structure of the bulk polymer. Figure 4 shows this transcrystalline structure in polyethylene, which had been melted and solidified in contact with copper.<sup>9</sup>

The transcrystalline structure is, of course, a boundary layer. It is a boundary layer for which some dynamic mechanical property data are available. Kwei's data<sup>10</sup> for transcrystalline polyethylene are shown in Table 2. The properties were measured in a direction normal to the columns. Both the storage and loss part of the Young's modulus are larger than for bulk material. The storage modulus is more than twice that of the bulk and the loss modulus almost  $3\frac{1}{2}$  times. So the mechanical properties of this surface region are very different from the bulk. This is an example of a boundary layer which was created in a different way and which has a different structure from the CASING layer. However, interestingly enough, it affects the joining properties in much the same way as the CASING layer. That is, joints made with polyethylene in which the inducing substrate had been etched away, presumably without disturbing the structure, gave strengths close to those of the same but CASING treated polyethylene.<sup>11</sup> The transcrystalline material, additionally, showed considerably higher  $\gamma_c$  values than

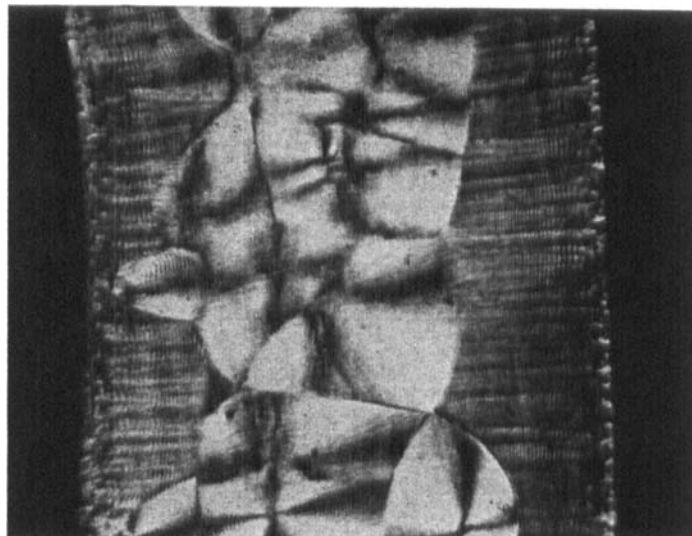


FIGURE 4 Transcrystalline region (columnar structure) in high-density polyethylene melted and solidified in contact with copper. (Courtesy H. M. Zupko)

TABLE II  
Dynamic mechanical properties of surface and bulk regions of high density Polyethylene<sup>a</sup>

	Young's modulus (dyne/cm <sup>2</sup> )	Loss modulus (dyne/cm <sup>2</sup> )
Bulk	$9 \times 10^9$	$2 \times 10^8$
Surface	$1.97 \times 10^{10}$	$6.7 \times 10^8$

<sup>a</sup> Ref. 10.

for normally molded polyethylene. However, on heating at 80°C for 1 hour in a nitrogen atmosphere, the  $\gamma_c$  returned to the normal lower value, without destroying the transcrystallinity and without affecting the increased joinability. Transcrystallinity has been said to be induced only by "high-energy" substrates but this was shown to be incorrect by Fitchmun and Newman.<sup>12</sup> Figure 5 shows an extensive, clearly defined transcrystalline region, prepared in the author's laboratory, in a high-density polyethylene melted and cooled against FEP Teflon.<sup>14</sup>

I think the broad conclusion to be drawn is that the response of polyethylene to mechanical influences which directly involve the surface region is governed primarily by the response of the surface region. This region behaves, in unmodified polymer, *as if* it has strength properties inferior to the bulk. The crosslinking treatments which we have been discussing modify the

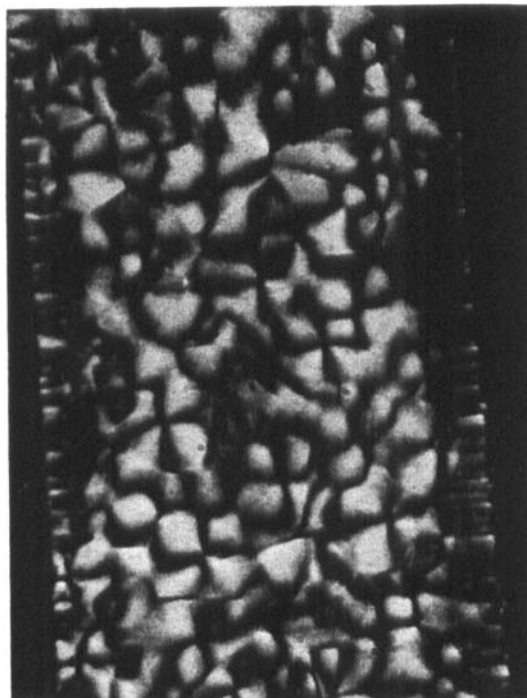


FIGURE 5 TranscrySTALLINE region in high-density polyethylene melted and solidified in contact with FEP Teflon.

mechanical properties of the surface region and shift the locus of failure from a superficial to a deeper site and also, probably, modify the mode of failure.

All of the preceding discussion has dealt with cases in which a boundary layer has been shown to be present, e.g., oxides on metals, a transcrySTALLINE or crosslinked surface region in polyethylene. Subsequent discussion will be concerned with cases in which a structure exhibits characteristic weak boundary layer behavior, but no weak boundary layer (in the sense of a discrete layer, with mechanical properties inferior to the bulk) has been shown to be present.

#### **"VIRTUAL" WEAK BOUNDARY LAYERS**

The presence or absence of a surface region of material with strength properties inferior to the bulk seems to have become the omnibus explanation for the weakness or strength of joints made between crystallizable thermoplastics

and higher modulus conventional adhesives. We seriously doubt that such layers exist, at least in the case of the particular work which we have been discussing. The evidence for their existence is purely inferential and related to joint strength alone. The reasoning goes that weak boundary layers are present because the joint is weak and, conversely, the joint is weak because weak boundary layers are present. There has been no evidence, independent of joint strength and related measurements, to demonstrate that they exist. Such evidence must be forthcoming in order to give this very tenuous concept some credibility.

We feel that the basis for a more reasonable explanation for the joint behavior may be found in the mechanics of the joint. Materials of different moduli and Poisson's ratios when joined will develop a stress concentration at the edges of the joint in response to an applied load. This stress concentration will be higher the greater the disparity in moduli and Poisson's ratios. Rigid epoxy adhesives typically have shear moduli in the range  $1.5 - 2.2 \times 10^5$  psi; high-density polyethylene typically in the range  $0.3 - 0.6 \times 10^5$  psi. Such a large disparity can lead to large stress concentration at the joint edge, no matter what the mode of loading. Such a large stress concentration can cause the composite structure to fail at loads which produce average stresses over the joint area far below characteristic failure stresses for the isolated bulk materials of the structure. Furthermore, the restraint exerted by the high on the low modulus material would be expected to be highly localized with respect to the interface. That is, the high stress field near the interface would decay rapidly with distance from the interface into the low modulus material to become characteristic of the larger scale stress field in the structure. Such a highly localized, high stress field would cause the low modulus (the "weaker") material to fail in a highly localized region near the interface, creating the illusion of a weak boundary layer. We are not prepared at this time to discuss in detail the effects of such a local stress field on the mechanical behavior of material near the interface. We simply wish to put forward this alternate hypothesis to explain certain instances of apparent weak boundary layer behavior.

There are other details of the problem which we have not touched upon but which, in certain instances, might be controlling for the joint behavior. For example, single lap joints stressed in tension attempt to deform to a shape involving minimum strain energy. In attempting to deform to this minimum strain energy configuration the joint develops large tearing stresses at the ends of the lap. These stresses, if not relieved by yielding of the adherends and/or of the structure (the adhesive) within the joint, will result in opening mode failure of the joint at relatively low loads. These stresses have been accounted for analytically and observed experimentally. They can be very large relative to the average stress in the joint.

Another detail of joint behavior which we have not discussed is the effect on joint strength of the wedge angle, at the joint edge, between the two materials making up the composite structure. We know that the stress concentration at the joint edge is probably related to the angle enclosed by the material faces.<sup>15</sup> Consideration must, therefore, be given to this angle and to the factors which determine it (rheology, wettability, details of joint preparation, etc.), and to the details of its effects on the mechanical behavior of the composite structure. Finally, some notice must be taken of the way in which the stress fields in the structure interact with each other and the effect(s) of this on the individual materials in the structure and the response of the structure as a whole.

The point to be made from all of this discussion is that a complex of (interacting) factors enter into the mechanical response of a composite structure to an applied load. It is, therefore, not productive nor useful to dismiss apparently unusual behavior by means of a succinct phenomenological characterization of such behavior—unless there is positive, credible evidence to support such a characterization. That is, one should not characterize apparently low joint strength as weak boundary layer failure unless one has rather good evidence that a weak boundary layer is, in fact, present. The breaking strength of a joint alone is a very sterile parameter on which to base conclusions regarding mechanisms or modes or causes of joint failure. It will be far more productive, in addition, to consider the energetics of the deformation and failure process and the detailed mechanics of the joint.

## CONCLUSIONS

(1) When one studies the deformation and failure of an adhesive joint, one is studying, first and foremost, a mechanical phenomenon. One is studying, directly, the mechanical response of a composite of materials to the application of a load. Therefore, it makes a great deal of sense to try to understand what that response means in mechanical terms.

(2) In many instances, boundary layers with properties different from the bulk materials are involved in the mechanical response of a composite structure. Therefore, attempts should be made to characterize such boundary layers and account should be taken of their effect on the response of the composite structure.

(3) There are cases in which composite structures exhibit breaking stresses considerably lower than one would deem reasonable on the basis of the breaking stresses of the materials comprising the structure. The behavior of such structures should not be succinctly characterized as weak boundary layer behavior without credible evidence that such boundary layers actually

exist. It may be that such behavior is due to the mechanics of the structure, and the boundary layer may, therefore, be virtual rather than real.

(4) Finally, the use of energy criteria and the consideration of the detailed mechanics of the joint are probably far more productive toward understanding joint response than the uncritical use of an average failure stress.

### Acknowledgment

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