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Durability of Composites and Adhesive Bonds

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Abstract
Any consideration of the durability of the high performance composite materials and structural adhesives used in aerospace construction must recognize that these are brittle materials and that their failure mode is characterized by flaw growth and propagation. One can easily anticipate a variety of flaws and defects; surface cuts, internal cracks due to stress relief and deliberate holes cut for fasteners. In this presentation we wish to discuss yet another type of flaw in fibrous composites and adhesive bonds that is inherently present because of the processing methods used to fabricate composites or bonded joints. These flaws are microvoids created by air entrapment that usually occurs when a viscous liquid is forcibly spread over a solid surface. Such forced spreading is characteristic of both adhesive bonding and composite fabrication.

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nondestructive testing, nondestructive evaluation

Disciplines
Materials Science and Engineering | Structures and Materials

DURABILITY OF COMPOSITES AND ADHESIVE BONDS

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Any consideration of the durability of the high performance composite materials and structural adhesives used in aerospace construction must recognize that these are brittle materials and that their failure mode is characterized by flaw growth and propagation. One can easily anticipate a variety of flaws and defects; surface cuts, internal cracks due to stress relief and deliberate holes cut for fasteners. In this presentation we wish to discuss yet another type of flaw in fibrous composites and adhesive bonds that is inherently present because of the processing methods used to fabricate composites or bonded joints. These flaws are microvoids created by air entrapment that usually occurs when a viscous liquid is forcibly spread over a solid surface. Such forced spreading is characteristic of both adhesive bonding and composite fabrication.

The static wetting behavior of a liquid on a solid surface is characterized by the equilibrium contact angle (θ) illustrated in Fig. 1. However, even if this equilibrium contact angle is zero, the dynamic angle (θ_D) is not. The situation is illustrated in Fig. 2 showing a film of liquid initially having $\theta = 0$ but, because of high viscous resistance at the solid/liquid boundary, the dynamic angle is nonzero. As a result the advancing liquid traps a thin air film which is unstable against surface tension forces and forms a bubble trapped at the interface.

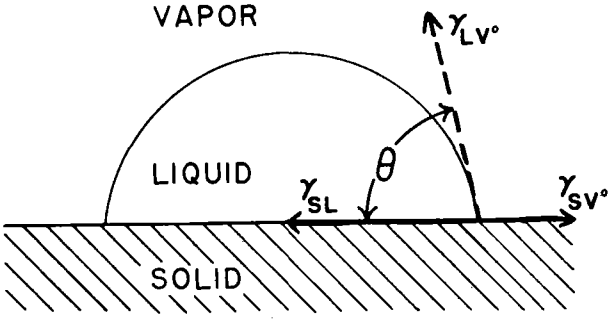


Figure 1. Equilibrium contact angle, θ. γ_{LV} = liquid surface energy, γ_{SV} = solid surface energy and γ_{SV} = solid/liquid surface energy.

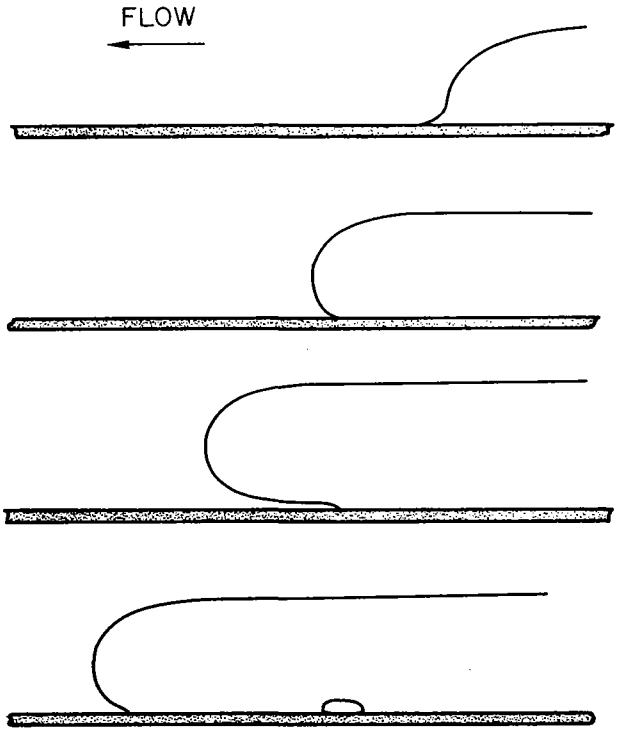


Figure 2. Schematic of a liquid film ($\theta = 0$) being forcibly spread over a smooth surface and trapping air.

There have been a number of analytical relationships developed for θ_D in terms of the viscous and surface chemical forces involved. Typical of these is the Friz equation (1,2),

$$\text{Tan } \theta_D = a \left(\frac{\eta v}{\gamma_{LV}}\right)^b \qquad (1)$$

where η is the liquid viscosity, v the average flow rate of the liquid film, i.e., spreading rate, γ_{LV} is the surface tension of the liquid and a and b are constants. Consider a typical case of an epoxy liquid resin ($\gamma_{LV} \approx$ 30 dynes/cm) and a spreading rate of 10 cm/sec. Even if the equilibrium contact angle is zero, Fig. 3 indicates that the dynamic contact angle approaches 90° even for moderately viscous liquids.

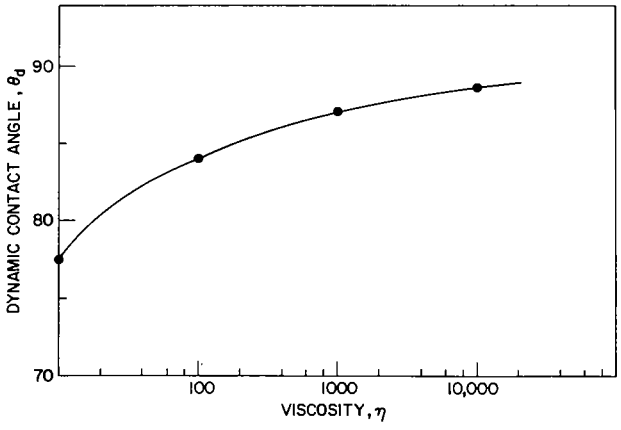


Figure 3. Plot of equation 1 for a liquid having γ_{LV} = 30 dynes/cm and a spreading rate of 10 cm/sec.

Air entrapment under conditions of forced spreading is by no means limited to flat surfaces. The situation of a rod being forced or pulled through a liquid surface is illustrated in Fig. 4. The air/liquid surface around the rod is forced down and the cylinder of air so formed may actually be carried on the rod into the liquid bath.

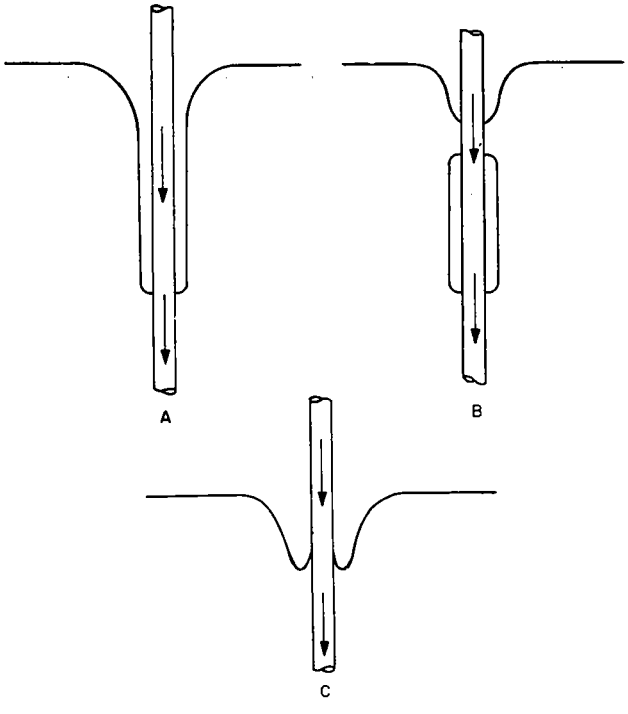


Figure 4. Schematic of air entrapment around a rod entering a liquid bath.

Resin/Fiber Composite Materials

A similar albiet more complex situation exists in wet winding of continuous filament composite. This technology involves strands of exceedingly thin (9μm) glass or graphite fiber being rapidly drawn through a bath of liquid resin. One need only observe the froth of air bubbles that accumulate in the resin bath to suspect that a process of air entrapment and release is occurring.

A study was made [3,4] of this air entrapment in filament winding by simulating the process so it could be observed microscopically. Figure 5 shows the experimental arrangement in which a strand (∿ 200 filaments) of glass fibers is pulled through a glass optical cell containing transparent resins and other liquids and onto a wind-up drum. Tension on the strand was maintained by a friction brake. The strand was observed as it entered the liquid bath and just before it emerged.

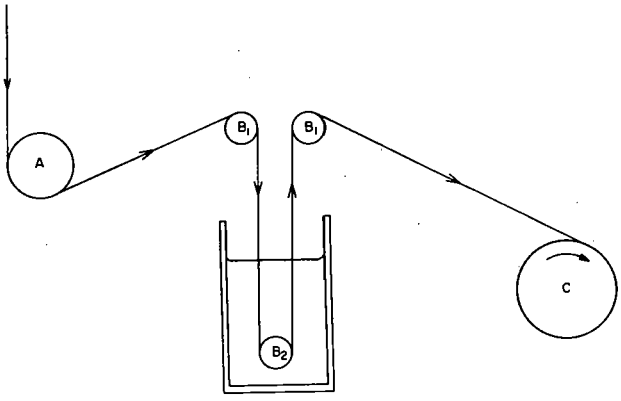


Figure 5. Experimental arrangement for observing air entrapment in filament winding. The strand is pulled from a spool (not shown) by the wind-up drum (C) and tension is maintained by a friction brake (A).

A photograph of the moving strand entering a bath of epoxy resin is presented in Fig. 6. The dark areas represent air surrounding the strand and being drawn into the bath. At typical winding rates not all of the air could be displaced by the liquid. Observed near the point of emergence from the liquid the trapped air has been rearranged into elongated voids as shown in Fig. 7. The voids are held in the strand in this elongated configuration because of the lateral constraint resulting from the tension on the filaments. Similar elongated voids can be seen in cured glass fiber-resin matrix composites.

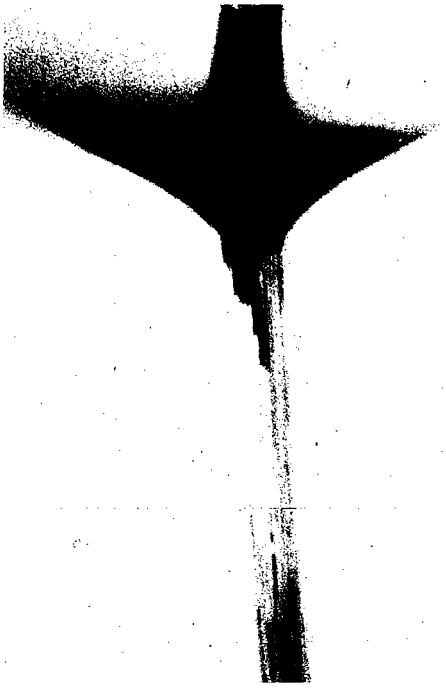
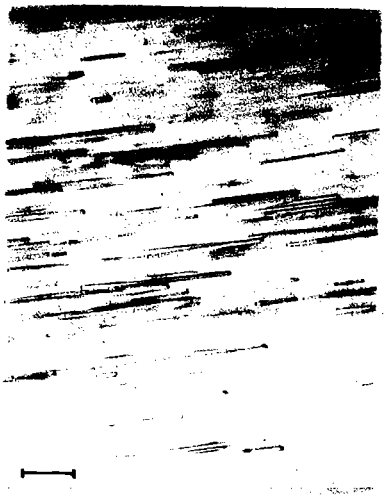
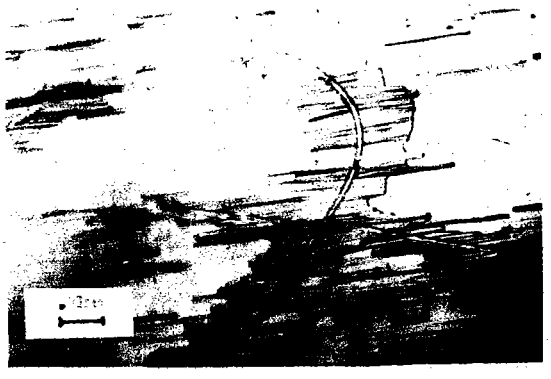


Figure 6. Photograph of strand entering a liquid bath. Dark areas are air.



A



B

Figure 8. Air voids in commercially prepared wetwound composites.

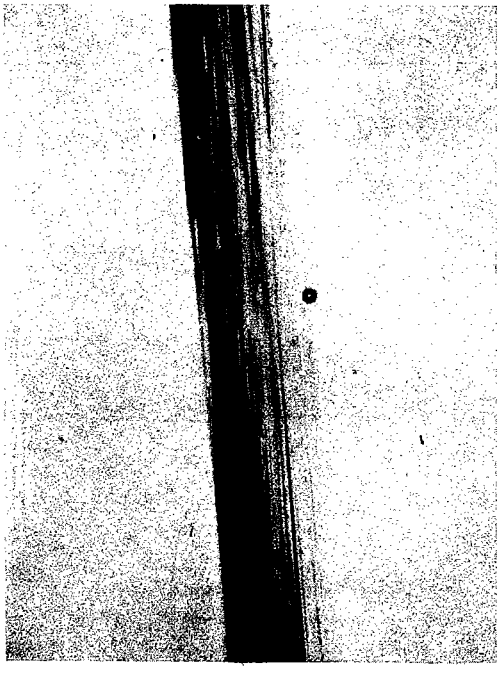


Figure 7. Photograph of strand just before emerging from the bath. Elongated features within the strand are trapped air bubbles.

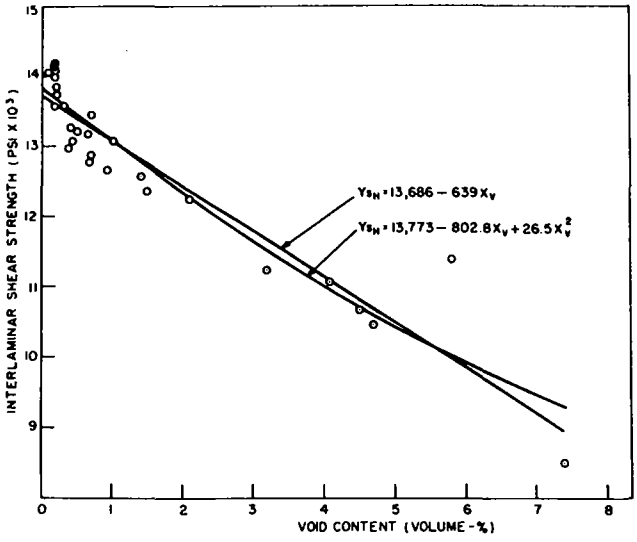


Figure 9. Effect of void content on NOL-ring interlaminar shear strength

There are two specific features of special interest in these photographs. First, that some of the air voids have sharp edges, notably where they intersect a filament (Fig. 8A). Secondly, that individual voids can collect into wide area debonds as in Fig. 8B where air has collected around a misaligned fiber. Note that the periphery of this debond is not especially smooth in that it presents sharp edges where the boundary intersects filaments. The importance of these sharp defects as opposed to the smoothly contoured air voids is the role of the former as points of stress concentration and thus, as structural defects.

In an effort to determine the extent to which this entrapped air affects composite strength, NOL-ring specimens (5) were fabricated with various void contents. The amount of trapped air was controlled by oscillating the tension on the strand during winding which allowed release of air when the filaments were relaxed. Fully void free specimens were prepared using a "vacuum release" technique[3] which simulates the effect of fabricating under pressure (autoclave) to reduce or collapse the air voids.

The effect of void content on interlaminar shear strength (ILSS) is shown in Fig. 9. This is essentially a resin dependent property and it is quite clear that reduction of void content to at least 1% significantly improves the shear strength.

Structural Adhesives

The opportunity for air entrapment is far greater in the case of adhesive bonding with structural adhesives than it is in filament winding. Commercial structural adhesives are supplied as slightly tacky films of resin supported on an open weave cloth of glass, polyester or nylon fiber. Their principal use is in aerospace construction to bond aluminum or composite skins to each other or to spars or honeycomb. In application these adhesive films, which are essentially semi-rigid solids, are pressed between rigid metal plates. The opportunity for air entrapment is exceedingly great because of the very high viscosity of the resin.

An experiment was devised to simulate this air entrapment process and to observe microscopically the fate of the trapped air as the resin film is softened by heat and then cured into a rigid solid[6] The experimental arrangement is shown in Fig. 10 and consisted of a vacuum chamber with windors at top and bottom. The specimen consisted of a film of commercial adhesive sandwiched between microscope slides and supported on a ring-shaped heater from an oil diffusion vacuum pump. Weight was applied to the sandwich by a brass cylinder bored through the center to pass a light beam. The events occurring within the film could be observed by viewing the lower glass/adhesive boundary with reflected-light microscopy or by viewing through the sandwich with transmitted light.

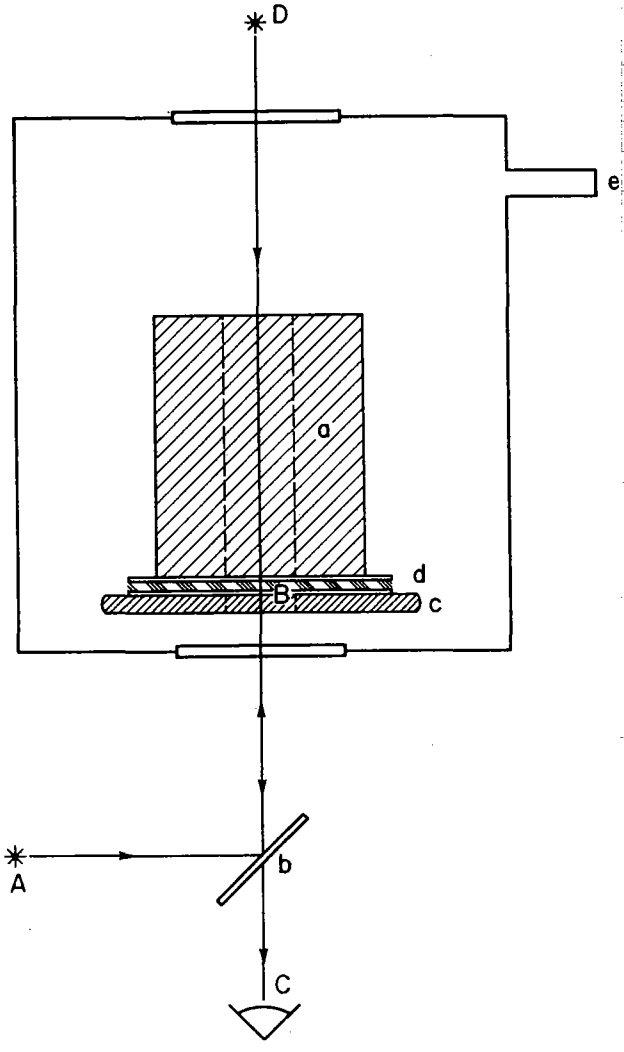


Figure 10. Experimental arrangement for viewing entrapped air at the adhesive/glass interface.

The photomicrographs presented in Fig.'s 11-15 demonstrate that considerable air is initially caught at the glass/adhesive interface but as the resin viscosity is reduced by heating it flows (under pressure from the brass weight) and the air is displaced from the interface and into the adhesive. The process is illustrated schematically in Fig. 16.

In photograph 11A the light areas represent trapped films of air and cover at least 50% of the interfacial area. Viewed in transmitted light (Fig. 11B) the trapped air film is too thin to be observed but the dark regions are believed to be air trapped at the intersection of filaments of the support cloth during manufacture of the adhesive film itself. As the resin softens the air is displaced and the regions of resin contact increase in area (Fig. 11C and 11D) and the air accumulates into bubbles thick enough to be observed in transmitted light (Fig. 12).

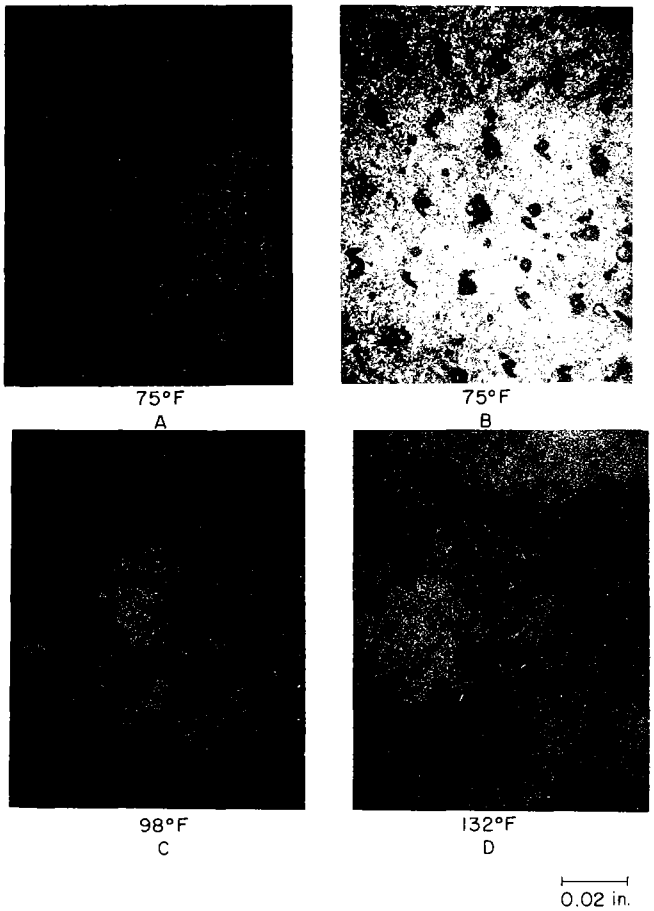


Figure 11. Photomicrographs of trapped air during resin cure (θ = 0)

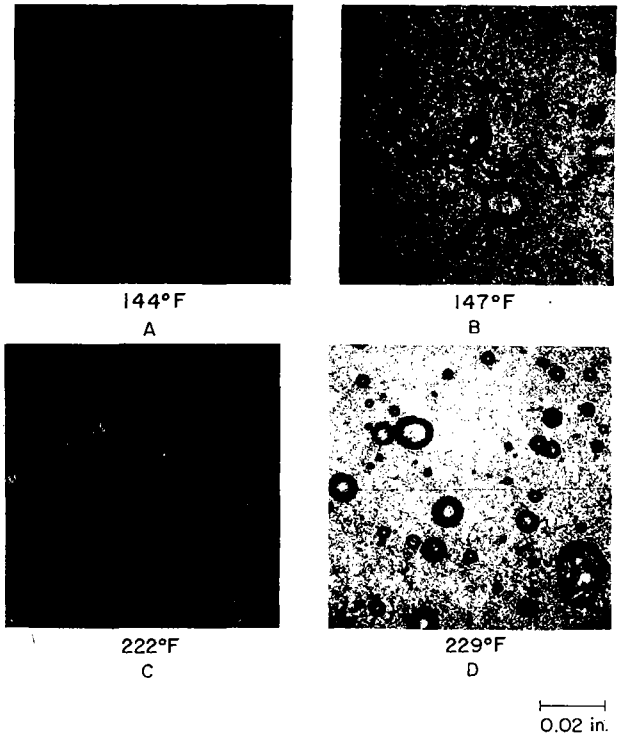


Figure 12. Photomicrographs of trapped air during resin cure (θ = 0)

Eventually, the air is fully displaced into the adhesive layer and tends to accumulate as elongated bubbles aligned along the fabric of the support cloth. At the end of the resin cure the adhesive film has thinned by flow-out along the edge of the specimen. This thinning is limited by the thickness of the support cloth. However, the process presses the trapped air bubbles against the glass surface so that they are again visible in reflected light (Fig. 13).

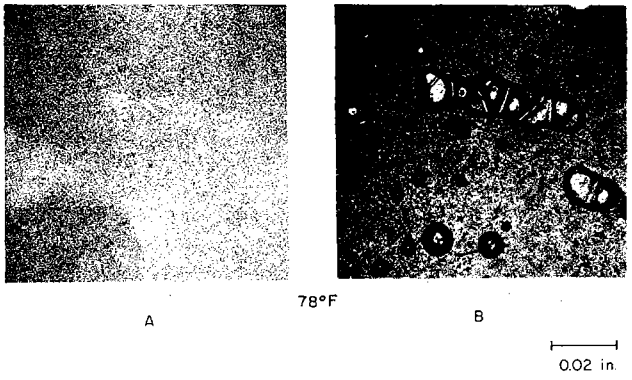


Figure 13. Final appearance of cured bond in reflected (A) and transmitted (B) light (θ = 0)

The air displacement process is truncated if the resin does not "wet" the adherend, i.e., exhibits a finite contact angle on the glass surface. In this situation displacement does not progress beyond step B in Fig. 16 as illustrated by the sequence of photographs in Fig. 14 and 15 from an experiment where the glass had been deliberately contaminated with a very thin film of silicone oil to make the glass oleophobic.[6]

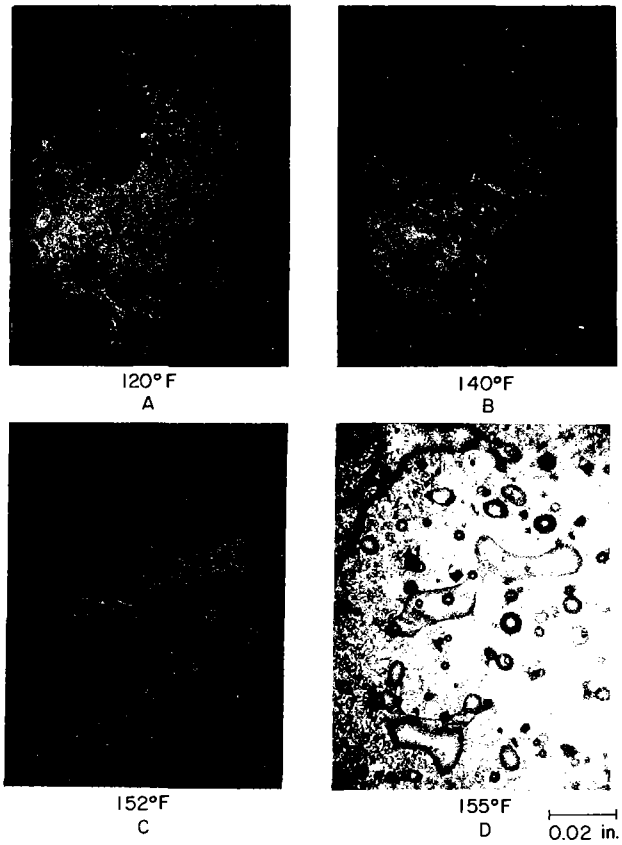


Figure 14. Photomicrographs of trapped air during resin cure. No further air displacement occurred upon continued heating (glass surface treated so that $\theta \neq 0$)

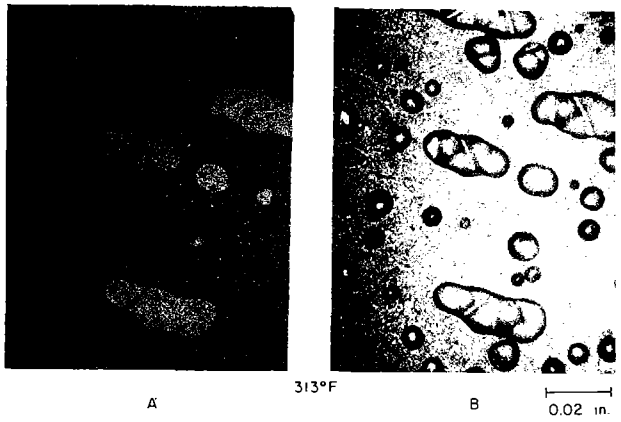


Figure 15. Photomicrographs of cured bond in reflected (A) and transmitted (B) light (glass surface treated so that $\theta = 0$)

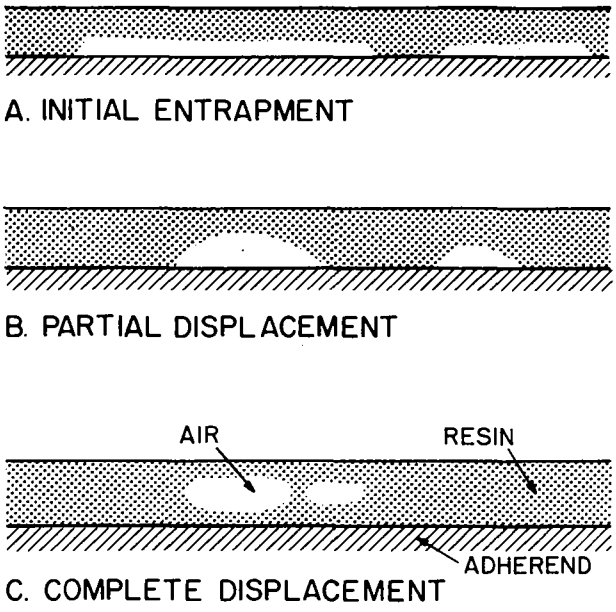


Figure 16. Air displacement process

Air entrapment in structural adhesive bonding is not prevented by curing under vacuum. All that occurs is that the initially trapped air film is evacuated along with the surrounding chamber. During the subsequent curing operation air is displaced either partially or fully into the resin layer. The only difference from what occurs at atmospheric pressure is that the air in the trapped voids is at a reduced pressure. In Fig. 17 the same array of bubbles is evident in specimens cured at 5 mm Hg and at 760 mm Hg. However, a vacuum release procedure can produce a void free bond (Fig. 17A). This technique involves evacuating ($\sim$ 5 mm Hg) the chamber initially but then returning to 760 mm Hg during the heat cure when the resin is most fluid. The hydrostatic pressure imposed on the resin causes the entrapped air bubbles to collapse to a size undetectable at 500X and higher. The actual volume reduction is of course $\sim$ 760/5.

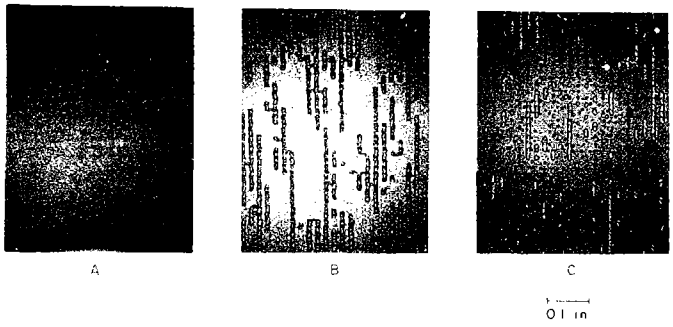


Figure 17. Low magnification views of glass-adhesive sandwiches bonded using the vacuum-release technique (A), vacuum through entire cure cycle (B) and no vacuum (C)

A point to be kept in mind is that the extent of air displacement and the effectiveness of the vacuum release technique (or autoclave pressurizing) depend on the resin becoming sufficiently fluid so that surface and hydrostatic forces can overcome the viscous resistance of the resin. Many adhesives are so highly loaded with inorganic fillers that they never attain this necessary degree of fluidity.

To test whether this entrapped air actually affects bond strength, adhesive specimens were prepared using aluminum sheet bonded with the same adhesive (modified epoxy) used in the microscopy studies. Peel test results are presented in Fig. 18. The top curve is for the adhesive without a support cloth and without any attempt to prevent air entrapment. Failure in this case was of a brittle, slip-stick nature and at a low peel strength. The slip-stick failure mode is considerably reduced and the peel strength improved with the inclusion of the scrim cloth (Fig. 18B) and still further improvements are attained in the absence of air voids (Fig. 18C). The recorder trace in Figure 18D is for another structural adhesive (nitrile-epoxy) and although there was as much as 30% air space in the bond, failure did not occur in the brittle slip-stick mode.

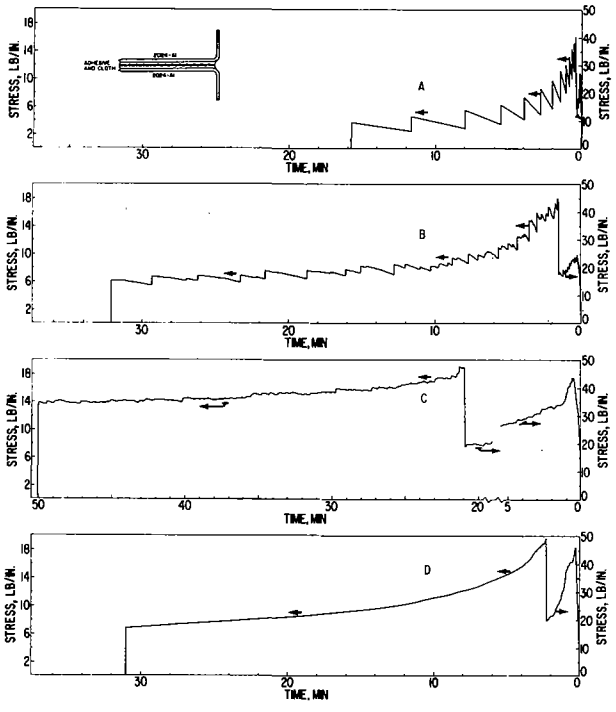


Figure 18. Stress-time curves for peel strength. A, modified epoxy with no cloth; B, modified epoxy with cloth; C, modified epoxy with cloth and void free; D, nitrile-epoxy with cloth.

Critical Flaw Size

It is quite evident from these two studies that these flaws inherent to the fabrication processing do in fact reduce material strengths - at least those dependent on resin properties. It is fair to ask if we could reasonably predict that these are serious flaws and worth removing or avoiding. The answer, at least to a crude approximation, comes from linear elastic fracture mechanics which relates the critical flaw size, r_c to the yield strength, σ_y, modulus E and fracture energy $\mathcal{G}_c$ (strain energy release rate (7));

$$r_c = Z \frac{\mathcal{G}_c E}{\sigma_c^2} \qquad (2)$$

where Z is a geometric factor dependent on the specimen shape and the loading conditions. The fracture energy, $\mathcal{G}_c$, is characteristic of the material and in Fig. 19 values of $\mathcal{G}_{Ic}$ for pure opening-mode (cleavage) fracture are compared. Note the relatively low toughness of the matrix resins but which, when formulated with elastomers, become high toughness (peel strength) adhesives. Unfortunately, the same micro-failure mechanisms which give rise to tough adhesives do not carry over into composites[8].

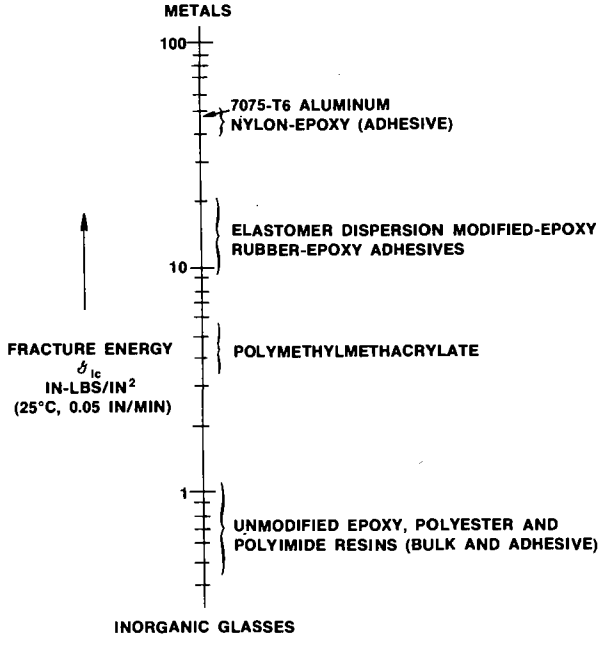


Figure 19. Ranking of $\mathcal{G}_{Ic}$ (1 in-lb/in^2 = 175.3 J/m^2).

In Table I the critical flaw size for matrix resins and the structural adhesives are listed along with the corresponding void size as determined in the microscopy studies. This elementary analysis clearly predicts that the air voids in the composite will cause matrix fracture.

TABLE I

	$\mathcal{G}_{Ic}$, J/m^2	r_c, μm	Microvoid Dimension, μm
Matrix Resin[a]	100	4	5
Structural Adhesive[b]	1700-3500	70-140	100-250

[a] bisphenol A diglycidyl ether/anhydride or amine systems

[b] "modified" epoxy systems

The $\mathcal{G}_{IC}$ and critical flaw size for structural adhesive vary depending on resin formulation and so for a very tough (high peel strength) adhesive the void dimension may be less than r_c. This situation might explain why the nitrile-epoxy adhesive (Fig. 18D) appeared to be insensitive to the presence of trapped air voids. When the flaw size is less than r_c failure occurs by resin yielding rather than fracture.

The use of equations such as (2) assumes an "infinitely sharp" edge at the flaw tip. More precisely, a crack tip radius, ρ, also characteristic of the material. It is for this reason that the point was made that at least some of the air voids have sharp edges. Notably, in Fig. 8 and when voids are not completely displaced from the adhesive/adherend interface (Fig. 16B). Smoothly contoured air bubbles do not meet the sharp tip criteria although fatigue loading, internal stress relief or other sources of microcracks which themselves would not be critical could provide the necessary sharp radius to make an air void a critical flaw.

Certainly there are other factors to be considered in any sophisticated analysis of critical flaw size. Hopefully, this elementary discussion has illustrated how flaws produced in materials processing and fracture failure analysis with NDE in predicting material strength.

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DISCUSSIONS

PROF. MAX WILLIAMS (Univ. of Pittsburgh): Do we have some questions for Bill Bascom?

I would like to stress the obvious in case you missed the point, that he's working with his early experiments with a transparent material where it's easy to see the flaw. In the fracture community, this is extremely important, as Bill and I have discussed before, because there are some rare cases, including the modified toothpick test, as I call it, that he showed first whereby pushing the rod down and entrapping the air just happens to be one of the problems that the mechanics in the community can solve. So it does have the extra added advantage of permitting a comparison between the NDE efforts and the fracture community efforts, and it's this bridge that I'm particularly interested in.

A question here?

DR. SAM K. NASH (Frankford Arsenal): Is there any reason for thinking that the initial air entrapment that you referred to is a manifestation of a lack of wetting, in other words, dirty interfaces?

DR. BASCOM: One of the main points I tried to make was that even with a perfectly smooth surface and a perfectly clean surface so that I have a zero contact angle, there are a number of equations that predict that the dynamic contact angle approaches 90 degrees in any real system - real in the sense of real flow velocities and viscosities and surface tensions. So the answer to your question is no, you can have a thoroughly clean surface and you still have the fundamental fact that the dynamic contact angle is greater than zero and would lead to air entrapment.

PROF. WILLIAMS: Bill, would you take your own questions until the time runs out? There's one in the back.

DR. BASCOM: Yes.

DR. ROBB THOMSON (National Bureau of Standards): What would happen and would it be successful if you wet the fiber with some kind of spray before you put it into the liquid to build up the layer? Then can you keep the air away from the fiber surface so that you get into the bubble situation instead of the crack situation?

DR. BASCOM: Yes, that is certainly feasible. In fact, it is possible to apply a coating so that the viscous resistance of the spreading resin at the boundary is reduced and θ_D is lower. However, it doesn't take much viscous resistance to overwhelm the thermodynamic surface forces.

DR. JERRY TIEMANN (General Electric): Has there been any recent progress in developing resins that have lower viscosities that also have good adhesive and strength properties?

DR. BASCOM: The trend seems to be to higher and higher viscosities-to melt forming for the high temperature resin. The high temperature polyimides, for example, are sometimes applied as melts with viscosities much higher than the conventional resins.

MR. ROBERT IRWIN (Northrop): It appeared in your commercial adherence interface versus wetting (or improved wetting properties) that you had a higher stress riser condition than usual.

DR. BASCOM: Yes.

MR. IRWIN: All right. What kind of NDT system did you utilize to prove that out or did you?

DR. BASCOM: To prove what out? That I--

MR. IRWIN: That you had a higher stress riser condition and--

DR. BASCOM: I am just presuming. If I have a sharp edge as opposed to a natural curvature, I assume I have a higher stress concentration.

MR. DAVE KAELBLE (Rockwell Science Center): I have a brief comment and then a question really for both Bill and Max.

The comment is this: that work that Bill has shown us this morning has not been lost in the wash. People concerned with prepreg and composite manufacture spend a lot of money and a lot of time attempting to use the curing cycle itself and at a certain stage of the cure, by following it by valid telemmetry, for example, to pinpoint a certain point in cure where pressure is applied. High pressure is applied in conjunction with the use of vacuum bagging at the early stages of curing, and these two things together seem to provide an approach to minimize this problem. So, in that sense you're early work has been very good.

DR. BASCOM: I'm glad to hear that.

MR. KAELBLE: The question that I have in my mind is: we know these flaws exist, and in your peel slide, you showed the slipstick type failure with the bubble specimen. Does that relate to a critical spacing between the flaws because throughout each flaw I note there's a stress field, and there is a sort of an idea that if the stress field overlapped, then you have this type of an interlinking or zipper effect. Maybe Max or Bill would have some comments on that.

DR. BASCOM: My only comment is that it certainly looked that way when we ran the test.

PROF. WILLIAMS: And theoretically your answer is yes, Dave.

DR. BASCOM: Are we out of time?

PROF. WILLIAMS: We have time for one or two more.

DR. JOSEPH JOHN (IFT): If I interpret what you have on the screen, is it fair to say that the idea here is to move the air bubble from the interface into the adhesive to increase the strength of the bond?

DR. BASCOM: This is the first improvement that you can make, yes.

DR. JOHN: Are there any data which indicate what the effect of the location of the air bubble; i.e., its distance from the interface, has upon the strength of the bond?

DR. BASCOM: Yes, there are. We have shown that failure tends to occur along the support cloth (especially glass). Voids have less effect if they are kept out of the cloth.

MR. DAVE KAELBLE: It appears that if you can displace the bubble two effective radii away from the surface, then the localization effects of the interface and the surface stress of the bubble tend to be diminished; in the bond line, generally, there is not that type of space available.

DR. RICHARD CHANCE (Grumman Aerospace): On the specimens where you showed a loss of strength due to the void condition in the prepreg specimens, were those specimens prepared using the standard method of vacuum bag, or was there vacuum used in making them at all?

DR. BASCOM: All our specimens were wet wound. We found we could shake the air out of single strands by slipsticking the tension. To reduce voids to 4 to 2 volume precent, we used a vacuum release technique to get to <|001.%.

DR. CHANCE: I was referring to the specimens that had the voids. How were they prepared?

DR. BASCOM: We oscillated the tension on the strand. In effect, shaking the air out of the strand before it came out of the bath.

PROF. WILLIAMS: I think that's fine. Thank you very much for your presentation, Bill.