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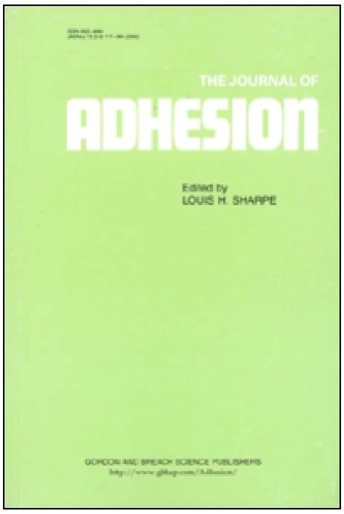

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Willard D. Bascom[a]; Robert L. Cottington[a]
[a] Naval Research Laboratory, Washington, D.C., U.S.A.

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Air Entrapment in the Use of Structural Adhesive Films

WILLARD D. BASCOM and ROBERT L. COTTINGTON

Naval Research Laboratory, Washington, D.C. 20390, U.S.A.

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Air entrapment during the preparation of bonds with structural adhesive films was examined by a microscopy study of glass/adhesive/glass specimens. It was observed that initially a thin film of air is trapped between the adhesive and adherend and covers over 50 % of the interfacial area. As the specimen is heat cured this air draws up into bubbles that are eventually displaced into the adhesive layer. Incomplete displacement occurs if the resin does not fully wet the adherend surface (contact angle greater than zero) or the resin does not become sufficiently fluid during the heat cure. The trapped air, whether displaced into the resin or held at the interface, could be eliminated from the bond by starting the cure in vacuum (5 mm Hg) and subsequently releasing the vacuum at the temperature at which the resin is in its most fluid condition. Specimens of bonded aluminum panels were tested in a T-peel configuration. An increase in bond strength of as much as 30 % could be realized by complete void removal using the vacuum release technique. It was also found that the nylon support cloth used in the adhesive film tends to stabilize crack propagation in the peel tests but that this stabilization is not fully realized unless the bond is void free.

INTRODUCTION

Adhesive bonding of metal structures offers greater joint strength and lower fabrication costs than conventional mechanical fasteners. Adhesives are especially attractive in aerospace construction since their use allows higher strength-to-weight ratios compared to riveted joints. In present technology adhesives are supplied as structural adhesive films—semi-rigid sheets of adhesive resin supported by a loose weave nylon or glass cloth. These films eliminate the tedious and costly handling of adhesive resin liquids or pastes.

The advantages of adhesive bonding are offset somewhat by the poor reliability of adhesive joints. In particular, they are susceptible to stress-corrosive attack by moisture and many of the more brittle adhesive resins have shown fatigue failure. Stress corrosion has created inordinate maintenance problems for military aircraft in tropic and subtropic regions.[1] Sometimes the cause of poor bond reliability can be traced to improper fabrication procedures. An obvious source of difficulty is air entrapment between the adhesive and adherend, especially when the adhesive is in the form of a semi-rigid film. In practice, bonded assemblies are placed in bags, a vacuum pulled on the bag to hold the pieces together and then the bagged assembly is placed in an autoclave for curing by heat and pressure. De Lollis notes that if the bags are vented during the cure there is a notable improvement in the bond strength which he attributes to the removal of air and volatiles[2]. We are also aware that in some bonding procedures the autoclave pressure is made high enough to compress entrapped air to a negligible volume. In the work reported here an effort is made to determine the extent of air entrapment, its fate as the adhesive is cured and the effect of trapped air on bond strength.

EXPERIMENTAL

Materials

The principal characteristics of the adhesive films studied here are listed in Table I. They were all obtained from commercial sources and are intended for air-frame construction. The last column of Table I gives the temperature (T_f) at which the adhesive resin becomes fluid as it passes from a semi-rigid consistency at room temperature to a rigid plastic at the cure temperature. The value of T_f was estimated by slowly heating small pieces of film on a hot plate and noting the temperature (from a surface thermometer) at which the resin is most fluid.

TABLE I
Structural adhesive films.

Film	Resin	Support Cloth	T_f(°F)
I	Modified epoxy	Nylon	255
II	Modified epoxy	None	255
III	Epoxy/nitrile elastomers	Nylon	255
IV	Metal-filled modified epoxy	Nylon	150 (tacky)
V	Metal-filled modified epoxy	Glass	150 (tacky)

The glass plates used in the microscopy study were 1 in. x 3 in. x 0.050 in. microscope slides (soda-lime glass) and were cleaned with a detergent solution, rinsed thoroughly with distilled water and dried in an oven at 250°F. The metal test panels were 0.032 in. thick 2024 ALCLAD aluminum cut into 1 in. x 5 in. strips. The following steps were taken to clean and prepare the aluminum panels for adhesive bonding:

(a) methyl ethyl ketone rinse,
(b) wash in a Soxlet extractor with C_6H_6—iso C_3H_7OH (1:1) for 30 minutes,
(c) tap water rinse,
(d) 30 minute soak in an alkaline detergent,
(e) 10 minute treatment with a dichromate solution at 150°F,
(f) 30 minute rinse flowing tap water,
(g) distilled water rinse,
(h) air dry at room temperature.

The dichromate solution used on the aluminum panels to be bonded with films I, II and III contained 28.5 gm/l of $Na_2Cr_2O_7$ and 285 gm/l of H_2SO_4 ($\rho = 1.84$) in distilled water. For the panels to be bonded with films IV and V, the dichromate solution contained 90.9 gm/l of $Na_2Cr_2O_7$ and 227 gm/l of H_2SO_4 ($\rho = 1.84$) in distilled water. Also, for IV and V, the detergent soak was omitted.

The adhesive-adherend "sandwich" specimens were cured by heating to 350°F (which took about 2-3/4 hours) under 5, 15 or 30 psi applied pressure, and held at that temperature for 1 hour and then were allowed to cool overnight (18–20 hours). The curing procedure and the metal cleaning procedures described above were within the recommendations of the adhesive film suppliers.

Microscopy study

An adhesive film was placed between cleaned microscope slides and the sandwich was mounted on a heating plate in the vacuum chamber shown schematically in Figure 1. The microscope, an inverted metallographic type, permitted observation of the lower adhesive/adherend interfaces by reflected light (path A-B-C) and observation through the sandwich by transmitted light (path D-B-C) for those films sufficiently transparent. The chamber could be evacuated to < 5 mm Hg and heated to 400°F or greater. The temperature was determined by a thermocouple mounted on the heating plate adjacent to the specimen. Mechanical pressure of $\sim$ 0.5 psi was maintained on the adhesive-adherend specimen by a brass weight (*a*, Figure 1) with a hole through its center to allow passage of the transmitted light beam.

Adhesive strength study

The test specimens were prepared by placing a 3.5 in x 1 in. strip of the adhesive film between two 5 in. x 1 in. aluminum panels so as to leave an unbonded length of 1.5 in. Six such specimens were placed in a spring-loaded holder that could be adjusted to apply a mechanical pressure of 5 to 50 psi. The loaded holder was placed in a vacuum oven to cure the adhesive-adherend sandwiches. The cured specimens were tested on a model TT-B Instron in a 180° "peel" test configuration (see insert Figure 9). The strain rate was 0.1 in./min in all cases.

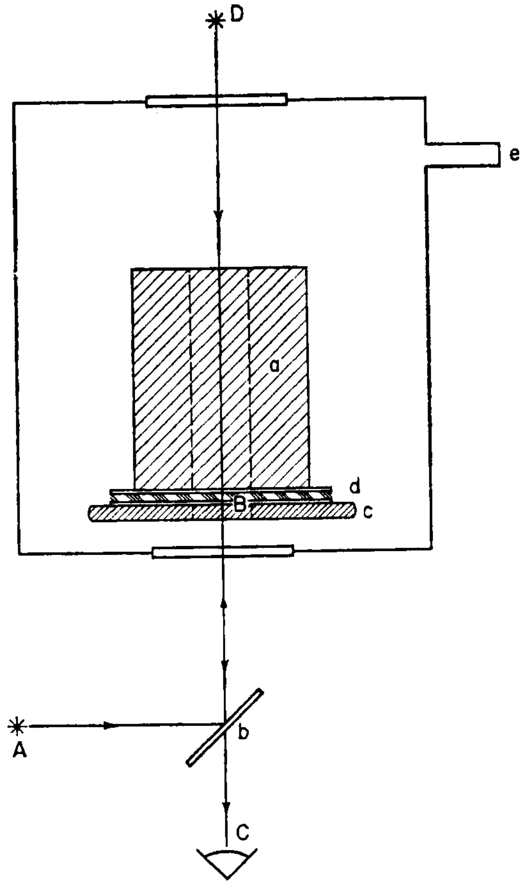

FIGURE 1 Heating and vacuum chamber for microscopy study of bond formation. a. brass weight, b. mirror, c. heating plate, d, glass slide-adhesive-glass slide specimen, e. evacuation port. $\overline{ABC}$-reflected light path, $\overline{DBC}$-transmitted light path.

RESULTS

Observation of air entrapment

Adhesive sandwich specimens of Film I between cleaned glass slides were observed microscopically in both reflected and transmitted light. The photomicrographs in Figures 2–4 illustrate the changes that took place as the adhesive was heat cured at atmospheric pressure and 0.5 psi mechanical pressure. Initially, a thin film of air covered about 50% of the interfacial area. This air appears as bright patches in Figure 2A. Viewed in transmitted light (Figure 2B) the air film was too thin to be observed but air bubbles

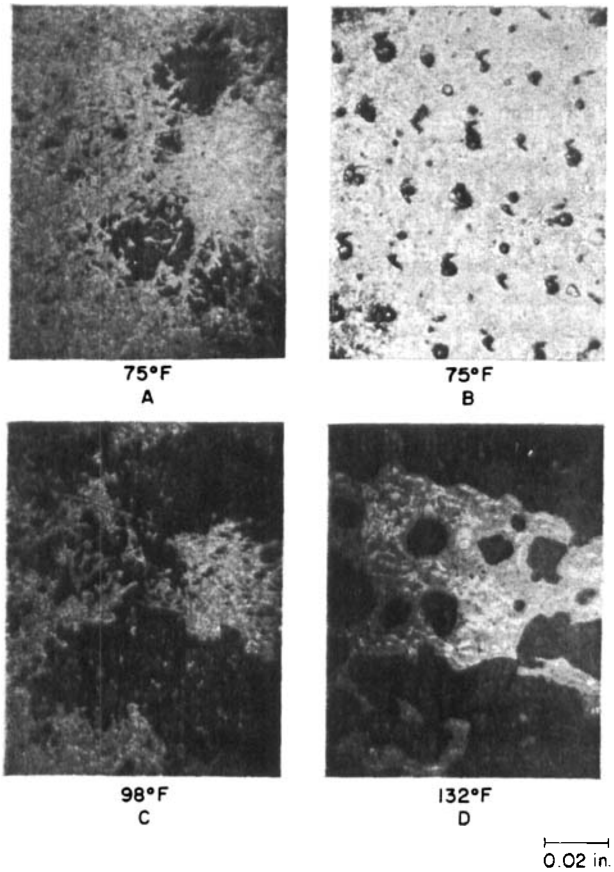

FIGURE 2 Progressive displacement of trapped air from adhesive/adherend interface. Film I against clean glass.

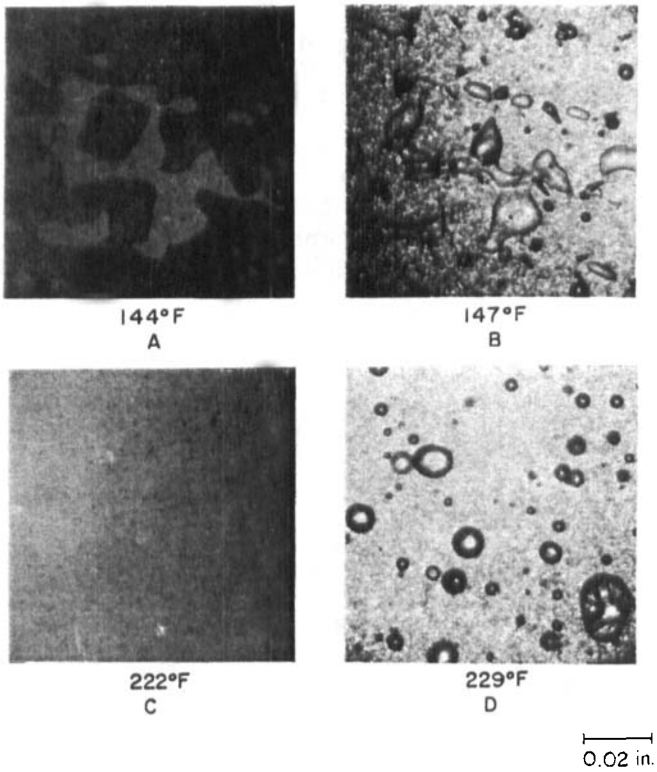

FIGURE 3 Progressive displacement of trapped air from adhesive/adherend interface. Film I against clean glass.

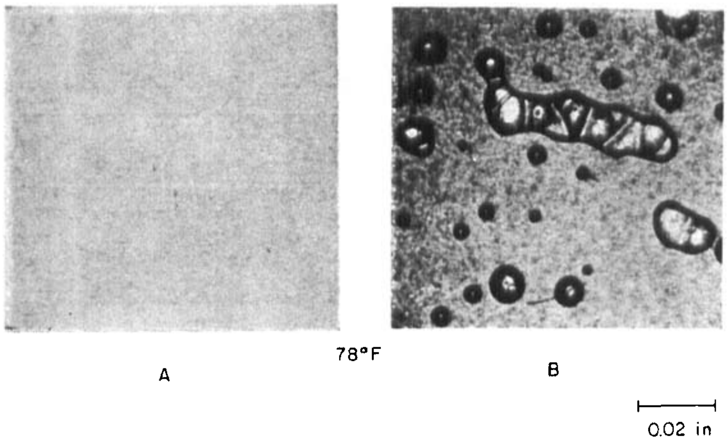

FIGURE 4 Final appearance of Film I against clean glass. Reflected light (A) and transmitted light (B).

and other inhomogeneities were evident in the resin layer itself. As the temperature was raised, the regions of trapped air progressively decreased in area (Figure 2C, D and Figure 3A). When the temperature reached 147°F the interfacial air had drawn up into bubbles large enough to be observed in transmitted light (Figure 3B) as well as in reflected light. At about 225°F all of the air had been displaced into the adhesive layer and was no longer visible in reflected light (Figure 3C). It then appeared in transmitted light as bubbles (Figure 3D) which moved about under small temperature and pressure gradients and could be seen to coalesce into elongated voids. Between 250°F and 300°F the resin was sufficiently fluid that some flowed out from between the glass plates thus thinning the adhesive layer. As a result the chains of air bubbles in the resin were pushed against the glass plate by the

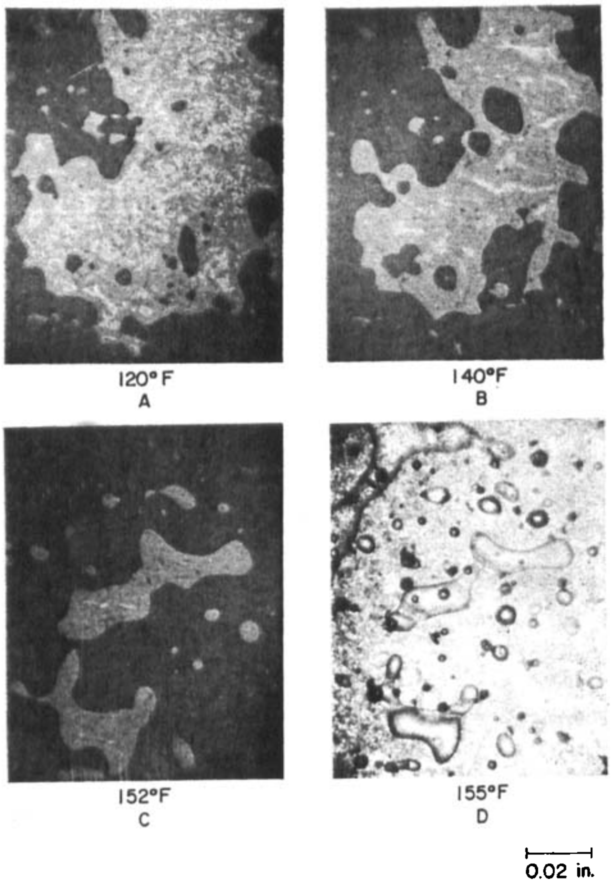

FIGURE 5 Progressive displacement of air from adhesive/adherend interface. Film I against oleophobic glass.

nylon cloth. Consequently, by the time the specimen had been cured and cooled, voids could again be seen in reflected light (Figure 4A) as well as in transmitted light (Figure 4B). Judging from the poor reflectivity of the void area in Figure 4A, the air had not displaced the resin from the glass. The lines running through the voids in Figure 4B are fibers of the reinforcing cloth.

The effect of adherend wettability on air entrapment was studied by making the glass slides oleophobic. Cleaned slides were coated with a polysiloxane oil (DC-200), then wiped and rinsed with copious amounts of benzene to remove all but the most firmly held siloxane molecules. The microscopy study was then repeated with Film I between these coated slides. As with the cleaned glass, the air film was progressively displaced from the interface (Figure 5). However, in contrast to the cleaned glass, the entrapped air seen in reflected light was never completely displaced into the adhesive layer. Thus, the appearance of the specimen at 313°F (Figure 6) was unchanged through the remainder of the cure.

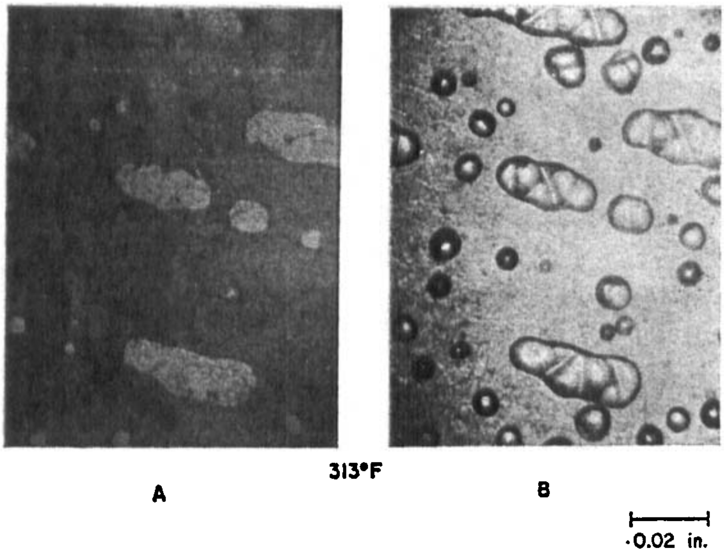

FIGURE 6 Incomplete displacement of air from Film I/oleophobic glass interface. Reflected light (A), transmitted light (B).

The events that occur as trapped air is displaced are presented schematically in Figure 7. When the resin does not spread spontaneously, i.e. non-zero contact angle), on the adherend surface the air displacement is incomplete and does not go beyond step B.

A similar study was made with specimens of Film III between cleaned

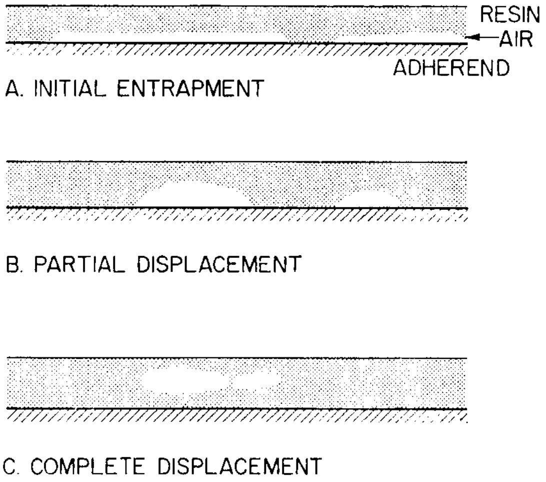

FIGURE 7 Air displacement process.

glass plates. This film has an epoxy resin on one side of the nylon cloth and a nitrile elastomer on the other side. At the epoxy/glass interface the initially trapped air was completely displaced when the temperature reached 225°F but at the elastomer/glass interface the displacement was incomplete even at the full cure temperature (350°F).

These experiments with Films I, II and III, were repeated with the chamber evacuated to a pressure of 2–5 mm Hg. The events were essentially the same as observed at atmospheric pressure. Even the area of trapped air and the volume of the bubbles appeared to be the same.

It was obvious that the voids could be eliminated if the evacuated chamber was opened to atmospheric pressure before the adhesive resin had cured to a solid. Viewed in transmitted light, the bubbles begin to collapse the moment the vacuum is released and in a few seconds they disappear. The most rapid and complete void removal was obtained if the chamber was opened near T_f, the temperature at which the resin is most fluid. This technique was successfully used to obtain void-free specimens of adhesive Films I, II and III between glass plates. In Figure 8 glass slides bonded with Film I are shown at low magnification and the effectiveness of the vacuum release procedure is obvious.

Studies were also made of air entrapment in preparing specimens of the metal-filled adhesives (IV and V) between glass plates. Since these films are opaque, they could be examined only in reflected light. The study indicated that some of the smaller regions of trapped air were displaced into the adhesive film. However, because these resins remain highly viscous during

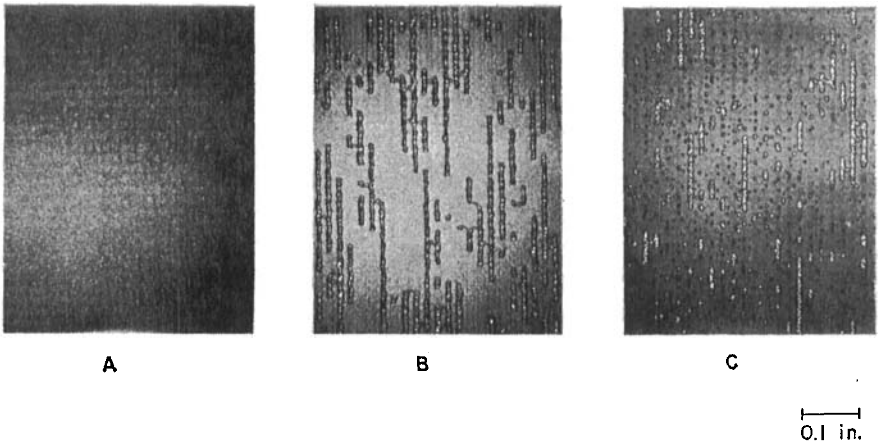

FIGURE 8 Photomicrographs of Film I—clean glass specimens viewed in transmitted light. A, cure started at 5 mm Hg but returned to atmospheric pressure at 255°F; B, pressure held at 5 mm Hg throughout cure; C, atmospheric pressure throughout cure.

the entire cure (much more so than the unfilled epoxy films) the air displacement was sluggish and usually incomplete for the larger areas of trapped air. This inefficient displacement did not appear to be a question of inadequate adhesive/adherend wetting but was due instead to a low rate of resin flow. Most of the displacement occurred near 150°F, the temperature at which these resins become tacky.

The "vacuum-release" technique for removing air voids did not work for the metal-filled adhesive. Although there was some decrease in void volume it was quite evident that most of the void space at the adhesive/glass interface remained after the chamber had been opened to the atmosphere.

Bond strength studies

The failure stress of aluminum panel sandwiches bonded with the various adhesive films was determined in the T-peel configuration at a low and constant strain rate (0.1 in./min). In many instances, the failure stress was too small to significantly deform the aluminum so that these tests would be better described as cleavage of the adhesive rather than as a peel failure. Typical stress-time curves are given in Figure 9. Note that the failure stress decreased progressively as the failure front moved away from the loading points. In Tables II–IV, the failure strengths are given for specimens prepared under various conditions. Each stress value represents the average of six specimens and the mean deviation is given in parenthesis. Two stress values are given; the initial maximum stress and the stress at one inch cross-head separation (CHS).

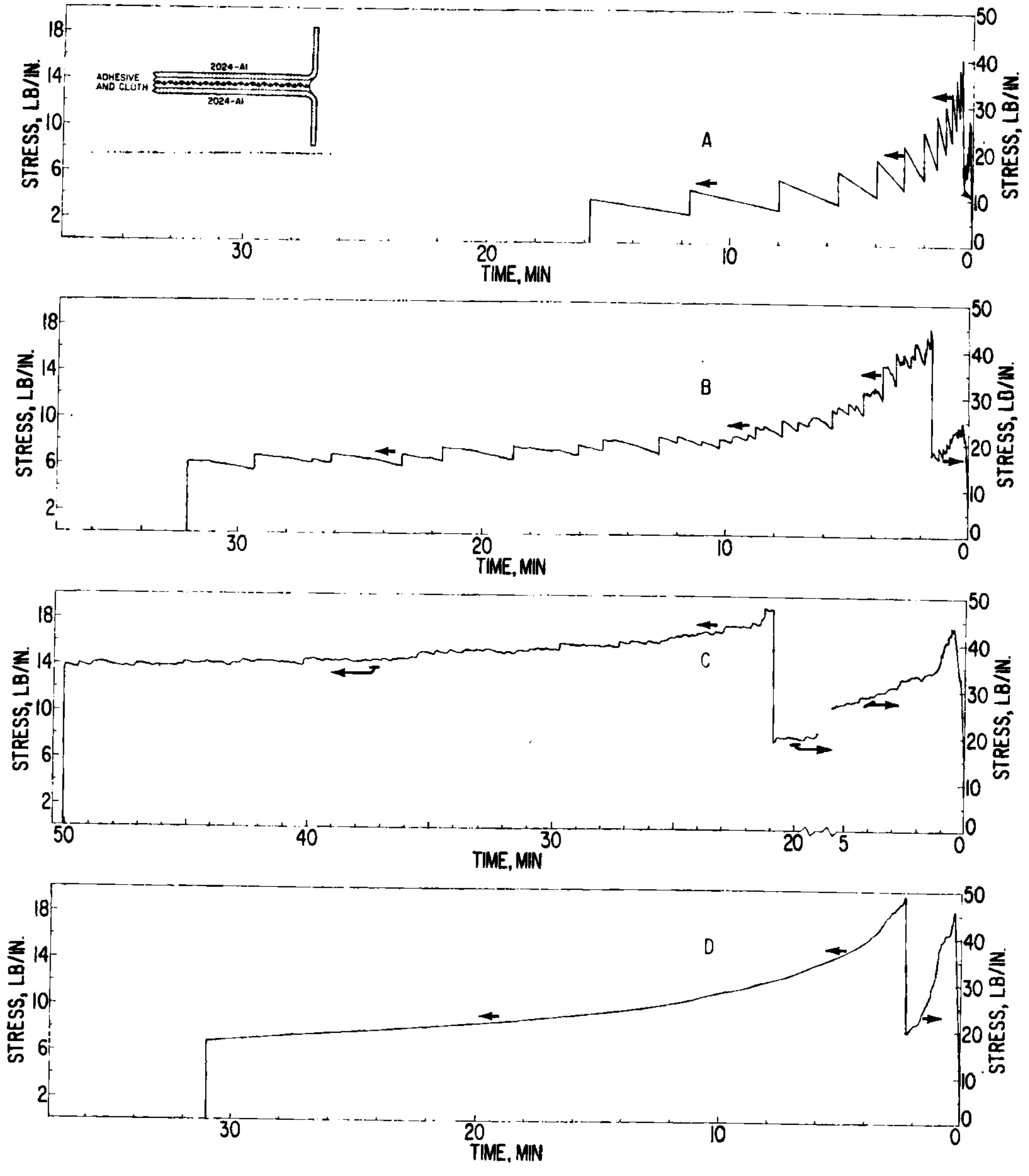

FIGURE 9 Stress-time curves. A, unsupported epoxy resin (Film II); B, nylon supported epoxy resin (Film I) with ~30% voids; C, void-free, nylon supported epoxy resin (Film I); D, void-free nylon-supported elastomer-epoxy (Film III).

TABLE II
The effect of void removal on failure stress.
(Film I, 30 psi applied pressure)

% voids[a]	Oven pressure	Failure stress, lb./in. Initial	1 in. CHS
~ 30	Atm.	27.7 (±1.1)	9.8 (±0.9)
~ 30	5 mm Hg	24.6 (±2.5)	9.9 (±1.9)
0	5 mm Hg → atm[b]	34.5 (±2.6)	12.1 (±1.3)

[a] Visual estimate.
[b] "Vacuum release".

TABLE III
The effect of applied pressure.
(Film I)
A

% voids[a]	Applied pressure, psi	Failure stress, lbs./in. Initial	1 in. CHS
0	30	34.5 (±2.6)	12.1 (±1.3)
0	15	39.9 (±0.7)	14.7 (±1.3)
0	0.5	44.3 (±1.6)	16.6 (±2.3)

The effect of void removal at low applied cure pressure.
(Film I)
B

~ 30	0.5	39.2 (±2.4)	17.2 (±1.7)
0	0.5	44.3 (±1.6)	16.6 (±2.3)

[a] Visual estimate.

TABLE IV
A comparison of the films.
(applied pressure = 0.5 psi)

Film	% voids	Failure stress, lbs./in. Initial	1 in. CHS
I	0	44.3 (±1.6)	16.6 (±2.3)
II	0	24.9 (±1.9)	3.6 (±0.6)
III	0	44.2 (±1.4)	11.0 (±0.2)
IV	30–40%	28.2 (±1.0)	10.8 (±1.0)
V	30–40%	19.8 (±0.7)	4.7 (±0.3)

The data in Table II indicate that complete removal of voids in specimens of Film I resulted in a 20–25% increase in failure stress. The void space was estimated after failure by examining the adhesive layer with the unaided eye. To obtain void free bonds the specimens were heated to 255°F with the oven evacuated to 5 mm Hg and with the specimen holder exerting the minimum mechanical pressure (0.5 psi). When the oven reached 255°F, it was opened to atmospheric pressure and the holder was adjusted to apply a pressure of 30 psi. When the oven was kept evacuated during the entire cure, the voids were not eliminated and the failure stress was actually lower than when the specimens were cured at atmospheric pressure. In examining the failed surfaces of specimens from which the voids had not been removed it was evident that the air bubbles had been displaced into the resin which indicates that for this epoxy the contact angle against the cleaned aluminum had been zero or very small.

The amount of mechanical pressure applied during the cure by the specimen holder had a marked effect on failure strength. In Table IIIA the data

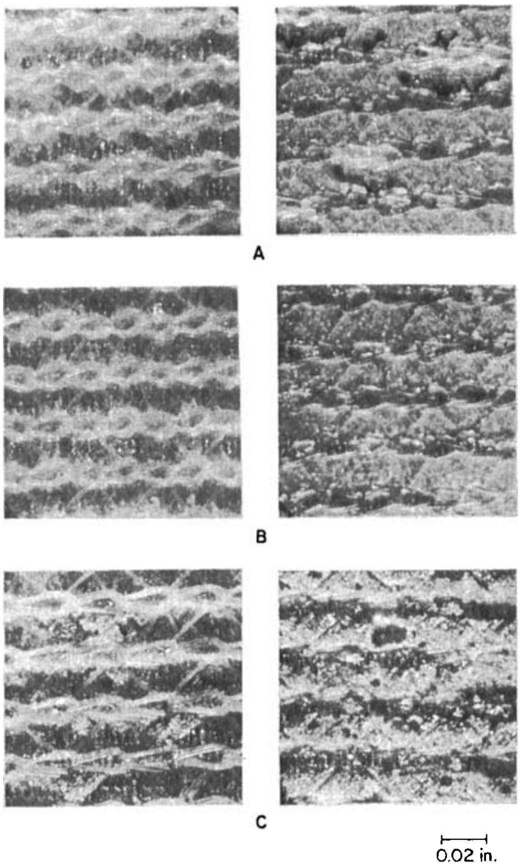

FIGURE 10 Failed surfaces. A, film I with voids; B, film I void-free; C, film IV with voids.

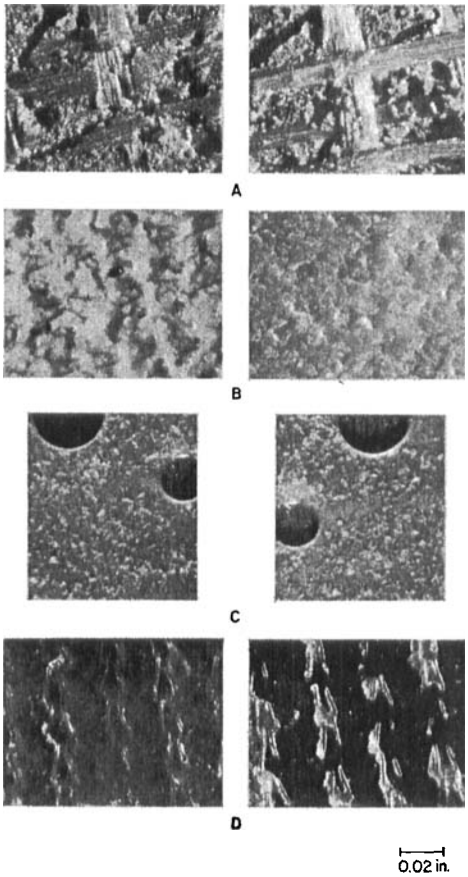

FIGURE 11 Failed surfaces. A, film V; B, film III; C, film II; D, film I from oleophobic (silicone oil treated) aluminum surface.

for void-free specimens of Film I indicate a 30% increase in failure stress in lowering the applied pressure from 30 psi to 0.5 psi. Furthermore, Table IIIB shows that void removal from specimens held at 0.5 psi had less of an effect on strength (5–15% increase) than it did when the applied pressure was 30 psi (20–25% increase, i.e. Table II).

In Table IV the failure strengths of specimens made using the different adhesives are compared. The epoxy (Film I) and the epoxy-elastomer (Film III) adhesives were essentially the same. Both had greater strengths than the metal-filled epoxy adhesives (Films IV and V) which is due in part to the voids in the latter which could not be removed by vacuum release. Note the much lower strength of Film V compared to Film IV. Both are metal-filled epoxy resins but Film V has a glass support cloth whereas the cloth in Film IV is nylon. Finally, Film II is the same resin as I but without any support cloth. Clearly the cloth adds to the adhesive strength.

The stress-time data for the various adhesive-adherend sandwiches differed not only in the stress levels but also in the "saw-tooth" character of the stress-time curves. In Figure 9, this feature is most pronounced for Film II, the unsupported adhesive (curve A), less so for Film I with voids (curve B) and essentially absent from the curves for the void-free bonds of Film I (curve C) and the epoxy-elastomer Film III (curve D).

The separated adhesive test specimens were examined microscopically in oblique reflected light. Photomicrographs are given in Figures 10 and 11 and each is representative of the failed surface all along the specimen. The epoxy resin-nylon cloth adhesive, Film I, and the metal-filled epoxy resin-nylon cloth adhesive, Film IV, failed between the cloth and the resin. Thus, the photomicrographs in Figure 10 show the clean separation of the nylon cloth from the resin with the cloth on one side (LHS of Figure 10) and the resin with the imprint of the cloth on the other (RHS of Figure 10). In contrast, the metal-filled epoxy-glass cloth adhesive (Film V) failed in the cloth (Figure 11A) and the elastomer-epoxy adhesive (Film III) failed in the elastomer near the boundary between the two resins (Figure 11B). Finally, the unsupported epoxy adhesive failed near the center of the adhesive bond (Figure 11C) and treatment of the aluminum panels with silicone oil caused the epoxy-nylon cloth adhesive (Film I) to fail at or near the interface (Figure 11D). The photographs on the right hand and left hand sides of Figures 10 and 11 do not necessarily represent corresponding areas of the failure surfaces except for 11C in which the circular features represent two air pockets bisected by the crack as it passed through the resin.

DISCUSSION

It is doubtful that air entrapment can be avoided in preparing bonds with structural adhesive films. Even for the small specimens used here and the care taken in their preparation, a thin film of air initially covered nearly fifty percent of the interfacial area. The fate of this trapped air as the adhesive is heat cured depends upon the viscous properties of the resin and the wetting behavior at the resin/adherend interface. If the resin is sufficiently fluid and has a zero contact angle against the adherend, it will displace the air from the interface into the adhesive layer. The driving force for this displacement is the decrease in surface area (and surface energy) as the trapped air film gathers into nearly spherical bubbles. The displacement is resisted by the work of displacement (W_D) for air by the resin from the adherend surface[3],

$$W_D = \gamma_{LV}(1 - \cos \theta)$$

which will be small or zero if the contact angle, θ, measured through the resin is small or zero ($\cos \theta = 1$). The term, γ_{LV}, is the surface tension of the liquid resin. The displacement is also opposed by the viscous resistance of the resin which, if the resin does not become fluid during the heat cure, can essentially prevent air displacement even if W_D is zero (i.e., zero contact angle).

Once displaced from the interface the air bubbles tend to coalesce into larger voids or channels along the warp of the support cloth (see Figure 8). Coalescence is resisted if the resin has a high viscosity or if there are surface chemical factors (i.e. certain surface active agents) stabilizing the smaller bubbles.

The trapped air could be removed by starting the heat cure at reduced pressure (5 mm Hg) but then returning to atmospheric pressure at a temperature at which the resin is fluid. The pressure of the trapped air film is reduced when the oven is evacuated so that later, when the oven is opened to atmospheric pressure, the volume of the voids is reduced by a factor of about 150 (i.e. 760 mm/5 mm). This "vacuum release" technique worked even when the resin did not wet the adherend. It was not successful when the resin was too viscous to allow the air voids to collapse.

The largest improvement in bond strength that could be realized by complete removal of trapped air was 20–30% increase in failure stress (adhesive Film I—Table II) which is roughly equal to the decrease in volume percent void content of the adhesive layer. This increase in failure stress was observed when the mechanical pressure applied during the cure was 30 psi. When the applied pressure was 15 psi or 0.5 psi, void removal had less of an effect (Table III B). In fact, with or without voids, the lower the applied pressure the greater the failure stress (Table III).

The interdependence of bonds strength on void content and applied pressure is probably related to the locus of failure characteristic of Film I. In these specimens, failure invariably occurred between the nylon cloth and the epoxy resin (Figure 10 A, B). In order for the voids to influence the failure stress they must lie in this boundary. It is reasonable that at the lower applied pressures a greater part of the void space lies in the resin layers on either side of the cloth. At the higher applied pressure more of the voids will be squeezed into the fabric and thus lie in the path of crack propagation. The locus of failure (and thus the effect of the voids) depends partly on the test configuration and partly on the mechanical characteristics of the resin and the support cloth. Consequently, the effect of voids on lap joint strengths may differ considerably from the effect observed for the T-peel configuration.

A study of the voids in lap shear specimens is in progress at NRL. The T-peel configuration does have one merit in that it imitates the lifting stresses experienced by aluminum skins on air frames so that failures at skin edges bonded to structural members would be similar to the peel failures observed here.

The comparison of the stress-time curves in Figure 9 indicates differences in the crack propagation characteristics of the adhesives and that the support cloth and trapped air voids can influence crack growth. In Figure 9, Curve A is for the unsupported epoxy adhesive (Film II) and the saw-tooth character of this curve indicates that failure took place by a stepwise crack advance. This occurs because of the instability of crack growth inherent in strain-rate sensitive materials such as the epoxy resins[4]. In contrast to the epoxy adhesive the elastomer-epoxy film gave a smooth stress-time curve characteristic of stable crack growth because it failed in the less strain-rate sensitive elastomeric resin. The top of each step, in Figure 9A, corresponds to crack initiation but instead of propagating smoothly it pops ahead of the machine. Because the "peel" configuration is essentially a cleavage test, there is a rapid load relaxation with crack movement so the crack arrests almost immediately until the specimen returns to the stress level for crack propagation. Comparing curves A and C it is clear that the crack advance is essentially continuous through the supported adhesive film even though the epoxy resin is the same in both films. Curve B is also for the nylon supported film but in this case the adhesive layer contains about 30% volume percent voids and it is evident that the presence of the voids detracts from the stabilizing effect of the cloth on crack growth.

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