

## Mode of Failure in Structural Adhesive Bonds

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### Synopsis

This paper attempts to prove the possibility of adhesive failure by preferential adsorption and adhesive displacement at the adherend surface. Data are presented to demonstrate different modes of failure that are possible after initial cohesive failure.

Adhesion is an interfacial phenomena of great importance because during application an adhesive bond creates or replaces one or more interfaces. As a result of this, theories of adhesion<sup>1-4</sup> have been created, modified, discarded, and recreated as more is learned of the formation of adhesive bonds.

Wettability<sup>5,6</sup> has also received considerable attention as a necessary companion of adhesion. Some attention has been given to the forces working against adhesion<sup>7</sup> including weak boundary layers.<sup>8,9</sup>

However, once a good bond is formed it has been assumed that only cohesive failure can result because the forces forming the bond far exceed the experimental failing loads.<sup>10</sup>

It has also been assumed that weak boundary layers are the primary reasons for poor bonds<sup>8</sup> and that once these weak boundary layers have been eliminated by crosslinking a barrier has been created to further permeation to the adhesive-adherend interface by low molecular weight materials, thus insuring that good bonds can be formed and maintained against the incursions of water, organic solvents, monomers, etc.

The results, described in this study, of the effect of continuous exposure of structural bonds to water both as a liquid and, as a vapor indicate that, depending on the nature of adhesive and the type of bond, both cohesive and adhesive failures are possible.

### Theoretical

Absorption and permeation of crosslinked organic systems by liquids such as water has been studied by Lee<sup>11</sup> and others.<sup>12</sup> Polyethylene is easily permeable by gases and vapors.<sup>13</sup> Henderson,<sup>14</sup> describing a study made of polyethylene containing oleamide, indicates that while flame treatment may remove oleamide which migrates to the surface, within 50 hr. the oleamide will have reestablished itself on the surface. However, an adhesive which has been preferentially adsorbed on the treated surface will not necessarily be displaced by the oleamide.

Once water or any other material of low enough molecular weight has

been absorbed and has permeated throughout the adhesive layer, the limit to further activity is the ability of the water or other molecules to be preferentially adsorbed on the adherend and thereby displace the adhesive at the interface.

Falconer et al.,<sup>15</sup> have proposed that water vapor does permeate organic resins and concentrate in a boundary layer at a hydrophilic metal surface. Elevated temperatures (80°C.) accelerate this permeation. A significant contribution to this mechanism of preferential adsorption and displacement at the interface would be the stress concentrations which tend to congregate at the interfaces and edges of a bond.<sup>16-18</sup>

Work has been done to show that liquid-liquid-solid systems<sup>19,20</sup> are not necessarily static, i.e., one liquid will tend to displace the other at the metal surface depending on the relative affinities. In a water-benzene-carbon system an equilibrium displacement pressure of 400 g./cm.<sup>2</sup> was measured,<sup>21</sup> i.e., the pressure necessary to halt the action of benzene in displacing water at the carbon surface. However, area tends to be meaningless when one realizes that displacement forces are acting along a front so that localized stresses could be considerably greater than any measured area stress.

Observation of the displacement of oil or air by water from a hydrophilic surface shows that the oil globules or air bubbles at the surface are displaced along a curvilinear front. The localized stresses along such a front could theoretically achieve infinity. However, since materials deform elastically along such a front the resultant stresses are probably finite but of appreciable magnitude.

Heats of wetting experiments<sup>22</sup> have shown that as little as 0.02% of water in benzene will produce a heat of wetting value with a polar solid which is practically the same as that for pure water and much greater than the heat of wetting of pure benzene on the polar solid. This indicates that benzene is probably completely displaced by water at the polar solid surface.

Polymer molecules above the glass transition point have mobility depending on the degree of crosslinking, temperature, and absorbed liquids so that in displacing an adhesive resin at the adhesive/adherend interface one is not dealing with an absolutely rigid system. Given the proper affinity of the displacing liquid for the adherend with the aid of time and temperature the resin can be displaced.

An interesting aspect of mode of failure<sup>24-27</sup> is that while the theoretical discussion emphasizes the probability of cohesive failure once a good bond is formed, most of the work, in improving the wet strength of glass resin laminates, is concerned with improving the bondability of the glass surface and minimizing the wicking action of water and resin displacement by water along the glass surface.

### Experimental

The brief study described in this report was limited to two structural adhesives. One, known to be sensitive to water was a nylon/epoxy ad-

hesive film used with a tack primer. This adhesive was air dried a minimum of 15 min. before assembly of the bond specimens then cured for 90 min. at 350°F. and 25 psi pressure.

The second structural adhesive was one known to be water resistant. This was a nitrile rubber phenolic adhesive film using a compatible nitrile rubber phenolic liquid primer. The primer was air-dried for 30 min., oven-dried for 30 min. at 290°F., then the bond specimen was assembled and cured for 90 min. at 350°F. and 25 psi pressure.

The type of specimen used for the study was a tensile lap shear per ASTM D 1002. The aluminum was treated with a sulfuric acid dichromate etch per Mil A 9067 prior to priming.

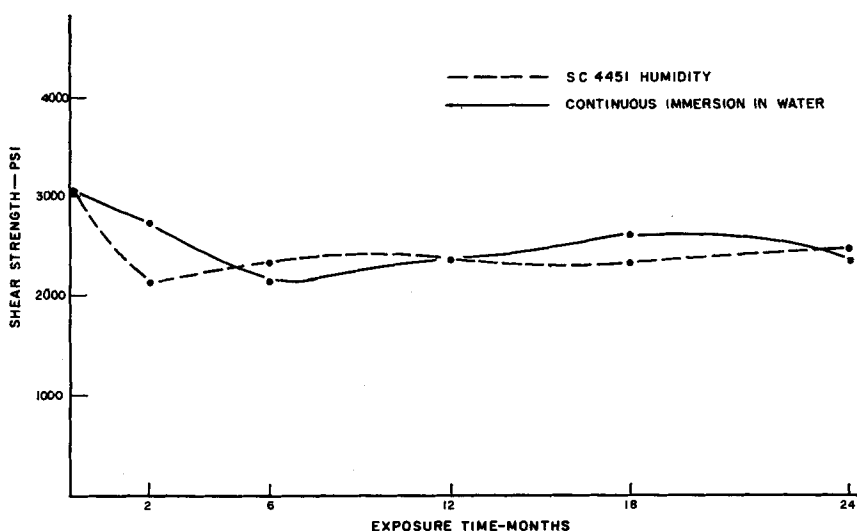


Fig. 1. Effect of aqueous exposure on tensile shear strength of nitrile rubber phenolic adhesive.

For continuous exposure to high humidity, the specimens were placed in a chamber programed per the SC4451 constant humidity environment. This consists of minimum 94% relative humidity with the temperature cycling between 149 and 86°F. over a 48-hr. period. Ordinarily one test consists of ten cycles but for the purpose of this study the specimens were exposed continuously and removed for test at the intervals shown in Figure 1 and Table I.

For continuous exposure to liquid water, the specimens were immersed in distilled water in a covered jar with the products of exposure being allowed to accumulate with time. The temperature of immersion was the ambient laboratory temperature with a mean of 75°F. The specimens were not allowed to dry before being tested.

TABLE I  
Effect of Water (Liquid and Vapor) Exposure on Tensile Shear Strength of Structural Adhesives

Adhesive Type	Environment	Controls	Shear strength <sup>d</sup> exposure (months), psi <sup>a</sup>				
			2	6	12	18	24
Nylon epoxy <sup>b</sup>	SC4451 <sup>c</sup> humidity	4,370 (4,220-4,560)	1,170 <sup>d</sup> (1,060-1,300)	950 (806-1,040)	795 (460-1,030)	1,025 (740-1,380)	850 (760-960)
	Immersion in distilled H <sub>2</sub> O		2890 <sup>d</sup> (1,850-3,800)	1,700 (1,074-2,640)	500 (40-870)	200 (160-280)	120 (70-210)
Nitrile rubber phenolic <sup>c</sup>	SC4451 humidity	3,052 (2,850-3,270)	2,180 (1,920-2,360)	2,370 (1,960-2,550)	2,830 (2,300-2,490)	2,350 (2,100-2,620)	2,440 (2,310-2,670)
Nitrile rubber phenolic	Immersion in distilled H <sub>2</sub> O		2,740 (2,270-3,260)	2,280 (2,050-2,720)	2,380 (1,940-2,740)	2,640 (2,460-2,950)	2,390 (1,480-2,940)

<sup>a</sup> All values are average of five specimens for humidity exposure and average of three for immersion exposure.

<sup>b</sup> Used with compatible primer—air dried minimum of 30 min.—cure 90 min. at 350°F. 25 psi.

<sup>c</sup> Humidity cycle 93% RH plus temperature cycle 149 to 89°F. in 48-hr. period.

<sup>d</sup> Starting with the two month test specimens all nylon/epoxy failures were adhesive.

<sup>e</sup> Used with compatible primer—air dried plus 30 min. bake at 280°F. before assembly—cure 90 min. at 350°F. 25 psi.

### Results

The results for nitrile rubber phenolic are plotted in Figure 1 and for nylon epoxy in Figure 2. The average values, number of specimens tested and high and low values are tabulated in Table I.

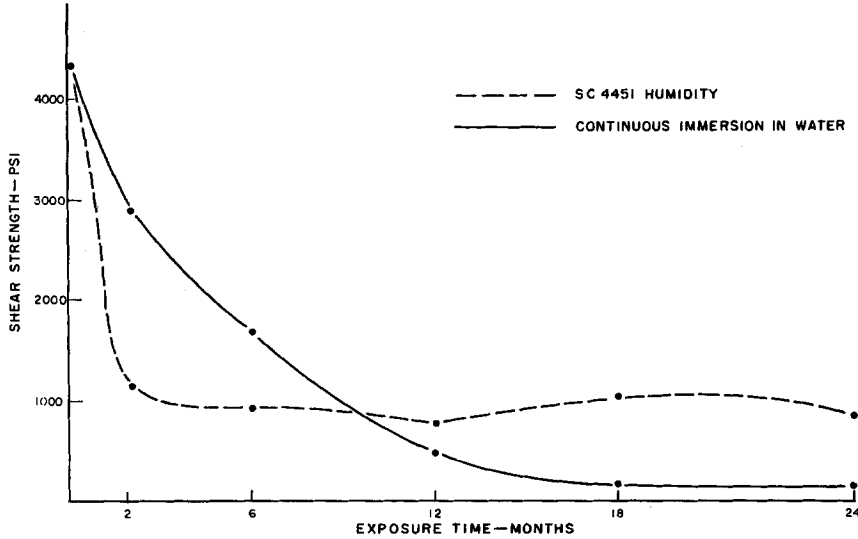


Fig. 2. Effect of aqueous exposure on tensile shear strength of nylon epoxy adhesive.

As expected, the nitrile rubber phenolic adhesive was more resistant than the nylon epoxy.

For the nitrile rubber phenolic there was not much difference between the two environments. The humidity exposed specimens achieved equilibrium within two months at about 2,200 psi from 3,000 psi and did not vary much for the remaining 22 months. The continuous immersion specimens reached the same state of equilibrium within six months. Both sets of specimens remained very close in shear strength at about 2,400 psi for the remainder of the test. For the nylon epoxy specimens, the continuous humidity exposed specimens achieved equilibrium at about 1100 psi within two months and dropped only slightly for the remainder of the test.

The immersion specimens dropped in shear strength for eighteen months and decreased slightly in the last six months to 124 psi. Besides the great difference in strength values between the two adhesives, there was a distinctive difference in mode of failure.

The nitrile rubber phenolic bonded specimens failed cohesively in the adhesive throughout the test while the nylon epoxy specimens went, from a cohesive failure in the adhesive to adhesive failure within 2 months. This suggests that the nitrile rubber phenolic achieved equilibrium by absorbing water physically in the body of the bond but not at the adhesive/adherent

interface. The nylon epoxy, not only absorbed water in the bond but underwent continuous displacement of the adhesive at the interface by the preferentially adsorbed water resulting in adhesive failure.

### Summary

The experimental results and their theoretical interpretation indicate:

(1) Two different adhesive systems bonded to identical adherend surfaces, which both show an initial cohesive failure can have one changing to adhesive failure given the proper environment.

(2) The nitrile rubber phenolic adhesive which did not succumb to failure through the mechanism of preferential displacement at the adhesive/adherend interface achieved equilibrium strength when the bulk adhesive material became saturated with water.

(3) The nylon epoxy adhesive which did succumb to failure through the mechanism of preferential displacement at the adhesive/adherend interface achieved equilibrium more quickly in the aqueous vapor environment than it did in the liquid water because of the more rapid permeation of the vapor.

(4) The nylon epoxy bonded assembly which was immersed continuously in water while weakening more slowly did not level off in strength and degraded continuously to an almost negligible bond strength (124 psi) in two years probably because of the liquid incompressibility and osmosis to the interface.

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### Résumé

Ce manuscrit tente à démontrer la possibilité de défauts d'adhésion par adsorption préférentielle et déplacement adhésif à la surface adhérente. Des résultats sont présentés pour démontrer différents modes de défauts qui sont possibles après le défaut de cohésion initiale.

### Zusammenfassung

In der vorliegenden Arbeit wird versucht, die Möglichkeit eines Klebeversagens durch präferentielle Adsorption und Verdrängung des Klebestoffes an der zu klebenden Oberfläche nachzuweisen. Es werden Daten angeführt, die verschiedene Arten des Versagens zeigen, welche nach einem zuerst eintretenden Kohäsionsversagen möglich sind.

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