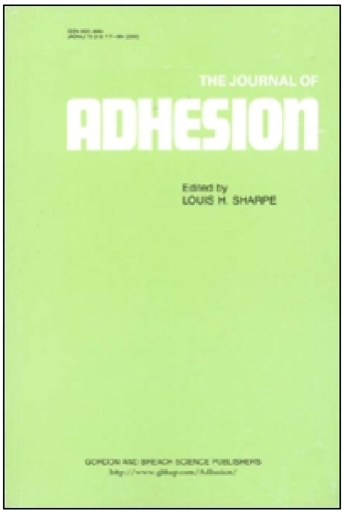

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Stress-Solvolytic Failure of an Adhesive Bond

Robert L. Patrick[a]; John A. Brown[a]; Lynn E. Verhoeven[a]; E. J. Rlpling[b]; S. Mostovoy[b]
[a] Alpha Research and Development, Inc., Blue Island, Illinois [b] Materials Research Laboratory, Inc., Glenwood, Illinois

To cite this Article Patrick, Robert L. , Brown, John A. , Verhoeven, Lynn E. , Rlpling, E. J. and Mostovoy, S.(1969) 'Stress-Solvolytic Failure of an Adhesive Bond', The Journal of Adhesion, 1: 2, 136 — 141
To link to this Article: DOI: 10.1080/00218466908078884
URL: http://dx.doi.org/10.1080/00218466908078884

Stress-Solvolytic Failure of an Adhesive Bond

ROBERT L. PATRICK, JOHN A. BROWN, LYNN E. VERHOEVEN
E. J. RIPLING, S. MOSTOVOY

Alpha Research and Development, Inc.
Blue Island, Illinois 60406
Materials Research Laboratory, Inc.
Glenwood, Illinois 60425

(Received April 7, 1969)

ABSTRACT

Stress solvolytic failure of an adhesive bond in an aqueous environment has been studied. Utilizing a beam specimen, with a precracked epoxide adhesive bond, static loads were applied and the interfacial cracking was observed. The interface cracking was independent of the center of bond precrack and occurred at an applied load which was twenty percent of the failure force.

INTRODUCTION

FAILURE OCCURS in structural adhesives by the extension of an initially present crack or flaw. The failure may be by extension of a stable crack at very slow rates, or by catastrophic extension of an unstable crack at extremely high rates. The latter occurs where a critical load is reached and a stationary or very slow moving crack is accelerated to a high velocity.

Earlier papers of three of the authors discussed in detail the study of fracture mechanics applied to special adhesive systems [1, 2] and, in particular, a series of epoxide systems [3]. The reader is referred to these papers for the background from which the current work derived.

This paper concerns the failure of adhesive bonds by the action of a liquid while the system is under stress. The failure may be referred to as stress-corrosion-cracking failure or, more descriptively, as solvolytic failure under stress.

DISCUSSION

The technique utilized in collecting the data was similar to that utilized in the determination of the fracture toughness of adhesive systems. A tapered-double cantilever beam[*] of known dimensions was used having the characteristics that the crack extension force $\mathcal{G}$ was proportional to the square of the applied load, P, and independent of the crack length, a. Normally, the test

---

[*] Abbreviated TDCB for convenience.

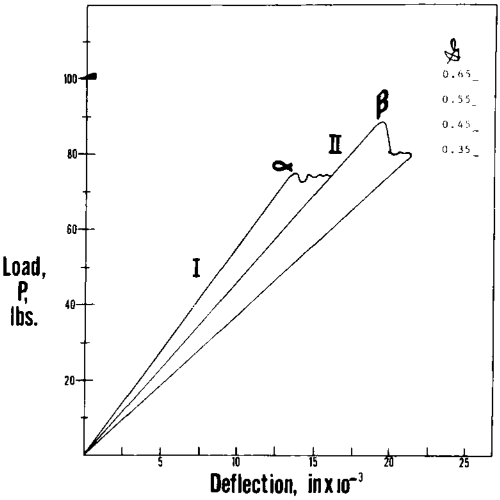

Figure 1. Typical load-deflection curve for precracked specimen: effect of water.

involved an increasing load function in which P was plotted as a function of its displacement, δ. A typical P-δ curve is shown in Figure 1, Curve I. The $\mathcal{G}$ value is calculated from the point of crack extension at α. The crack extends from the initial precrack and is self-arresting, the crack extension being produced by constant displacement. The crack produced in this way is referred to as a "center of bond" fracture (*CoB*). Only under anomalous conditions can one develop a crack near the interface in an increasing load system.

It is of interest to note that experiments have shown that the addition of water to the crack, followed by reapplication of the continuous load, results in an increase in the toughness of the system as shown by a higher $\mathcal{G}$ value, β. Schematically, this is shown by Curve II of Figure 1 where the crack propagation occurs at a higher load than was necessary to propagate the crack developing Curve I.

In all cases involving increasing load the specimens failed as *CoB* cracks. However, the evaluation of static-load specimens provided rather different results from those anticipated. Indeed, static loads resulted in slow crack extension at or near one of the other interfaces at humidities above four per cent. It should be pointed out that the specimens were precracked in an opening mode to determine the $\mathcal{G}_c$, or critical crack propagation value.

The experimental specimens were prepared as follows. Tapered-double cantilever-beam specimens, Figure 2, were prepared at Materials Research Laboratory using a tetraethylene pentamine cured epoxide (DER 332) as the bonding agent. The bonds were 10/180* epoxide with 2024-T4 aluminum adherends. The specimens were precracked in an opening mode by continuous loading, resulting in a precrack which was *CoB* and ran for approxi-

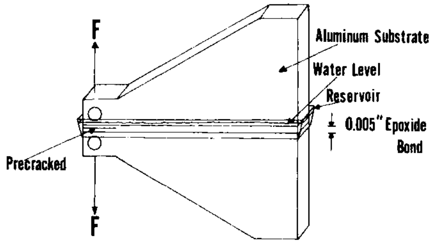

Figure 2. Stress-corrosion-cracking specimen with liquid water.

mately one inch prior to arresting. Following the precracking, a reservoir was prepared which allowed for complete immersion of the bond line in the liquid to be studied. The specimen, supported by the upper beam, was placed in a suitable load cell and a static weight hung from the lower-beam loading hole. The assembly was placed in an isolation chamber, the reservoir filled with water, and weights placed on the weight plan. The static load which was applied was 0.2 $\mathcal{G}_c$, or, in other words, two tenths of the load which would cause unstable cracking. The crack generated by stress-solvolysis occurred at the interface (IF), Figure 3, and was not a continuation of the *CoB* precrack. Rather, the IF crack started at the edge of the specimen, in the vicinity of the crack top, at the air-adhesive-adherend junction. The *IF* cracks propagated inward from the edges until they joined or reached the other edge. They did not, in any case, join the *CoB* crack. Often, the crack initiated at the upper and lower interfaces and the crack extended across both interfaces, at which time double debonding occurred along the entire length of the specimen.

The location of the initiation of interfacial failure was of some significance. Generally, it occurred just below or slightly behind the *CoB* crack tip. This was the area of the interaction of the stress field due to the crack tip and the adherend surfaces.

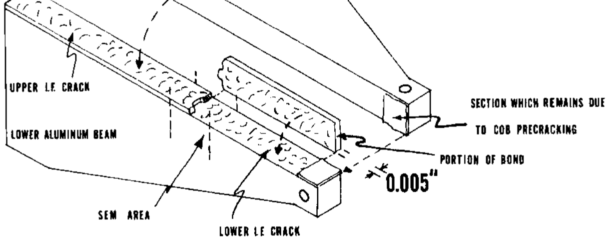

Figure 3. Schematic: stress-solvolytic-cracking failure—aluminum/epoxide bond.

---

[*] 10/180 follows the nomenclature of Mostovoy & Ripling[8], indicating 10 parts of TEPA per hundred parts of epoxide resin cured at 180°F.

The rate of cracking is quite slow and a reasonably accurate value of this can be determined by observing the average rate following 100 hours exposure, or some arbitrary time. The rate data calculated on 10/180 specimens, both with liquid water and with 96 per cent R. H., are virtually identical.

While rapid cracking of the epoxide bond results in *CoB* failure, slow crack extension in a humid environment, or liquid water, always takes place in the interface. Stress-corrosion-cracking requires that the corroding media be available, along with a high stress concentration. If the liquid or vapor is excluded, no cracking will occur until $\mathcal{G}_c$ is reached.

Figure 3 is useful in describing the stress-corrosion phenomenon which occurred during these experiments. Following the precracking, the static load, in the presence of water, caused interfacial failure at the lower interface. Independently, the upper interfacial failure initiated and both *IF* failures continued to the end of the specimen. After both cracks had propagated well past the mid-point of the specimen the tongue of the adhesive bond sheared off as is shown in the schematic allowing a section of the bond to be removed. The shear failure was a function of the geometry rather than stress-corrosion-cracking.

SCANNING ELECTRON MICROSCOPE TECHNIQUE

The scanning electron microscope has made it possible to examine, in great detail, surface phenomena and surface effects far more readily than it has ever been possible before. Sample preparation is straight-forward, allowing one to essentially evaluate the surface with which he is involved, rather than to perform the arduous and often unsatisfactory task of preparing replicas as is required by the transmission machine. It should be pointed out that it is often necessary to apply an extremely thin metallic coating to dielectric specimens in order to eliminate the possibility of charging by the electron beam. However, this metallizing coating thickness is generally less than 200 angstroms which is below the resolving power of the SEM.

The fact that it is not necessary to prepare replicas of the surface to be examined makes the production of information very simple and many samples can be examined in the course of a very few hours. Of course, the fact that replicas are not required eliminates the possibility of the generation of artifactual information, accordingly, reducing one of the major objections to electron microscopy.

The SEM is especially useful in the examination of bond failures following the destruction of an adhesive by many of a number of methods. The fact that bonds can be failed and that within minutes the specimens may be inserted into the scanning electron microscope for visual examination, makes for an extremely powerful tool. The technique lends substantial informative support to the phenomenological study of adhesion, and can aid markedly in studying failure modes of adhesively bonded systems.

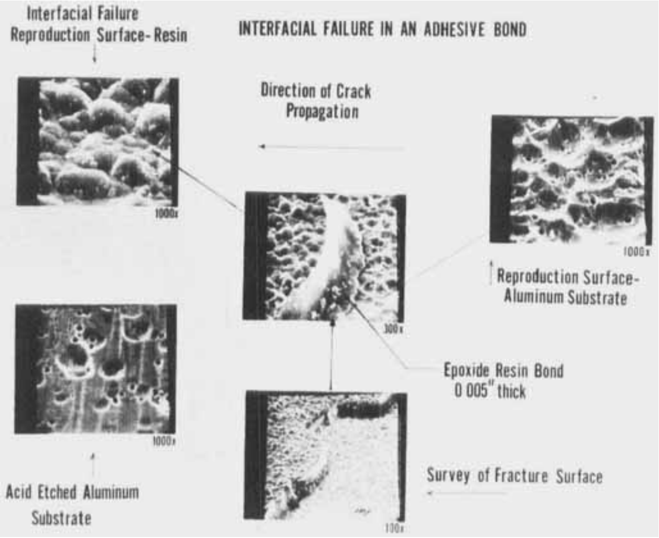

Figure 4. Interfacial failure in an adhesive bond.

SCANNING ELECTRON MICROSCOPY OF A STRESS-SOLVOLYTIC FAILURE

Figure 4 is a montage of several scanning electron photomicrographs obtained with 10/180 TEPA cured epoxide bonded to the aluminum substrate. The electron photomicrographs are taken after the upper beam has been removed. The observation is of those areas where two interfacial cracks were propagating simultaneously. The areas are delineated by dotted lines in Figure 3.

The crack propagation in this particular specimen was from right to left. The cliff-like structure is a shearing of the 0.005″ bond due to the geometry of the specimen, and is not directly involved in the interfacial failure phenomena. It does, however, make it simple for one to observe the specimen following the stress-corrosion-cracking.

The area to the lower right in the 300X photomicrograph is the surface of the lower aluminum beam. A higher magnification of this aluminum substrate is shown in the upper right-hand photomicrograph. The dimpled surface clearly shows that the aluminum is essentially free of the epoxide adhesive. The holes which are generated by the cleaning solution are, however, partially filled with the epoxide resin. One may compare the surface which had been part of the adhesive bond with the photomicrograph in the lower left of the figure showing a control aluminum surface which was etched with the same cleaning solution; albeit, for a shorter period of time. The control surface had not been utilized in an adhesive bond. A comparison of the photomicrographs of the surfaces shows remarkable similarity.

The upper left-hand photomicrograph shows the epoxide surface after the upper aluminum substrate of the TDCB had been removed. One may clearly see the finely detailed surface structure of the aluminum replicated in the epoxide surface. One may also note the protrusions emanating from the surface having obviously been torn out of the holes in the aluminum surface. It is quite apparent that the adhesive bonds in the interface of the epoxide and the aluminum have been failed by a combination of stress and solvolytic action. The load was then carried completely by the material in the holes in the aluminum and these protrusions apparently failed through mechanical loading rather than by stress-corrosion.

It is felt that this series of scanning electron photomicrographs of a typically stress-solvolytically failed specimen shows dramatically the effect of solvolytic failure under low loads in the presence of flaws. The experiments quite conclusively prove that interfacial failure accompanies stress-solvolysis-cracking. We will later be concerned with mechanically stressed bonds and will report the types and mechanisms of mechanical non-interfacial failure.

It has been reported that glass/resin interfacial failures have been observed in glass bead reinforced structures [4, 5]. The writers feel that glass is a special case. Work is being carried out at this point which will be substantially more definitive concerning glass surfaces.

SUMMARY

1. When a combination of stress and solvolysis is applied to TDCB specimens containing a precrack, true interfacial failure is possible.
2. The resin-aluminum bonds were cleaved by a combination of chemical and mechanical action rather than by mechanical action alone.
3. The system generated gross failure characteristics at one or both interfaces at $\mathcal{G}$ levels well below $\mathcal{G}$ critical [2].

ACKNOWLEDGMENT

Acknowledgments are due to Dr. Neil M. Cameron for many helpful comments during the manuscript preparation.

REFERENCES

1. E. J. Ripling, S. Mostovoy, and R. L. Patrick, "Measurement of Fracture Toughness of Adhesive Bonds," Mater. Res. Stand., *64*, (1964), p. 129.
2. S. Mostovoy and E. J. Ripling, Stress-Corrosion-Cracking of an Epoxy Adhesive in a Humid Environment. Accepted for Publication Jour. Appl. Poly. Sci., Winter 1969.
3. S. Mostovoy and E. J. Ripling, Fracture Toughness of an Epoxy System, Jour. Appl. Poly. Sci., *10*, (1966), pp. 1351-71.
4. A. S. Kenyon, "Role of the Interface in Glass-Epoxy Composition," J. Coll. and Interface Sci., *27*, (1968), pp. 761-71.
5. A. Wambach, K. Trachts, and A. DiBendetto, "Fracture Properties of Glass Filled Polyphenylene Oxide Composites," J. Comp. Materials., *2*, (1968), pp. 266-83.