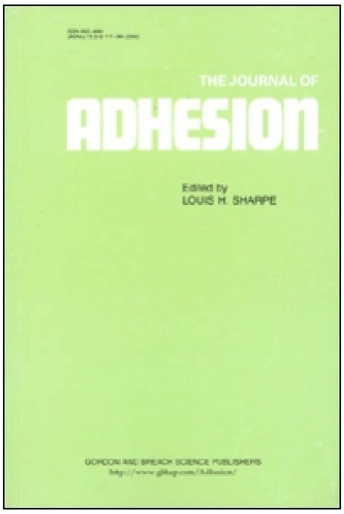

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Continuum and Fracture Mechanical Studies of Contaminated Bonding Surfaces

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Continuum and Fracture Mechanical Studies of Contaminated Bonding Surfaces*

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The importance of fracture mechanics testing of contaminated bonding surfaces is discussed. The sensitivity of adhesive bond systems to contamination may increase dramatically when macroscopic cracks are present. A bond system is shown to retain a significant level of tensile adhesion strength at relatively high levels of contamination, yet have near zero mode I fracture toughness at very low levels of the same contaminant. Silane adhesion promoter is shown to reduce greatly the system fracture toughness sensitivity to contamination, especially at lower levels of contamination.

KEY WORDS fracture mechanics; tensile adhesion; silane adhesion promoter; butt joint; tapered double cantilever beam (TDCB); sensitivity to contamination.

INTRODUCTION

Contamination insensitivity of adhesives is a very important property in industrial bonding operations. With improved NDE techniques which quantify material flaws and increased reliance on such techniques for quality assurance, the importance of contamination insensitivity is increased. This is due, in part, to the fact that NDE methods generally do not distinguish interfaces which are weakened by contamination. In cases where the maximum allowed contamination level can be assured by such techniques as OSEE (optical stimulated electron emission), IR-scanning or black-light inspection, the effects of the maximum level on the bond system capability must be clearly understood.

Two analytical methods are commonly employed in the analysis of adhesive joints: continuum mechanics and fracture mechanics. Continuum mechanics views materials as continua in which there exist no macroscopic flaws and measures bond

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capability as strength. Fracture mechanics analyzes the response of materials to existing macroscopic cracks and flaws, quantifying the resistance of materials to the propagation of the cracks and flaws. The energy required to propagate an existing macroscopic crack per unit area of new surface created by the crack propagation is termed the adhesive fracture energy or fracture toughness. Since most adhesives fail due to the initiation and subsequent propagation of flaws and cracks, the application of fracture mechanics and fracture mechanical testing of adhesive systems is very important.[1,2]

The utility of fracture mechanical testing in contamination sensitivity studies has been observed and is reported in this paper. Two adhesives were tested for contamination sensitivity employing tensile adhesion butt joint specimens, representing continuum mechanics testing, and tapered double cantilever beam (TDCB) specimens, representing fracture mechanics testing.

Silane adhesion-promoting primers have been used extensively in industry to improve initial strength and durability of bondlines. Many mechanisms have been proposed to explain the utility of silane primers.[3,4] These mechanisms include: interdiffusion of the coupling agent with the adhesive network,[5] chemical linking of the coupling agent to the bond surfaces through covalent bonds formed from condensation reactions between bonding surface hydroxyl groups and the hydrolyzed alkoxy groups of the primer[6,7] and improved bond surface wetting due to the low viscosity of the primer.[8] It was suspected that the use of silane primer would reduce the system sensitivity to contamination as well as improve initial bond capability and durability. Thus, the use of silane primer was investigated in this effort as a means of improving the bond system robustness by reducing the system sensitivity to contamination.

SPECIMEN GEOMETRIES AND ADHESIVE PROPERTIES

Tapered double cantilever beam (TDCB) specimens developed by Mostovoy and Ripling[9,10] and outlined and discussed in ASTM-D3433 and tensile adhesion buttons specified in ASTM-D897 were employed in the study. The TDCB geometry followed the ASTM standard precisely. The tensile adhesion buttons, however, were slightly modified to allow the incorporation of annular spacers to control bond thickness. The button diameter was 31.5 mm (1.24 in). The spacers fit snugly over the buttons, separating a pair of buttons by the desired bond thickness and reducing the diameter of the bondline to 28.7 mm (1.129 in). A cross section of the modified tensile adhesion button geometry is shown in Figure 1. The adherends for both geometries were made of D6AC steel. The contaminant used was Calcium HD-2 grease, a light paraffin oil mixed with a calcium soap, manufactured by Conoco, Inc. HD-2 grease is applied to D6AC steel surfaces during refurbishment of Space Shuttle booster rocket nozzle components to reduce corrosion during transportation and storage prior to reuse.

The two adhesives studied were two-part, amine-cured epoxy structural adhesives formulated by Dexter-Hysol: EA 946, a low-modulus and high-elongation adhesive, and EA 913NA, a high-modulus and high-strength adhesive. Table I presents per-

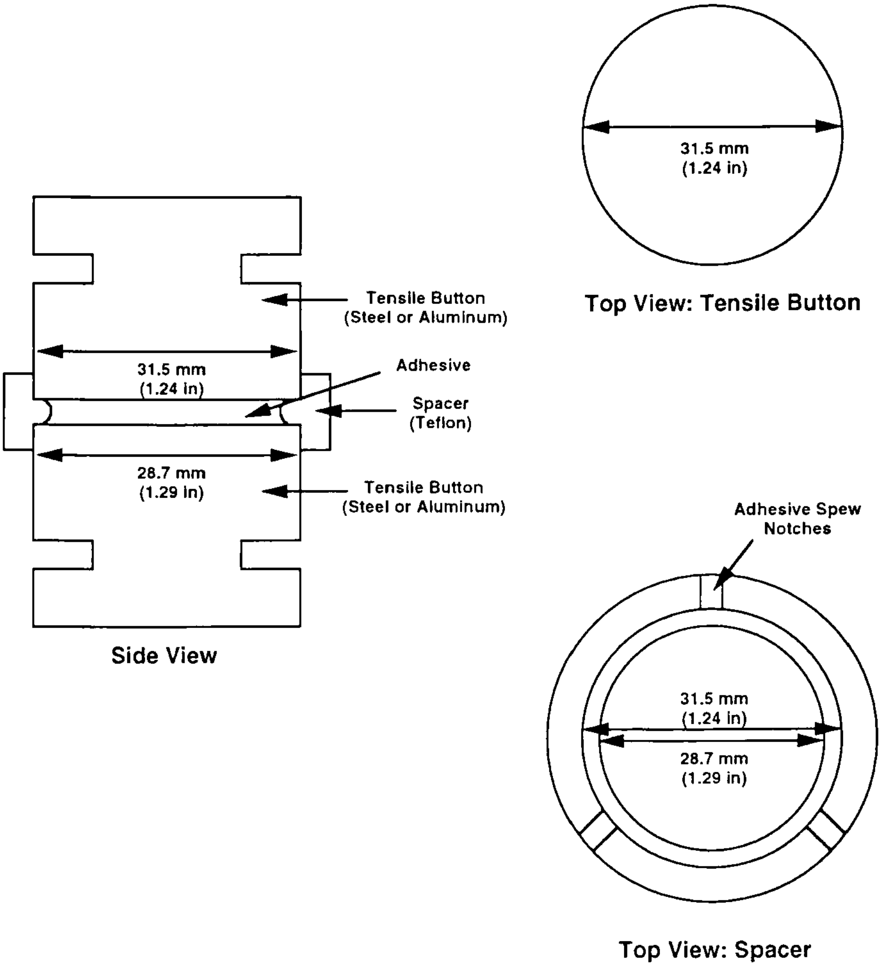

FIGURE 1 Modified geometry of the tensile adhesion specimen.

TABLE I
Adhesive and adherend material properties

Material	Modulus (MPa)	Poisson's ratio	Ultimate elongation (percent)	Uniaxial tensile strength (MPa)
D6AC Steel	204,000	0.32	8.0	1380
EA 913NA*	2,810	0.41	4.2	45.7
EA 946*	41.4	0.40	77	14.8

*Test Rate = 1.3 mm/min
Test Temperature = 25°C

tinent material properties of the two adhesives and the adherend material used in the study.

SPECIMEN PREPARATION

The adherends were vapor degreased using methyl chloroform (1,1,1 trichloroethane). The vapor degreasing was followed by a grit blast and a dry wipe using Rymplecloth® or a dry nitrogen blast to remove any grit residue; no difference was measured between the two residue removal methods. Finally, another methyl chloroform vapor degrease, a grit blast with fresh grit and another grit residue removal cycle were performed just prior to contamination, priming or bonding.

For silane-primed specimens, UF-3296 primer was applied prior to contamination. UF-3296 is a solution containing 40% toluene, 40% absolute ethanol, 5% distilled/deionized water, 5% n-butanol, 5% 2-butoxyethanol, 5% γ-glycidoxypropyltrimethoxysilane (A-187, manufactured by Union Carbide Corporation), and 0.3% acetic acid. The primer was applied using a nylon bristle brush and single brush strokes. The primed surfaces were allowed to air dry for a minimum of one hour at ambient conditions prior to bonding.

The HD-2 grease was thinned to a given concentration (0.5 to 2%) in methyl chloroform. The solution was then sprayed onto the bond surface using an air brush. The sweep pattern of the air brush was controlled by an XY-plotter. An aluminum foil sheet was placed next to the specimens being contaminated and sprayed during the same contamination sweep as the test specimens to provide a "witness panel" for a precise measurement, by weight (± 22 mg/m^2), of the contamination level. Only one bonding surface was contaminated for each specimen. That surface was marked with a "C," and the failure surface of adhesively failed specimens was noted by the technicians performing the tests. The methyl chloroform solvent was allowed to evaporate for fifteen minutes prior to bonding.

Vacuum-mixed adhesive (EA 913NA or EA 946) was applied to both bonding surfaces with an excess of adhesive in the center to avoid air entrapment during mating of the adherends. The specimens were mated within a bonding fixture with spacers to insure a 1.3 mm (0.050 in) bond thickness, the chosen bond thickness representing a production bondline. The fixture and specimens were then placed in an oven for curing at 40 ± 3°C for a minimum of 36 hours. A weight (1.8 kg per specimen) was set on top of the specimens to assure good mating during the cure.

TEST PROCEDURES AND DATA ANALYSIS

Testing of the TDCB's was performed in an Instron mechanical testing device which is capable of low displacement rate loading. In order to form a precrack in the low toughness, contaminated specimens without catastrophically failing the specimens, the specimens were clamped with a C-clamp just beyond the beginning of the taper as shown in Figure 2. The specimens were then loaded at a constant displacement rate of 0.5 millimeters per minute, using the Instron, until the load leveled or

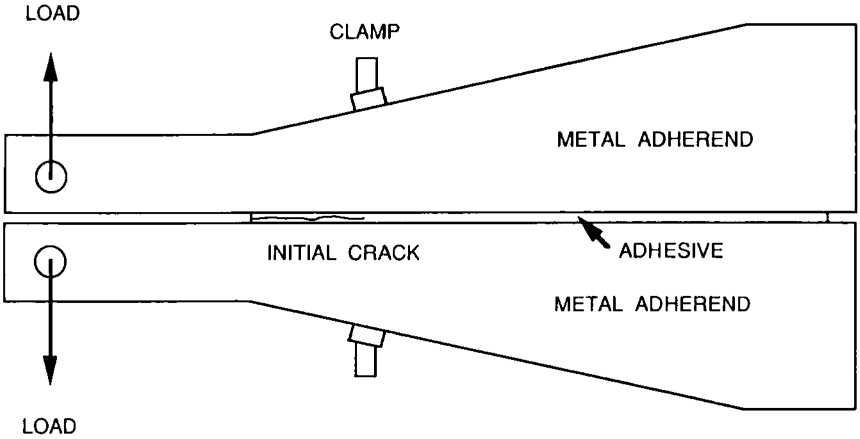

FIGURE 2 Tapered double cantilever beam geometry showing loading mode and precracking arrangement.

decreased sharply, signaling the initiation of a crack which was also observed visually. The specimens were then unloaded, the clamps were removed and the specimens were tested to measure the average critical load for crack propagation at a constant displacement rate of 0.125 millimeters per minute. All testing was performed at ambient conditions (22 ± 2°C and 10–40% relative humidity).

Due to the geometry of the TDCB specimen, the data reduction was simple. The fracture toughness was calculated employing the following equation (from ASTM D3433):

$$G_{IC}=\frac{4P_C^2 m}{E w^2} \qquad [1]$$

where:

G_{IC} = mode I fracture toughness
P_C = average critical load
E = modulus of beam material (193 GPa)
w = width of specimen (= 25.4 mm)

and

$$m=\frac{3a^2}{h^3}+\frac{1}{h} \qquad [2]$$

where:

a = crack length
h = adherend thickness

The geometric factor m was a constant equal to 3.5 mm^{-1} due to the taper of the adherend.

Testing of the tensile buttons was performed at 1.25 millimeters per minute. Average stress values at failure were recorded from the tensile button testing.

RESULTS AND DISCUSSION

Figures 3 and 4 show the sensitivities of the bond systems to HD-2 grease contamination in the continuum and fracture mechanical realms. Each datum represents the average of five replicate tests, and the error bars depict the ranges of test values. All failures in the tensile button testing switched from cohesive in the adhesive to interfacial between the adhesive and the steel (determined by visual inspection) at the lowest tested level of contamination. TDCB failures were all interfacial. At the highest contamination levels tested, all of the bond systems retained a considerable degree of strength.

Although the strengths of the two bond systems at higher levels of contamination are roughly equivalent, a large difference in behavior was observed in fracture mechanical measurements. While the EA 946 bonds retained a considerable portion of their fracture toughness at fairly high levels of contamination, EA 913NA bond systems exhibited almost no fracture toughness, resistance to crack growth, at very low contamination levels.

The sensitivity of EA 913NA to contamination in the fracture mechanics realm has been demonstrated by failures in laboratory simulation motors. The first failure was observed during a static motor firing in which pressure ports were bored through the steel housing to the D6AC steel/EA 913NA bondline. The ports were placed in an area of bond-normal tensile stress where failure was later calculated to have initiated due to stress concentrations around the pressure ports. The failure initia-

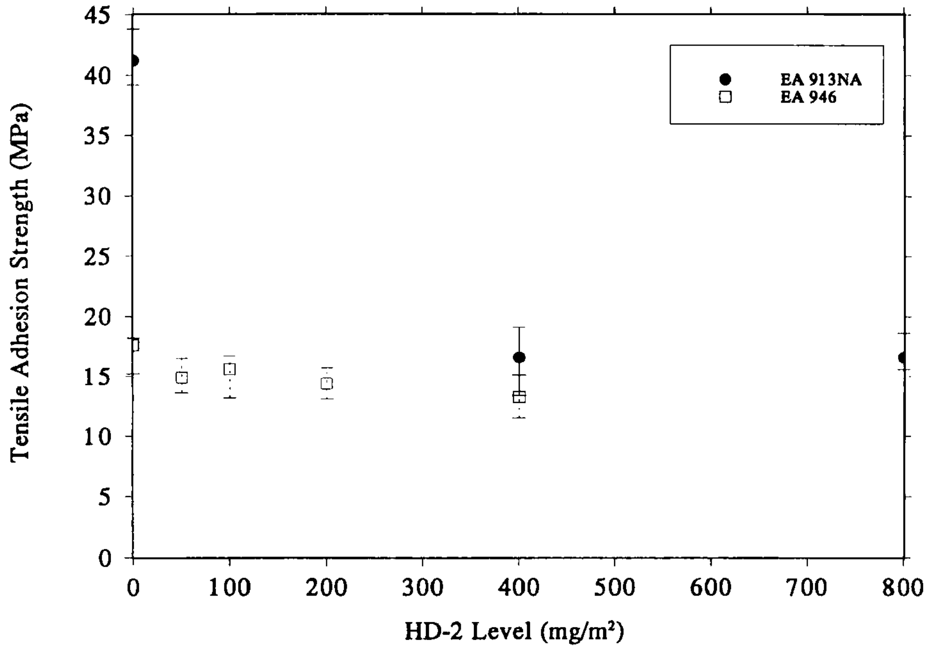

FIGURE 3 Tensile strength reduction due to HD-2 grease contamination.

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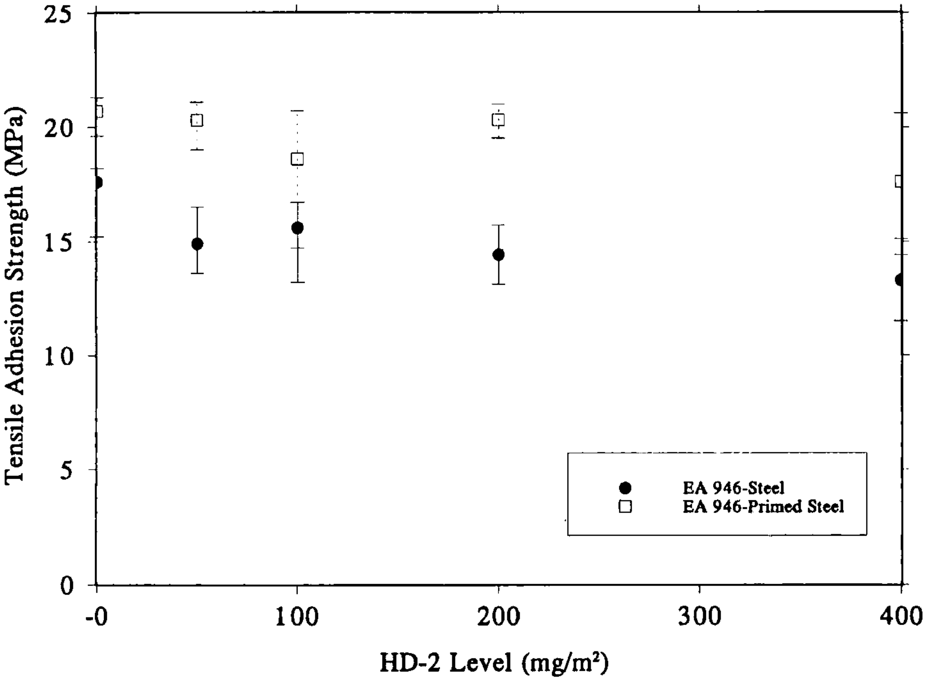

FIGURE 5 Effect of silane primer on tensile strength contamination sensitivity.

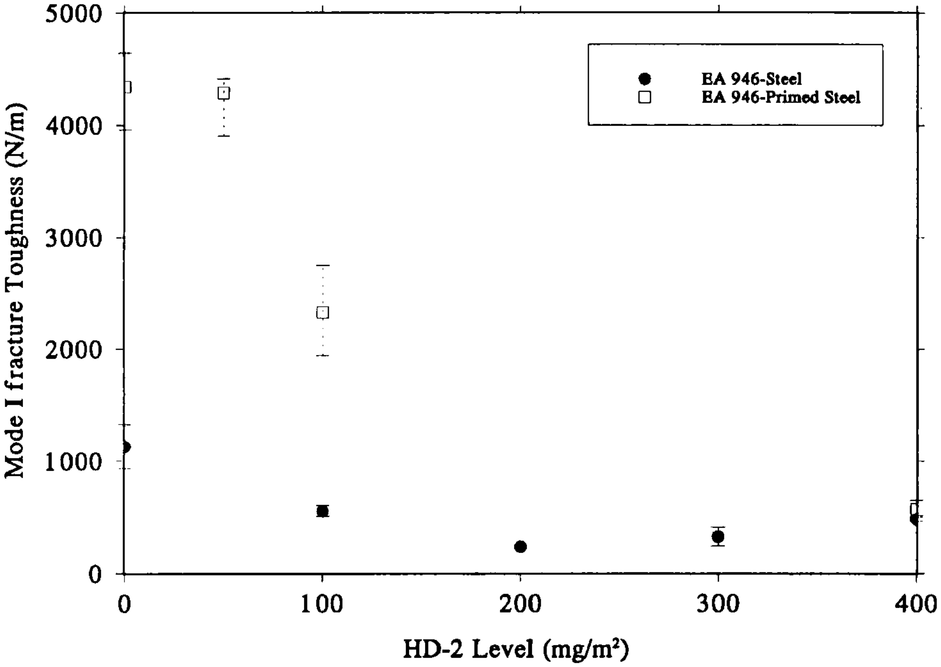

FIGURE 6 Effect of silane primer on mode I fracture toughness contamination sensitivity.

the adhesive layer in the primed control samples. Importantly, the failure mode remained cohesive up to contamination levels of 205 mg/m^2. The use of silane adhesion promoter realizes several significant benefits in the system tested, with no apparent disadvantages.

SUMMARY AND CONCLUSIONS

The importance of studying the effects of contamination sensitivity on the strength (in the continuum realm) and resistance to crack growth (in the fracture realm) of two adhesive systems has been shown. While both adhesives reacted similarly to contamination in the continuum realm, in which a significant percentage of the strength remained at fairly high levels of contamination, the resistance of the two adhesive systems to crack growth at the contaminated interface was quite different. While a considerable fracture capability remained with one bond system at moderate contamination levels, the second system maintained almost no resistance to crack growth at very low levels of contamination. Neglecting the contamination sensitivity in the fracture realm has led to failure in laboratory simulation bondlines containing macroscopic cracks.

The use of silane adhesion promoter can greatly decrease the contamination sensitivity of an adhesive bond, especially at lower levels of contamination. This was demonstrated in both strength and fracture toughness measurements.

Acknowledgments

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