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A fracture analysis of cathodic delamination at polyurea/steel interfaces ☆

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ABSTRACT

A fracture mechanics approach to accelerated life testing of cathodic delamination between steel and polyurea is presented. This required the hyperelastic behavior of the polyurea to be described by the Marlow model based on uniaxial tension and plane strain compression tests. Time-dependence was also considered but could be neglected if proper test protocols were followed in cathodic delamination tests using a strip blister specimen. The variation of J-integral with specimen geometry and loading parameter was obtained, which allowed the resistance to cathodic delamination to be expressed in terms the J-integral and the crack speeds obtained from the tests at several temperatures. The approach established that both temperature and stress can be used to accelerate the cathodic delamination, thereby providing a quantitative and rational basis for conducting accelerated testing. In addition, the discriminating nature of the approach for design purposes was exemplified by quantitatively establishing differences in the delamination resistance of three surface treatments.

1. Introduction

Cathodic delamination can be viewed as an example of environmentally assisted crack growth, an example of slow, subcritical fracture that can eventually transition to fast fracture and complete failure of the interface. The environmental or chemical aspects of the problem have been studied for a number of polymer/metal pairs [1–10], as reviewed in [11] and have the potential to be coupled with mechanical effects [11–18], thereby improving our understanding of the problem. This in turn can motivate accelerated life testing protocols and the development of new surface treatments with a view to eliminating or at least minimizing cathodic delamination in naval and automotive structures.

In the current study, we examine the potential for cathodic delamination in systems where steel is coated with polyurea, often for blast protection [19,20]. The elements of the approach are threefold; determining the time-dependent, hyperelastic behavior of the polyurethane, conducting a stress analysis of the specimen to be used in the cathodic delamination experiment in order to obtain J-integral values as a function of crack length and conducting cathodic delamination experiments and determining the crack velocity profiles for the polyurea/steel interface as a function J-integral and temperature. The details of these steps are presented in Sections 2 and 3 followed by results and discussion in Section 4.

2. Experimental

In this section, we describe the experiments that were conducted to determine the nonlinear mechanical behavior of the polyurea and the cathodic delamination of polyurea from steel.

2.1. Polyurea constitutive behavior

The polyurea considered in this study was formed by the reaction of a modified diphenylmethane diisocyante prepolymer (Isonate 143 from Dow Chemical) with an oligomeric diamine curative (Versalink P-1000 from Air Products). A ratio of 1:4 prepolymer to curative by weight was used herein. The Versalink was heated to 50 °C until its viscosity dropped sufficiently for processing. It was then degassed under vacuum at room temperature with constant stirring until no bubbles were observed. The Versalink and Isonate were then mixed under vacuum in a weight ratio of 1:4 for 5 min. Polyurea was poured into a rectangular sheet mold. This sheet of polyurea was then cut to prepare samples for

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uniaxial tension and plane strain compression tests. The cure time for the material was 2 weeks at room temperature.

The uniaxial tension specimens were strips ($17.5 \times 0.8 \times 0.33$ cm) that were gripped at each end, leaving a 5 cm gage length, and were loaded to failure in an electromechanical testing device under displacement control at various rates. The load and overall extension of the specimen were measured using the load cell and crosshead displacement sensor of the device. The engineering stress in the specimen was obtained from the load and original cross section area. A camera (Lumenera INFINITY3) was set up to measure the axial and transverse displacements in the gage section of the specimen using horizontal and vertical lines that were marked on the specimen surface. The temperature at which the tests were conducted was 22 °C.

In the plane strain compression test, polyurea sheets were compressed across their width by narrow bars (Fig. 1), which were made of ground tool steel with 0.13-cm radii to minimize stress concentrations [21]. The bars were mounted between self-aligning platens that were attached to the crosshead and base of the electromechanical loading device. The dimensions of the sheet (Fig. 1) were $L_0 = 7.8$, $b_0 = 7.8$ and $t_0 = 0.44$ cm, while those of the bar were $w = 1$, $b = 15$ and $h = 2.5$ cm. In order to ensure that the deformation under the bars is essentially homogeneous, the ratio of bar width to strip thickness at any instant in the test should be between 2 and 4 [22]. This choice of dimensions w/t_0 satisfied this criterion initially but violated it once the true strain was -0.5. Consequently, any data outside this regime should be considered in light of this restriction. A release agent was applied to the surfaces of the polyurea as a lubricant in order to minimize friction. The load and platen displacement were measured as before and the camera was used to measure the displacement of the grips 0.5 cm from the contact surfaces. Images were recorded every 20 s. The tests were conducted in displacement control at a strain rate of 9.2×10^{-5}/s.

2.2. Cathodic delamination

The strip blister specimen [11] (Fig. 2) was used to characterize the resistance to cathodic delamination between polyurea and steel. The steel substrate was 11.5 cm long by 1.27 cm wide by 2.54 cm thick, with polyurea layers whose thickness t was 7.6 mm.

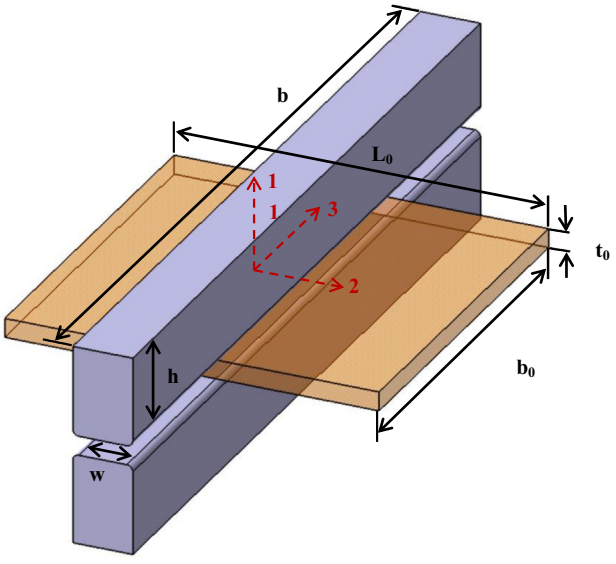

Fig. 1. A schematic of the plane strain compression test and specimen. The dimensions were $L_0 = 7.8$, $b_0 = 7.8$, $t_0 = 0.44$ and $w = 1.0$ cm.

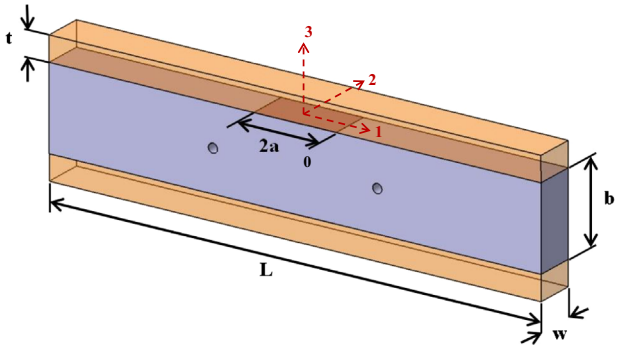

Fig. 2. A schematic of the strip blister specimen with layers of polyurea bonded to steel with a primer PR-420. The dimensions were $L = 11.5$, $w = 1.27$, $b = 2.54$, $t = 0.76$ and $2a = 2.54$ cm.

The initial crack length $2a_0$ was 2.54 cm. The fabrication steps were as follows: The steel surfaces were grit blasted with #50 angular steel grit at a pressure of 0.6 MPa. The adherends were then placed in an ultrasonic bath filled with methyl ethyl ketone (MEK) for 15 min, once to remove major debris and then again as a final cleansing. The region for the initial crack was then masked with Teflon® tape and PR-420 (PRC-DeSoto) metal primer was applied to the remainder of the steel surface and allowed to dry for 2 h. Mold walls were applied to specimen and the gap was filled with previously evacuated polyurea to the thickness specified above. The polyurea was cured for 2 h at room temperature, while the polyurea for the second layer was prepared. The specimen was then turned over and the second layer of polyurea was applied in the same way. This procedure provided two potentially different interfaces to evaluate because the primer dried for 4 h on the second interface prior to the application of the polyurea. The interfaces were designated 2 h and 4 h, respectively. The assembly was allowed to cure at 22 °C for 2 weeks and the mold walls were removed.

A separate set of specimens were fabricated in the manner just described, except for the fact that there was no primer between the steel and polyurea. In this case, the first polyurea layer cured for two more hours than the second layer, but, since the total cure time was 2 weeks, no distinction was made between the respective interfaces.

For the cathodic delamination experiment itself, a 4.8 mm-diameter stainless steel dowel was inserted between the polymer and metal at both interfaces at the center of the initial crack to provide a wedge loading to the specimen. The specimen was then allowed to relax for several hours prior to environmental exposure in order to minimize any viscoelastic effects.

The conditions for cathodic delamination were provided by placing the preloaded specimens in an artificial sea water solution [23] in an aquarium (Fig. 3) and applying a suitable electrical potential to the specimen. Air was directly injected into the artificial sea water using a Bubble Bar®, which, in conjunction with a ventilator, ensured that there was a homogeneous and sufficient supply of oxygen for the cathodic delamination reaction to occur. The artificial sea water was maintained at several temperature levels in separate tests. A potentiostat was used to maintain the metal parts of the specimen at a constant potential of -0.9 V with respect to a standard calomel electrode (SCE). A graphite rod was used as the anode. The current flow in the tank was measured periodically throughout each experiment and remained constant at about 1 mA. The specimens were periodically removed in order to measure the crack length with vernier calipers. The measurements were made on both edges of the crack fronts and the average for each interface (2 h and 4 h) was recorded as the effective crack length.