



Characterization of Functionally Graded Adhesives Using Radiation Curing

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Grading adhesive properties across a bondline can lead to more uniform stresses and increased strength without altering the geometry of the adherends. In this research, radiation sensitizers have been added to adhesives to create a secondary cross-linking possibility that is activated with radiation. In this way the adhesive stiffness and strength can be controlled by controlling the exposure to radiation. In this paper, a system of grading adhesive properties is introduced and the double cantilver beam test results show that the gradation not only changes stiffness and strength, but also mode I fracture properties. Additionally, specimens were created with graded properties along the bondline and test results will be presented in the final paper.

I. Introduction

Adhesively bonded joints are becoming more standard in composite material applications. Fasteners introduce holes which cut fibers and cause significant stress concentrations and premature failure in composite materials. Adhesives spread the load more evenly over the composite while facilitating a lighter overall structure.

However, the load path eccentricity in a joint still introduces a stress concentration at the ends of the adhesive layer. This leads to inefficiency and often to early failure initiation. Different methods of reducing the stress concentrations includes tapering the end of the adherend¹, increasing thickness of the adhesive at the end, fillets², novel joint geometries³, and joint insertions⁴, to name a few. These methods involve local details of adherend geometry (except the adhesive fillets), which typically increases part complexity and cost.

Another method of relieving the stress concentration in the adhesive is through grading the adhesive properties across the bondline. Early research on functionally graded adhesives uses bi-material adhesives, with a softer adhesive near the stress concentration and stiffer adhesive elsewhere^{5–11}. While large gains have been shown, the effectiveness of the joint has been shown to be highly sensitive to the boundary between the two adhesives. More recently, functionally graded adhesives with continuously graded properties have been of interest in the research community. Early theoretical works have shown that the stress reduction potential for a continuous gradation is much greater than that of discretely graded adhesives^{12,13}. Since these two works, there have been many theoretical studies on functionally graded joints^{14–20} using analytical formulations or finite elements.

While there has been a large amount of theoretical studies on functionally graded adhesive joints, there have been very few experimental studies. In one of the first examples, the gradation was created using differing concentrations of glass beads¹². However, this method was difficult to repeat and manufacture. More recently, a gradation was created by differing amounts of induction heating along a joint, which effectively varied the amount of curing in the joint²¹. However, post-cure effects lead to unstable benefits²².

In the current study, and method of grading the adhesive via graded radiation exposure is investigated. The adhesive has two crosslinking systems: one standard crosslinking system activated by temperature similar to many adhesives today. The second crosslinking system is activated by radiation. Therefore, a joint can be cured as in standard manufacturing procedures, then exposed to radiation for a secondary cure. This method has the advantage that the gradation is not altered by flow of liquid adhesive during manufacturing, since the adhesive is already in

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place and cured before the radiation is applied. Second, this method of gradation does not rely on over or under curing, which is often not stable in the long run and can have adverse effects to other properties. Double cantilever beam (DCB) joints were created with different levels of radiation exposure to show how this can change with radiation. Finally, specimens with linearly graded adhesive were made using radiation shielding, and results will be presented in the final paper.

II. Methods

A. Materials

The developed adhesive in this study is an epoxy system of DGEBA-NMA-CTBN 15%wt, in which the NMA is the hardener and CTBN is the chain extender. The NMA and CTBN are components that control the sensitivity of the adhesives to γ irradiation. The effects of γ irradiation on the properties of the adhesives was measured through thermomechanical analysis as well as tensile tests. Bisphenol A diglycidyl ether (DGEBA, D.E.R.332), Nadicmethyl anhydride (NMA, $\geq 95\%$) and Dicarboxy terminated Poly(acrylonitrile-co-butadiene) (CTBN, $M_n = 3800$, Acrylonitrile 8-12wt%) were sourced from Sigma-Aldrich Chemical Co.; 1,8-diazabicyclo [5.4.0]-undec-7-ene (DBU, 98%) was sourced from Alfa Aesar. The DGEBA-NMA-CTBN 15%wt epoxy system was prepared was created using the following procedure: DGEBA and 15 wt.% of CTBN (15.15 g) were added in a mixing cup. Then, 0.1wt.% of DBU, as an accelerator, was added to the mixture, followed by mixing in a speed mixer at 1200 rpm for 2 mins (FlackTek, Inc. DAC 600.1 VAC-P). The mixture was heated at 65°C for 4 h. NMA was then added to the reaction mixture and mixed again in the speed mixer 1200 rpm for 2 mins. The mixture was heated at 65°C for another 4 h, followed by mixing and degassing under vacuum in the speed mixer at 1200 rpm for 2 min, in order to obtain a homogeneous mixture.

B. Surface Preparation

For the DCB specimens, the adhesive was applied to aluminum bars. For better adhesion, a two step surface treatment was conducted. First a mechanical abrasion followed by chemical surface treatment was done as shown in Figure 53. In the first step, the aluminum surfaces were sanded using an orbital sander which creates random patterns. The Al bars were then washed and heated in a conventional oven for 10 min at 110°C , after which they were cleaned with acetone to remove organic impurities. For the second step, the aluminum bars were prepared for chemical surface treatment with silane. Next, the aluminum bars were immersed in a pH. 2 aqueous sulfuric acid bath for 5 minutes at 25°C . Acid washing created a more reactive surface that allowed for better wetting of and stronger bonding by the silane. The panels were then washed with deionized water and dried at 110°C for 10 min. Dispersions of silane coupling agent (7% w/w of anhydride-functional silane) containing the relevant NACURE catalyst (3% w/w) were obtained in a mixture of water and ethanol (80:20). The coupling agent dispersions were applied to the cleaned substrates using a wet film applicator (wire size 4, S4), and the coated panels were transferred to a convection oven at 110°C for 20 min. A wet film applicator gave a silane-rich layer that produced excellent adhesion.

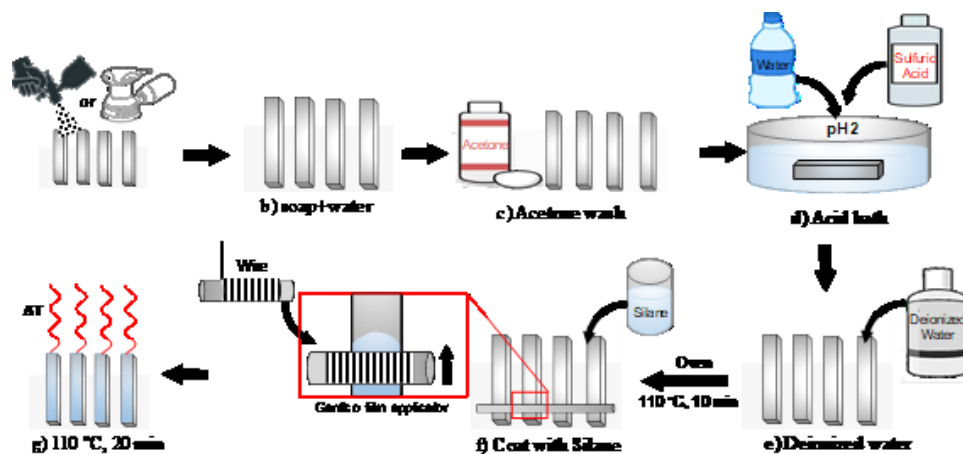


Figure 1. Workflow for surface treatment of DCB joints.

C. Specimen Radiation Exposure

Once the first curing cycle (thermal curing) was completed, specimens were prepared for the second curing cycle with γ irradiation. The γ radiation source consisted of Cobalt-60 pencils (C—60) located at the bottom of a deionized water pool. The DCB samples were vacuum sealed in a plastic bag in order to prevent oxidation during radiation exposure. Three samples per radiation dose were placed in a tube shaped can referred to as “sub can”. This sub can setup allowed the samples to be exposed evenly from both sides. The sub can was transferred to the radiation source under the water. Samples were exposed to four different radiation doses which were 50, 250, 500, and 1250 kGy, and the average dose rate was 11 kGy/h. The specimens were taken out of the sub cans, in which the color difference was obvious from low dose exposure (50kGy) to high dose exposure (1250 kGy). For the graded DCB joints, the specimens were surrounded by linearly increasing shielding (Tungsten) as shown in Figure 2 and exposed to 500 kGy and 250 kGy radiation.

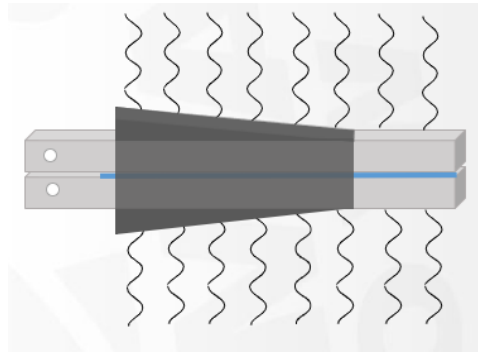


Figure 2. Angled shielding grades the adhesive radiation exposure across the joint, creating a functionally graded adhesive.

γ

D. Tests

The DCB test was conducted using ASTM D3433 [122] using a tensile machine as shown in Figure 3. The crosshead speed was set to 0.25 mm/min, and three specimens were tested per radiation dose. A speckled pattern was applied to the specimens for digital image correlation, and a digital camera was used to record the crack propagation during the loading. By tracking a jump in the rate of deformation across the interface, the crack tip was tracked in post-processing.

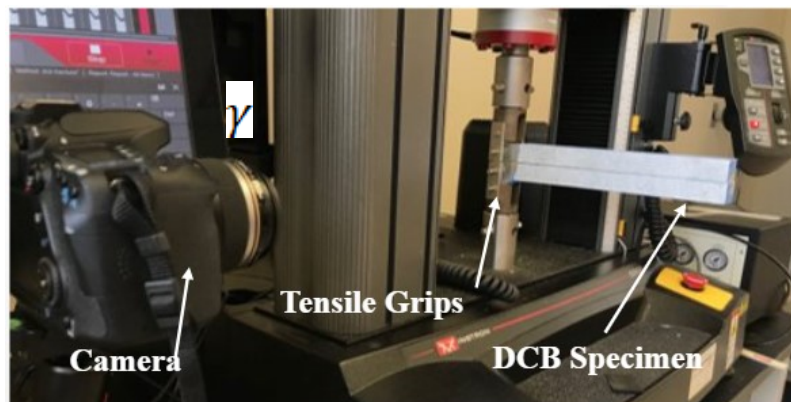


Figure 3. DCB setup for obtaining the fracture toughness of specimens with different levels of radiation exposure.

III. Initial Results

Initial results are displayed in Figure 4. This shows that as the radiation level increased and the cross-linking in the secondary system increased, the fracture toughness also increased. However, with an exposure of 1250 kGy, the exposure was high enough that the degradation from the exposure overcame any additional cross-linking that may have been happening. When the graded DCB is tested, we will be able to see whether we can characterize the properties as a function of exposure with progressive cracking. If this is the case, then we will show that we can fully characterize our gradation method with only one test, rather than requiring tests at various levels of exposure and interpolation of results in between. Finally, this method will be eventually used to grade a joint that is much

more common in application such as a single or double lap joint. It is expected that the gradation will allow us to spread the stress more evenly along the joint and increase joint strength. Finally, the radiation exposure can be applied in industry through E-Beam exposure, which is common for curing of some polymers and films.

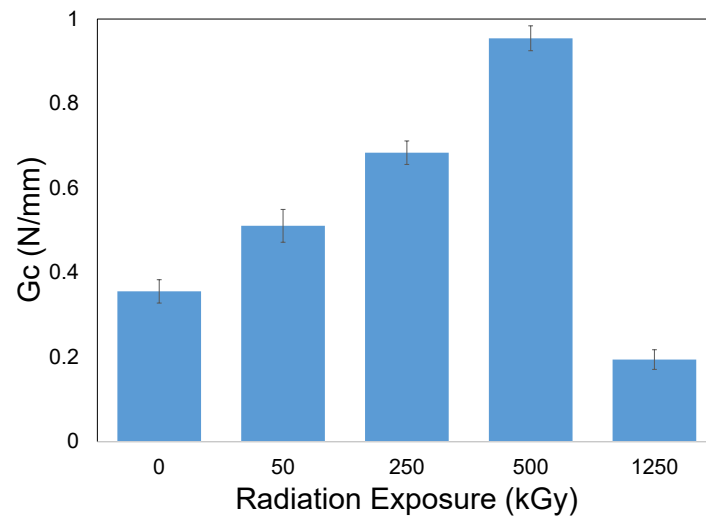


Figure 4. Critical fracture toughness as a function of radiation exposure.

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