A Radiation Sensitive Adhesive System for Functionally Graded Composite Joints

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ABSTRACT

Adhesively bonded composite joints can help reduce weight in structures and avoid material damage from fastener holes, but stress concentrations formed at the edges of the adhesive bond line are a main cause of failure. Stress concentrations within the adhesive can be reduced by lowering the stiffness at these edges and increasing the stiffness in the center of the joint. This may be achieved using a dual-cure adhesive system, where conventional curing is first used to bond a lap joint, after which high energy radiation is applied to the joint to induce additional crosslinking in specific regions. Anhydride-cured epoxy resins have been formulated to include a radiation sensitizer enabling the desired cure behavior. Tensile testing was performed on cured systems containing varying levels of radiation sensitizer in order to evaluate its effects on young's modulus as a function of radiation dose.

INTRODUCTION

Adhesively bonded joints are used because they can aid in reducing weight and avoiding weakening composite materials by making holes for fasteners. A major issue with these joints is that stress concentrations form at the end of the bond line which causes cracking and adhesive failure. Methods for reducing stress concentrations have been tried which include increasing the thickness of the adhesive[1], adding glass beads[2], spatial variations in cure temperature[3-4], mixing the resin with hardener[5], and radiation[6-7]. Radiation has stood out as a more viable option for the task of making adhesives functionally graded for two main reasons. The first reason being that the gradation is not affected by the flow of adhesive during the curing process. Secondly, radiation does not require different levels of cure. Specifically, the adhesive is completely cured, so it could be used at its base state or irradiated to a state with increased stiffness. Additionally,

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enhancing polymers with radiation is a common process in the plastics industry, so this method has potential in both novel and commercial adhesive systems depending on the sensitivity of the system to radiation and desired properties. Stapleton, Najafian, and Cassano showed potential methods for doing this process, but chose a system that did not have significant enough changes in stiffness to be conclusive[7]. This paper will explore similar, but slightly modified versions of their adhesive system, to find one whose sensitivity would be viable for making FGA joints.

METHOD

1.1 3.1 Adhesive Making Procedure

First, 50 grams of Bisphenol A diglycidyl ether (DGEBA) was mixed with 0.12 grams of 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU) and either 15.15, 25.25, 50.50, or 75.75 grams of Poly (acrylonitrile-co-butadiene) dicarboxy terminated (CTBN), depending on the formulation that was being tested. This mixture was then heated at 65°C for four hours, and the mixture was put into a speed mixer at 900 rpm for two minutes every two hours. Once the first four-hour cycle was finished, 51 grams of Methyl Nadic Anheydride (NMA) was added and put into the speed mixer at the same settings as before. The mixture was put through another 4 hours in the oven at 65°C and was speed mixed every 2 hours. After this cycle was completed, the finished adhesive would either be put under nitrogen, vacuum sealed, and put into a freezer, or it was made into tensile bars. These ratios were commonly multiplied by 2.5 to make enough adhesive for 24 tensile bars.

1.2 3.2 Tensile Tests

The dog bone shaped tensile specimens were made in accordance with sample type 1 in ASTM D638 [8]. A silicon mold with six dog bone shaped cavities was used to manufacture the specimens. The mold was put into an oven for 12 hours at 90°C and 24 hours at 120°C. Once removed from the oven, the thickness of the bars were brought down to between 2.85 and 2.95 millimeters by grinding them with 160 grit sandpaper on a Bueler MetaServ 250. Each specimen had tension applied by a Instron Universal testing machine with a 10 KN load cell and pulling rate of 5mm/min. The tests were performed according to ASTM D638 [8]. Digital image correlation (DIC) was used to calculate the strain and displacement fields of the tensile specimens. To prepare the pecimens for DIC, each was air brushed with matte white spray paint as a base, and then black dots were added. Pictures were taken using the Cannon EOS 80D DSLR camera (figure 1).

Once the images were on the computer, they were batch cropped and renamed using IrfanView. After the images were prepared, the free version of GOM Correlate was used to do the actual DIC analysis. The last step of the DIC was to match the strain values from GOM correlate to the stress values from the Instron universal tensile tester. GOM Correlate generated the strain at each point for each image. The points were spread equidistantly across the sample every 2mm (figure 2). The strain in the vertical direction for each point in each image was taken and averaged to have one average strain in the vertical direction for each image.

Figure I. DIC and tensile test setup.

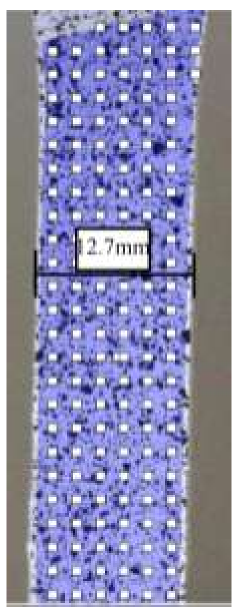

Figure II. Example of spacing of the points where GOM correlate reported strain values for the reference image of the CTBN50% 500kgy sample 1.

A MATLAB script was written to match the load measurements from the tensile testing machine to the strain measurements. This was necessary because the tensile testing machine took data points at a much greater frequency than the frame rate of the camera.

RESULTS AND DISCUSSION

In this section, the change in mechanical properties of DGEBA-NMA-CTBN25%, 50%, and 75%(CTBN##%) from previously studied DGEBA-NMA-CTBN15% (CTBN15%) will be explored. The change in these properties will be quantified and their implications for functionally graded adhesive joints discussed.

4.1 Tensile Test

The CTBN15% studied in the dissertation by Najafian [6], can be seen in table 1. For the CTBN15%, there was no clear significant changes in the mechanical properties due to the radiation exposure. The young's modulus, elongation at break, and break stresses from Najafian's study of CTBN15% show that the properties can be changed using radiation, but this system does not have the range in stiffness necessary for FGA joints. Past papers have used models with stiffnesses varying from 1GPa to over 3 GPa[7]. However, table 1 only shows values ranging from 2.5-3.3 GPa and too much variation for this range to be considered reliable.

Table I. DGEBA-NMA-CTBN15% mechanical properties.

Dosage(KGy)	Youngs modulus(GPa)	Elongation at break(%)	Break Stress(MPa)
0	2.56 (±0.12)	4.00 (±0.9)	69.47 (±3.59)
250	3.08 (±0.43)		71.47 (±2.18)
500	2.99 (±0.43)	4.32(±1.77)	72.97 (±1.20)
1250	3.34 (±0.47)	4.00(±1.02)	59.68 (±0.11)

From the tensile bar testing, the stress strain curves in the three new formulations of CTBN25%, 50%, and 75% were produced and can be seen in figure 3. It can be observed from this figure that, as the CTBN content rises, the young's modulus tends to decrease, elongation at break tends to increase, and breaking stress tends to increase. To gauge the significance of these trends, the data points summarized in tables 2-4 were plotted and visually checked for large changes in properties and whether these changes were not from the variation in test results.

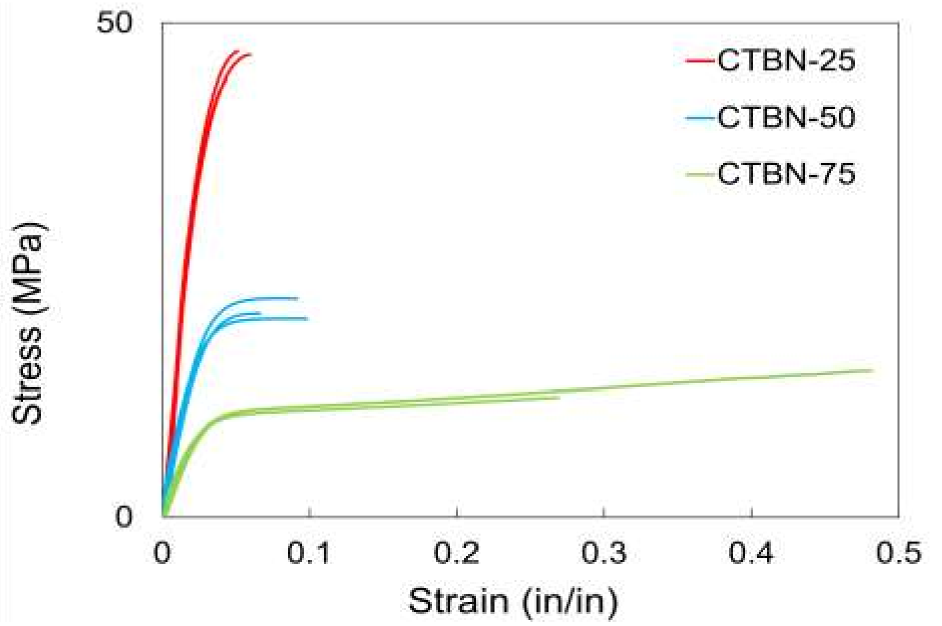

Figure III. The stress strain curve for three samples at CTBN25%, CTBN75%, and CTBN50% with no radiation exposure.

TABLE II. TENSILE PROPERTIES FOR DGEBA-NMA_CTBN25% FORMULATION AT EACH DOSE.

Dosage(KGy)	Youngs Modulus(GPa)	Elongation at break(%)	Break Stress(MPa)
0	1.71 (±0.18)	4.83 (±1.20)	44.30 (±2.19)
250	1.78 (±0.12)	5.32 (±0.86)	51.85 (±4.24)
500	1.97 (±0.11)	4.70 (±0.57)	59.92 (±1.44)
1250	2.57 (±0.083)	2.88 (±0.58)	60.02 (±5.35)

TABLE III. TENSILE PROPERTIES FOR DGEBA-NMA_CTBN50% FORMULATION AT EACH DOSE. '*' INDICATES THAT FIVE SAMPLES WERE USED INSTEAD OF THE USUAL SIX.

Dosage(KGy)	Youngs modulus(GPa)	Elongation at break(%)	Break Stress(MPa)
0	0.71 (±0.04)	8.35 (±1.29)	20.44 (±1.44)
250	0.97 (±0.07)	7.56 (±3.60)	28.03 (±3.18)
500	1.71 (±0.08)	3.19 (±1.37)	40.88 (±8.34)
1250*	2.15 (±0.11)	2.32 (±0.40)	47.68 (±5.49)

TABLE IV. TENSILE PROPERTIES FOR DGEBA-NMA_CTBN75% FORMULATION AT EACH DOSE.

Dosage(KGy)	Youngs modulus(GPa)	Elongation at break(%)	Break Stress(MPa)
0	0.34 (±0.08)	36.5(±9.18)	13.31(±1.33)
250	0.48 (±0.05)	22.8 (±5.73)	19.98 (±1.85)
500	1.03 (±0.09)	8.21 (±3.43)	31.54 (±2.34)
1250	2.15 (±0.13)	2.44 (±1.10)	42.98(±12.25)

To determine whether the change in stiffness was significant between the different formulations and the different radiation doses, Figure 4 was made where the average of the six sample's young's moduli from tables 1-4 were plotted. From the plot, it can be observed that the four formulations have significantly different stiffnesses from each other. Additionally, CTBN15% and CTBN25% do not seem to have very significant changes in stiffness due to radiation, except for the stiffness gained from exposing CTBN25% to 1250kGy of radiation. In contrast, CTBN50% and CTBN75% undergo statistically significant changes in stiffness between each radiation dose. Moreover, CTBN50% has the second largest range in stiffness of around 1.44GPa which is 67% and 85% different than the ranges of CTBN25% and CTB15% respectively. Similarly, CTBN75% has the greatest range of 1.81GPa. Another insight observed from Figure 4, was that the largest change in properties for the CTBN50% system tends to be in between the 250kGy and 500kGy range. This trend can be further corroborated in Figures 5 a and b in how the elongation at break drops by around 40% and the stress at break rises by around 46%. Much higher variation is observed in the elongation and stress at break because those properties were very dependent on the condition of the tensile bars and the performance of the test. Specifically, it was affected by bubbles present within the adhesive and or specimens which broke nearer to the clamps. In contrast to the CTBN50%, CTBN75% has a much more constant increase in stiffness after 250kgy. Considering, that higher radiation doses take more time, understanding where the adhesives change in properties the most could be useful in terms of optimizing manufacturing time of the FGA joint. Additionally, CTBN-75 appears to trend towards being able to go toward higher stiffnesses with higher radiation doses, because it does not appear to level off at 1250kGy as much as other samples.

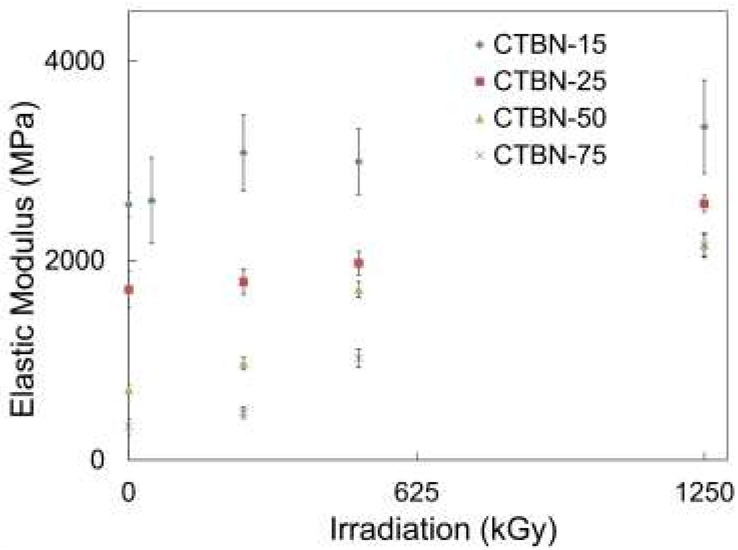

Figure IV. Average elastic modulus of each CTBN formulation at radiation doses of 0kGy, 250kGy, 500kGy, and 1250kGy.

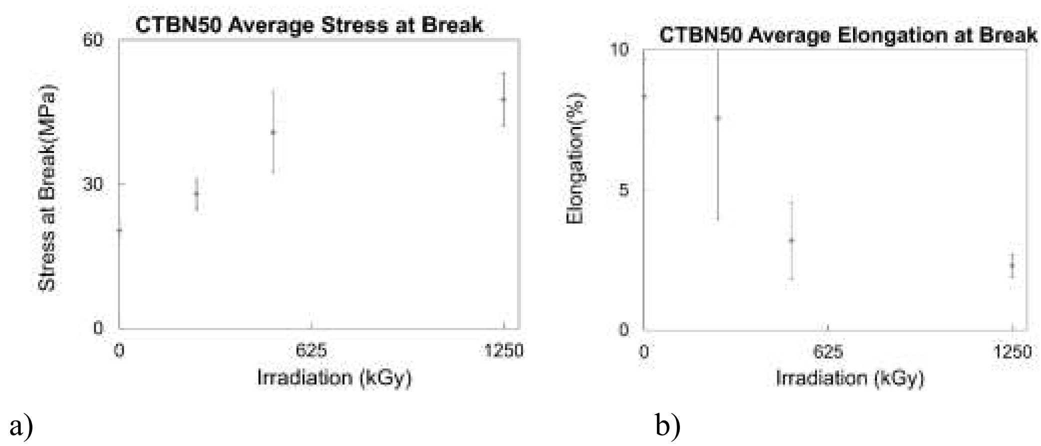

Figure V. The stress at break of the CTBN50% formulation at 0, 250, 500, and 1250kGy, and b) the elongation at break of CTBN50% at the same 4 radiation doses at figure 'a'.

SUMMARY AND CONCLUSIONS

Amongst the different formulations with varying CTBN percentages, CTBN75% stood out with the largest range in stiffness values. With a total range of over 1.8GPa, it comes close to the around 2GPa range used for past studies examining the efficacy of FGA joints. Moreover, it shows that it can be more reliably manufactured for these stiffnesses than its CTBN15% predecessor. The next steps will be to further investigate the novel adhesive formulations with thermomechanical testing to better quantify the sensitivity these varying formulations have to the radiation. Another important question that will be studied is how the CTBN75% system performs in an actual bonded joint. These studies will include analyzing mode I fracture toughness in a homogenous Double cantilever beam(DCB) bonded joint and then moving on to experimenting with FGA DCB samples in order to gauge the benefits to strength that FGA with these adhesive formulations can produce.

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