AIAA SciTech Forum
6-10 January 2020, Orlando, FL
AIAA Scitech 2020 Forum

10.2514/6.2020-1929

Functionally Graded Adhesives Using Radiation Curing

Scott E Stapleton,[1] Alessandro Cassano[2], and Sara Najafian[3]
University of Massachusetts Lowell, Lowell, MA, U.S.A, 01854.

Daniel F. Schmidt[4]
Luxembourg Institute of Science and Technology (LIST), Hautcharage, Luxembourg, L-4940.

Adhesively bonded joints contain stress concentrations at geometric and material discontinuities within the joint, causing the joint to be inefficient. This study investigates a method to grade the material properties of an adhesive across the bondline to have a soft, flexible adhesive near the stress concentration and a stiff, strong adhesive elsewhere. Theoretical studies and a few experiemental studies have shown an that the load is distributed more evenly along the joint and strength is increased. Adhesive gradation is achieved through a secondary crosslinking system in the adhesive which is activated via radiation. After an adhesive is initially cured, the joint can be exposed to varying levels of radiation to grade the properties. Initial results demonstrate the ability to grade stiffness using radiation shielding, and final results will demonstrate the application in an adhesively bonded joint.

I. Introduction

WITH the increasing demand for fiber reinforced composites in lightweight structures, adhesively bonded joints are becoming more critical than ever. Bolts and rivets 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 results in early failure initiation and yielding. Different methods of reducing the stress concentrations includes tapering the end of the adherend [1], increasing thickness of the adhesive at the end, fillets[2], novel joint geometries [3], and joint insertions [4], 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 used 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]. Following these two reports, there have been many theoretical studies on functionally graded joints [14–20] using analytical formulations or finite elements.

While there have been many 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 beads [12]. 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 joint [21]. However, post-cure effects lead to unstable benefits [22].

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. This allows a joint to be cured as in

[1] Assistant Professor, Mechanical Engineering, University Ave. 1, Lowell, MA 01854, AIAA Member.
[2] Research Assistant, Mechanical Engineering, University Ave. 1, Lowell, MA 01854, non-AIAA Member.
[3] Research Assistant, Mechanical Engineering, University Ave. 1, Lowell, MA 01854, non-AIAA Member.
[4] Group Leader, Green Polymers, 5 Rue Bommel, Hautcharage, Luxembourg L-4940, non-AIAA Member.

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 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. This study demonstrates early efforts to grade the adhesive in an adhesively bonded joint via radiation and proposes adhesive property changes for stronger joints.

II. Methods

A. Model

The software Joint Element Designer (JED) was used for the gradation design. The model was created to provide a rapid-sizing solution for adhesively bonded joints [23], but was extended to include functionally graded adhesives [12,24]. The model utilizes joint elements whose shape functions are derived by solving a structural model for two plates under cylindrical bending between elastic foundations. By solving for shape functions rather than prescribing them, one element can be used through the thickness of the joint and one element along the joint when material properties remain linear elastic. Additionally, a co-rotational formulation was included to consider large rotations, [25] and adaptive shape functions and an internal adaptive mesh include the effects of material nonlinearities and crack growth [26]. Finally, a modified Von Mises formulation is used to include plasticity of the adhesive layer in the framework of a thin adhesive layer constrained by two stiff adherends [24], along with an interpolation strategy between data curves for the continuously graded adhesive.

Once an adhesive system and gradation method are identified and characterized, the model can take the individual constitutive responses of the adhesives under different amounts of gradation (Figure 1a), and design a gradation to optimize the strength as shown in Figure 1b and c. Additionally, since the manufactured specimen will inevitably deviate from the ideal specimen, a parametric study can be run to look at sensitivity of the strength to the exact gradation shape as demonstrated in [12].

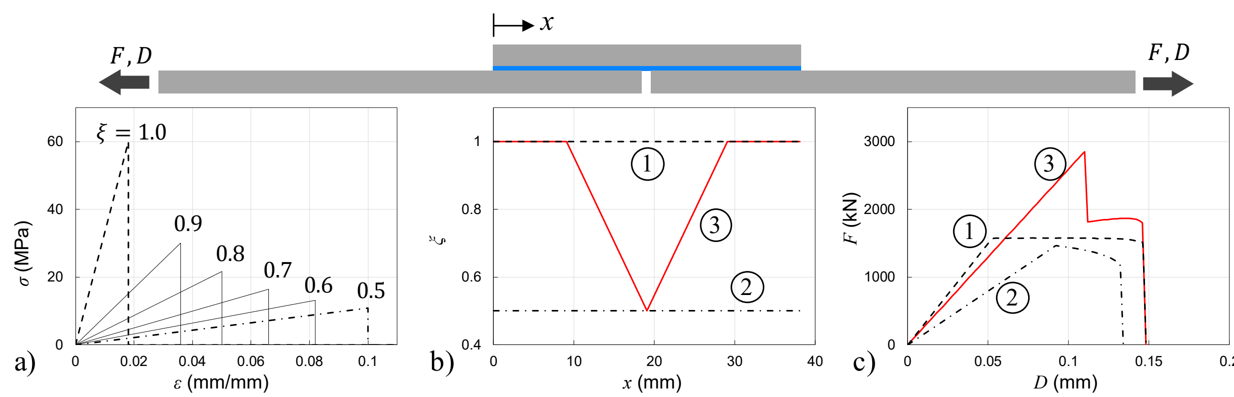

Figure 1. A theoretical study showing that when an adhesive is a) graded by a grading variable ξ, which in this case changes the strength and stiffness of the adhesive while preserving the area under the stress-strain curve, then b) grading the adhesive along the length of the bondline to be soft at the stress concentration location, the c) strength of the adhesive can be improved over the exact same joint with a homogenous adhesive at either end of the gradation spectrum (ξ=0 or 0.5).

B. Experiments

Bisphenol A diglycidyl ether (DGEBA, D.E.R.332), Nadicmethyl anhydride (NMA), 2,2'-Diallylbisphenol A (DBPA) and Dicarboxy terminated poly(acrylonitrile-co-butadiene) (CTBN) were all purchased from Sigma-Aldrich Chemical Co. 1,8-diazabicyclo [5.4.0]-undec-7-ene (DBU) was purchased from Alfa Aesar. Tungsten-filled polyamide 12 material (Ecomass Compound 1700TU96) was purchased from EcomassTechnologies. Two adhesive system formulations were prepared based on carefully selected components containing different types of (radiation-sensitive) double bonds, namely the DGEBA-NMA-DBPA system and the DGEBA-NMA-CTBN system. The DGEBA-NMA-DBPA adhesive system was created using the following procedure: the specified amount of DBPA was added in a mixing cup (mixing cup is made by polypropylene, the cup size dependent on batch size) with DGEBA. Then, 0.1 w.% of DBU was added to the mixture as an accelerator, followed by mixing in a speed mixer (FlackTek, Inc. DAC 600.1 VAC-P speed mixer) at 1200 rpm for 2 minutes. The mixture was heated at 65°C for 4 h in a Lindberg Blue M forced air convection oven. NMA was added to the reaction mixture, and then mixed and degassed in the speed mixer at 1200 rpm for 2 mins under vacuum. After a homogeneous mixture was formed, it was poured into a custom-made silicone rubber mold in the convection oven. The curing program was 90℃ for 12h and 120℃ for 24h. The molar ratio of total epoxy, hydroxyl and anhydride groups was fixed at 1:0.665:1.335, to ensure an equal number of carbon-carbon double bonds from DBPA and NMA. In addition, the DGEBA-NMA-CTBN system was prepared by adding 15 wt.% of CTBN to DGEBA in a mixing cup. Then, 0.1 wt% of DBU, as an accelerator, was added to the mixture, followed by mixing in the speed mixer at 1200 rpm for 2 mins. The mixture was heated at 65℃ for 4 h in the convection oven. NMA was then added to the reaction mixture and mixed again in the speed mixer at 1200 rpm for 2 mins. The mixture was heated at 65℃ for another 2 h in the convection oven, followed by mixing and degassing in the speed mixer at 1200 rpm for 2 mins under vacuum, in order to obtain a homogeneous mixture. Then, it was poured in a custom-made silicone rubber mold in the convection oven. The curing program was 90℃ for 12h, 120℃ for 24h. A molar ratio of total epoxy groups to anhydride groups was fixed at 1:1.95, with two carboxylic acid groups from CTBN counted as equivalent to one anhydride group.

The mechanical properties of the two adhesives were characterized by tensile testing for non-irradiated samples as well as samples irradiated at two different radiation doses (500 and 1250 kGy) with the dose rate of 15kGy/h from a ^{60}Co cell. The specimens were vacuum sealed in polyethylene bags prior to irradiation in order to avoid oxidation. Digital image correlation (DIC) was used to measure the strain, which was subsequently used with the load measurements to get theYoung's modulus for the linear elastic portion of the response under tensile loading. Quasi-static tensile tests were performed on an Instron 5966 machine, with crosshead displacement rate of 5 mm/min, according to ASTM D638 [27]. The tensile specimens were manufactured using a custom silicone mold for Type I specimens. At least five specimens for each formulation and radiation dose were tested.

Radiation shielding was created from a tungsten-filled polyamide 12 material, which can be compression molded or machined to the desired dimensions. After initial curing of the epoxy adhesive at elevated temperature, gamma irradiation causes additional crosslinking, due to the radiation sensitivity of double bonds built in to the network. The increased crosslink density can increase the glass transition temperature, Young's modulus and tensile strength of the thermoset. The shielding decreases the adhesive's exposure to radiation. By controlling the length of exposure and shielding thickness, one can control the amount of irradiation the specimen is exposed to, which in turn controls the final crosslink density of the adhesive.

Figure 2 shows some tensile specimens which were thermally cured, then exposed to 500 kGy of radiation. Shielding was placed over half of the specimen, limiting the crosslinking in that half of the specimen. The specimens were then tested under tensile loading, and digital image correlation (DIC) was used to measure the strain gradient in the specimen between the fully exposed region to the shielded region. This demonstrates the ability to control the stiffness of the adhesive through strategic use of radiation shielding.

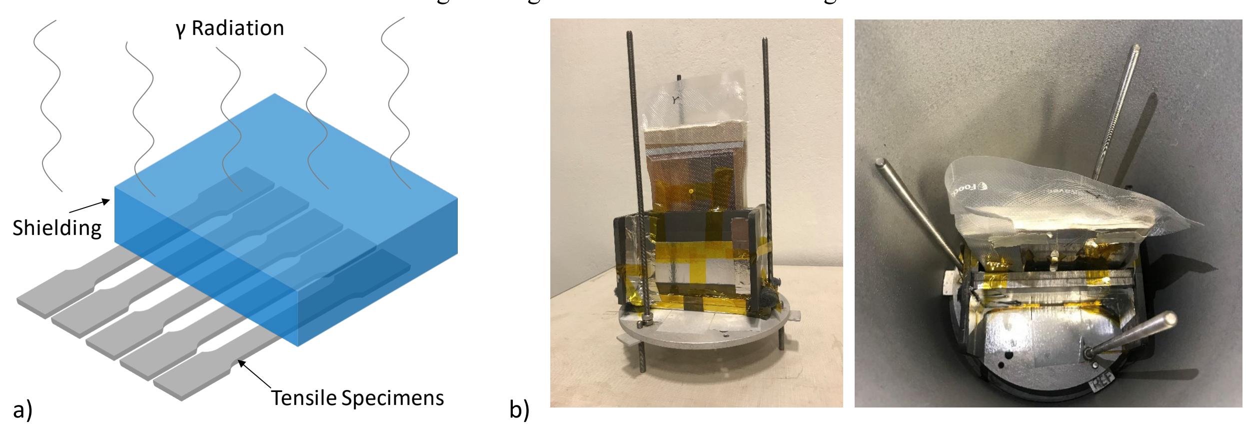

Figure 2. Gradations in adhesive properties were created using a secondary crosslinking system which are activated by exposure to γ-radiation. By a) shielding half of tensile specimens and b) exposing them to 500 kGy radiation, tensile specimens were created to have a gradation of properties under load.

C. Adhesive Gradation Design

A strap joint was used as a numerical example for the functionally graded adhesive (FGA) design study. The overlapping region of the joint is implemented in the JED using two elements, as shown in Figure 3. One element was used to represent the homogenous part of the adhesive, whereas the second element defined the graded part of the adhesive using the adhesive material input curves from the tensile testing. The adherends were considered to be carbon fiber reinforced composites with a Young's modulus of 105 GPa. The ratio l/l_0 was used as a parameter for the numerical study, where l_0 is the length of the graded part and l is the total length of the bonded region. Although in previous numerical studies linear or exponential gradation shapes were found to be more beneficial for FGA's, in this study a step gradation was used (Figure 3b) to replicate the shape of the radiation shield.

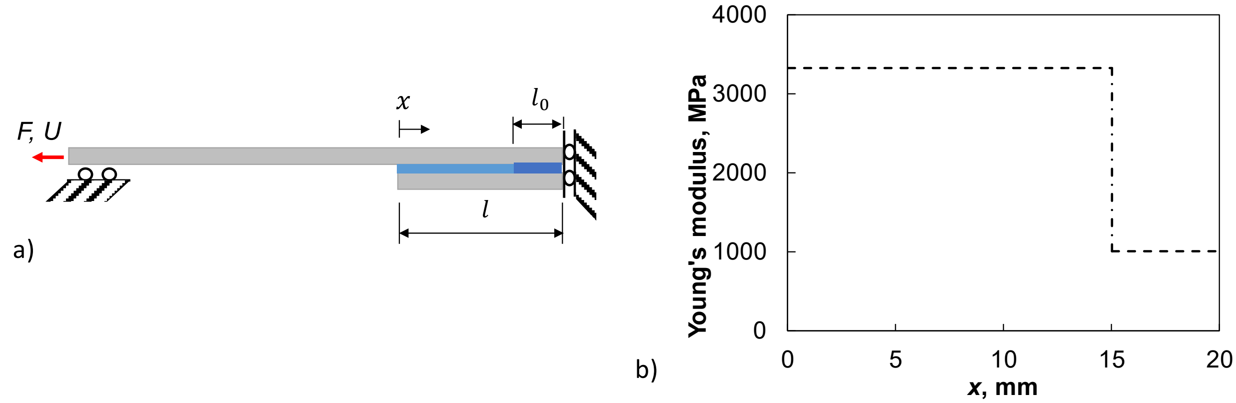

Figure 3. Strap joint geometry with a) gradation parameters and boundary conditions in JED and b) step gradation shape.

III. Results and discussion

A. Experimental results

In this section, the mechanical properties of the DGEBA-DBPA-NMA and DGEBA-NMA-CTBN adhesive formulations are discussed. Figure 4 shows the average stress-strain curves measured in tension for two different epoxy formulations as a function of radiation dose (0, 500 and 1250kGy).

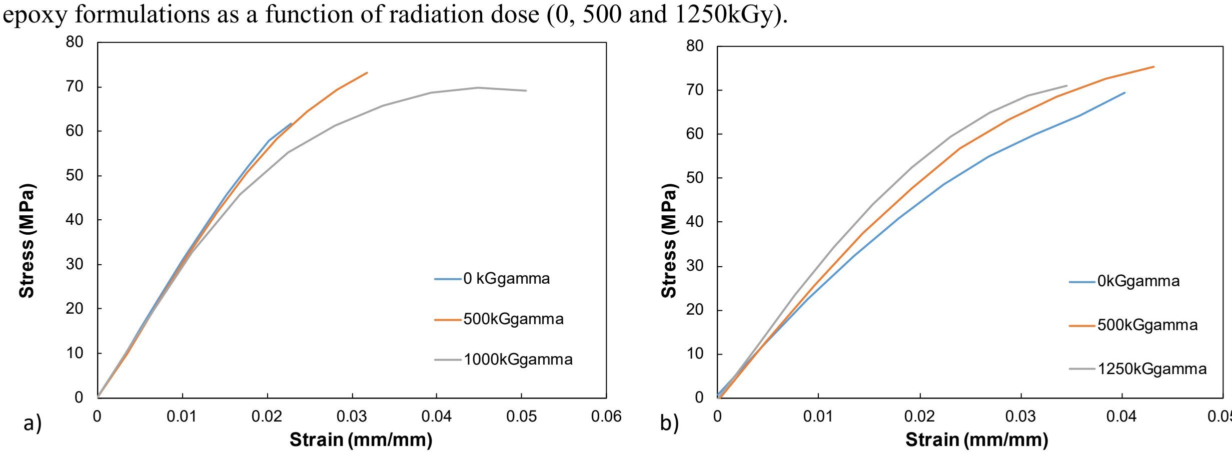

Figure 4. Stress-strain curves (measured in tension) for epoxies exposed to doses of 0, 500 and 1250 kGy based on the a) DGEBA-DBPA-NMA and b) DGEBA-NMA-CTBN adhesive formulations.

For the DGEBA-DBPA-NMA adhesive there is no significant change in Young's modulus but the elongation at break increases as a function of the radiation dose. As a result, the total strain energy density to failure also increases with radiation dose. In the DGEBA-NMA-CTBN system, a change in modulus of about 33% can be observed from 0 kGγ to 1250 kGy exposure. Results from the tensile test are summarized in Tables 1 and 2.

Table 1. Tensile properties for DGEBA-NMA-DBPA formulation at each dose.

Dosage (kGy)	Young's modulus (GPa)	Elongation at break (%)	Break stress (MPa)
0	3.27 (±0.14)	3.68 (±0.81)	68.74 (±8.73)
500	3.21 (±0.11)	5.17 (±1.33)	75.10 (±2.54)
1250	3.12 (±0.20)	5.00 (±1.87)	67.51 (±6.01)

Table 2. Tensile properties for DGEBA-NMA-CTBN formulation at each dose.

Dosage (kGy)	Young's modulus (GPa)	Elongation at break (%)	Break stress (MPa)
0	1.74 (±0.09)	4.03 (±0.9)	65.73 (±5.76)
500	2.08 (±0.18)	4.32 (±1.77)	70.08 (±9.86)
1250	2.32 (±0.17)	4.00 (±1.02)	73.65 (±3.03)

Specimens were also prepared with only half of the specimen shielded for the DGEBA-DBPA-NMA system. The radiation dose for the unshielded part was 500kGy. Figure 5a shows the strain along the specimen length (*y*-direction) measured using DIC and averaged across the width (*x*-direction) at a load of 3.1 kN. The specimen showed a significant gradient in the strain, indicating that the shielding strategy can be a suitable technique to create FGA joints. However the results were not easily repeatable for the DGEBA-DBPA-NMA system and other specimens did not display a definite gradient. It is possible that this is attributed to the fact that while the strain to failure is significantly increasing with radiation level, the rest of the constitutive response remains unchanged. Therefore, failure in less-exposed areas would most likely occur before the property increase is evident. However, when gradations are created where the modulus is affected, a graded tensile specimen is expected to yield more repeatable and conclusive results about the spatial distribution of material gradation, even within the linearly elastic portion of the response.

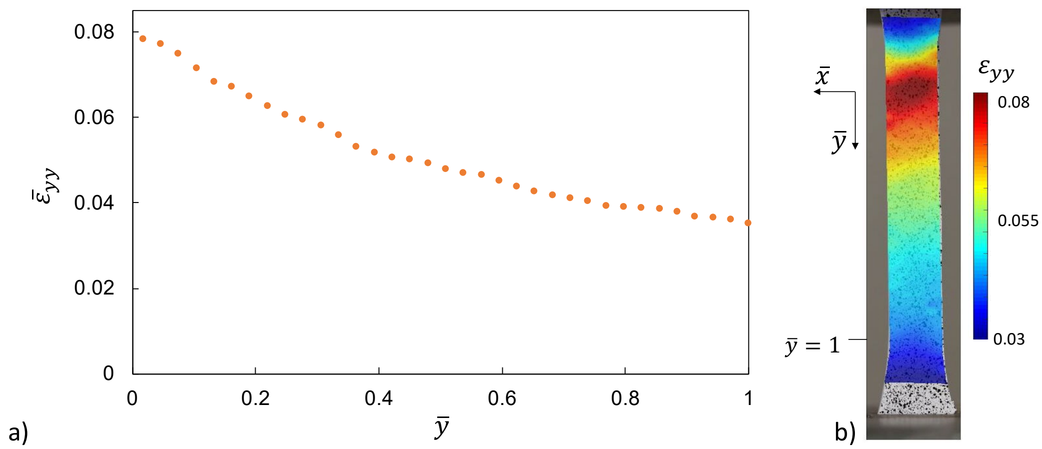

Figure 5. Average cross-sectional strain along a tensile specimen before break for half-shielded DGEBA-DBPA-NMA specimens with a radiation dose of 500kGy using DIC measurements and b) strain contour plot of the specimen just before break.

B. Parametric Study with JED

A functionally graded strap joint was simulated using the JED software and the stress-strain curves shown in Figure 4 for the DGEBA-DBPA-NMA and the DGEBA-NMA-CTBN networks. The stiffer adhesive was used as homogenous part of the bondline and the more compliant one as graded adhesive. The length of gradation over the length of the overlapping region l/l_0 was used as a parameter to optimize the FGA. Figure 6 shows the results for the DGEBA-DBPA-NMA system. Although strain at break and strain energy density is much higher at 1250 kGy for this adhesive system it seems to be not beneficial in the context of an FGA joint.

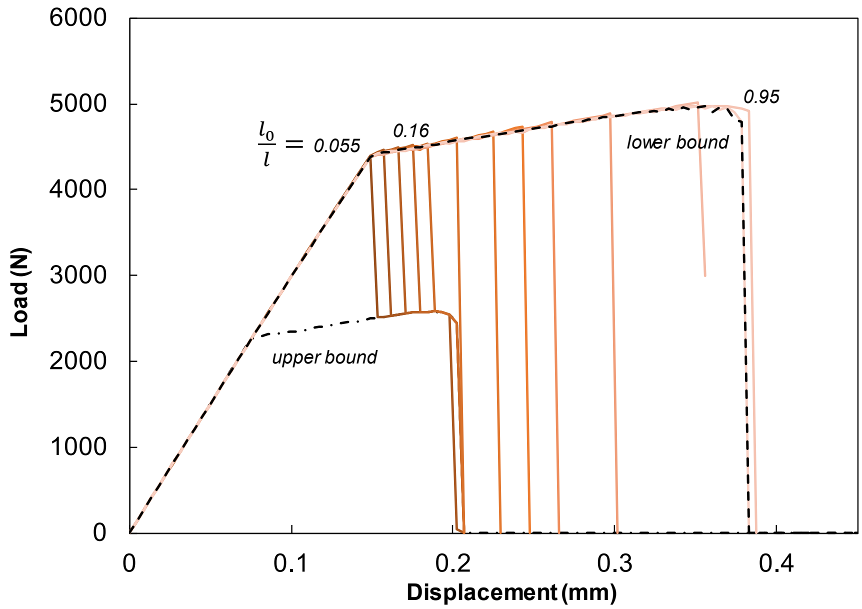

Figure 6. Load vs displacement plot for different values of gradation length l/l_0 and homogenous adhesive (dashed lines).

The parametric study results for the DGEBA-NMA-CTBN network are summarized in Figure 7. This second adhesive system seems to be more promising for FGAs because of the variation in elastic modulus of 33% from the 0kGy to 1250kGy radiation dose. However, the gain in strength for FGA compared to the homogenous adhesive joint is about 6% and the gain in strength is not visible for values of l/l_0 higher than 0.16.

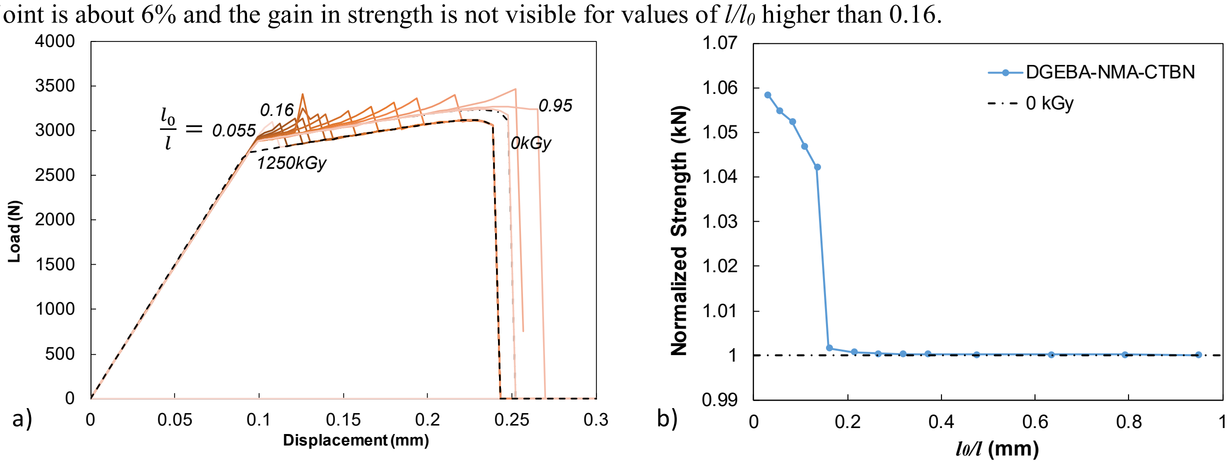

Figure 7. Parametric study on FGA's for DGEBA-NMA-CTBN adhesive showing a) load-displacement curves for different l/l_0 ratios and b) normalized strength vs. normalized length, showing the expected strength increase by properly designing the gradation shape.

IV. Conclusions

Adhesives have been formulated which form secondary crosslinks upon radiation exposure, and initial tensile testing has shown that property gradations within the adhesive can be created by using shielding during exposure. Initial results have demonstrated the ability to control the strain to failure, but have only afforded minimal changes to the stiffness. Design models predict that the current formulations will not be able to positively influence the strength of the joint, but suggest that a greater change in modulus could lead to the desired stress distribution and stronger joints. With this in mind, further adhesive formulations are being formulated and tested in joint configurations.

V. Acknowledgements

This material is based upon work supported by the National Science Foundation under Grant No. 1663502. The authors would like to thank Jamal Husseini and Christopher Day for their assistance in specimen preparatation, testing, and analysis. Additionally, thanks to Barbara Fleschutz at Hochschule Damrstadt for shielding manufacturing.

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