

Functionally Graded Adhesives via High-Energy Irradiation

Weiqing Xia, Sara Najafian, Alessandro G. Cassano, Scott E. Stapleton, and Daniel F. Schmidt*

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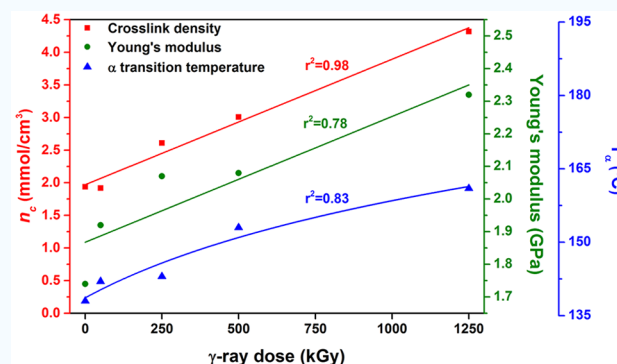


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Supporting Information

ABSTRACT: A thermally cured epoxy/anhydride system is shown to exhibit dose-dependent increases in cross-link density, glass transition temperature, and modulus. The addition of various sensitizers further boosts sensitivity toward radiation-induced cross-linking. A theory proposed by Shibayama relating T_g with cross-link density provides a useful means to predict the dose at which a particular set of properties may be produced. This combination of an approach to materials formulation and processing and the identification of simple analytical models to predict resultant properties provides a useful strategy for the generation of functionally graded materials.



KEYWORDS: functionally graded adhesives, functionally graded materials, dual curing, γ -rays, radiation sensitizers, epoxy resins

Functionally graded materials (FGMs) belong to a class of advanced functional material whose composition, structure, and (most importantly) properties are locally modulated in one or more dimensions.¹ Inspired by the advantages of polymeric FGMs, for instance in reducing stress concentrations,² improving bond strength,³ and enhancing damping capacity,⁴ a variety of formulations and production technologies for polymer-based FGMs have been developed. Material grading can also be applied to adhesively bonded joints, which are then referred to as functionally graded adhesives (FGAs).⁵ One major drawback of conventional adhesive joints is the existence of stress concentrations at the edges of the adhesive layer. In FGAs, the goal is to tune adhesive properties to produce a more uniform stress distribution within the joint.⁶ The advantages of FGAs have been described theoretically, but experimental studies on FGAs are rare.⁵ This is due to the fact that the techniques traditionally used to prepare polymeric FGMs, such as lamination,⁷ frontal polymerization,⁸ centrifugal casting,⁹ and bipolar electrochemistry,¹⁰ are difficult to apply to FGAs.¹¹ Attempts to prepare FGA joints have so far focused on one of two approaches. One method involves the manual creation of variations in composition (filler content and/or mix ratio).^{6,12–15} This method is effective in producing a stable gradient, but it is also labor-intensive and difficult to apply consistently, given the need to prepare and precisely apply multiple compositions of matter throughout the bond-line. A second method involves modulating the extent of cure of a single adhesive formulation along the bond line, typically through the application of localized heating.^{3,6,15} This approach also produces gradients in properties, though as they are achieved through the creation of zones where the adhesive remains capable of conventional curing, they have

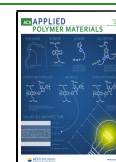
been shown to be effective but unstable.¹⁶ This is consistent with literature on the so-called “cold curing” of epoxy adhesives used in civil engineering applications, where large shifts in modulus are observed as a function of aging under ambient conditions.¹⁷ In addition, from a practical standpoint, neither approach is convenient or readily scalable. Hence, a question arises as to how one could produce FGAs with consistent, well-defined, stable gradients in properties. In particular, is it possible to develop complementary materials compositions and preparation techniques that allow the tuning of properties following conventional curing of an adhesive joint?

A new and promising approach is proposed involving the use of penetrating high-energy radiation. In particular, γ -rays, with neither charge nor mass, are known for their ability to cause chain scission and/or cross-linking in polymers.¹⁸ In this work, new thermal/radiation dual-cure epoxy formulations are reported whose thermal and mechanical properties may be controlled via γ -irradiation following conventional curing. The novelty of this approach lies in the utilization of two independent reaction steps to achieve the desired result: a stable, precisely defined gradient in cross-link density and properties. The first step involves the application and complete curing of the material through conventional (e.g., thermal)

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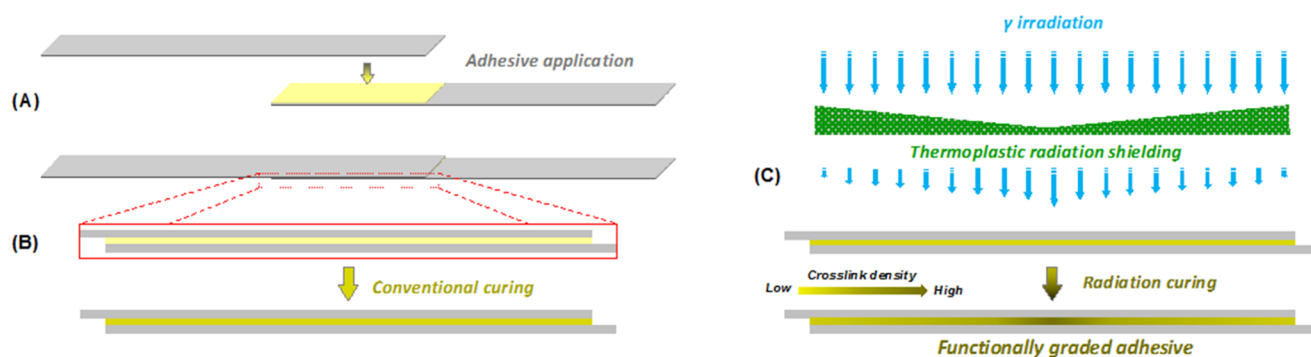


Figure 1. Schematic demonstrating a new approach to FGA formation through the use of novel dual-cure adhesives: (A) a single adhesive composition is applied; (B) the adhesive is conventionally cured to stabilize the joint; (C) selective irradiation is used to realize functional gradations in the conventionally cured material.

means via reactions between functional groups found in typical adhesive formulations, this providing a stable joint with which to work. The second step involves the use of high energy radiation to trigger additional cross-linking reactions within that joint and in a dose-dependent fashion, taking advantage of the presence of a second set of intentionally added functional groups that are stable under use conditions but susceptible to cross-linking by high energy radiation.

To provide an example of the application of this approach in practice, the epoxy-anhydride reaction system was selected as the basis for conventional curing, with carbon–carbon double bonds included as groups stable under normal conditions but susceptible to radiation cross-linking. First, the diglycidyl ether of bisphenol A (DGEBA) was combined with nadic methyl anhydride (NMA) and thermally cured. Then, γ -irradiation was used to examine its stability and capacity to undergo additional cross-linking reactions, e.g. through activation of the carbon–carbon double bonds ($C=C$) in the norbornyl substituent of the NMA. The resulting changes in properties were monitored as a function of dose. Second, the sensitivity of this system to radiation-induced cross-linking was increased through the addition of additives containing terminal unsaturation. In particular, both rigid and flexible additives were studied as radiation sensitizers for incorporation into the DGEBA-NMA epoxy: diallyl bisphenol A (DBPA) and carboxyl-terminated liquid butadiene-acrylonitrile rubber (CTBN). Both radiation sensitizers enhanced the response to radiation curing at relatively low levels (refer to [Supporting Information](#)). The use of thermosets designed with such dual-cure characteristics in mind, in tandem with precision-formed polymeric radiation shielding (tungsten-filled thermoplastics designed for lead replacement), enables the creation of FGs with well-controlled gradients in radiation dose. This also provides a convenient route to FGA formation given the ease with which high energy radiation penetrates common adherends.

Figure 1 illustrates the general strategy for the generation of FGAs through the use of dual-cure adhesives. A dual-cure resin is applied to commonly used adherends, then conventionally cured (**Figure 1A** and **1B**). The cross-link density of the adhesive can be further modulated following conventional joint formation by designing the radiation shielding and radiation exposure conditions to generate a gradient in radiation dose following conventional curing (**Figure 1C**). In contrast with all other methods for FGA formation described to date,¹⁵ this novel approach provides the convenience of using a single

material composition while fully decoupling joint formation and the creation of functional gradients. It is currently being investigated for the generation of both FGs and FGAs based on the epoxy formulations described here.

The thermal curing of DGEBA-NMA involves ring-opening polymerization (refer to the [Supporting Information](#)). Following thermal curing of the epoxy, the cured networks were then subjected to 50, 250, 500, and 1250 kGy of γ -irradiation using a ^{60}Co source (refer to the [Supporting Information](#)). To investigate the impact of γ -irradiation on the structure of the epoxy network, ATR-FTIR analysis was carried out before and after irradiation at all dose levels (**Figure S1A**, [Supporting Information](#)). The generally accepted mechanism of radiation-induced chain scission in epoxy networks involves the cleavage of ($C-C$) and ($C-H$) bonds, resulting in a decrease in the intensity of the $C-H$ absorption region in FTIR spectra.¹⁹ In contrast, the ATR-FTIR spectra of the irradiated materials produced here display a systematic increase in absorption intensity of peaks associated with $-CH_2-$ (2925 and 2849 cm^{-1} , $C-H$ stretching; 1450 cm^{-1} , $C-H$ bending) and a decrease in the intensity of peaks associated with $C=C-H$ (3057 cm^{-1} , $C-H$ stretching) as a function of dose (**Figure S2A**, [Supporting Information](#)). Consistent with the recognized resistance of epoxy resins to radiation damage,²⁰ these results indicate that cross-linking reactions involving the consumption of unsaturated groups are the primary outcome of the γ -irradiation process. The mechanism of γ -irradiation induced cross-linking involves the cleavage of $C=C$ π bonds to form free radicals, followed by coupling with neighboring free radicals to form cross-links. In addition, a systematic increase in the intensity of the $-C-OH$ absorption band (3380 cm^{-1} , $O-H$ stretching) coupled with the decreasing intensity of the absorption band associated with unreacted epoxy groups (910 cm^{-1} , $C-O$ bending) implies that the small number of residual epoxy groups that remain in the system following thermal curing are also consumed (**Figure S2A**, [Supporting Information](#)).²¹

Having confirmed that cross-linking was being favored over degradation, the impact of γ -irradiation on the thermal properties and cross-link density (n_c) of the epoxies was then evaluated via TGA, DSC, and DMA (**Figures S3A–S7A** and **Table S1**, [Supporting Information](#)).

Addressing the TGA data first, the thermal stability of the DGEBA-NMA epoxy was observed to increase slightly with radiation dose (**Table S1**, [Supporting Information](#)). One possible explanation for this is that the radiation-induced

cross-linking of the norbornyl groups present in the network impedes subsequent thermally induced retro-Diels–Alder reactions considered to be primarily responsible for thermal degradation in such materials.²²

The glass transition temperature was determined both using DMA (T_g from peak E'') and DSC (T_g from second heating). The effect of γ -irradiation on the thermal properties, especially the glass transition, is associated with changes in cross-link density, which may in turn be assessed using the rubbery plateau modulus from DMA (Equation S1, Supporting Information).²³ While there is some scatter in the data, Figure 2A nevertheless shows a clear increasing trend in cross-link

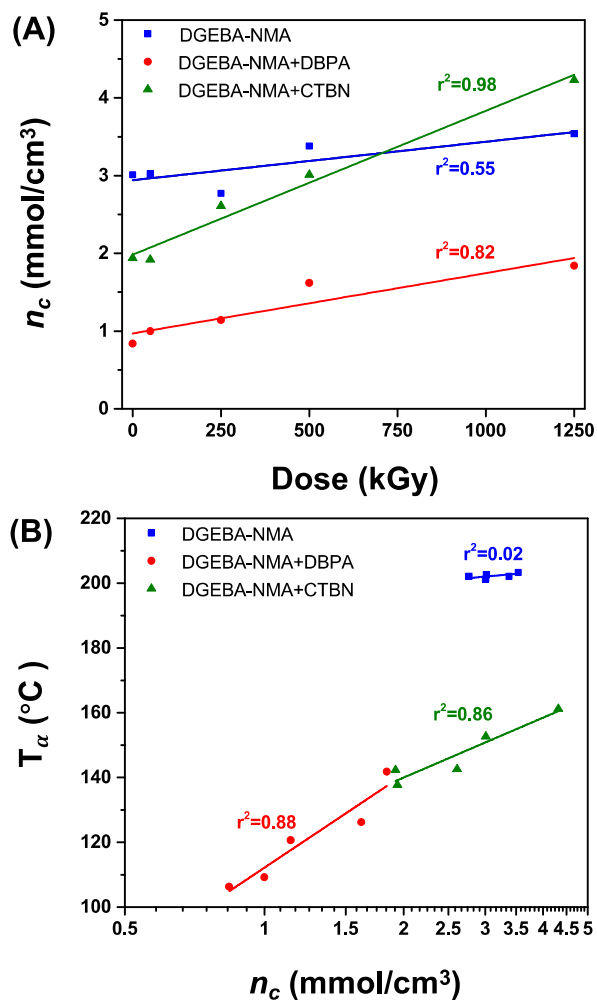


Figure 2. (A) Plot of n_c versus radiation dose for all networks. (B) Plot of T_g versus $\log(n_c)$ of all networks. Lines represent linear fits.

density with radiation dose. Parallel increases in both T_g and T_g were also observed, implying that the increase in the glass transition temperature was a direct result of this increase in the cross-link density. Shibayama has linked glass transition temperature and cross-link density based on a free volume argument that accounts for the volume shrinkage resulting from cross-linking²⁴ and proposes the following relation between the two:

$$T_g(^{\circ}\text{C}) = K_1 \log(K_2 n_c) = K_1 \log(K_2) + K_1 \log(n_c) \quad (1)$$

which has been successfully applied to a wide range of epoxies as well as cross-linked networks more broadly.²⁵ For a network

consisting of chains attached via cross-links, K_1 characterizes the degree of restraint on chain motion imposed by an increase in cross-link density (lower values imply smaller changes), while K_2 depends on the interactions and rigidity of the chains between the cross-links (lower values imply weaker interchain interactions/lower chain rigidity). The application of such a model helps us to better understand and predict changes in network properties observed as a function of γ irradiation of the dual cure epoxies described here. The resulting fits are shown in Figure 2B. For the irradiated DGEBA-NMA system, the values obtained were $K_1 = 10$ and $\log(K_2) = 23$. Here, it is emphasized that the relatively small variations in T_g observed in this system result in a low r^2 value and mean that these values should be treated as order of magnitude estimates at best. Nonetheless, the aforementioned K_1 and $\log(K_2)$ values are consistent with the high cross-link densities observed in these systems and the rigidity of the components used to produce these networks and imply very little increase in molecular restraint due to additional cross-linking (thus the lack of large increases in T_g).

The use of FGAs to improve joint strength requires adhesives with graded mechanical properties, especially the Young's modulus.^{5,7,8} With this in mind, the effect of γ -irradiation on the mechanical properties of DGEBA-NMA was studied via tensile testing (Table S4, Supporting Information). The nonirradiated DGEBA-NMA showed tensile properties similar to those published elsewhere.²⁶ The Young's modulus of this material was observed to increase linearly with radiation dose (Figure 3A). In contrast, no statistically significant changes were observed in failure stress or failure strain at any dose (Figures 3B and C).

The fact that glass transition temperature, thermal stability and modulus can be varied in a predictable fashion via postcure radiation cross-linking of DGEBA-NMA demonstrates the promise of this approach as a means of realizing FGMs and FGAs. However, greater variations in modulus are needed to achieve a more uniform stress distribution along a joint.^{5,12} The limited changes in modulus may be explained in light of the fitting parameters derived from application of the Shibayama model and their implications for the behavior of this material. Effectively, what the K_1 and $\log(K_2)$ values tell us is that the network is already so rigid and heavily cross-linked that additional cross-linking results in minimal changes in properties.

To address this point, additives were selected to enhance the sensitivity of the network to radiation-induced cross-linking (through the inclusion of more reactive terminal C=C bonds) and to reduce the cross-link density following thermal curing (to increase the relative impact of the introduction of additional cross-links). Diols such as bisphenol A (BPA) that function as epoxy chain extenders have previously seen use as modifiers in epoxy networks.²⁷ With this in mind, DBPA was chosen as an additive for the DGEBA-NMA network (DGEBA-NMA+DBPA; refer to the Supporting Information). During conventional curing the DBPA is expected to act as a rigid chain extender, reducing cross-link density without substantially compromising T_g or modulus. Following conventional cure, the allyl groups present in DBPA promise increased sensitivity to radiation-induced cross-linking.

CTBN was chosen as the second additive for the DGEBA-NMA network (DGEBA-NMA+CTBN; refer to the Supporting Information). As with DBPA, CTBN also contains terminal C=C bonds (in the form of poly(1,2-butadiene) repeats),

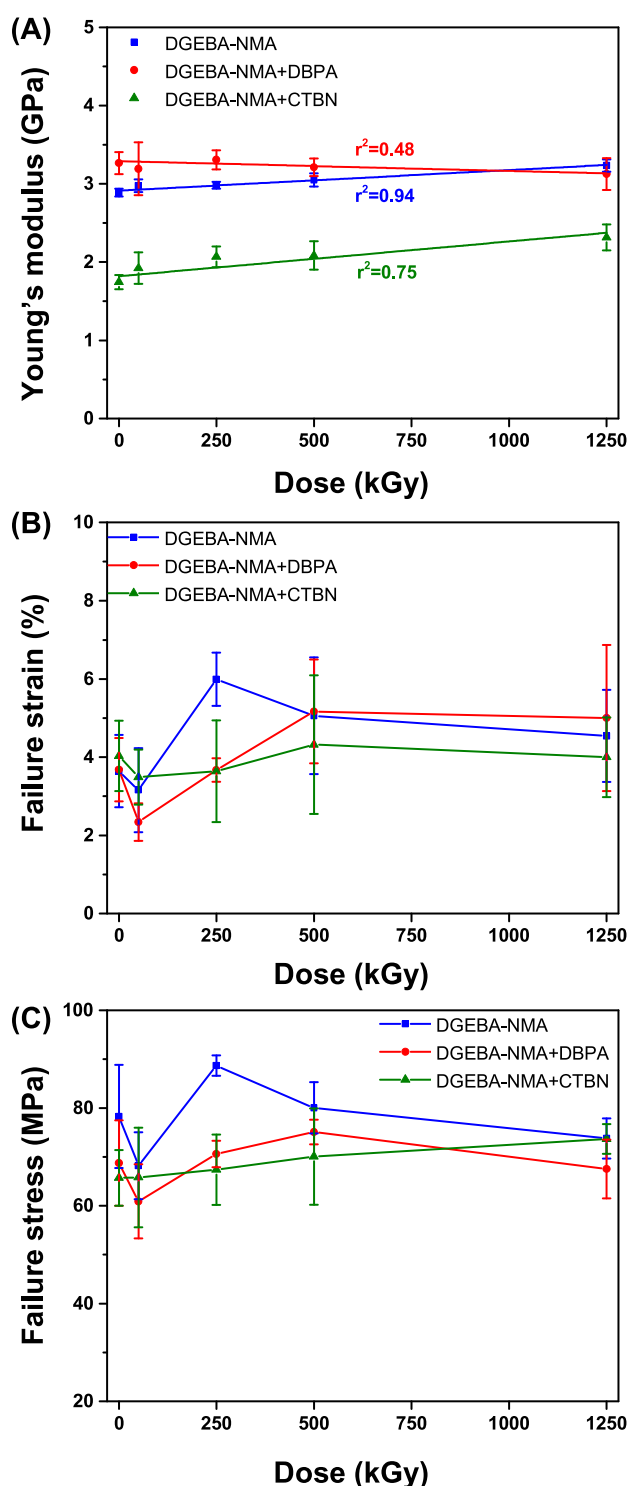


Figure 3. (A) Young's modulus versus ^{60}Co γ -ray dose for all networks; lines represent linear fits. (B) Failure strain versus ^{60}Co γ -ray dose for all networks; lines connect adjacent data points. (C) Failure stress versus ^{60}Co γ -ray dose for all networks; lines connect adjacent data points.

promising increased radiation sensitivity in addition to its well-known capacity for increasing toughness with a relatively low loading used to avoid excessive reductions in T_g and modulus.²⁸

Subsequent ATR-FTIR analyses confirm that the addition of the aforementioned additives can indeed improve the radiation

sensitivity of the DGEBA-NMA network. The observation of significant increases in the intensity of the $-\text{CH}_2-$ absorption bands (2922 and 2850 cm^{-1} , C–H stretching; 1454 cm^{-1} , C–H bending) coupled with reductions in the C=C–H absorption bands (3071 cm^{-1} , C–H stretching; 1636 cm^{-1} , C=C stretching) confirmed the increased radiation sensitivity of the DGEBA-NMA+DBPA network (Figures S1B and S2B, Supporting Information). Following irradiation of DGEBA-NMA+CTBN networks at different doses (Figure S1C, Supporting Information), ATR-FTIR spectra indicated continuous reductions in the intensity of the C=C–H absorption bands (3055 cm^{-1} , C–H stretching; 1636 cm^{-1} , C=C stretching) as a function of dose (Figures S1C and S2C, Supporting Information), consistent with consumption of C=C double bonds. However, in contrast with the DGEBA-NMA+DBPA system, in the DGEBA-NMA+CTBN system, the highest intensity of the $-\text{CH}_2-$ absorption bands (2922 and 2850 cm^{-1} , C–H stretching) was reached at 500 kGy (Figure S2C, Supporting Information), with a decrease observed at 1250 kGy . While further study is needed to confirm the origins of this observation, some level of CTBN degradation cannot be ruled out at this highest dose. Nonetheless, these results once more confirm that the desired increases in radiation sensitivity have been achieved in both formulations.

Subsequent thermal characterization results confirm that the addition of the additives studied here can boost the sensitivity of the thermal properties of the DGEBA-NMA epoxy to irradiation. At the highest dose (1250 kGy), the degradation temperature (via TGA) increases by $\sim 47^\circ\text{C}$; the T_g (via DSC) and T_α (via DMA) increase by ~ 34 and $\sim 36^\circ\text{C}$, respectively, and the cross-link density increases by $\sim 119\%$ (Figures S3B–S7B and Table S2, Supporting Information) for the DGEBA-NMA+DBPA network. Likewise, for DGEBA-NMA+CTBN network, the degradation temperature increases by $\sim 30^\circ\text{C}$; the T_g and T_α increase by ~ 24 and $\sim 34^\circ\text{C}$, respectively, and the cross-link density increases by $\sim 123\%$ (Figures S3C–S7C and Table S3, Supporting Information). The plots of cross-link density versus dose show a clear linear trend (Figure 2A), and the Shibayama model is successfully applied once more to these networks, as shown in Figure 2B. In this case, the obtained fitting parameters of two networks (DGEBA-NMA+DBPA network: $K_1 = 107$ and $\log(K_2) = 4$; DGEBA-NMA+CTBN network: $K_1 = 61$ and $\log(K_2) = 5$) confirm the ability of the DBPA and CTBN to enhance the sensitivity of the network to additional cross-linking while maintaining some level of chain rigidity. Indeed, these parameters are quite similar to those obtained for conventional epoxies as a function of the extent of (thermal) curing.²⁹

Given the above results, it is surprising to note that, upon γ -irradiation of the DGEBA-NMA+DBPA epoxy system, the mechanical behavior of irradiated samples (Table S5, Supporting Information) differed greatly from expectations. In particular, no statistically significant changes were observed in modulus, failure stress or failure strain as a function of dose (Figures 3A–C). While this may seem counterintuitive, one key observation in this case is that the addition of DBPA resulted in an increase in Young's modulus even prior to irradiation. As irradiation was shown to produce only modest increases in modulus in the base DGEBA-NMA system, none of which reached the level of the unirradiated DGEBA-NMA+DBPA system, it follows that the effect of DBPA addition is to render radiation cross-linking even less significant as far as its effects on modulus are concerned. In contrast, DBPA

addition results in a substantial decrease in both unirradiated cross-link density and glass transition temperature, thus providing the system with much greater capacity to respond as far as irradiation-induced changes in these quantities are concerned.

In contrast to the DGEBA-NMA+DBPA case, the addition of the CTBN produces the desired effect of reducing the modulus of the DGEBA-NMA system while simultaneously enhancing its sensitivity to radiation-induced increases without compromising other properties (Table S6, Supporting Information). Changes in Young's modulus follow a linear trend with radiation dose, increasing by ~33% at the highest dose (Figure 3A). No statistically significant changes are observed in failure strain, while failure stress shows a clearly increasing trend with radiation dose, albeit one that is within experimental uncertainty (Figures 3B and C). Based on these results, it is concluded that any radiation-induced degradation processes that may be occurring in the DGEBA-NMA+CTBN system do not appear to have a negative impact on quasi-static mechanical performance. Additionally, the shifts in performance reported here validate this approach as a means of generating materials appropriate for the preparation of FGAs.

In conclusion, a series of thermal/ γ -irradiation dual cured epoxy resins has been reported whose properties may be controlled via postcure irradiation dose level. ATR-FTIR characterization confirms the cross-linking mechanism active during γ -irradiation. Based on the thermal characterization data, material properties were dominated by cross-linking, not degradation, even at doses as high as 1250 kGy. The addition of relatively low levels of additives with terminal C=C bonds (DBPA or CTBN) successfully enhanced the sensitivity of the DGEBA-NMA formulations vs radiation cross-linking, with much more significant increases in cross-link density observed in the DGEBA-NMA+DBPA network (119%) and the DGEBA-NMA+CTBN network (123%) than the DGEBA-NMA network (15%) at the highest radiation dose (1250 kGy). Mathematical relationships were established between dose, cross-link density, modulus and T_g in each case, providing insights into materials behavior and enabling predictions of irradiation-induced changes in relevant properties. Mechanical testing indicates that the DGEBA-NMA+CTBN system is the most promising given the large range of Young's moduli accessible as a function of radiation dose. Additionally, in the absence of radiation, CTBN-toughened anhydride-cured epoxy has been shown to provide a consistent modulus vs long-term aging,³⁰ supporting the supposition that FGAs fully cured via conventional means prior to supplemental localized radiation cross-linking will maintain stable modulus gradients over time. In sum, these results demonstrate the significant potential of the approaches and materials described here in enabling the preparation of FGMs and FGAs. Continued efforts along these lines and with the aim of further expanding the range of accessible properties as a function of radiation dose will be the subject of future reports.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge on the ACS Publications Web site. The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.0c01137>.

Details of materials, synthetic procedures, characterization techniques, and supporting data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Daniel F. Schmidt – Department of Plastics Engineering, University of Massachusetts Lowell, Lowell, Massachusetts 01854, United States; Department of Materials Research & Technology, Luxembourg Institute of Science & Technology, L-4940 Hautcharage, Luxembourg; orcid.org/0000-0003-2511-1906; Email: daniel.schmidt@list.lu

Authors

Weiqing Xia – Department of Plastics Engineering, University of Massachusetts Lowell, Lowell, Massachusetts 01854, United States

Sara Najafian – Department of Mechanical Engineering, University of Massachusetts Lowell, Lowell, Massachusetts 01854, United States

Alessandro G. Cassano – Department of Mechanical Engineering, University of Massachusetts Lowell, Lowell, Massachusetts 01854, United States

Scott E. Stapleton – Department of Mechanical Engineering, University of Massachusetts Lowell, Lowell, Massachusetts 01854, United States

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsapm.0c01137>

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Notes

The authors declare no competing financial interest.

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