

Directed Oligomer Structure by Controlled Radical Polymerization For Use In Photocurable Thin Films.

By Jon Scholte, Soon Ki Kim, and C. Allan Guymon

Introduction

Photopolymerization is a broadly expanding field with many industrial applications. Photocurable epoxy resins in particular are used for their optical clarity and adhesive properties. While these materials are also known for their hardness, they are often considered too brittle for many applications.¹ Recent research has shown, however, that hybrid epoxy-acrylate resins achieve an overall hardness similar to that of neat epoxy materials while reaching greater conversion at shorter irradiation times.² These hybrid systems often require dual cationic and radical photoinitiator packages to achieve sufficient conversion of both moieties, which limits their ease of application.²

Modification of mechanical properties in epoxy resins is accomplished primarily through the incorporation of prepolymers. While traditional prepolymers are comprised of a range of molecular weights and functionality, the ability to more directly control the structure could be of great benefit. Such control for prepolymers could be achieved with a variety of controlled radical polymerization techniques, including nitroxide mediated polymerization (NMP).³ This technique uses the highly stable nitroxide radical to mediate the propagation of growing radical polymer chains and thus to maintain a low polydispersity index. Further, molecular weight and architecture of prepolymers can be controlled by changing the reaction feed, an ability facilitated by the long life of radical species generated during NMP.

Phase separation, which may induce properties that are favorable in certain applications, may be established using prepolymer architectural control. Previous work has shown that the incorporation of hyper-functionalized star polymers into epoxy resins can be utilized to modify the resulting photocured polymer network to improve various mechanical properties including impact strength.^{4,5} In addition, free radical photopolymerization induced phase separation has been documented when linear nonreactive oligomers are incorporated in a system.⁶ Here, we report that the incorporation of epoxy functionalized acrylate prepolymers strengthen epoxy resins while simultaneously establishing multiple glass transition regimes. Linear functional prepolymers were synthesized using a facile NMP method. Further, we demonstrate that the location of reactive groups along the linear prepolymer backbone affects the strength of the resulting polymer network.

Experimental

Novel prepolymers were synthesized utilizing BlocBuilder RC-50 (Arkema) as both the initiating and mediating radical source. A 2L reactor was filled with BlocBuilder RC-50 and

butyl acrylate in an equivalent weight of ethyl acetate as solvent. End functionalized prepolymers were synthesized in three steps using different feeds. A primary feed of butyl acrylate and cycloaliphatic epoxy methacrylate was used. A secondary feed consisting of butyl acrylate was added after the first feed, followed by a final feed identical to the first. This scheme allows the epoxy moieties to be placed at the end sections of the monomer.. Similarly, random prepolymers were also synthesized with an initial reactor volume containing BlocBuilder RC-50, butyl acrylate, and ethyl acetate, however, only a single feed consisting of butyl acrylate and cycloaliphatic methacrylate was used. Once synthesized, ethyl acetate and residual monomers were removed via rotary evaporation and the products were analyzed using GPC to determine molecular weight and distribution. Table 1 contains the target MW and functionality of the synthesized prepolymers used in this report.

Table 1. Prepolymer Target Weights and Functionalities

Prepolymer Target Molecular Weight	Target Functionality	
End Architecture Prepolymer		Films were fabricated with varying concentrations of prepolymer and crosslinker (3,4-Epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate, EEC). Diaryliodonium hexafluoroantimonate (IHA, Satomer) and Isopropylthioxanthone (ITX, Albemarle) were used as the photoinitiating package and added to the prepolymer/crosslinker mixture at 2% and 1% by weight, respectively. Formulations were then photopolymerized between two quartz plates, each covered with a release
20,000	16	
10,000	8	
Random Architecture Prepolymer		
20,000	16	
10,000	8	

substrate, for 30 minutes using a 13.5 mW/cm² medium pressure mercury arc lamp emitting 250-500 nm light. Samples were then cut to dimensions of 0.25 mm x 6 mm x 25 mm (thickness x width x length) for mechanical testing via dynamic mechanical analysis. To measure the tan (δ) and moduli, samples were cooled to -100°C and heated to 150°C under constant strain using a cycle of 1Hz. For adhesion testing, samples were photopolymerized for one minute under the same conditions on a stainless steel substrate. A second piece of stainless steel was then applied at a pressure of 2-3 metric tons to 0.5 cm² of the sample for lap shear adhesion testing. To measure creep, a constant stress of 4 MPa was applied to each thin film sample for 10 minutes while strain was monitored. After 10 minutes, the stress was removed and strain recovery was monitored for 30 minutes.

Results and Discussion

One of the key factors in determining the utility of a photocured system is its glass transition temperature. Here, we explore the use of photopolymerizable novel prepolymer species to modify the thermomechanical properties of epoxy resins using EEC as a cationic chain extender.

Glass transition temperatures were identified using dynamic mechanical analysis to monitor $\tan(\delta)$ as a function of temperature. Figure 1 shows the $\tan(\delta)$ profiles of films with 70 wt% prepolymer (functionality = 16) with two different architectures and 30 wt% EEC. The end functional architected oligomer exhibits 2 maxima in the profile, representing 2 distinct glass transition temperatures. The lower glass transition temperature is due to the long uninterrupted butyl acrylate backbone, while the second, more prominent maximum originates from the highly crosslinked continuous glassy phase originating from the EEC crosslinking monomer. In contrast, the profile of the randomly functionalized oligomer species has a single broad peak. This suggests that the resulting polymer network lacks separation of butyl acrylate and EEC, leading to a much broader glass transition temperature.

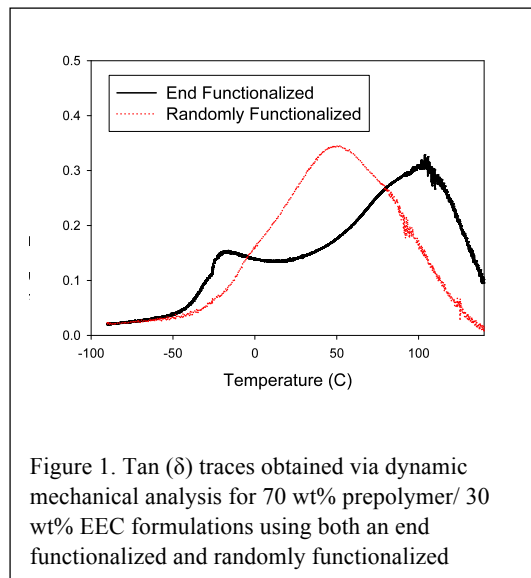


Figure 1. $\tan(\delta)$ traces obtained via dynamic mechanical analysis for 70 wt% prepolymer/ 30 wt% EEC formulations using both an end functionalized and randomly functionalized

Based on the large changes in glass transition temperatures, the architecture of prepolymers is also likely to modify mechanical and surface properties. Films consisting of these novel oligomers and EEC as a crosslinker were again used to examine elongation and mechanical resistance as well as lap shear adhesion. The average ($n=3$) results for these tests are found in Table 2. Utilizing different weight ratios of oligomer and EEC, films were fabricated as described and elongated until the samples yielded. As predicted, greater incorporation of oligomer species leads to materials that experience greater elongation for both oligomer architectures. The ultimate material properties

Table 2. Summary of test results for mechanical toughness and lap shear adhesion using 20,000 Molecular Weight Prepolymers

Oligomer/EEC	Rupture Strain (%)	Rupture Stress (MPa)
Random Architecture		
60/40	33±3	20±2
70/30	42±4	15±2
End Architecture		
60/40	33±2	21±2
70/30	37±2	16±1

upon failure are not significantly different based on the oligomer architecture. However, the continuous glassy domain present in the end functionalized epoxy samples leads to greater tensile moduli during the plastic deformation of these samples as compared to their randomly structured counterparts. Lastly, to ensure sufficient tack for adhesion to stainless steel substrates, the shear adhesion of films consisting of high concentrations of oligomer species were examined in using a lap shear test as summarized in table 3. The reinforcement of the uninterrupted butyl acrylate backbone in the end architected prepolymer samples leads to a greater stress needed to cause lap shear failure compared to the randomly functionalized oligomer.

Table 3. Summary of lap shear adhesion test results

Oligomer/EEC	Lap Shear Adhesion (MPa)
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Random Architecture

Creep can also be modulated by incorporating photopolymerizable prepolymers with different architectures. The end functionalized oligomer species are expected to show less creep under similar stresses as compared to the randomly architected oligomer. This is due to the “coiled” butyl acrylate chain acting as a restoring force as compared to the random samples, which lack this feature. Table 3 shows the strain and strain recovery of each sample after the application of 4 MPa stress. Randomly functionalized prepolymer/EEC samples experienced significantly higher strains with the 70wt% oligomer/30 wt% EEC breaking immediately after the stress was applied. The 60wt% oligomer/40wt% EEC experienced significantly more strain as compared to the same ratio of the end functionalized sample, which experienced an average of only 1.9% strain. The 70wt% end functionalized oligomer/30wt% EEC sample experienced an average of 23% amount of strain as compared to the previously mentioned 70/30wt% randomly functionalized oligomer sample, which broke after the application of stress. During the recovery period, the end architected prepolymer samples recovered as much or more than the randomly architected samples, up to 90%. These results suggest that utilizing these different oligomer species, we can directly manipulate the viscoelastic properties of epoxy resins.

Table 3: Elongation of architected prepolymer and EEC films under constant stress using 10,000 MW prepolymers (creep).

Architected prepolymer/EEC	% Strain	% Strain Recovery
	Random	
60/40	35±10	69±3
70/30		Broken
	End	
60/40	1.90±0.07	91±2
70/30	23±3	68±1

Conclusions

Controlling photopolymerizable oligomer architecture has been shown to be a versatile method of modifying the thermomechanical properties of epoxy resins. While prepolymers are known to impart greater flexibility to materials, herein we report a new method of generating phase separation while also modifying the mechanical properties. The incorporation of different architectures shows the ability to modify the $\tan(\delta)$ behavior: end functionalized oligomers show the ability to impart more glassy behavior into the traditionally glassy EEC epoxy network. The end functionalized oligomer species also can be used to enhance the toughness a photocured film as compared to a randomly architecture oligomer. Interestingly, the formulations using end functionalized oligomer architected materials show less irreversible strain and greater strain recovery after experiencing the same stress.

Works Cited

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