A "DROP-IN" COMPOSITE MATRIX VIA AZIDE-ALKYNE CYCLOADDITION

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ABSTRACT

Since the inception of carbon fiber-reinforced polymers (CFRPs) they have steadily gained in popularity due to their light weight, high tensile strength and modulus, and environmental toughness. However, curing of CFRPs of the thermosetting type generally must be performed within an autoclave, whose fixed, physical dimensions effectively limit the maximum size of the part. Alternative curing chemistries may potentially eliminate the requirement for an autoclave, which would allow creation of much larger panels. This project seeks to develop a thermoset composite matrix that is radiation-curable using the Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) click reaction. Previously, Storey *et al.*[1,2] reported that the azide-modified epoxy resin, di(3-azido-2-hydroxypropyl) ether of bisphenol-A (DAHP-BPA), could be cured by reaction with polyfunctional alkyne crosslinkers under mild conditions using Cu(I) catalysis. In the absence of reducing agents, Cu(II) compounds are catalytically inactive; however, upon exposure to ultraviolet light, they are reduced to Cu(I), which then catalyzes the reaction, allowing it to progress to a high degree of cure at room temperature. Herein, we report the kinetics of photo-induced CuAAC polymerization of the DAHP-BPA and several polyfunctional propargyl amine based crosslinkers, monitored by real-time FTIR as well as mechanical properties of fully cured materials. Polymerizations were studied as a function of Cu(II) compound type, Cu(II) concentration, UV light (365 nm) intensity, and duration of irradiation.

1. INTRODUCTION

In many application areas of thermoset polymers, including coatings, adhesives, sealants, and composite matrices, a two-component system is utilized consisting of resin and crosslinker that are mixed immediately prior to application. Such a system is typically characterized by a finite working time or pot life, which can be a processing limitation. In such cases, a triggered or on-demand cure can be highly advantageous.

In several recent reports[1–4] we described a two-component thermosetting polymer system based on the Cu(I)-catalyzed azide alkyne cycloaddition (CuAAC) reaction.[5–7] The system consisted of the azide-functionalized resin, di(3-azido-2-hydroxypropyl) ether of bisphenol-A (DAHP-BPA) and various polyalkyne crosslinkers. We discussed the thermal curing of these two-component systems, either catalyst-free with highly reactive alkynes such as propiolates, or in the presence of Cu(I) with less reactive alkynes.

The CuAAC reaction can be performed by the direct addition to the reaction of a Cu(I) compound, or by the addition of a Cu(II) catalyst precursor, from which Cu(I) can be generated *in situ*. Cu(I) has been directly added in the form of Cu(I) salts,[8] carbene complexes,[9] Cu(I) on immobile phases,[10,11] and copper containing nanoparticles.[12] In addition, Cu(II) can be reduced photochemically.[13] The *in situ* generation of Cu(II) presents the possibility of a triggered cure. Spectroscopic studies have shown that Cu(II) complexes have a strong absorption at 300 nm and can undergo redox reactions during UV-irradiation.[14] This wavelength correlates to the ligand-to-metal-charge transfer that is responsible for the reduction of Cu(II).[15]

Herein, we explore the use of UV light to induce the on-demand cure of the DAHP-BPA/tripropargyl amine system, via photo-reduction of various Cu(II) species. The ultimate goal is a composite matrix resin system that may be cured on-demand at room temperature for out-of-autoclave applications such as field repair.

2. EXPERIMENTAL

2.1. Materials

Copper(II) 2-ethylhexanoate (CEH), copper(II) acetylacetonate (CuAA) (97%), copper(II) bromide ($CuBr_2$) (99.999%), copper(II) acetate ($Cu(OAc)_2$) (98%), copper(II) sulfate ($CuSO_4$anh) (anhydrous, ≥99%), copper(II) sulfate pentahydrate ($CuSO_4$penta) (~99%), dichloro(1,10-phenanthroline)copper(II) (DCPC) (98%), bromotris(triphenylphosphine)copper(I) (BTTPP) (98%), EOSIN Y (dye content ~99%), and 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959) (98%) were purchased and used as received from Sigma Aldrich. Tripropargylamine (TPA) (97%) was purchased and used as received from GFS Chemical. The diglycidyl ether of bisphenol-A (EPON 825) was donated by Hexion Specialty Chemicals and used as received. Synthesis of the azide functional resin, di(3-azido-2-hydroxypropyl) ether of bisphenol-A (DAHP-BPA), and the difunctional alkyne tetra(ethylene glycol) dipropargyl ether (TEGDPE) were accomplished following procedures developed by Gorman, *et al.*[2]

2.2.Instrumentation

Reaction conversion during exposure to UV radiation was monitored using real-time FTIR (RT-FTIR) by observing the disappearance of the azide and alkyne peaks that are coincident at *ca.* 2,100 cm^{-1}. The RT-FTIR studies were conducted using a Nicolet 8700 spectrometer with a KBr beam splitter and a DTGS detector and an Omnicure S2000 ultraviolet light source with a 320−500 nm filter. Overall lamp intensity was 25 mW/cm^2, with peak intensity at 365 nm. FTIR analysis was conducted using a horizontal sample holder designed especially for this purpose. Approximately 0.05-0.10 mL of the sample was sandwiched between two 25 mm NaCl salt plates and placed into the sample holder. Data acquisition was begun, and spectra were taken approximately every 1 s for the duration of the experiment (experiments ranged ~10-60 min) with each spectrum consisting of 1 scan. After a 10 s delay, the UV irradiation was turned on, signifying the start of the reaction (t = 0 s). The ten second delay

between the start of data acquisition and the onset of UV light allowed for the establishment of a stable baseline prior to the beginning of the reaction.

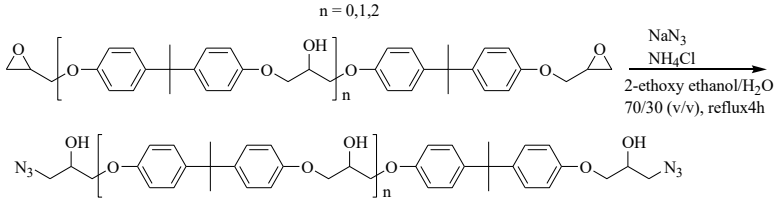
Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained using a 300.13 MHz Varian Mercury^{plus} NMR (VNMR 6.1C) spectrometer. Typical acquisition parameters were 5 s recycle delay, 7.8 µs pulse corresponding to a 45 degree flip angle, and an acquisition time of 1.998 s. The number of scans acquired for each sample was 32. All ^{1}H chemical shifts were referenced to TMS (0 ppm). Sample solutions were prepared at a concentration of approximately 10 wt% in DMSO-d_6 containing 1% TMS as an internal reference and the resulting solution was charged to a 5 mm NMR tube.

2.3.Synthesis

2.3.1. Di(3-azido-2-hydroxypropyl) Ether of Bisphenol-A (DAHP-BPA)

Commercially available EPON 825 was reacted with excess NaN_3 and NH_4Cl in a refluxing mixture of two parts 2- ethoxyethanol and one part deionized water. The nucleophilic azide attacks the ring-strained epoxide (~25 kcal/mol of ring strain[16]) of EPON 825, which opens the ring while adding the azide end group to the less hindered carbon atom (Scheme 1).

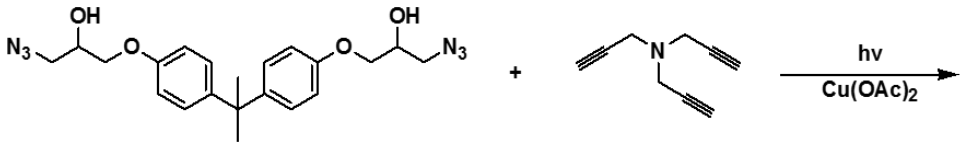
Scheme 1: Synthesis of DAHP-BPA.



2.3.2. Real-time FTIR Sample Preparation

Samples were prepared by first mixing DAHP-BPA and tripropargylamine at 1:1 stoichiometric equivalence in a 20 mL scintillation vial. Cu(II) catalyst precursor, at an appropriate concentration relative to azide, was then added to the vial, and the mixture was stirred by hand for 5 min. A control formulation was prepared similarly, to which was additionally added photoinitiator (Irgacure 2959) at 5 mol% relative to azide. A representative preparation was as follows: DAHP-BPA resin (2.00 g, 4.69 mmol) and TPA (0.41 g, 3.13 mmol) were charged to a 20 mL scintillation vial. $Cu(OAc)_2$ (4.24 mg, 0.024 mmol, 0.25 mol% relative to azide) was next added to the vial, and the mixture was stirred by hand for 5 min.

Scheme 2: UV curing of CuAAC networks.



3. RESULTS AND DISCUSSION

3.1.1. Neat Linear Polymerization for Reaction Conversion Monitoring by ^{1}H NMR

To provide soluble samples for ^{1}H NMR analysis of reaction conversion, a neat, linear polymerization was conducted by reacting DAHP-BPA resin with the difunctional alkyne, tetraethylenglycol dipropargyl ether (TEGDPE), at a molar ratio of azide:alkyne = 1:1 and 0.25% $Cu(OAc)_2$ relative to azide. Thus, TEGDPE (2.04 g, 7.54 mmol), DAHP-BPA (3.21 g, 7.53 mmol), and $Cu(OAc)_2$ (0.007 g, 0.039 mmol) were combined and mixed for 5 min to create a masterbatch, and then 0.1 g aliquots of this mixture were charged to a series of 20 mL glass scintillation vials, which served as individual polymerization reactors. The aliquots were cured under UV light irradiation (Omnicure S2000 lamp with a 320−500 nm filter at an intensity of 25 mW/cm^2), and individual vials were removed from the light at t = 0, 5, 10, 20, 30, 40, 50, and 60 min. These vials were immediately dissolved in DMSO-d_6 to quench the reaction. Conversion was determined via ^{1}H NMR by monitoring the increase in intensity of the combined 1,4- (8.72 ppm) and 1,5-disubstituted triazole ring protons (8.29 ppm), relative to the $C_{3,5}$ phenyl protons (7.12 ppm) of the DAHP-BPA resin. The latter protons served as a convenient internal standard whose intensity remained constant over the course of reaction. By way of illustration, Figure 1 shows spectra acquired prior to and after 1 h of irradiation. The triazole proton resonances are labeled a (1,4 isomer) and b (1,5 isomer) and the $C_{3,5}$ phenyl protons are labeled c. Reaction conversion, p, was calculated according to equation 1,

$$p = 2\frac{A_{a+b}}{A_c} \tag{1}$$

where, A_{a+b} is the combined integrated intensities of peaks a and b and A_c is the integrated intensity of peak c.

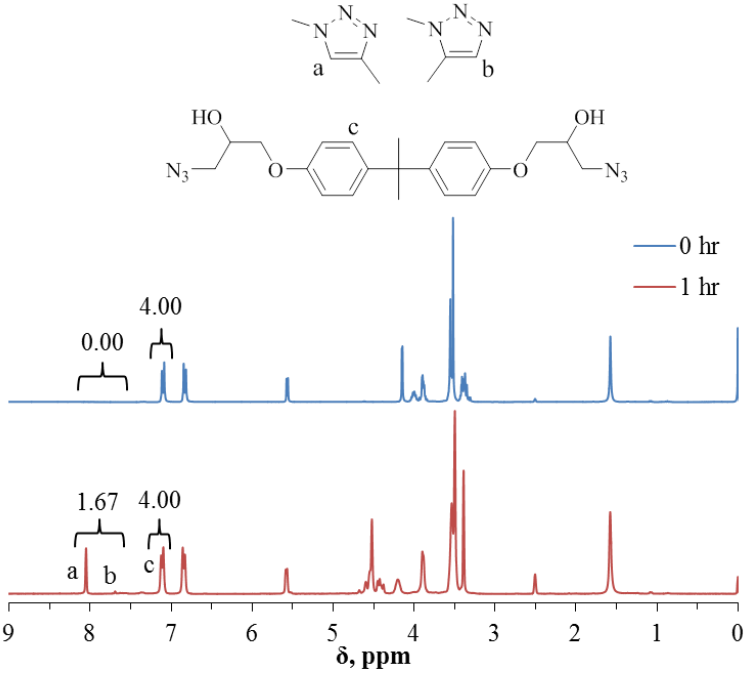


Figure 1: ^{1}H NMR spectra of a DAHP-BPA/TEGDPE/0.25 mol% $Cu(OAc)_2$ sample prior to (upper) and after (lower) 1 h irradiation by 365 nm light at an intensity of 25 mW/cm^2. Reaction conversion was calculated as the integrated intensity of the combined 1,4- and 1,5-

disubstituted triazole ring protons, peaks a and b, relative to that of the $C_{3,5}$ phenyl protons of DAHP-BPA, peak c.

Conversion data obtained by real-time FTIR were validated using ^{1}H NMR as a second method. DAHP-BPA was reacted with the difunctional alkyne, TEGDPE. (Scheme 1) using UV irradiation and the catalyst precursor, $Cu(OAc)_2$, to produce a linear polymer that could be analyzed by ^{1}H NMR. Reaction was carried out in a glass reactor; aliquots were collected, and conversion was determined by integration of the triazole peaks, as described above. Real-time FTIR monitoring was applied to an identically formulated sample reacted between NaCl plates, and monitored for 60 min. Equal light intensity (25 mW/cm^2) was applied in the two reactor configurations. The results, shown in Figure 4, indicate excellent agreement between FTIR and NMR data. These results validate the RT-FTIR data, and show that the reaction proceeds at the same rate regardless of reactor configuration (scintillation vial vs. thin film between NaCl plates).

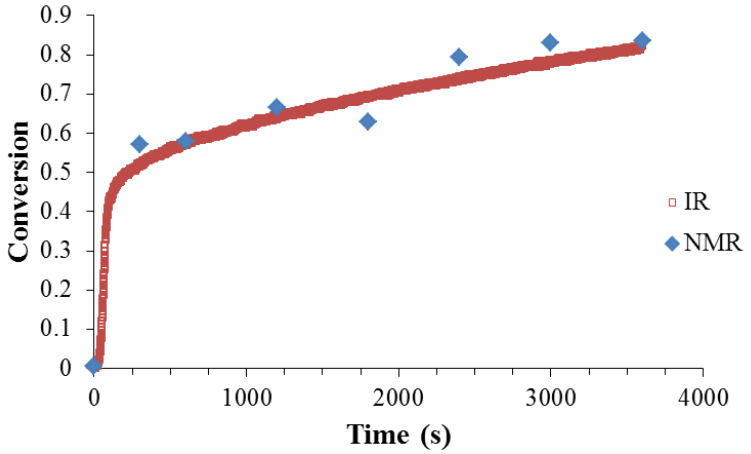


Figure 2: Conversion vs. time for the DAHP-BPA resin/TEGDPE system. Data from ^{1}H NMR (aliquots) and FTIR (real time) are compared. Azide:alkyne was 1:1 (mol:mol). $Cu(OAc)_2$ was 0.25 mol% relative to azide. UV irradiation (25 mW/cm^2) began at t = 0 s and persisted continuously for 3,600 s. Aliquots for NMR were taken at 0, 5, 10, 20, 30, 40, 50, and 60 min of UV irradiation.

Tasdelen and Yagci showed that no photoinitiator was required to begin CuAAc in solution, and also that once initiated, the CuAAC reaction will continue without further UV irradiation, *i.e.*, the reaction will continue in the dark.[17] In the current work, we have conducted experiments to establish whether these findings also hold for reactions conducted in the bulk, involving polymer network-forming reactants. Figure 3 shows CuAAC conversion as a function of time for the DAHP-BPA resin/tripropargylamine/$Cu(OAc)_2$ system, irradiated for various times with 365 nm light at an intensity of 25 mW/cm^2. In view of the report by Tasdelen and Yagci, the systems were irradiated in the absence of a photoinitiator. Control experiments conducted in the absence of UV irradiation (0 s) and in the presence of UV irradiation and photoinitiator (5 mol%, relative to azide, Irgacure 2959) (600 s PI) were also performed. Reaction did not occur in the absence of UV radiation (0 s curve), indicating that $Cu(OAc)_2$ is ineffective under these conditions. The presence of photoinitiator had no significant effect on the rate or extent of photopolymerization,

and thus the findings of Tasdelen and Yagci regarding the superfluity of a photoinitiator, apply also to the bulk DAHP-BPA/TPA system. However, the use of a photoinitiator can broaden the range of wavelengths of light that can be used to trigger the polymerization. For irradiation times > 30 s, the rate and extent of photopolymerization was also independent of the duration of UV irradiation. For all irradiation times above this threshold, rapid photopolymerization began after a brief induction period (25-30 s); photopolymerization continued in the dark for those samples irradiated for relatively short times (30 and 60 s), and then slowed rather abruptly when the conversion reached the 70-80% range. The abrupt slowing of the reaction is ascribed to vitrification of the reaction mass, caused by a rise of the glass transition temperature of the forming polymer network above the temperature of the system. The sample irradiated for only 15 s displayed a significantly reduced rate of photopolymerization and a significantly lower conversion at 600 s. The mechanism of photoreduction of Cu(II) to Cu(I) has been reported to occur by a ligand-to-metal charge transfer. Under the conditions of Figure 3, photoreduction is apparently complete between 15-30 s irradiation, thereby reducing all available copper to Cu(I).

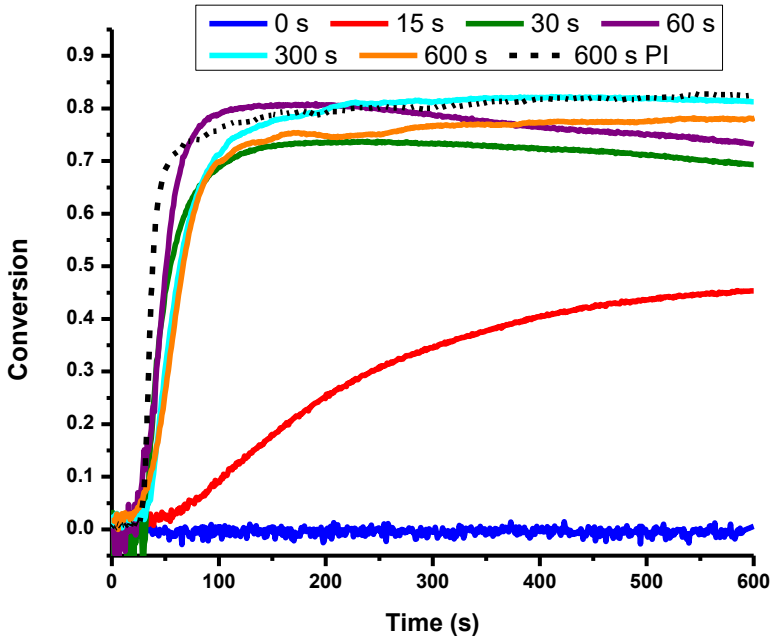


Figure 3: Conversion (real-time FTIR data) vs. time for the DAHP-BPA resin/tripropargylamine/Cu(OAc)$_2$ system, as a function of time of irradiation with 365 nm light at an intensity of 25 mW/cm^2. Azide:alkyne was 1:1 (mol:mol). Cu(II) was 0.25 mol% relative to azide. The control sample with photoinitiator (600 s PI) contained Irgacure 2959 at 5 mol% relative to azide and was irradiated for 600 s. The control sample in the absence of UV irradiation (0 s) did not contain photoinitiator. UV irradiation began at t = 0 s.

We next examined seven different Cu(II) species to detect any differences that might arise due to solubility of the salts within the DAHP-BPA system: CEH, CuAA, $CuBr_2$, $Cu(OAc)_2$, $CuSO_4$anh, $CuSO_4$penta, and DCPC. Real-time FTIR data for each Cu(II) compound are shown in Figure 4. Figure 4 shows data from samples of relatively longer path length as indicated by an initial peak intensity at 2,100 cm^{-1} of ≥ 1 absorbance unit. All seven Cu(II) compounds performed essentially the same with respect to their

effectiveness as a catalyst. When sample thickness (reacting mass) was controlled, all Cu(II) species produced similar rates of photopolymerization and similar final conversions. This simple conclusion was initially confused by different sample thicknesses. The CuAAC reaction is highly exothermic, and small differences in reaction mass can produce detectable differences in reaction rate. Figure 4, which shows data from relatively longer path-length samples, shows higher initial polymerization rates compared to those from shorter path-length samples (data not shown). We hypothesize that the greater reaction rate in the longer path-length samples is due to a slightly greater rise in temperature due to the exothermic reaction in the larger reacting mass. This phenomenon has no effect on the final conversions of the photopolymerization as the final conversions were all in the 80-90% range, regardless of the Cu(II) species and regardless of sample thickness (initial peak intensity at 2,100 cm^{-1}).

Visual observation of the formulated systems prior to irradiation suggested that only CEH was readily and fully soluble within the DAHP-BPA resin. All other Cu(II) compounds produced turbid mixtures with DAHP-BPA suggesting only partial or marginal solubility. Although CEH did not show greater effectiveness as a catalyst regarding rate or final conversion, its greater solubility might confer process advantages in a practical system.

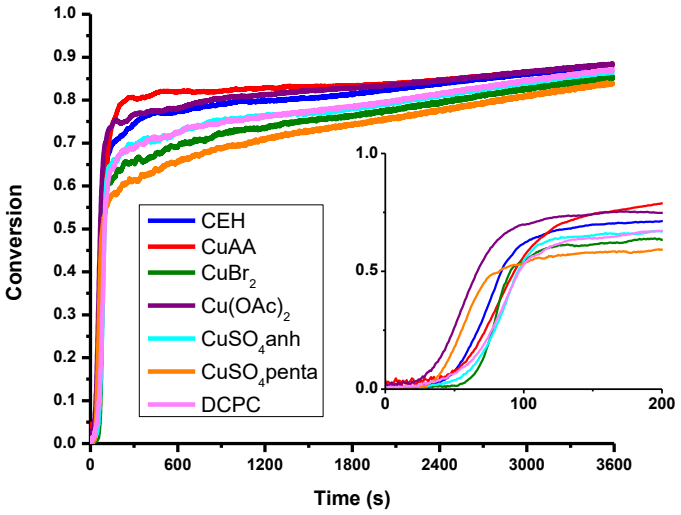


Figure 4: Conversion (real-time FTIR data) vs. time for the DAHP-BPA resin/TPA system as a function of Cu(II) source: CEH, CuAA, CuBr2, Cu(OAc)2, CuSO4anh, CuSO4penta, and DCPC. Azide:alkyne was 1:1 (mol:mol). Cu(II) was 0.25 mol% relative to azide. UV irradiation (25 mW/cm^2) began at t = 0 s and persisted continuously for 3,600 s.

4. CONCLUSION

The objective of this research was to explore the UV-light triggered cure of the azide functional resin (DAHP-BPA) with polyalkyne crosslinkers and Cu(II) as a photo-reducible catalyst precursor. Specifically, we wished to determine whether the UV-

triggered CuAAC reaction could be carried out in the absence of a photoinitiator, as reported by Tasdelen and Yagci,[17] for thermosetting reactions conducted in the bulk. Photo-reduction of Cu(II) was indeed efficient using 320-500 nm filtered UV light (maximum at 365 nm) in the absence of a photoinitiator. Using RT-FTIR, it was observed that after 60 s of UV irradiation ~60% of the reaction had taken place. Then upon further irradiation for 1 h, the conversions increased to >80%. It was also shown that the rate and extent of cure are independent of the Cu(II) compound utilized, for a group of seven Cu(II) compounds analyzed, composed of various counterions/ligands. The only distinction observed among the seven catalysts was the exceptional solubility of CEH within the DAHP-BPA system. Although CEH did not show greater effectiveness as a catalyst with regard to rate or final conversion, its greater solubility might confer process advantages in a practical system.

^{1}H NMR was used to verify the RT-FTIR data, and good agreement was achieved between the two methods. Optimal amount of copper catalyst loading was determined to be about 0.05 to 0.25 mol% relative to azide. Lower amounts can be used, but the rate of reaction decreases dramatically below 0.05 mol%. It was also shown that conversion was independent of the UV irradiation time as long as irradiation time was at least 30 s at 25 mW/cm^2.

5. REFERENCES

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