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Curing kinetics and characterization of dual-curable thiol-acrylate-epoxy thermosets with latent reactivity

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ABSTRACT

A new dual-curing scheme was developed for thiol-acrylate-epoxy mixtures. A photo-initiated latent catalytic system was used to carry out thiol-acrylate Michael addition at 35 °C (Stage 1) followed by thiol-epoxy click reaction (Stage 2) at 80–110 °C. The intermediate materials were shown to have several days of storage stability. The use of a radical inhibitor has suppressed radical mediated acrylate homopolymerization which would otherwise lead to unreacted thiols remaining. Kinetics of Stage 2 was analyzed mathematically using iso-conversional differential method and Kamal model regression. Glass transition temperatures (T_g) of samples with varying contents of epoxy and different types of acrylates were measured. Epoxy-rich formulations gave the highest final T_g. Although not as influential as the epoxy content, using higher functional and more rigid acrylate monomers resulted in higher intermediate and final T_g. The proposed curing scheme and the resulting materials could be useful in applications such as adhesives, industrial coatings with high chemical resistance, optical and electronic materials.

1. Introduction

Over the last few years, dual-curing polymer systems have attracted a great interest because of the facility they provide in polymer processing and application. A dual-curable system consists of two distinct crosslinking reactions that are triggered independently using stimuli such as heat and UV irradiation. Separating the two curing reactions enables one to attain an intermediate stage of curing where one type of polymer network has developed and a significant amount of unreacted monomers is present. This intermediate stage ensures the storage and processing flexibility demanded by certain applications. At a later stage, when desired, the second curing reaction could be triggered and the unreacted monomers would crosslink to yield the ultimate material with a dual network structure. To ensure high yields at desirable reaction conditions, click chemistry is a requirement for these systems [1]. Nair et al. demonstrated the use of dual-curability in a medical application. They synthesized intermediate materials with shape memory property which could be deployed from a catheter. Once they attain their shape inside the body, the second curing stage could be triggered to fix the shape permanently [2]. Chatani et al. adopted a similar approach and synthesized triple shape memory materials using a single reaction mechanism but two different monomers with significantly different reactivities so as to allow two-stage curing [3]. Peng et al. used two sequential click reactions to produce holographic materials. The intermediate stage materials allowed large refractive index gradients to be recorded onto them [4].

Michael addition reactions are used widely in dual-curing formulations as they often fit the click criteria. It is the nucleophilic addition (i.e. the Michael donor) to an electrophilic olefin (i.e. Michael acceptor). The reaction proceeds through an anionic intermediate which is stabilized by the electron withdrawing group possessed by the Michael acceptor. Common Michael donors are amines, thiols and phosphines. Michael acceptors are more numerous and include acrylates, methacrylates, sulfones and many other electron deficient groups [5,6]. In our work, we use thiol-acrylate Michael addition reaction as it has many advantages such as low polymerization shrinkage, low oxygen inhibition and gelation at higher conversions when compared to chain-growth acrylate homopolymerization [7–10]. However, due to the flexible structure of the thiol-acrylate thermoset, it has limited use in demanding applications requiring superior hardness, modulus and glass transition temperatures (T_g) [11].

To ensure separability of two curing steps, many researchers make use of latent catalytic systems which are dormant under storage conditions, but liberate catalytic species when stimulated by heat and/or UV light. Using photobase generators (PBGs) are one option to exploit such latent reactivity [12–14]. Jian et al. combined a PBG based on a sodium tetraphenylborate salt of TBD with isopropylthioxanthone (ITX), a photosensitizer for carrying out thiol-acrylate Michael addition

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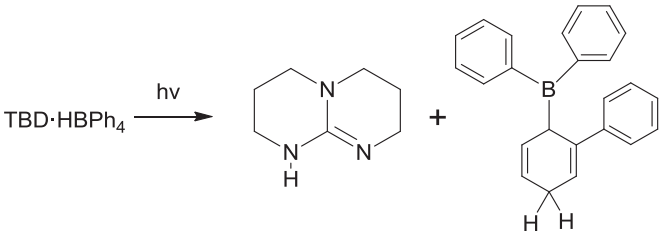

Scheme 1. Liberation TBD from its $HBPh_4$ salt when subjected to UV radiation [12].

[11]. The mechanism of TBD liberation is shown in Scheme 1.

However, radicals are generated due to ITX which give way to radical mediated thiol-acrylate reaction and acrylate homopolymerization, which in turn would lead to off-stoichiometric thiol conversion. Radical inhibitors such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) are used to avoid this [13].

Another widely used reaction in dual-curing polymer research is the thiol-epoxy reaction which fits the high-yield criteria of click reactions [15]. Epoxy resins are one of the most widely used thermosetting resins due to their superior properties such as high chemical and mechanical resistance, excellent adhesion and low polymerization shrinkage [16,17]. Due to these desirable features, many researchers have incorporated the thiol-epoxy reaction to obtain a hybrid thiol-acrylate/thiol-epoxy system which offsets the setbacks of a purely thiol-acrylate network [11,18]. Thiol-epoxy reaction is the base catalyzed, nucleophilic attack of a thiol group to an epoxy ring. The base deprotonates the thiol, yielding a thiolate anion, which in turn attacks and opens the epoxy ring [15].

In this work, we present a set of novel thiol-acrylate-epoxy thermosets which is cured using a photocatalytic system. In particular, we use a PBG of TBD, together with a photosensitizer ITX. The catalytic properties of the same PBG were characterized in an earlier work with thiol-epoxy reaction [19]. To suppress the formation of radicals during UV irradiation, we use TEMPO as radical inhibitor. We first study the reaction kinetics of both stages by experimental and computational methods. We then investigate how the T_g of our final materials change as the acrylate-to-epoxy ratio and also the acrylate type in our formulations are changed. To the best of our knowledge, no other research attempted to obtain a thiol-acrylate/thiol-epoxy system while allowing minimal radical mediated reactions through use of a radical inhibitor. Although for certain applications, it could be desirable to have unreacted monomers remaining, for certain others such as industrial coatings with high chemical resistance, obtaining a fully crosslinked product is crucial [20].

2. Materials and methods

All materials except the epoxy resin were supplied by Sigma Aldrich and used as received. The epoxy resin, coded as DG187, was supplied by Hexion Specialty Chemicals (traded as EPIKOTE™ Resin 828, with an epoxy equivalent weight of 187) and was dried under vacuum at 80 °C for 30 min prior to use. The chemical structures of all materials used are given in Scheme 2.

2.1. Synthesis of the photobase generator

PBG was synthesized using a procedure reported previously [21]. Firstly, TBD was solubilized in methanol (10 mmol in 10 mL MeOH) and slightly acidified with 36% HCl solution. $NaBPh_4$ was also solubilized in a small amount of MeOH and added with a slight excess to the acidified TBD solution. The formed salt was filtered, washed thoroughly with distilled water and MeOH, recrystallized from a 4:1 mixture of MeOH and $CHCl_3$, and dried under mild heat and vacuum.

2.2. Sample preparation

Samples with PBG were prepared in 5 mL glass vials by adding the PBG into DG187 and heating up to 110 °C under agitation using an electric heater equipped with a magnetic stirrer. Mixing was continued until a clear solution was obtained. The mixture was left to cool down, after which the acrylate (HDDA, TMPTA or TCDDA, depending on the formulation), S4 and ITX were added. In all formulations, amount of S4 was in stoichiometry with acrylate and epoxy groups combined. Also, in all samples with PBG, the amount of PBG and ITX were 0.5% and 0.25% w/w based on total reactants, respectively. For our preliminary experiments, the neat base DMAP was added lastly during sample preparation. Samples were coded as DGxHDDAy where x and y stand for molar percentages of DG187 and the acrylate (HDDA in this case), respectively. When necessary, samples were also coded as TEMz where z is the TEMPO content by mass percentage. In between experiments, the sample vials were stored under − 20 °C wrapped in aluminum foils to avoid light exposure and loss of latency. Table 1 shows the formulations used.

2.3. Differential scanning calorimetry (DSC)

Calorimetric analyses of materials were carried out on a Mettler DSC822e thermal analyzer both to measure T_g and to monitor functional group conversions. UV irradiation of materials were performed on a Mettler DSC821 thermal analyzer using a Hamamatsu LC5 light source equipped with a Hg-Xe mid-pressure lamp conveniently adapted to the DSC by means of fiber optics probes. UV light intensity was approximately 36 mW cm^{-2} measured at 365 nm using a radiometer. Both analyzers were calibrated using an indium standard (heat flow calibration). Samples of 4.5 mg (± 0.1 mg) were placed in aluminum pans and were scanned in either analyzer using various temperature programs depending on the type of measurement. Functional group conversion as a function of time is denoted by $x(t)$ and is calculated using Eq. (1).

$$x(t) = \frac{\Delta H(t)}{\Delta H_{total}} \tag{1}$$

where $\Delta H(t)$ is the heat flow measured during the curing reaction integrated until time t, and ΔH_{total} is the same integral until complete conversion is achieved. For storage stability experiments, conversion was calculated by Eq. (2) by using residual heats of reaction.

$$x = 1 - \frac{\Delta H_{residual}}{\Delta H_{total}} \tag{2}$$

where $\Delta H_{residual}$ is found by integrating the heat flow signal throughout the exothermic peak of curing of a sample stored for a specified duration of time, and ΔH_{total} is the same integral for a recently prepared and UV irradiated sample.

The T_g of the samples at the intermediate and final stages of curing were determined from a scan at 10 °C min^{-1}, and taken as the half-way point in the jump in the heat capacity step, following the DIN 51007 method in the STARe software by Mettler. To compare with experimental results, T_g's were calculated using the Fox equation [22] given below.

$$\frac{1}{T_g} = \frac{x_1}{T_{g,1}} + \frac{(1 - x_1)}{T_{g,2}} \tag{3}$$

Where x_i and $T_{g,i}$ are the mass fractions and T_g of the constituent polymer network denoted by subscript i. For a material at the intermediate curing stage, the constituent networks would be a fully-cured thiol-acrylate network and an uncured thiol-epoxy network.

2.4. Fourier transform infrared spectrometry (FTIR)

We used a Brucker Vertex 70 FTIR spectrometer equipped with an

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