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Dear Editor,

We are submitting our manuscript titled "Curing kinetics and characterization of dual-curable thiol-acrylate-epoxy thermosets with latent reactivity" to *Reactive & Functional Polymers* to be considered as a Research Article.

In our work, we present a new thiol-acrylate-epoxy ternary system synthesized using a dual-curing scheme. The first stage is a photo-initiated thiol-acrylate Michael addition at near ambient temperature, followed by thiol-epoxy click reaction at a moderately elevated temperature. No solvent is required for neither stage and no by-products are formed. We study curing kinetics in detail, discuss possible reaction mechanisms, and demonstrate separation of the two curing stages and the storage stability of intermediate materials. Although previous work has been conducted on similar ternary systems, no other paper has demonstrated the separability of the thiol-acrylate and thiol-epoxy reactions which enables processability at the intermediate stage.

We use Differential Scanning Calorimetry, IR Spectroscopy and kinetic modeling methods such as Friedman isoconversional method and Kamal auto-catalytic model. Besides curing kinetics, we investigate the impact of acrylate:epoxy ratio, and acrylate rigidity/functionality in our formulations on intermediate and final glass transition temperatures. We believe that this novel ternary system could be useful in applications such as adhesives, industrial coatings, and optical/electronic materials.

Please let me know if you have any questions. Thank you for your time.

Kind regards,

Ali Osman Konuray

(on behalf of all authors)

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 have suppressed radical mediated acrylate homopolymerization which would otherwise lead to unreacted thiols remaining. Kinetics of Stage 2 was analyzed mathematically using isoconversional 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.

Keywords: dual-curing, thiol, acrylate, epoxy, latent catalysts

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

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 was 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].

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 minutes prior to use. The chemical structures of all materials used are given in Scheme 2.

Scheme 2

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. NaBPh₄ 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 CHCl₃, and dried under mild heat and vacuum.

Sample preparation

Samples with PBG were prepared in 5mL 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.

Table 1

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 4.5mg (+/- 0.1mg) 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.

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

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.

$$x = 1 - \frac{\Delta H_{residual}}{\Delta H_{total}} \quad (2)$$

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 $10 \text{ }^\circ\text{C min}^{-1}$, 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.

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

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.

Fourier Transform Infrared Spectrometry (FTIR)

We used a Bruker Vertex 70 FTIR spectrometer equipped with an attenuated total reflection (ATR) accessory (GoldenGate™, Specac Ltd.) which is temperature controlled in order to monitor thiol and acrylate conversions during the thiol-acrylate Michael reaction and thiol and epoxy conversions during the thiol-epoxy click reaction. Spectra were collected in absorbance mode with a resolution of 4 cm⁻¹ in the wavelength range from 4000 to 600 cm⁻¹ averaging 20 scans for each spectrum. To capture the fast kinetics of UV-initiated thiol-acrylate reaction, scans were performed every 5 seconds until acrylate groups are depleted. UV irradiation equipment and intensity of irradiation were the same as in the DSC experiments. The absorbance peaks that we used to monitor conversion were 1620-36 cm⁻¹, 2570 cm⁻¹, and 3600 cm⁻¹ for acrylate, thiol, and hydroxyl (formed due to epoxy conversion), respectively. Also, the absorbance peak at 915 cm⁻¹ which is directly due to epoxy groups was also monitored for cross-checking. Due to overlapping signals that produce the absorption peaks at 915 cm⁻¹ and 2570 cm⁻¹, they could only be analyzed qualitatively. Acrylate conversion of functional groups is calculated by Eq. 4, whereas epoxy conversion is calculated by Eq. 5.

$$x = 1 - \frac{A'}{A_0'} \quad (4)$$

$$x = \frac{A'}{A_\infty'} \quad (5)$$

here A' is the absorbance of the functional group of interest (area under the absorbance peak), A_0' and A_∞' are the initial and final absorbances of hydroxyl groups (3600 cm⁻¹), respectively. All absorbances were normalized with that of the ester group (1720 cm⁻¹) of each scanned sample

Isoconversional differential method

The reaction rate equation can be expressed as a product of two terms, one of which is a function of temperature and the other is a function of fractional conversion x . That is,

$$\frac{dx}{dt} = f(x)k(T) \quad (6)$$

where T is the reaction temperature and $k(T)$ is the rate expression which follows the Arrhenius law. It is given as

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \quad (7)$$

where E is the activation energy, k_0 is the pre-exponential factor, and R is the universal gas constant. To be able to use Eq. 6, one would need to know the kinetic

model function $f(x)$, and the constants k_0 and E . We use the differential method first proposed by Friedman [23] which does not necessitate information about the kinetic model $f(x)$. We start by inserting Eq. 7 inside Eq. 6 and taking the natural logarithm of both sides.

$$\ln\left(\frac{dx}{dt}\right) = \ln[k_0 f(x)] - \frac{E}{RT} \quad (8)$$

At constant conversion,

$$\frac{d}{d\left(\frac{1}{RT}\right)}\left(\frac{dx}{dt}\right) = -E \quad (9)$$

Therefore a plot of $\ln\left(\frac{dx}{dt}\right)$ versus $\frac{1}{RT}$ at a given fixed conversion, at different heating rates or at different isothermal temperatures will be a line with slope $-E$ and y-intercept $\ln[k_0 f(x)]$. This is usually carried out in regular conversion steps so as to have a set of kinetic parameters for all the conversion range [24]. Once the activation energy E and the term $\ln[k_0 f(x)]$ are found in this manner, one can run an isothermal simulation in which the reaction rate can be calculated for each conversion by integrating Eq. 8 numerically to obtain the conversion-time curves for a given temperature programme.

Kamal model

A useful model that has been shown to accurately represent the auto-catalytic curing kinetics of such thermosetting polymers is the Kamal model [25,26]. It is expressed as

$$\frac{dx}{dt} = (k_1 + k_2 x^m)(1 - x)^n \quad (10)$$

where m and n are the exponents of each autocatalytic function; k_1 and k_2 are the Arrhenius rate constants with different apparent activation energies. They are defined as

$$k_1 = k_{01} \exp\left(-\frac{E_1}{RT}\right) \text{ and } k_2 = k_{02} \exp\left(-\frac{E_2}{RT}\right)$$

As epoxy systems cure through complex reaction steps, one can use a multi-term Kamal model to account for the contribution of these different reaction steps. The multiterm Kamal model that we use in this study is based on previous works [27,28] and is given in Eq. 11.

$$\frac{dx}{dt} = (k_1 + k'_1 x^{m_1})(1 - x)^{n_1} + \sum_{i=2}^4 k_i x^{m_i} (1 - x)^{n_i} \quad (11)$$

where $k_i = k_{0i} \exp\left(-\frac{E_i}{RT}\right)$

A multi-variate nonlinear regression method was used to determine all the kinetic parameters. The parameters were used in simulation runs whose results were compared with experimental data.

Storage stability

To determine the latency at the intermediate stage, a number of DG50HDDA50 samples were prepared, UV irradiated and placed in a thermostatic bath at 30°C inside glass tubes filled with silica gel in order to minimize moisture-related effects. To monitor storage stability, samples were analyzed daily. The fractional conversion x of functional groups during storage was determined by DSC as explained previously. To establish a range of storage temperatures, the same procedure was repeated using a thermostatic bath temperature of 40°C with a new sample set.

RESULTS AND DISCUSSION

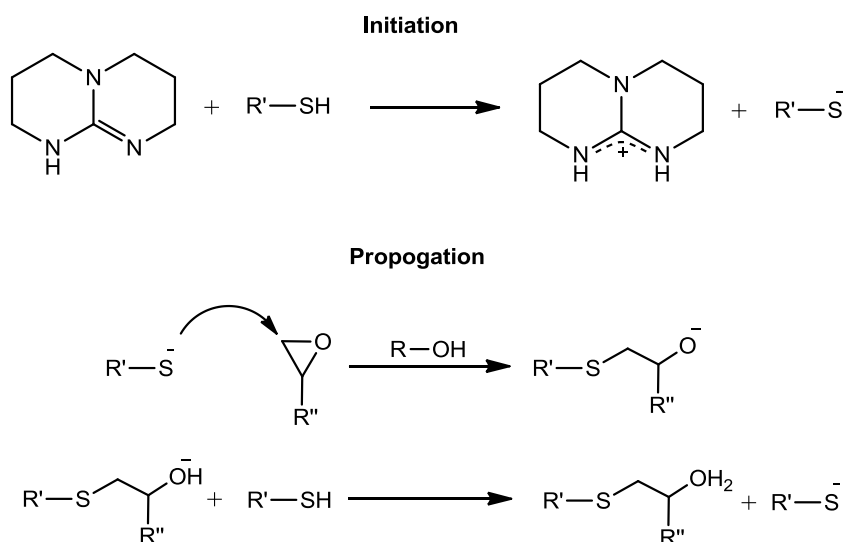
Reaction mechanisms

The thiol-acrylate Michael addition reaction starts with the formation of a thiolate anion which could take place via two different mechanisms [29] as shown in Scheme 3.

Scheme 3

Depending on the pK_a and nucleophilic strength of the catalyst, the formation of the thiolate can follow either mechanism. When a strong base such as TBD is used, the base catalyzed mechanism is favored.

Thiol-acrylate Michael addition reaction can take place at fast rates at room temperature, whereas the thiol-epoxy reaction requires considerably longer times, higher temperatures and/or higher catalyst concentrations. When a strong base such as TBD is used as catalyst, the thiol-epoxy reaction starts with a base-catalyzed deprotonation of the thiol (upon heating or UV irradiation) [30]. The reaction propagates through the nucleophilic attack of the thiolate anion to the oxirane ring [8]. The overall mechanism is depicted in Scheme 4.



Scheme 4. The thiol-epoxy click reaction catalyzed by TBD.

Even without the use of a photocatalytic system, the two reactions can proceed sequentially so that one can obtain a stable intermediate material. In our preliminary work, we established dual-curability when DMAP was used as catalyst. We used FTIR spectrometry to monitor conversion of relevant functional groups. The reader is directed to the supporting information file for details.

Analysis of thiol-acrylate Michael reaction triggered by the PBG (Stage 1)

In the kinetic analysis that follows, we use the DG50HDDA50 formulation which contains PBG (of TBD) as catalyst, and ITX as photosensitizer. The amounts of PBG and ITX are 0.5% and 0.25% w/w, respectively, based on total reactants. In Figure 1, FTIR conversions are given together with DSC thermograms of two DG50HDDA50 samples, one containing TEMPO at 0.25% w/w (TEM025), and one neat (TEM0). UV irradiation was carried out at 35°C. The heat flow peaks result from a combination of events: Activation of radicals, radical mediated polymerizations, liberation of base from the PBG, and thiol-acrylate Michael reaction. The sharp peak observed in TEM0 sample suggests there is significant radical formation and thus acrylate homopolymerization. On the other hand, in TEM025 sample, radical reactions seem to be suppressed as indicated by their moderate heat flow peaks. As can be seen, in both samples, heat release continues until approximately the fifth minute of irradiation, despite complete conversion of acrylates by the first minute. Since no other reaction could have taken place, the heat release after the first minute should be due to further liberation of base

catalyst. The complete liberation of base is crucial for desirable reaction kinetics at Stage 2. To test higher TEMPO concentrations, a TEM05 sample was also scanned by DSC and no significant difference was observed in thiol-acrylate reaction kinetics. Therefore, TEMPO percentage was fixed at 0.25% w/w in all samples prepared for further analysis.

Fig. 1

Analysis of thiol-epoxy reaction (Stage 2)

For the TEM025 formulation, reaction onset temperatures in dynamic DSC scans have been observed to be sufficiently high to allow separation of thiol-acrylate and thiol-epoxy reactions as can be seen in Fig. 2a. Compared to the thiol-acrylate Michael addition carried out at 35°C, thiol-epoxy reaction onset was approx. 100°C. This sequential nature of curing is in agreement with our preliminary results with DMAP as catalyst (See supporting information). On the other hand, it is in contrast with the system of Jian et al. where both reactions proceed simultaneously with no latency [11]. In the rate curves (bottom graph in Figure 2a), shoulders appear at temperatures higher than 150°C, which are believed to be due to a purely thermal thiol-epoxy reaction since neat thiol-epoxy mixtures were shown to start curing at these temperatures [19].

Fig. 2

The differential isoconversional analysis was performed on a kinetic dataset containing dynamic scans with rates 2.5, 5, and 10°Cmin⁻¹, as well as isothermal scans at 80, 90, 100, and 110°C. In Figure 3, the activation energy for the reaction calculated as a function of epoxy group conversion is given. Once the auto-catalytic mechanism kicks in, the activation energy drops as reaction proceeds.

Fig. 3

As explained previously, the 4-term version of the Kamal model as given by Eq. 11 was used to fit the same kinetic datasets obtained by DSC. To solve for the model

parameters, GRG Nonlinear Solving method (MS Excel) was used to minimize the average relative error which is given by the following equation.

$$\text{Average relative error} = \sum \frac{\left| \left(\frac{dx}{dt} \right)_{exp} - \left(\frac{dx}{dt} \right)_{calc} \right|}{\left(\frac{dx}{dt} \right)_{calc}} \quad (12)$$

where $\left(\frac{dx}{dt} \right)_{exp}$ and $\left(\frac{dx}{dt} \right)_{calc}$ are the experimentally measured, and the calculated reaction rates, respectively. Adding more than 4 terms to the model did not reduce the error any further. The resulting model parameters are given in Table 2. It could be noted that the activation energies of the different terms are similar to the ones plotted in Figure 3.

Fig. 4

Figure 4 shows conversion-temperature and conversion-time plots for DSC dynamic and isothermal data together with Kamal multi-term model fits. A numerical integration was performed to the Kamal rate expression given in Eq. 11. An induction temperature and an induction time were assigned in simulating dynamic and isothermal data, respectively, where a conversion of 1% is reached at the induction temperature, or at the induction time. The good fits on Fig. 4 suggest that it is safe to assume an auto-catalytic mechanism for Stage 2 of our dual-curing system. Thus, using the Kamal model, one can simulate different processing conditions.

Table 2

Using the Kamal model, comparable reaction temperatures can be simulated for the DG50HDDA50 material. In Figure 5, we show simulations for 70 and 120°C together with experimental data. Experimental data were obtained by isothermal DSC runs at the given temperatures. Whereas at 120°C the fit is highly accurate, at 70°C the model performs rather poorly. Apparently, extrapolation to lower temperatures produces greater error. Interestingly, a simulation at 63°C fits almost perfectly our experimental data at 70°C. This suggests that the error originates mostly from the extrapolation of the Arrhenius temperature dependence.

Fig. 5

Storage stability

As explained previously, storage stability of DG50HDDA50 (containing TEMPO, PBG, and ITX at 0.25, 0.5, and 0.25% w/w, respectively) was determined by analyzing samples stored at a thermostatic bath for several days. Conversion of samples were calculated from the residual reaction heats measured by DSC. The one-day stability at 30°C is particularly remarkable as no epoxy conversion was observed. Using the Flory-Stockmayer relation, the theoretical gel point conversion for DG50HDDA50 (at Stage 2) is calculated as 58% [31]. Since thermosets maintain handleability below gel point conversions, we can argue that DG50HDDA50 has storage stabilities of 5 and 6 days, at 40°C and 30°C, respectively.

Fig 6

Effect of acrylate-to-epoxy ratio

In all the formulations that follow, the catalytic system composes of PBG, ITX and TEMPO at 0.5, 0.25 and 0.25% w/w on total reactants, respectively. For the calculations, we used experimentally determined initial and final T_g 's of neat epoxy-thiol and acrylate-thiol samples.

Fig. 7

Increased epoxy content results in remarkably higher T_g at the end of Stage 2. There is a difference of about 40°C in final T_g 's of DG25 and DG75. Experimental results are in good agreement with the ones calculated using Fox equation as can be seen from Figure 7. The final T_g measured for DG50HDDA50 is in good agreement with the one reported by Jian et al. for the same formulation [11].

Effect of acrylate type

Instead of a linear diacrylate (HDDA), when an acrylate having a more rigid backbone (TCDDA) or an acrylate with higher functionality (TMPTA) is used, higher T_g 's could be achieved at all stages. When TCDDA and TMPTA are used at the same weight percentage, the formulations yield slightly higher final T_g 's as can be seen in Table 3.

CONCLUSIONS

A new latent dual-curing scheme has been developed for mixtures of a tetra-functional thiol, a DGEBA epoxy resin and a selection of polyacrylates. The photolabile catalytic system ensures separability of the two curing steps and yields an intermediate material with a storage stability of at least 5 days. Whereas the first curing stage can be activated by UV light and carried out at near-ambient temperatures, the second stage can be triggered at moderately elevated temperatures. Full cure times under 6 hours is possible above 80°C. It has been shown that with the use of TEMPO, it is possible to suppress radical mediated acrylate homopolymerization which would otherwise lead to a significant amount of unreacted thiols remaining at the end of the scheme.

An isoconversional analysis has confirmed the auto-catalytic behavior of the thiol-epoxy reaction which is indicated by a decrease in activation energy with conversion. A multi-term Kamal model has been shown to represent experimental data with good accuracy and as such, could be a computational tool to study this reaction further.

It has also been shown that formulations with higher epoxy content attain significantly higher T_g especially at the final stage. The choice of acrylate, although not as influential as epoxy content, plays a role in the glass transition temperature of final materials. The higher the functionality and backbone rigidity of the acrylate monomer used, the higher are the T_g at the intermediate and final stages. The proposed curing scheme and the resulting materials could be useful in applications such as adhesives, protective coatings for highly corrosive environments, and optical/electronic materials.

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Scheme 1. Liberation TBD from its HBPh₄ salt when subjected to UV radiation [12].

Scheme 2. Chemical structures of the materials used in the work

Scheme 3. Thiol-acrylate reaction mechanism. Thiolate anion may form via two distinct mechanisms: Catalysis by base, or nucleophile.

Fig 1. FTIR acrylate conversion – time plots and DSC heat flow curves of UV irradiation at 35°C to show the effect of TEMPO on thiol-acrylate Michael reaction kinetics. Sample is DG50HDDA50 with 0.5 and 0.25% w/w of PBG and ITX, respectively.

Fig 2. DSC conversion and reaction rate curves of DG50HDDA50 with 0.25% w/w TEMPO scanned at different heating rates (a) and isothermally (b) after UV irradiation at 35W/m² for 15 minutes.

Fig 3. Activation energy calculated by differential isoconversional method. Regression coefficient R² averages at 0.98.

Fig 4. Kamal model fits to experimental kinetic data for DG50HDDA50. Average relative error of fit is 9.5%.

Fig 5. Experimental (DSC) and simulated (Kamal) conversions for stage 2 curing of DG50HDDA50 which contains TEMPO, PBG and ITX at 0.25, 0.5, and 0.25% w/w, respectively.

Fig 6. Epoxy conversion of DG50HDDA50 at two different storage conditions. Conversions were calculated from DSC data.

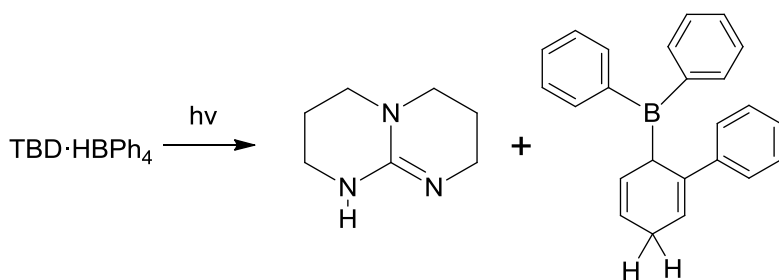
Fig 7. T_g at different stages of curing as a function of acrylate content. Purely acrylate and purely epoxy containing systems are also shown, together with the Fox Equation fits.

Table 1. Formulation of samples used in the work

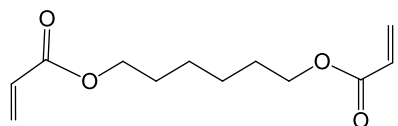
Table 2. Parameters of the 4-term Kamal auto-catalytic model

Table 3. T_g of formulations with different acrylates. ^a Epoxy; ^b Acrylate; ^c Experimental; ^d Calculated.

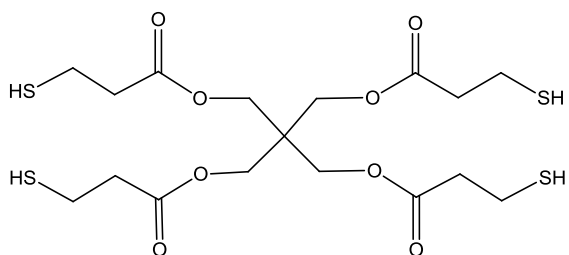
Scheme 1



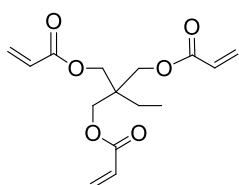
Scheme 2



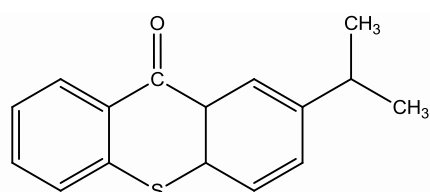
Hexanediol Diacrylate (HDDA)



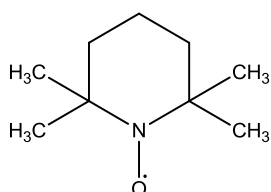
Pentaerythritol tetrakis(3-mercaptopropionate) (S4)



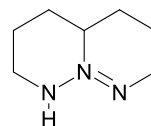
Trimethylolpropane triacrylate (TMPTA)



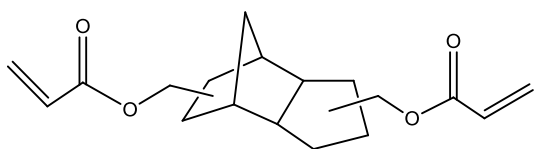
Isopropylthioxanthone (ITX)



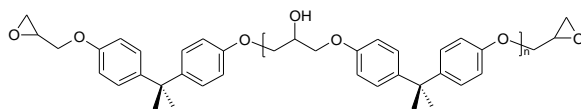
2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO)



1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD)



Tricyclo[5.2.1.0]decanedimethanol diacrylate (TCDDA)



Epoxy Resin DG187 (n=0.12)

Scheme 3

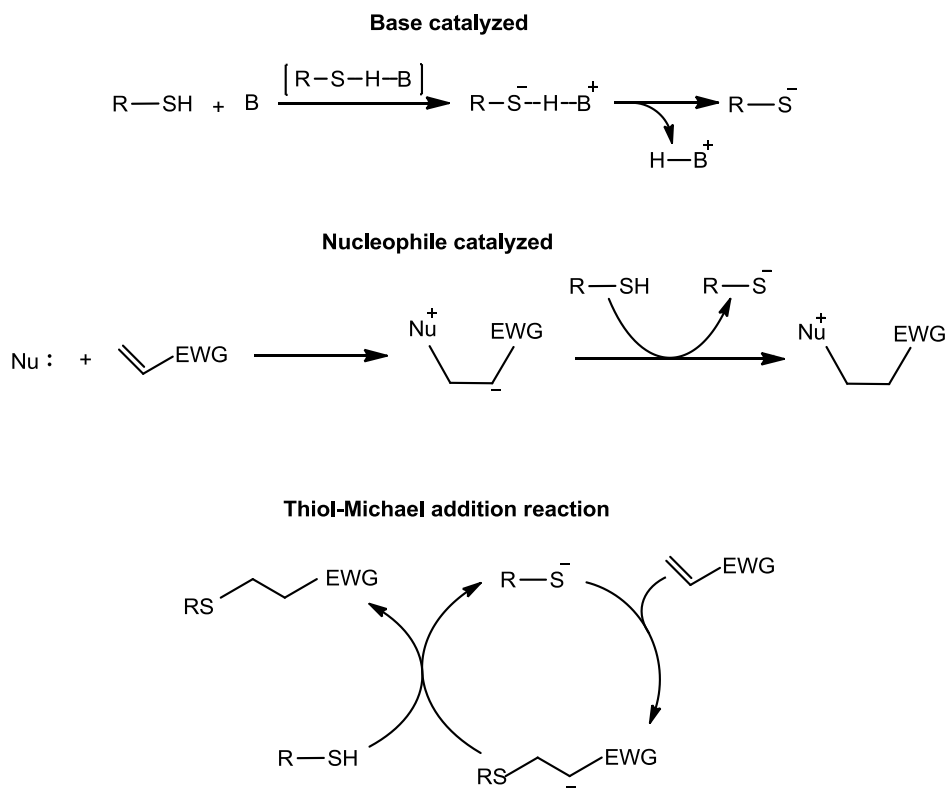


Fig. 1

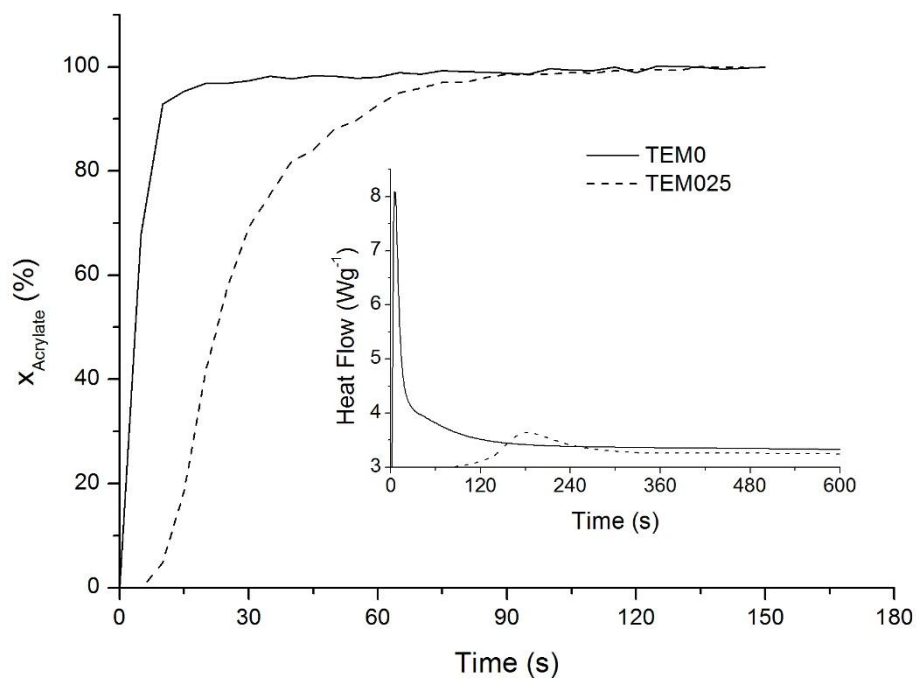
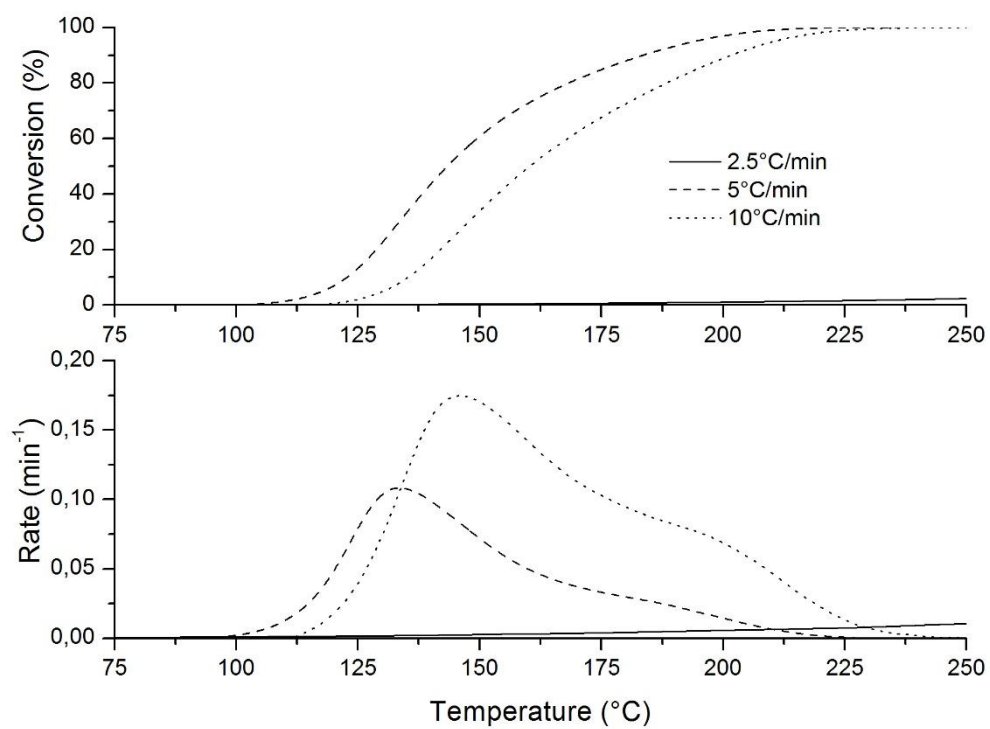
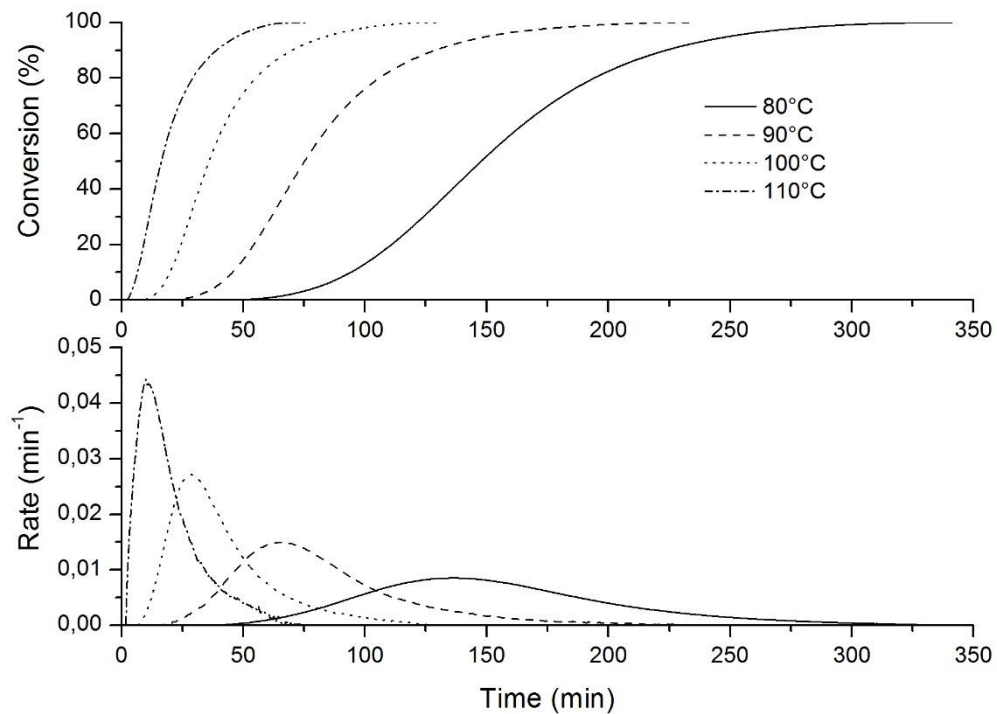


Fig. 2



(a)



(b)

Fig 3

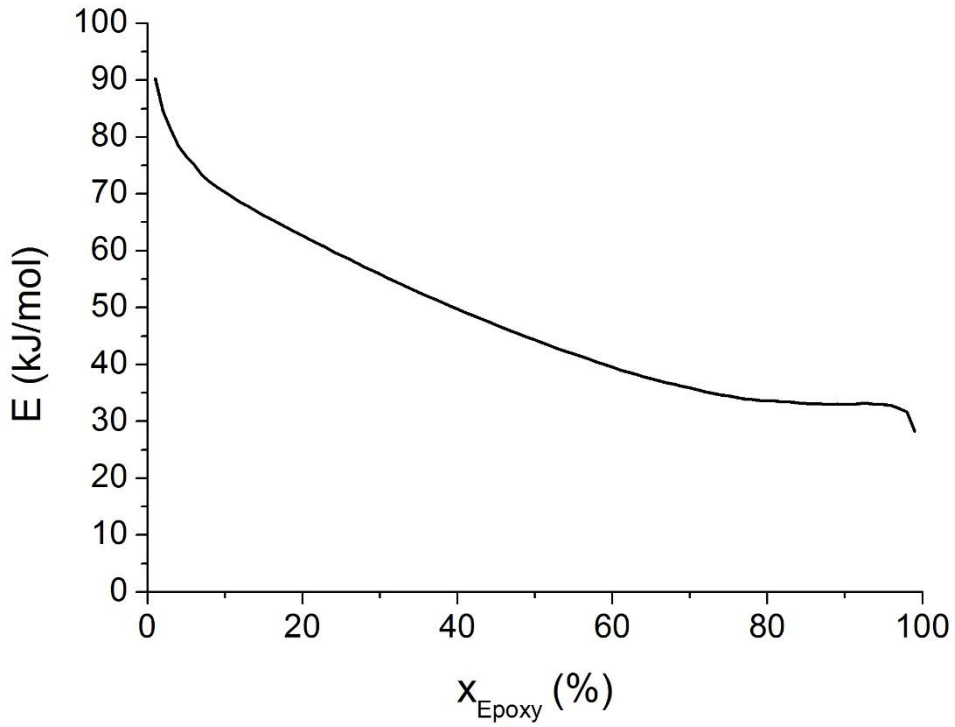


Fig 4

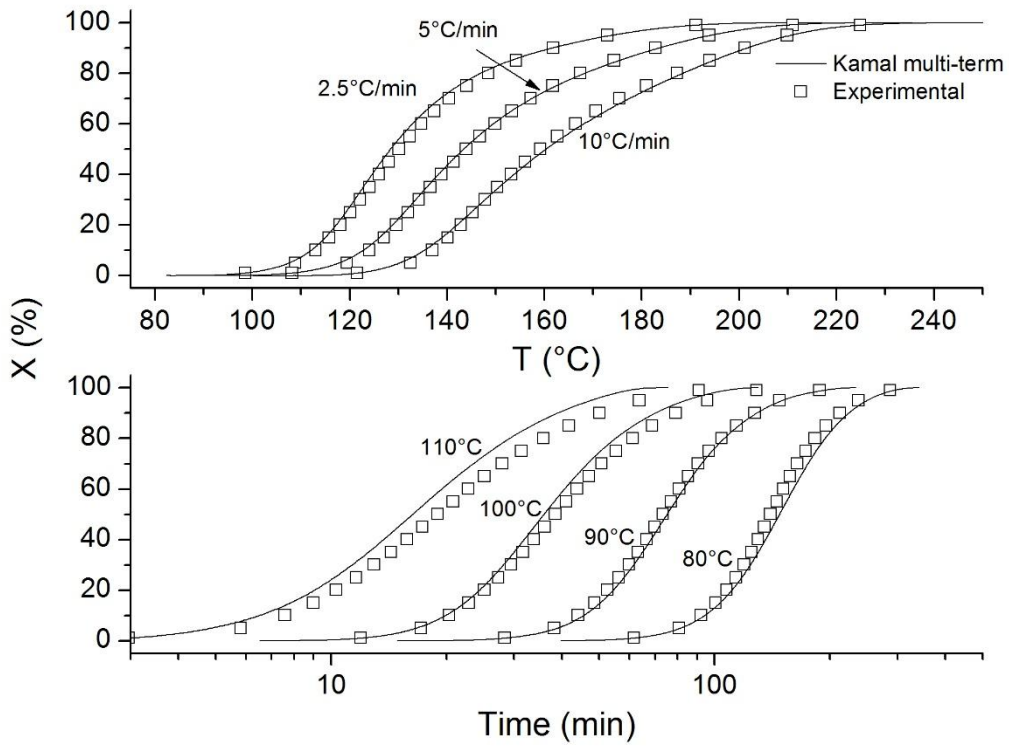


Fig 5

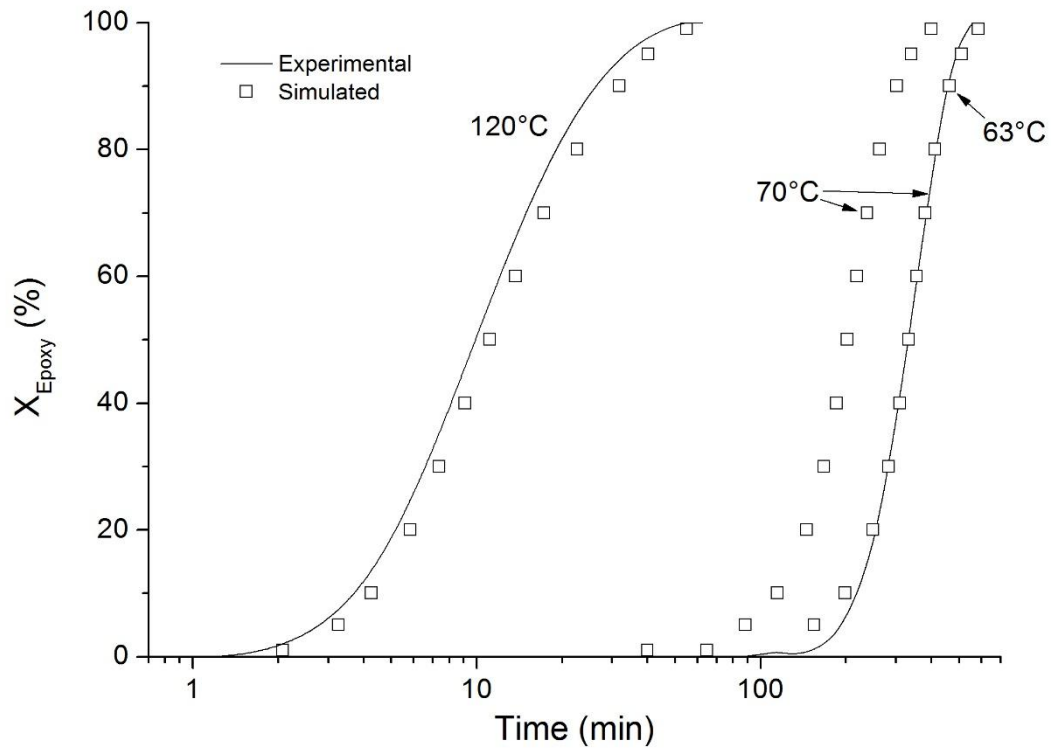


Fig 6

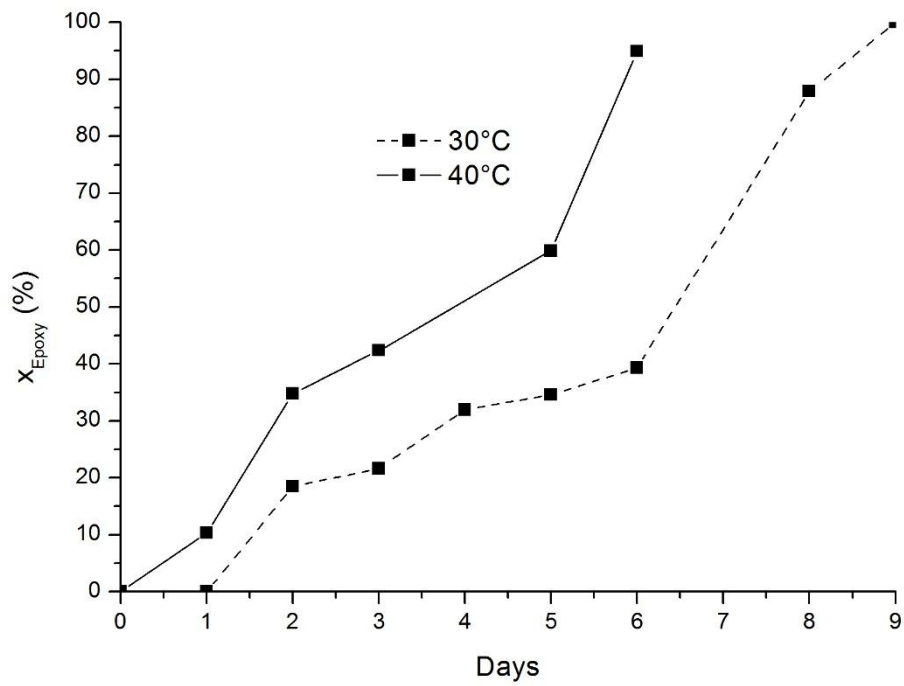


Fig 7

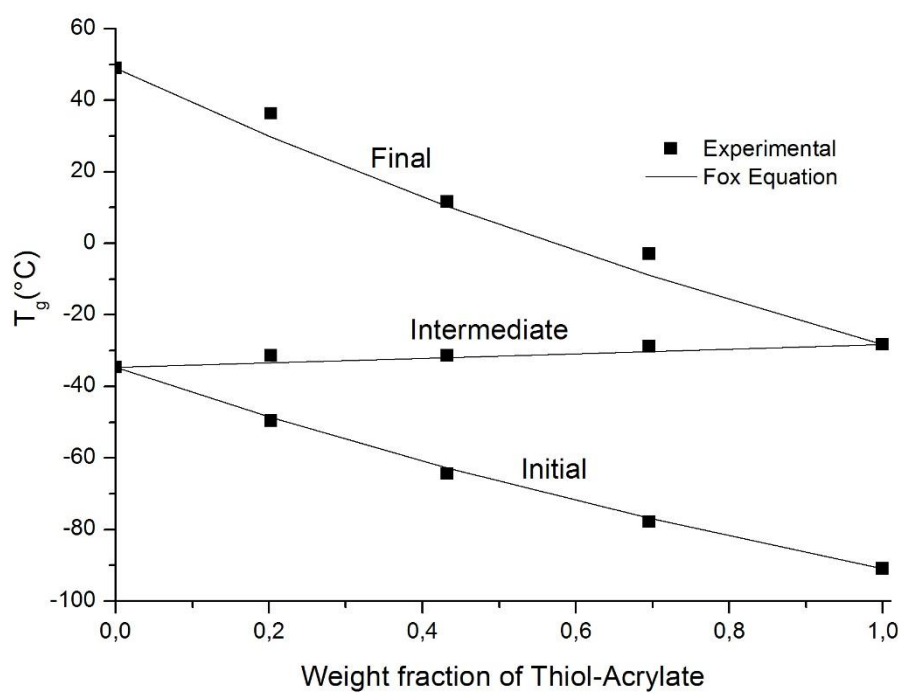


Table 1

Sample	DG187 % w/w	S4 % w/w	HDDA % w/w	TMPTA % w/w	TCDDA % w/w
DG0HDDA100	0	0,5189	0,4811	0	0
DG25HDDA75	0,1843	0,4811	0,3346	0	0
DG50HDDA50	0,3437	0,4484	0,2079	0	0
DG75HDDA25	0,4827	0,42	0,0973	0	0
DG100HDDA0	0,605	0,395	0	0	0
DG0TCDDA100	0	0,445	0	0	0,555
DG50TCDDA50	0,3206	0,4184	0	0	0,261
DG0TMPTA100	0	0,5526	0	0,4474	0
DG50TMPTA50	0,353	0,4606	0	0,1864	0

Table 2

i	n_i	m_i	E_i (kJ/mol)	$\ln k_{0i}$
1	1,81	6,25	64,81	0,41
1'			161,04	38,38

2	6,10	0,92	72,07	17,80
3	3,04	2,46	40,52	8,67
4	0,96	3,51	22,35	0,01

Table 3

Sample	Wt. Frac.		$T_{g,0}$ (°C)		$T_{g,int}$ (°C)		$T_{g,f}$ (°C)	
	Ep ^a	Ac ^b	Exp ^c	Calc ^d	Exp	Calc	Exp	Calc
DG50TCDD50	0,53	0,47	-48,07	-47,76	-12,47	-14,82	40,91	30,44
DG50TMPTA50	0,58	0,42	-48,20	-47,94	-20,90	-19,96	37,80	28,58
DG50HDDA50	0,57	0,43	-64,44	-62,74	-31,39	-31,94	11,59	10,37
DG0TCDDA100	0	1	-60,88	-	-	-	11,94	-
DG0TMPTA100	0	1	-64,21	-	-	-	3,99	-

Supplementary Data

[Click here to download Supplementary Data: SUPPLEMENTARY INFO_TAE.docx](#)