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Design and analysis of dual-curing systems

by

Ali Osman Konuray

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DESIGN AND ANALYSIS OF DUAL-CURING SYSTEMS

Ph.D. Thesis

as collection of published articles

by

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Department of Heat Engines



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*“We’ll ride the spiral to the end.
And may just go where noone’s been.”*

- Maynard J. Keenan

To lifelong learning...

Summary

Dual-curing processing is a method to prepare thermoset materials through two polymerization reactions carried out simultaneously or sequentially. In these processes, a firm understanding of reaction mechanisms enables the design of catalytic systems to control reaction kinetics and to impart sequentiality to the curing reactions. Material properties at different curing stages are dictated by the choice of monomers. Furthermore, by employing click-based approaches, eco-friendly and efficient dual-curing processes can be designed.

In this thesis, a number of sequential dual-curing systems were prepared and characterized. Sequentiality was either intrinsic due to the monomers used or it was achieved by employing latent catalysts. The dual-curing systems were designed with an objective of improved physical and mechanical properties of the fully cured materials. The majority of the monomers were processable through click reactions, although a few processes did not strictly fit click criteria. In terms of the characterized properties, this did not pose any shortcoming.

Due to the limited number of related publications, the thiol-epoxy reaction was investigated in more detail. Accurate phenomenological and mechanistic models of reaction kinetics were developed to study reaction kinetics in and out of dual-curing context.

For reactive latency, a new family of photobase generators (PBGs) were developed. As the name implies, these PBGs liberated base catalysts upon UV irradiation. The possibility of thermal initiation of some of these PBGs was also demonstrated. Storage stabilities of uncured and partially-cured (i.e. intermediate) materials were significantly improved since PBGs allowed temporal control over curing stages.

In some dual-curing systems, step-wise click polymerizations such as Michael additions were combined with chain-wise homopolymerizations such as acrylate photopolymerizations. In these systems, the initial step-growth process delivered intermediate materials with desirable properties such as polymer network homogeneity, high gel point conversion, and low polymerization shrinkage. The chain-wise process was carried out as a second curing stage, at the end of which final materials were obtained with increased crosslinking density, hardness and T_g . In all dual-curing systems presented here, final materials had significantly improved properties compared to intermediate materials, regardless of the nature of the curing processes.

In one part of the project, a new set of catalyst comonomers were designed. These comonomers, which were also prepared using click-based procedures, had pendant allyl functionalities and wielded tertiary amine groups in their structure. The tertiary amines catalyzed a thiol-acrylate reaction carried out as a first curing stage in a dual-curing system. Later, as a second curing stage, the pendant allyl groups of the comonomers participated in thiol-ene polymerizations with the excess thiols initially present in the formulation, thereby getting incorporated into the final polymer network.

The dual-curable materials developed here can be used in diverse applications ranging from high-performance adhesives, to rigid shape-memory materials. As a matter of fact, a preliminary demonstration of these two applications is provided. Prospectively, the materials presented here could benefit from a more detailed characterization in the context of specific applications. Without a doubt, such an effort would increase the possibility of successful commercialization of these formulations.

Resumen

El curado dual es una metodología utilizada para preparar materiales termoestables mediante la combinación de dos procesos de polimerización que pueden tener lugar de forma simultánea o secuencial. Conocer en profundidad los mecanismos de reacción que rigen estos procesos es la herramienta clave para el diseño de sistemas catalíticos que permitan controlar la cinética de la reacción y conseguir la secuencialidad de las etapas de curado. Las propiedades del material en las diferentes etapas de curado están determinadas por la elección de los monómeros. Además, la utilización de reacciones de tipo *click* permite diseñar procesos de curado más ecológicos y eficientes.

En esta Tesis, se prepararon y caracterizaron diferentes sistemas de curado secuenciales. La secuencialidad en el curado se consiguió con la selección adecuada de monómeros o mediante el empleo de catalizadores latentes. Los sistemas de curado dual se diseñaron también con el objetivo de mejorar las propiedades físicas y mecánicas de los materiales completamente curados. La mayoría de los monómeros fueron curados mediante reacciones de tipo *click*. Aunque algunas de las etapas de curado no se ajustaban estrictamente a los criterios aceptados para las reacciones *click*, esto no supuso un problema en cuanto a las propiedades de los materiales preparados.

La cinética de reacción tiol-epoxi se investigó con más detalle, dado el número limitado de publicaciones existentes sobre este tema. Se desarrollaron modelos fenomenológicos y mecanísticos avanzados para estudiar la cinética de esta reacción dentro y fuera del contexto del curado dual.

Para conseguir sistemas latentes, se desarrolló una nueva familia de fotobases latentes. Como su nombre indica, estas fotobases, tras ser irradiadas mediante luz UV, liberan una base que actúa como catalizador del curado. También se demostró la posibilidad de activar térmicamente las fotobases. La utilización de estas permitió el control temporal de las etapas de curado, aumentando significativamente la estabilidad durante el almacenamiento de los materiales no curados y parcialmente curados, después de la primera etapa.

En algunos sistemas duales, se combinaron polimerizaciones *click* por etapas tales como las adiciones de Michael con homopolimerizaciones en cadena tales como la fotopolimerización de acrilatos. En este tipo de sistemas, la polimerización por etapas en la primera etapa de curado permite obtener materiales intermedios con propiedades deseables tales como alta homogeneidad y conversión a la gelificación y baja contracción durante el curado. La polimerización en cadena que tiene lugar durante la segunda etapa de curado, permitió obtener materiales finales con mayor densidad de entrecruzamiento, dureza y temperatura de transición vítrea. Independientemente de la naturaleza de los procesos de curado utilizados, todos los materiales finales presentaron propiedades térmicas y mecánicas significativamente mejoradas en comparación con los materiales intermedios.

En una parte de esta Tesis, se diseñó una nueva familia de comonómeros que actuaban simultáneamente como catalizadores. Estos comonómeros, que también se prepararon mediante procedimientos basados en la química *click*, tenían funcionalidades alílicas terminales y aminas terciarias en su estructura generadas durante su síntesis. Estas aminas actuaron como catalizadores de la primera etapa de curado tiol-acrilato en un sistema de curado dual. En la segunda etapa de curado, los grupos alilo terminales de los comonómeros reaccionaron con grupos tioles en exceso presentes en la formulación mediante una reacción tiol-eno fotoinducida.

Los materiales preparados mediante curado dual en este trabajo se pueden utilizar en una amplia gama de aplicaciones avanzadas que van desde adhesivos de alto rendimiento hasta materiales con memoria de forma. Aunque en esta memoria solo se muestra una demostración preliminar de estas dos aplicaciones, un desarrollo exhaustivo de las mismas podría conducir potencialmente a la comercialización de algunos de los sistemas desarrollados.

Resum

El curat dual és una metodologia utilitzada per preparar materials termoestables mitjançant la combinació de dos processos de polimerització que poden tenir lloc de forma simultània o seqüencial. Conèixer en profunditat els mecanismes de reacció que regeixen aquests processos és l'eina clau per al disseny de sistemes catalítics que permetin controlar la cinètica de la reacció i aconseguir la seqüencialitat de les etapes de curat. Les propietats del material en les diferents etapes de curat estan determinades per l'elecció dels monòmers. A més, la utilització de reaccions de tipus *click* permet dissenyar processos de curat més ecològics i eficients.

En aquesta Tesi, es van preparar i caracteritzar diferents sistemes de curat seqüencials. La seqüencialitat en el curat es va aconseguir amb la selecció adequada de monòmers o mitjançant l'ús de catalitzadors latents. Els sistemes de curat dual es van dissenyar també amb l'objectiu de millorar les propietats físiques i mecàniques dels materials completament curats. La majoria dels monòmers van ser curats mitjançant reaccions de tipus *click*. Encara que algunes de les etapes de curat no s'ajustaven estrictament als criteris acceptats per les reaccions *click*, això no va suposar un problema pel que fa a les propietats dels materials preparats.

La cinètica de reacció tiol-epoxi es va investigar amb més detall, atès el nombre limitat de publicacions existents sobre aquest tema. Es van desenvolupar models fenomenològics i mecanístics avançats per estudiar la cinètica d'aquesta reacció dins i fora del context del curat dual.

Per aconseguir sistemes latents, es va desenvolupar una nova família de fotobases latents. Com el seu nom indica, aquestes fotobases, després de ser irradiades mitjançant llum UV, alliberen una base que actua com a catalitzador del curat. També es va demostrar la possibilitat d'activar tèrmicament les fotobases. La utilització d'aquestes va permetre el control temporal de les etapes de curat, augmentant significativament l'estabilitat durant l'emmagatzematge dels materials no curats i parcialment curats, després de la primera etapa.

En alguns sistemes duals, es van combinar polimeritzacions *click* per etapes com ara les addicions de Michael amb homopolimeritzacions en cadena tals com la fotopolimerització d'acrilats. En aquest tipus de sistemes, la polimerització per etapes en la primera etapa de curat permet obtenir materials intermedis amb propietats desitjables com ara alta homogeneïtat i conversió a la gelificació i baixa contracció durant el curat. La polimerització en cadena que té lloc durant la segona etapa de curat, va permetre obtenir materials finals amb major densitat d'entrecruament, duresa i temperatura de transició vítria. Independentment de la naturalesa dels processos de curat utilitzats, tots els materials finals van presentar propietats tèrmiques i mecàniques significativament millorades en comparació amb els materials intermedis.

En una part d'aquesta Tesi, es va dissenyar una nova família de comonòmers que actuaven simultàniament com a catalitzadors. Aquests comonòmers, que també es van preparar mitjançant procediments basats en la química *click*, tenien funcionalitats alíliques terminals i amines terciàries en la seva estructura generades durant la seva síntesi. Aquestes amines van actuar com a catalitzadors de la primera etapa de curat tiol-acrilat en un sistema de curat dual. En la segona etapa de curat, els grups al·lil terminals dels comonòmers van reaccionar amb grups tiols en excés presents en la formulació mitjançant una reacció tiol-è fotoinduïda.

Els materials preparats mitjançant curat dual en aquest treball es poden utilitzar en una àmplia gamma d'aplicacions avançades que van des d'adhesius d'alt rendiment fins a materials amb memòria de forma. Encara que en aquesta memòria només es mostra una demostració preliminar d'aquestes dues aplicacions, un desenvolupament exhaustiu de les mateixes podria conduir potencialment a la comercialització d'alguns dels sistemes desenvolupats.

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Chapter 1

Introduction

1. Introduction

1.1. The dual-curing philosophy

Global plastic production has increased from 15 million tonnes in the sixties to 311 million tonnes in 2014 and is expected to triple by 2050, when it will account for 20% of global annual oil consumption [1]. Although thermoplastics constitute the majority, thermosetting resin production also shares the growth rate of the industry. An 2014 estimate of global annual thermoset production was 53 million tons [2].

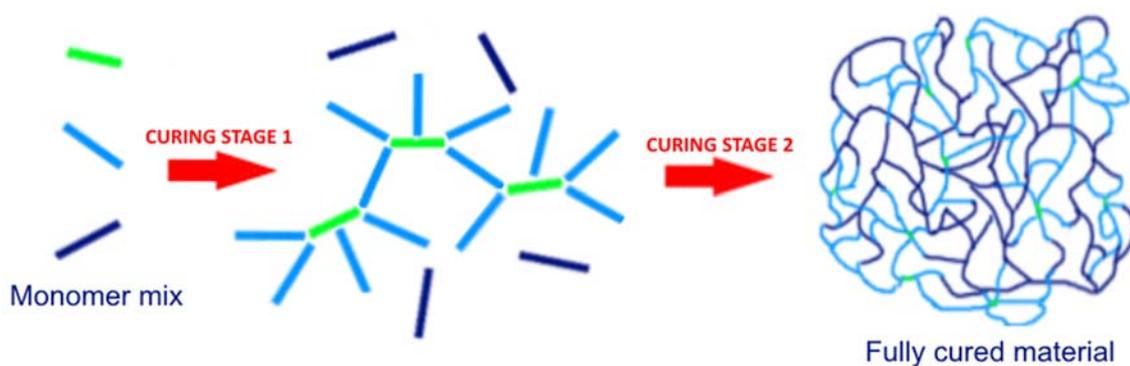
The first half of the 20th century witnessed the development of thermosets such as phenolic plastics produced by Baekeland in 1907, urea and melamine plastics produced by John and Henkel in 1918 and 1935, alkyds patented by Kienle in 1933, and epoxy resins patented by Schlack in 1933 [3]. These resin systems are still used globally in many industry areas and everyday life. Among the many thermoset technologies, dual-cure processing continues to attract attention due to its many advantages which will be outlined followingly.

Dual-cure processing refers to a combination of two thermoset polymerization reactions taking place either simultaneously or sequentially. The two reactions may have different triggers such as heat or UV light. Depending on the choice of monomers and reaction types, covalently bound interpenetrating polymer networks (IPNs) can be obtained.

There are several motivations behind dual-cure processing schemes. For instance, post-polymerization of excess reactants in off-stoichiometric stepwise polymerizations is used to enhance the thermal and mechanical properties of thermosets [4–6]. In cases where UV or visible light photo-polymerization is employed, although fast cure can be achieved superficially, through-cure at deeper layers takes place more slowly [7]. Only a second stage of thermal polymerization would ensure full conversion of reactants in such a system. Similarly, for coatings that are cured by UV light, dual-curing formulations containing photoabsorbers can achieve complete, or at least sufficient cure in shadowed sections [8].

As simultaneous dual-curing is only relevant for end-product properties, the majority of recent research is directed towards sequential dual-curing systems. Unlike a simultaneous dual-curing process, sequential dual-curing provides processing flexibility as long as the intermediate materials (i.e. after the first curing reaction) are non-reactive. Sequential dual-curing methodology is developed from multi-stage (or B-stage) processing techniques. Multi-

stage processing is well known from the early times of crosslinked polymers, with the development of Bakelite in the early 20th century [9]. Conventionally, a multi-stage thermoset refers to a one-pack adhesive, usually of epoxide origin, that can be partially pre-cured after application to a substrate. The substrate can then be transported and/or further processed (e.g. in final assembly stage), and the full cure of adhesive could be initiated whenever desired by using appropriate stimuli (e.g. heat or UV light). The same processing technique is employed in composite industry as well [10,11]. A general representation of dual-curing processing is shown in **Scheme 1.1**



Scheme 1.1 An exemplary dual-curing system. Monomer functionalities are 5,4, and 2 for green, dark blue and light blue, respectively. At curing stage 1, green polymerizes with light blue, leaving dark blue unreacted. At curing stage 2, there is both light blue-dark blue copolymerization and homopolymerization of each monomer. No unreacted species left at the end of the process. Adapted from [12].

In sequential dual-cure processing, the extent of both curing reactions and the intermediate material properties can be easily regulated by formulation composition. The material will have stable intermediate properties after the first curing stage. No further polymerization will take place unless the second reaction is triggered. This storage stability might be critical in certain applications. Certain applications require that the material be adhesive or flexible before it is fully employed at the final stage of application. **Figure 1.1** shows a polymeric coil developed for a biomedical application. The material is flexible after the first curing stage which facilitates its intravenous deployment using a catheter.

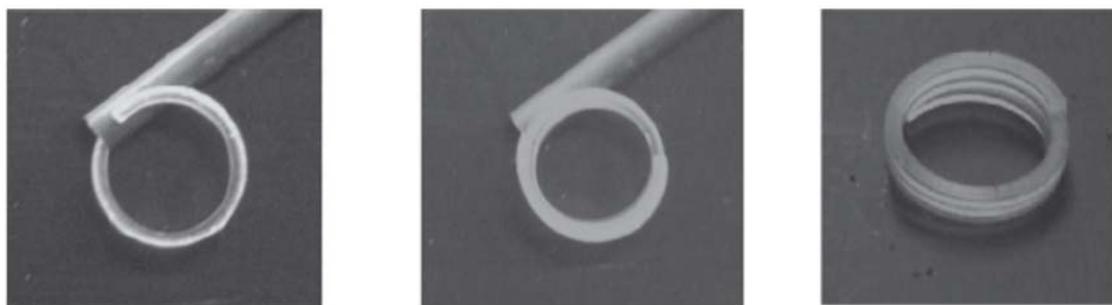


Figure 1.1 Endovascular coils. Intermediate stage polymers are deployed from a catheter. Once strain-free, the polymer recovers the original coil shape. At the physiological temperature (38°C), the final curing reaction is triggered and the shape is fixed. Reproduced with permission from [13].

In dual-curing formulations, processing and compounding is made much easier than in conventional prepolymer formulations. These prepolymers are produced *in situ* starting from a mixture of low molecular weight monomers, rather than large polymeric components. Dual-cure processing takes this approach one step further by introducing tailor made chemistries that originate from different types of polymerization reactions in a single pot. As such, dual-curing systems prove successful in a number of advanced, high added-value applications [13–15].

Two main requisites of sequential dual-cure processing are as follows:

- i. The two polymerization reactions must be compatible within themselves and each reaction must be selective to certain monomers. This ensures no undesired inhibition or reactivity effects;
- ii. They must be triggerable by different stimuli such as UV light or heat, or else they must have disparate reaction rates so as to allow selectivity of reactions (i.e. Reactions must take place at different temperatures and/or times)

A variety of polymerization reactions fit these criteria. Among them, “click” polymerizations are of interest as they are orthogonal, selective, and efficient with virtually quantitative yields and take place in mild and solventless conditions [16,17]. To ensure stability of partially-cured intermediate materials, the use of latent catalysts is common. These latent catalysts can be activated either photolytically or thermally depending on their chemistry. They are employed in base- or acid-catalyzed reactions or radical polymerization reactions, facilitating the design of one-pot dual-curing formulations with good storage stability of the monomer mix and also of intermediate materials [18–21]. Ionic liquids (i.e. Liquid curing agents

composed of organic cations or anions) [22] or blocked species [23] are also used in storage stable dual-curing systems. In case the second curing stage is a thermally triggered reaction, the exothermicity of the first stage should be controlled carefully to avoid loss of intermediate storage stability [24]. This is also a concern relevant to quality control in composite processing [11]. Reader is directed to the book chapter by Ramis et al [25] for an excellent review of click-based dual curing systems and their applications. In another paper, reaction mechanisms and applications of acrylate based dual-curing systems are reviewed [12].

In dual-cure processing, the polymer network formation should be monitored carefully to ensure that properties develop as desired. The intermediate and final properties of dual-curing materials depend strongly on the network structure at the end of each polymerization stage. The key parameters are monomer functionality, structure and feed ratio. Relevant structural parameters are mass-average molecular weight, gel point conversion, cross-linking density, and gel fraction. By characterizing the rheological or thermomechanical properties of partially or fully cured materials, these parameters can be determined. Network buildup in multistage processing has been studied using stochastic models in the past [26]. Recently, some criteria for designing dual-curing systems and preliminary network structure analysis was developed based on ideal network buildup models [5,27]. However, in certain cases, these idealized stepwise network buildup models fail to explain the complex structure-property relationships. A more profound understanding of the effects of monomer structure, functionality, and feed ratio on the intermediate and final properties is necessary [28].

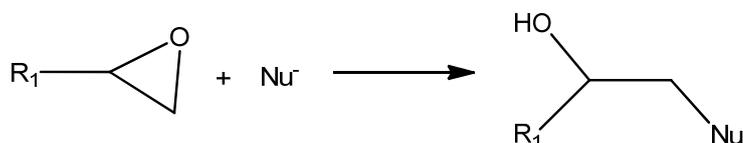
1.2. Click and non-click reactions in dual-curing systems

Sharpless et al. first coined the word “click” to refer to a variety of chemical reactions that are orthogonal, selective, and highly efficient [16,17]. Click reactions have the following characteristics: (a) high yields; (b) regio and stereospecificity; (c) insensitivity to oxygen or water; (d) mild, solvent-free, or aqueous reaction conditions; (e) orthogonality with other common organic reactions; and (f) availability of a wide array of starting compounds [28,29]. The click chemistry concept made it possible to employ a modular construction approach, as opposed to conventional synthesis methods [29,30]. Most often, post-purification step is not needed thanks to high yields of reactions. In an extensive review, Tunca reported the

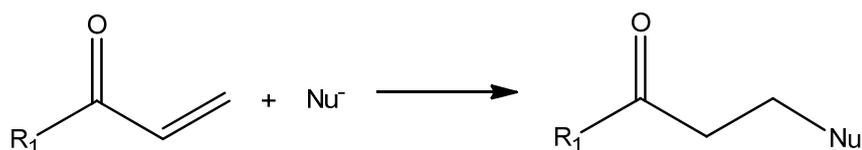
combination of two or more orthogonal click processes to synthesize complex architectures [31].

Click reactions can be carried out under mild and solvent-free conditions and therefore can be designed in an environmentally friendly manner. A large number of chemical functionalities show click behaviour with chemically and mechanistically distinct reaction pathways, so that they can be combined in dual curing methodologies. Some click reactions commonly used to prepare dual-curable materials are summarized in **Scheme 1.2**.

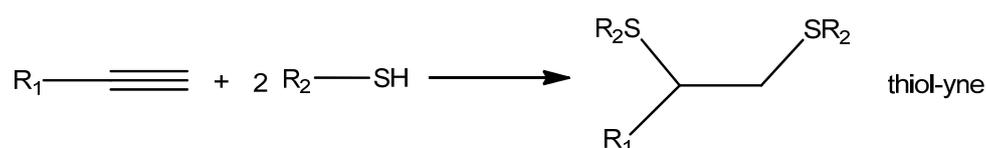
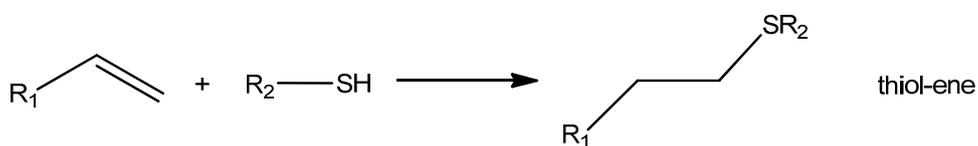
a. Nucleophilic ring opening reactions



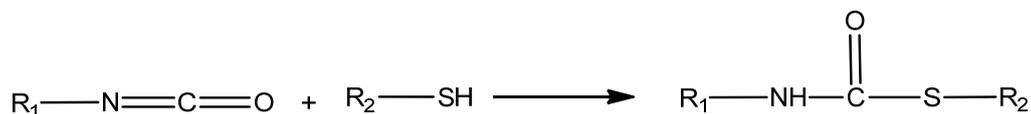
b. Michael addition reactions



c. Photochemical addition of thiols to alkenes and alkynes



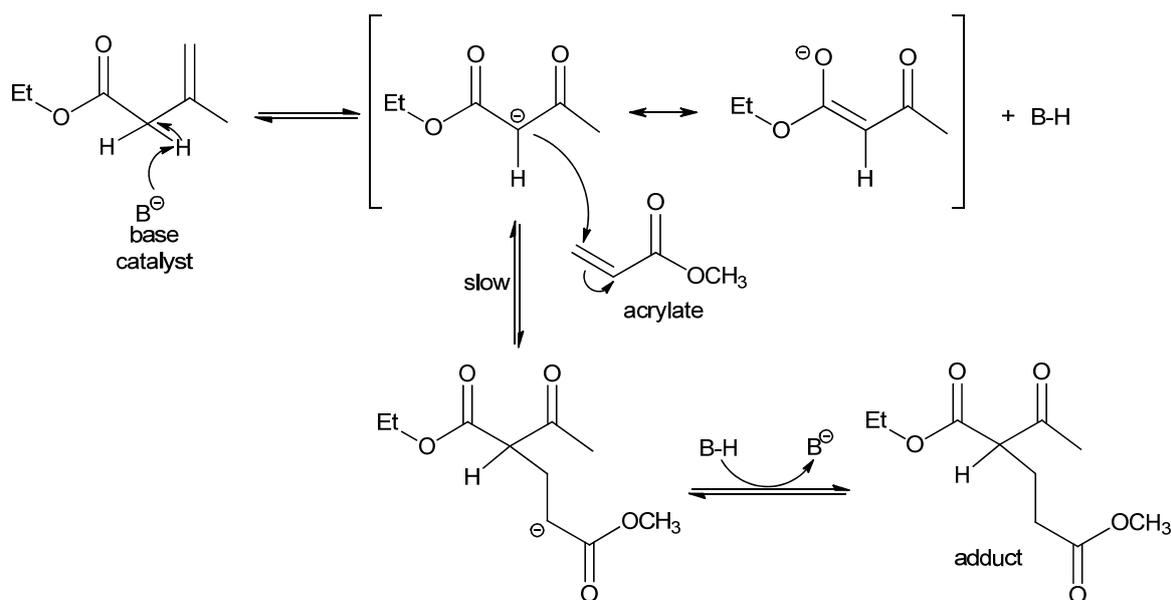
d. Carbonyl addition of thiols to isocyanates



Scheme 1.2 Some common click based polymerization reactions used in dual-curing systems

1.2.1. The Michael addition

A versatile click reaction is the Michael addition and is commonly used in dual-curing systems. Michael addition is defined as the 1,4-addition (or conjugate addition) of resonance-stabilized carbanions to activated double bonds [32]. Michael-type addition reactions are used widely in dual curing processes thanks to the variety of commercially available nucleophiles (Michael donors) and activated double-bond compounds (Michael acceptors). Typical Michael donors are amines, thiols, acetoacetates and phosphines. The group of Michael acceptors is more numerous and includes acrylates, acrylonitrile, acrylamides, maleimides, alkyl methacrylates, cyanoacrylates, and vinyl sulfones. A variety of basic and, especially, nucleophilic catalysts can be used to trigger Michael addition in a controlled way making it possible to combine Michael-type reactions in dual-curing systems with a variety of other reactions in a controlled and sequential way, that is, radical-induced polymerizations [32,33]. The general Michael reaction is shown in **Scheme 1.3**.

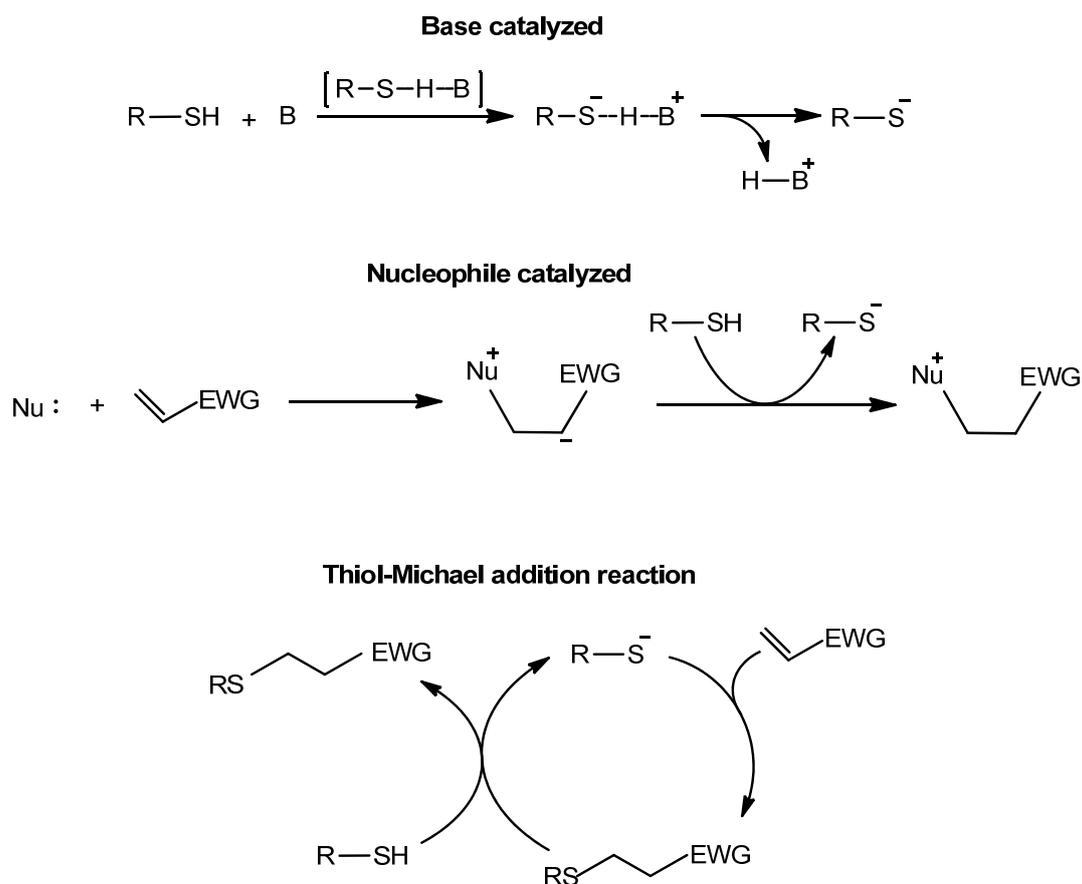


Scheme 1.3 Michael reaction mechanism. The Michael donor (acetoacetate) is deprotonated by the base catalyst. The formed enolate anion attacks the acrylate double bond and regenerates the base. The formed adduct may undergo a second but slower Michael addition [34].

Among the set of monomers used in dual curing systems, thiol monomers are arguably the most common. Thiols are clickable with a variety of coreactants under favorable reaction conditions. They can participate in thermal nucleophilic and radical UV-initiated reactions [35].

Thiols impart good transparency to final materials and low polymerization shrinkage (and thus reduced internal stresses). On the other hand, the long carbon-sulfur bonds render thiol-based polymers somewhat flexible. The C-S bond length is 1.8 Å whereas a C-C bond length is in the range 1.2-1.5 Å. This limits the mechanical properties of the cured materials, such as hardness, modulus, and glass transition temperatures (T_g). Using higher functional or more rigid monomers (such as those wielding aromatic rings) is a strategy to compensate for this flexibility.

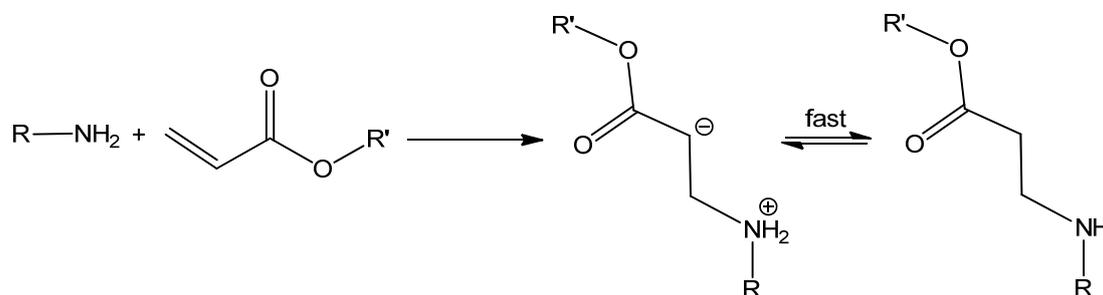
Thiols can undergo Michael reactions as they are susceptible to deprotonation by a number of basic or nucleophilic species. In **Scheme 1.4**, thiol-acrylate Michael reaction is shown.



Scheme 1.4 Thiol-Michael addition to activated olefins. The thiolate anion can either be produced through a basic (top) or nucleophilic (middle) mechanism.

The kinetics of thiol-Michael addition is a strong function of the solvent type, solvent polarity, nature (basic or nucleophilic) and concentration of catalyst [36]. It is not straightforward to predict optimum reaction conditions based solely on the pK_a values of thiols and bases since basic and nucleophilic mechanisms might be operational simultaneously [33]. Strong bases and nucleophiles complicate the sample preparation process since the reaction starts too early and too fast. When weak nucleophiles are used an induction period can be achieved allowing a window of workability [37]. Latent catalysts also come in handy to prepare chemically stable dual-curing systems with thiols [38]. If the latent catalyst is photo-activated, there is a risk of concurrent radical formation. In this case, a radical scavenger would be needed to preserve stoichiometry [39].

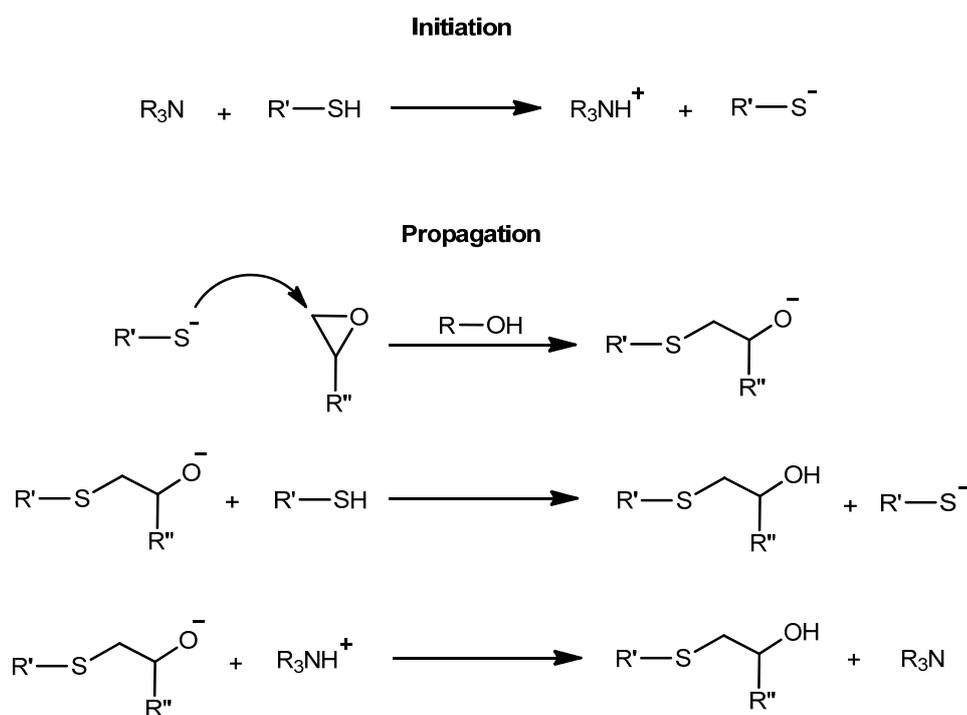
Another common Michael type reaction encountered in dual curing systems is Aza-Michael reaction. The reaction mechanism is similar to that depicted in **Scheme 1.3**. As Michael donors, amines have some advantages in comparison to thiols or acetoacetates: (a) Amines are more available commercially; (b) catalysts are not required since amines can act as both nucleophiles and bases; (c) radicals or other active species are not formed during their polymerization; (d) the formation of tertiary amines during aza-Michael addition avoids the intrinsic oxygen inhibition of free-radical vinyl polymerizations and allows the curing to be performed without inert blanketing [40] and (e) these tertiary amines can act as co-initiator when type II photoinitiators (i.e. photoinitiators that require a co-initiator or synergist to produce initiating radicals) are used. A drawback of aza-Michael reactions is the lower reactivity of secondary amines, which may lead to incomplete double bond conversions. Nevertheless, subsequent photopolymerization of the unreacted Michael acceptor groups would lead to full conversion [41].



Scheme 1.5 Aza-Michael addition of a primary amine to an acrylate monomer. The resulting adduct (secondary amine) may undergo a second but slower aza-Michael reaction.

1.2.2. Thiol-click reactions

Thiols readily react with a variety of other substrates through mechanisms different than the Michael addition depicted in **Scheme 1.4**. A prominent click reaction of thiols commonly encountered in recent dual-curing systems is the thiol-epoxy reaction [5,42–45]. Conventionally, this reaction has been used in many biosynthetic and biomedical applications [35]. It also is the reaction of choice in polymer functionalization due to the hydroxyl groups it delivers which can undergo a second functionalization [46]. The reaction can be carried out without the use of solvents, under mild conditions, and with high yields. **Scheme 1.6** depicts the mechanism of thiol-epoxy reaction catalyzed by triazabicyclodecene (TBD), a strong base. The formed hydroxyl group catalyzes epoxy ring opening, thereby imparting an auto-acceleration effect. As a result, the reaction kinetics can be simulated using auto-catalytic models [47–49].

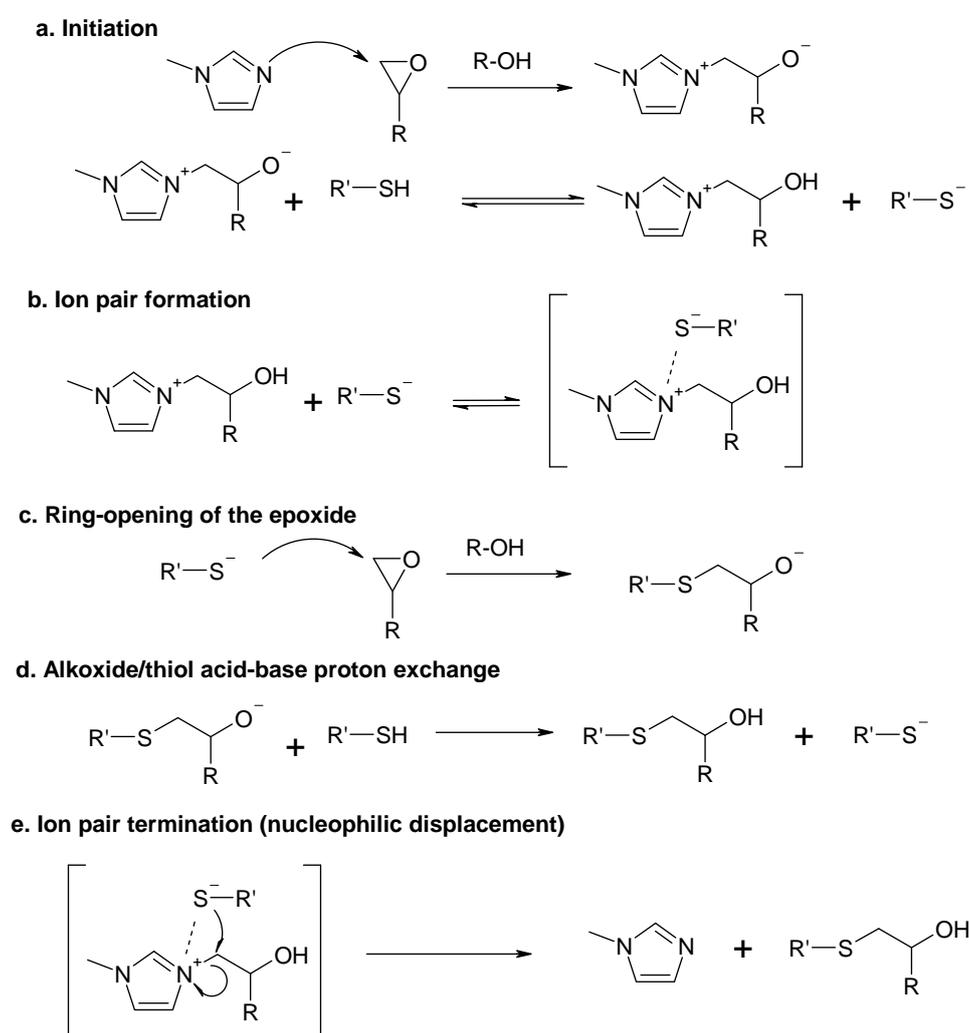


Scheme 1.6 The base catalyzed thiol-epoxy reaction. Base deprotonates the thiol, producing the thiolate anion, which attacks the alpha-carbon of the epoxy ring. Chain transfer reactions regenerate the thiolate and the base.

For temporal and spatial control of the reaction, photobase generators (PBG) attracted attention recently [35,50,51]. Many PBG chemistries exist, with different activation methods (including thermal activation). Catalytic species are liberated upon irradiation of the PBG with light at appropriate wavelengths (or upon heating).

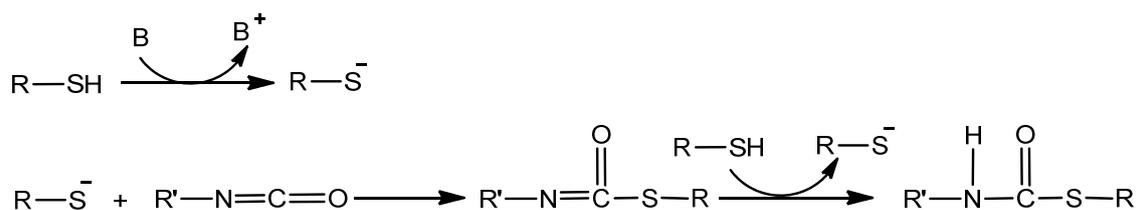
Thiol-epoxy reaction proceeds to completion given that appropriate catalysts are used. A nucleophilic reaction route is also plausible as shown in **Scheme 1.7**. As a matter of fact, the mechanism of thiol-epoxy reactions is a promising research topic since the chemistries involved during the reaction steps are relatively more complex and less understood than other click schemes [35,52].

The main difference between this process and the base-catalyzed reaction is the formation of the propagating thiolate (nucleophilic attack leading to formation of strong base + acid-base exchange, reaction a), and the ion-pair / termination (reaction e)



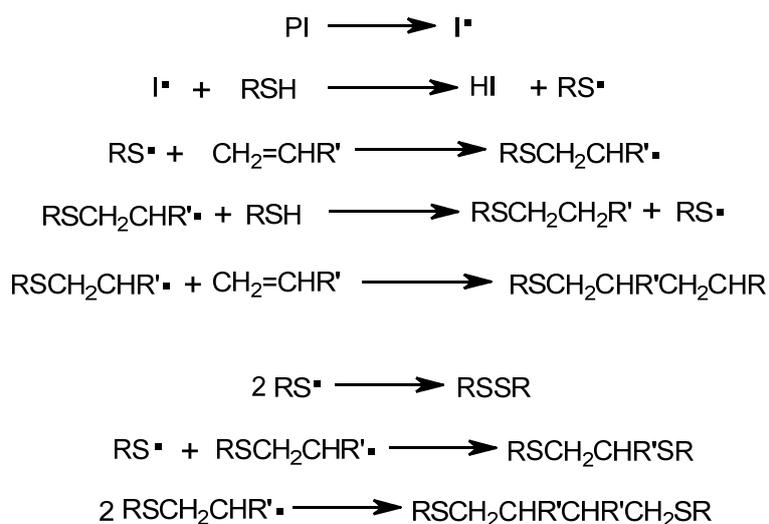
Scheme 1.7 Nucleophilic mechanism for thiol-epoxy reaction. A zwitterion is formed after nucleophilic ring opening of the epoxy (reaction a). An ion-pair formation (reaction b) seems a valid explanation for observed effect of catalyst amount on reaction kinetics, similar to ion-pairs formed during cationic homopolymerization of epoxy [53]. Thiolate propagation (reaction c) and regeneration (reaction d) are analogous to the base catalyzed mechanism. Termination of the ion-pair via a unimolecular mechanism (reaction e) regenerates the base.

Thiols also react with isocyanates in a click fashion to yield polythiourethanes with similar properties to polyurethanes [35]. This reaction proceeds through an anionic chain transfer-propagation mechanism similar to thiol-ene radical polymerization as depicted in **Scheme 1.8**. The reaction takes place at milder conditions than alcohol-isocyanate (polyurethane) reactions. The thiourethane product has desirable properties which find use in high refractive index materials [35]. The reaction is frequently employed in dual curing systems [54–56].



Scheme 1.8 The thiol-isocyanate click reaction. The thiolate anion is regenerated by proton transfer to the thiourethane product [35].

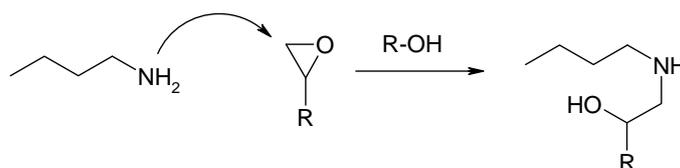
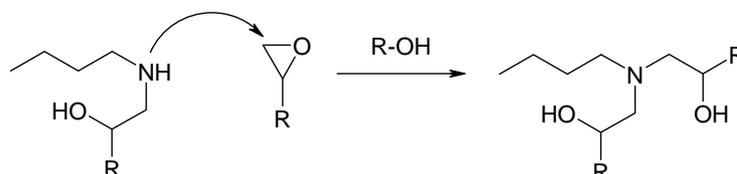
Thiols react through free radical mediated reactions as well. The so-called radical thiol-ene (and thiol-yne) reactions have remarkably fast kinetics, are robust, and afford products with high yields [12,35,57]. In these reactions, the polymer network evolution proceeds in a step-growth fashion. Combining this advantage with the high reactivity of radicals generated, the radical thiol-ene reactions find use in numerous areas, including electronics, optics, and protective coatings. Both light and heat is used, in combination with suitable photoinitiators (PIs) and photosensitizers, to generate radicals. Activation by light facilitates temporal and spatial control over the reaction, wherein the irradiation wavelength, intensity and duration determine the rate and extent of reaction. Radical thiol-ene reactions are readily combined with other click reactions such as Michael additions or thiol-epoxy reaction to design efficient dual-curing systems [24,42–44,58]. The radical thiol-ene reaction steps are depicted in **Scheme 1.9**.



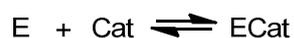
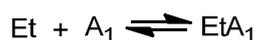
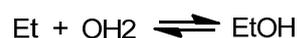
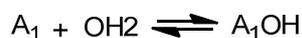
Scheme 1.9 Radical mediated thiol-ene (or -yne) reaction [59,60]. Once the PI is cleaved, thiyl radicals start forming at a high pace. The propagation reaction proceeds until quantitative conversion given that thiol groups and double bonds are in stoichiometry and no physical impediments at the molecular level. Possible radical termination schemes are also given.

1.2.3. Epoxy-amine click reaction

As a matter of fact, the most common curing agent for epoxy resins are polyamines [53,61,62]. Epoxy groups readily react with amines at ambient conditions, without requiring added catalysts, to yield highly crosslinked thermosets. The hydroxyl groups formed during the reaction exert an autocatalytic effect [62]. In cases where amine groups are in stoichiometric defect, hydroxyl groups may react to form ether linkages [62,63]. Both primary and secondary amines can react with epoxides as shown in simplified form in **Scheme 1.10**. The actual reaction mechanism is fairly complicated due to the formation of multiple reactive and non-reactive equilibrium complexes [53,64,65]. The reactions of these complexes are shown in **Scheme 1.11**.

a. Primary amine reaction**b. Secondary amine reaction**

Scheme 1.10 Simplified representation of the epoxy-amine reaction. The hydroxyl groups formed, as well as those already present in the reaction medium exert a catalytic effect.

Reactive complexes**Primary and secondary amine-epoxy reaction****Non reactive complexes**

Scheme 1.11 Equilibrium complex formation in epoxy-amine polycondensation [64]. A_1 , A_2 , and A_3 are the primary, secondary, and tertiary amines, respectively. OH is the hydroxyl formed during the reaction; Cat is either OH or A_1 ; ECat is an equilibrium complex; and Et is the ether group of the epoxy.

It was documented that the reaction is initiated by the equilibrium primary amine-epoxy complex [64]. However, the reactions between the primary and the secondary amine with a reactive epoxy-hydroxyl complex soon dominates the overall reaction kinetics. When the reaction temperature is within or below the T_g range of the fully-cured epoxy-amine polymer, the curing polymer vitrifies before reaching complete conversion.

1.2.4. Other reactions in dual-curing processes

Dual-curing schemes may also involve polymerization reactions that do not necessarily fit the click criteria. Mostly, these reactions require certain initiators and special conditions (such as high temperatures) to attain quantitative conversions of monomers. In the majority of times, these non-click procedures are employed as a second curing stage, after a self-limiting click reaction [25]. Preparation of off-stoichiometric formulations with an excess of acrylates, methacrylates or epoxy groups is a commonly employed dual-curing method [4,5,41,66,67]. The excess functionality undergoes homopolymerization in the second stage, significantly increasing the crosslinking density of the final polymer, hence resulting in better physical and mechanical properties. Furthermore, if the intermediate materials (i.e. after the first curing stage) have storage stability, they can be shaped (if gelled), applied onto substrates as adhesives (if not gelled) and/or be transported to the site of final use where they could be fully cured by initiating the second curing stage. Two possible applications of this approach are illustrated in **Figure 1.2**.

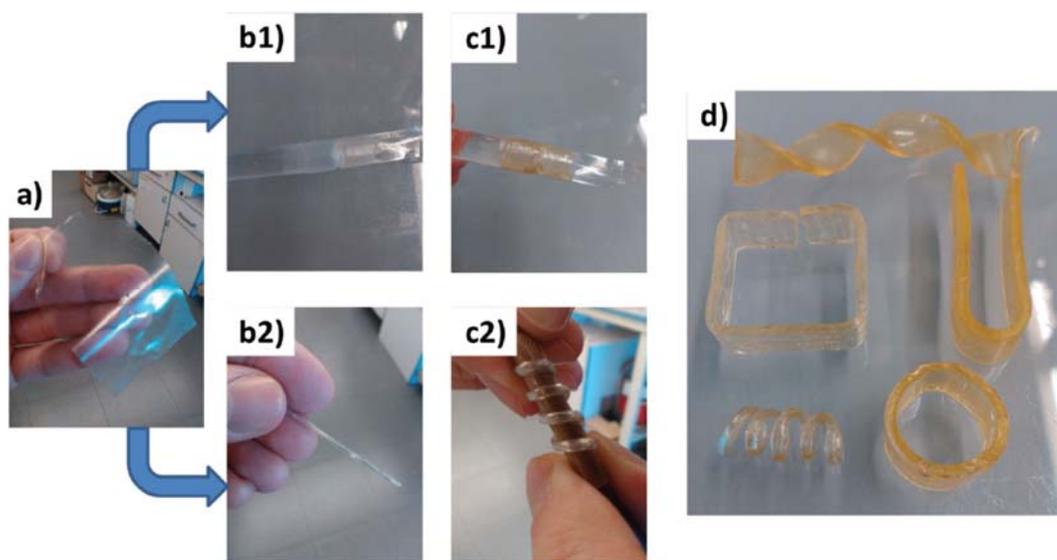
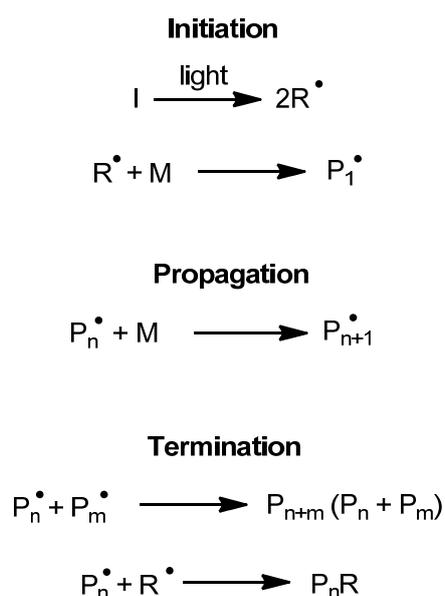


Figure 1.2 Dual-curing process of an off-stoichiometric thiol-epoxy system. Pipe joint repair (sequence a–b1–c1), and creation of spring-shaped materials (sequence a–b2–c2) and other complex shapes (d). The materials are easily deformed after the first curing stage. The second stage is triggered to fix the shape. Reproduced with permission from [5]. Published by The Royal Society of Chemistry.

The intermediate properties depend on the choice of monomer type, structure, functionality and feed ratio. Usually, a step-growth polymerization (first stage) precedes a chain-growth (second stage) polymerization, at the end of which complete cure is achieved. In these systems, a step-growth process delivers an intermediate material with desirable properties such as polymer network homogeneity, high capacity for mechanical dampening near its T_g , high gel point conversion, and low polymerization shrinkage. The second stage curing of such an intermediate would result in a significant increase in hardness and T_g , rendering it suitable for demanding applications.

The two most common homopolymerizations encountered in dual-curing systems is acrylate/methacrylate free radical homopolymerization [41,68,69] and anionic epoxy homopolymerization [5,42,66,70,71]. The free radical homopolymerization of acrylates/methacrylates has been studied extensively [72–74] and the reaction mechanism is established as in **Scheme 1.12**.

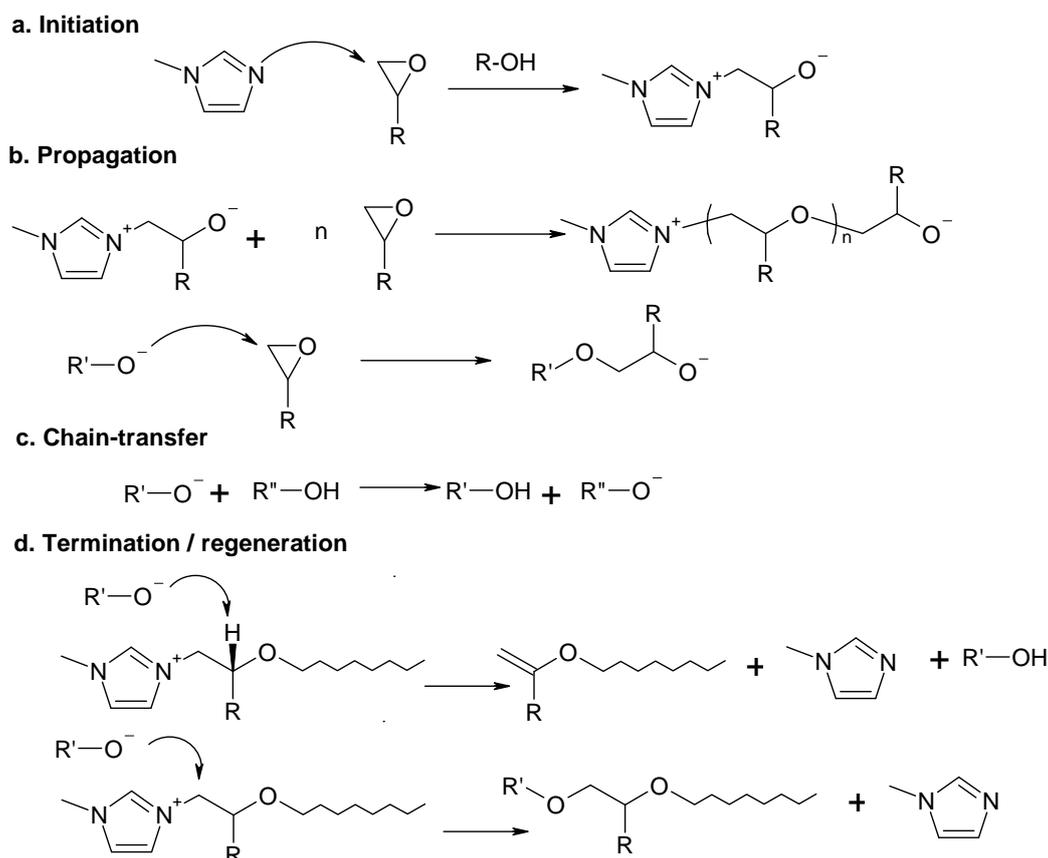


Scheme 1.12 The photolysis of the initiator yields two equally reactive radicals. The radicals initiate the chain by reacting with an acrylate monomer. The chain propagates by reaction with other monomers. Termination occurs when the propagating polymer reacts either with another growing polymeric radical or with a primary radical.

Although the initial radical formation can be accomplished by thermal means [75], photoinitiation offers numerous advantages such as spatial and temporal control over the reaction, high reaction rates and low energy requirement [76]. In photoinitiated polymerizations, reaction kinetics are governed by parameters such as light intensity, and

irradiation duration, apart from intuitive parameters such as initiator concentration and initiation efficiency [59]. However, in these photocuring systems, formulators must be mindful about polymerization induced shrinkage which can reach up to 20% with certain monomers [77].

Similar to off-stoichiometric dual-curing systems based on vinyl functionality, epoxy-based dual curing-systems can be formulated with an excess of epoxy groups [5,66,78]. The second stage of such systems is usually an anionic epoxy homopolymerization. In certain epoxy systems, kinetics of both curing stages (i.e. copolymerization and homopolymerization) benefit from each other [78]. The anionic epoxy homopolymerization reaction is catalyzed by tertiary amines, some resulting in faster kinetics than others [79]. In **Scheme 1.13**, the epoxy homopolymerization is initiated by an imidazole.



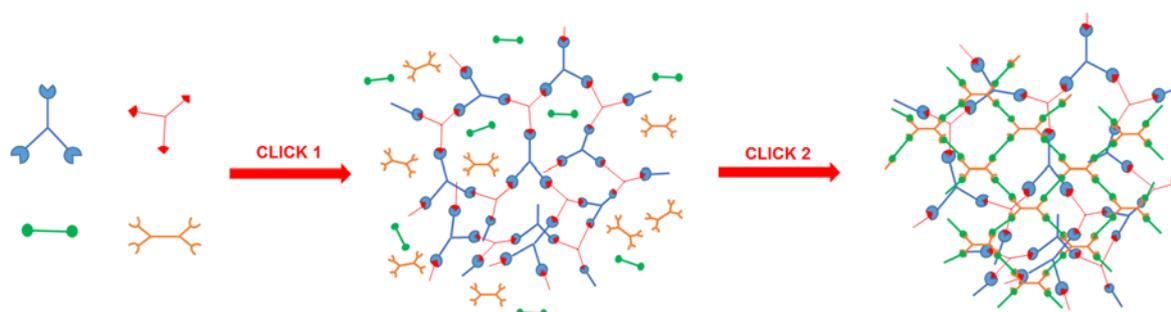
Scheme 1.13 Anionic homopolymerization of epoxides using 1-methylimidazole as initiator. The reaction is initiated by the nucleophilic attack of the imidazole to the epoxy ring, propagation by the different alkoxide anions present in the system (b), alkoxide-hydroxyl proton exchange (c) and two different termination or regeneration mechanisms (d), one by hydrogen abstraction (β -elimination) and another one by nucleophilic displacement of the imidazole, each one with a clearly different effect in terms of network build-up. Scheme adapted from [5].

This reaction can be used in dual-curing systems in which both reactions share the same initiator but have disparate reaction rates [5] or in systems in which the initiator is used only in the second curing stage [66]. In the latter case, a latent catalytic system might be necessary to achieve sequentiality in curing.

1.3. Approaches for the design of dual-curing systems

1.3.1. Dual-click procedures

As click reactions are fairly robust, orthogonal and selective, two different click reactions can be safely combined in dual-curing systems to yield materials with superior final properties. In **Scheme 1.14**, an exemplary dual-curing process consisting of two sequential click reactions is depicted. Depending on the reaction kinetics of the second curing stage, intermediate storage stability can be achieved. Some monomers might have more than one type of functional groups and can participate in both click stages.



Scheme 1.14 A dual-curing process based on two orthogonal click reactions carried out sequentially. Click 1 is between blue and red monomers, with a functionality of 3 for both. Click 2 is between green and yellow monomers which have functionalities of 2 and 4, respectively. The final material consists of a polymer network with high crosslink density and no extractable content.

A common dual-click procedure employs click thiol-ene with thiol-epoxy reaction. Carioscia et al [80] developed a thiol-ene/thiol-epoxy hybrid system with tailorable curing kinetics. The resulting materials had high crosslink density, high T_g and reduced polymerization induced shrinkage. By modifying composition of formulations, network development can be controlled as desired. In another paper, Carlborg et al [44] presented a photocured thiol-ene/thiol-epoxy system with 24h of intermediate storage stability. The thiol-epoxy reaction was triggered by a photolabile base which, upon UV irradiation, liberated a tertiary amine capable of deprotonating the thiol. More recent papers investigate similar thiol-ene/thiol-epoxy systems combining photoinitiated thiol-ene with thermally initiated thiol-epoxy

reaction [24,81]. Feature similar click characteristics to thiol-ene, the thiol-yne reaction has also been successfully combined with thiol-epoxy curing [58].

Other thiol-click chemistries were also employed in dual-curing processes. Chan et al used phosphine catalyzed nucleophilic thiol-ene with radical thiol-yne in a sequential fashion. They found that a wide selection of commercially available thiols are compatible with this procedure and the resulting materials may be suitable for biomedical applications [82]. Later, Peng et al published two papers about dual-curing systems in which Michael-type thiol-acrylate reactions are combined with either radical thiol-allyl [83] or thiol-yne [84] reactions. They showed that both systems are promising in the field of holographic image patterning (See **Figure 1.3**). The two curing stages are easily separated in both systems, where the base catalyzed thiol-acrylate Michael reaction affords writable substrates with desirable properties.

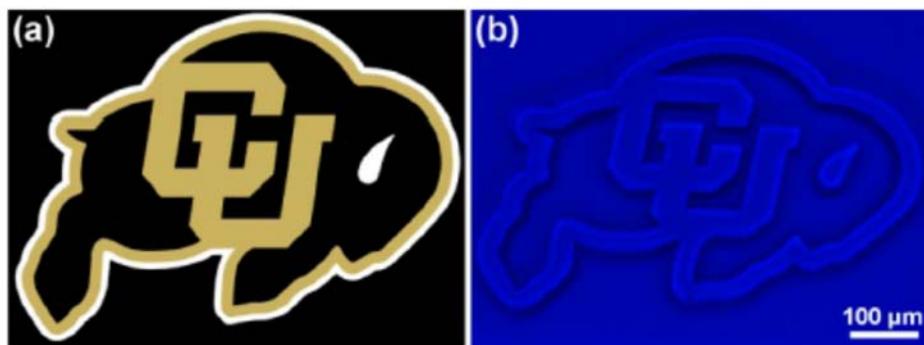


Figure 1.3 Holographic image patterning. (a) Original image used as a digital mask and (b) the directly patterned image on the stage 2 material composed of thiol/acrylate/alkyne. Reprinted (adapted) with permission from [84]. Copyright 2014 American Chemical Society.

In another paper, nucleophile catalyzed thiol-acrylate Michael addition was combined with thiol-epoxy reaction in a simultaneous dual-curing process [48]. The resulting materials exhibited two different glass transitions at different temperatures. By employing thiols with different functionalities, the crosslink density of the networks could be controlled and a wide range of mechanical properties could be attained.

Thiol-isocyanate click reaction has also been used in dual-curing procedures. Shin et al [55] showed the possibility of carrying out base-catalyzed thiol-isocyanate with radical thiol-ene both sequentially and simultaneously depending on the catalytic system employed. When they used a PBG of a strong base, both reactions took place concurrently upon UV irradiation, whereas when a thermally active base catalyst was used, thiol-isocyanate reaction preceded

the photoinitiated thiol-ene reaction. They saw that the inclusion of a thiourethane network helped improve physical and mechanical properties due to additional hydrogen bonding in the final polymer. A similar improvement was observed by McNair et al [85] in a dual-curing system composed of a base catalyzed thiol-isocyanate reaction and a photoinitiated thiol-ene reaction, carried out sequentially. In a more recent paper, Perrot et al [54] combined thiol-isocyanate and thiol-epoxy reactions, both catalyzed by a PBG of a strong base. Although the thiol-isocyanate reaction was complete in a matter of seconds, the thiol-epoxy reaction extended over several days leading to a post-consolidation of materials. They recorded enhanced mechanical properties due to increased hydrogen bonding, similar to previous dual-curing systems with thiol-isocyanate coupling.

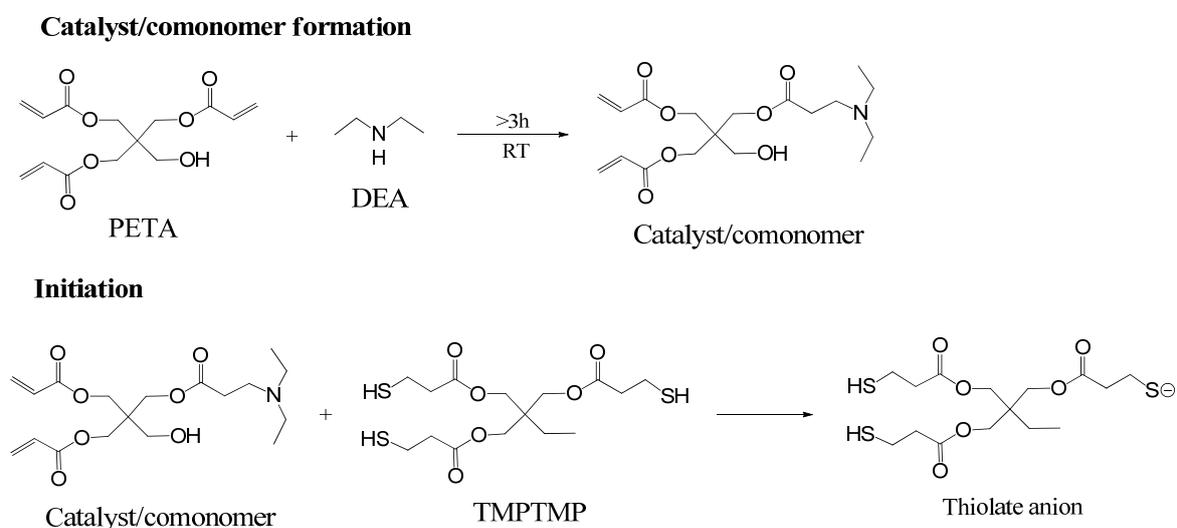
1.3.2. Common click mechanism with different monomers

Within the same click reaction, different monomers may exhibit different polymerization kinetics depending on their chemical structure. As it was previously shown by Chatani et al [27] that, compared to acrylates, vinyl sulfones react more rapidly with thiols through a Michael type mechanism, thanks to their greatly electron deficient vinyl groups. Exploiting this property, they were used in combination with acrylates to design sequential dual Michael-type click procedures [86]. This process afforded materials with triple shape memory properties based on the dual polymer network formed. Although the click reaction type and the catalyst were the same, the acrylate and vinyl sulfone monomers had drastically different reaction kinetics. Furthermore, by employing two different thiols (i.e. mercaptoacetate and mercaptopropionate) with different reactivities, the two curing stages were easily separated. The mercaptoacetate-vinyl sulfone Michael reaction took place easily at ambient temperature, followed by mercaptopropionate-acrylate Michael reaction at elevated temperatures. Both reactions were catalyzed by a time-controlled nucleophilic initiation system.

Similarly, acrylates and methacrylates have very distinct reactivities with respect to the thiol-Michael addition. Due to the pendant methyl group it possesses, a methacrylate is a poor Michael acceptor [32]. However, given a strong catalytic environment they can be incorporated into the addition reaction. As a matter of fact, Xi et al [38] used a photocaged superbase to carry out photoinitiated Michael addition of thiols to methacrylates, preceded by

a base catalyzed and thermally induced thiol-acrylate Michael addition. The photocaged base enabled efficient temporal and spatial control over the process.

Another interesting idea is to use an in-situ catalyst/comonomer that could participate in the polymerization reaction. Higham et al [87] investigated the use of an in-situ synthesized allyl functional tertiary catalyst/comonomer in a Michael reaction of triacrylate and trithiol monomers. The in-situ synthesis of the catalyst/comonomer and the subsequent initiation of thiol-Michael reaction is given in **Scheme 1.15**. The idea was employed in the production of microfluidic devices via a soft lithography process [88]



Scheme 1.15 Employing catalytic comonomers in dual-curing systems [88]. The catalyst/comonomer yields tertiary amine groups that deprotonate the thiol. PETA: Pentaerythritol triacrylate; DEA: Diethanolamine; TMPTMP: Trimethylolpropane tris(3-mercaptopropionate). The formed thiolate may propagate the polymerization both with the catalyst/comonomer, and the triacrylate PETA.

1.3.3. Combination of a click reaction with acrylate homopolymerization

The use of off-stoichiometric monomer mixtures is a widely adopted practice in dual-curing system design. The excess part of the monomers undergo homopolymerization reactions which significantly enhance final network properties. Often times, the first curing stage is a self-limiting click reaction between two multifunctional monomers and usually proceeds in a step-growth fashion. The subsequent homopolymerization of the excess monomer is a thermo- or photo-induced chain growth reaction. The inclusion of a step-growth polymer network imparts network homogeneity, high gel point conversion, and reduced polymerization shrinkage. On the other hand, the chain-wise polymer network that would

result from the second curing stage would have greatly increased crosslinking density, increased hardness, and higher T_g . Depending on the initial composition, the type and functionality of the monomers, intermediate materials (i.e. at the end of the first curing stage) can be gelled or not; final materials can be loosely or tightly crosslinked. This versatility can be exploited in custom-tailoring intermediate and final material properties with regards to application requirements.

One of the off-stoichiometric dual-curing formulation was reported by Moszner et al [89] in mid-90s. Their procedure consisted of a Michael addition of multifunctional acetoacetates to multiacrylates, followed by radical homopolymerization of excess acrylate groups. They also tested formulations with added dimethacrylates which cured upon irradiation in the second stage and yielded materials with improved hardness. A few years later, they provided a more thorough characterization of the same dual-curable materials [90]. They documented that the added excess of vinyl monomers acts as a reactive diluent for the first curing stage and helps achieve higher conversion, homogeneity and crosslink density. Despite the potential of multifunctional acetoacetates in such dual-curing systems, the lower reactivity of the second hydrogen of the acetoacetate group poses limitations on crosslink density. In fact, Pietschmann et al [91] showed that chemical pre-treatment of the acetoacetate monomer with certain amines increases the reactivity. The formed enamine tautomeric structure is believed to be responsible for the enhanced reactivity.

As mentioned previously, the versatile chemistry of thiols comes in handy in dual-curing systems with Michael-type networks. Nair et al published a number of papers about dual-curing systems based on off-stoichiometric mixtures of thiols and acrylates, where acrylate groups were in excess [13,69,92]. The first stage was an orthogonal thiol-acrylate Michael addition followed by photoinitiated radical homopolymerization of acrylate groups at a later stage. Depending on the monomer types and the stoichiometry, they showed the possibility of obtaining materials having a wide range of properties. In some cases, they observed 20-fold increases in moduli, as well as drastic increases in T_g of their materials, after the second curing stage. Once the materials are characterized, they tested them as substrates for shape memory materials, impression materials and as optical materials to record refractive index patterns. In an elegant way, an off-stoichiometric thiol-acrylate system was used to fabricate wrinkles [93]. The first stage was thiol-acrylate radical reaction, followed by acrylate photopolymerization. By using photoabsorbers, the UV light could be constrained in a thin

skin layer. The intermediate materials were first strained in predetermined configurations after which they were UV cured (for very short durations) through photomasks to generate wrinkles in desired forms as shown in **Figure 1.4**.

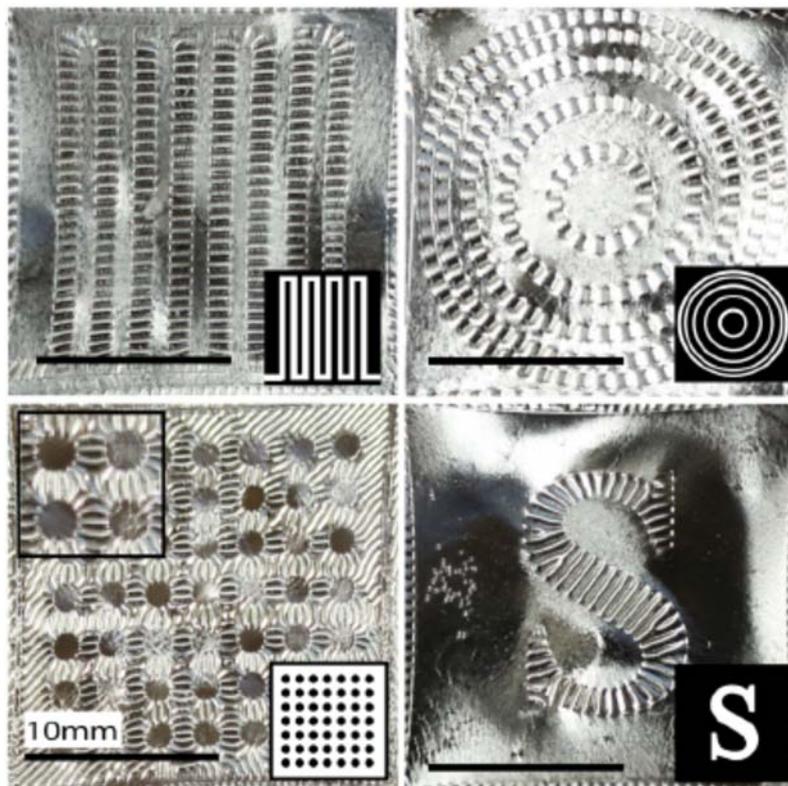


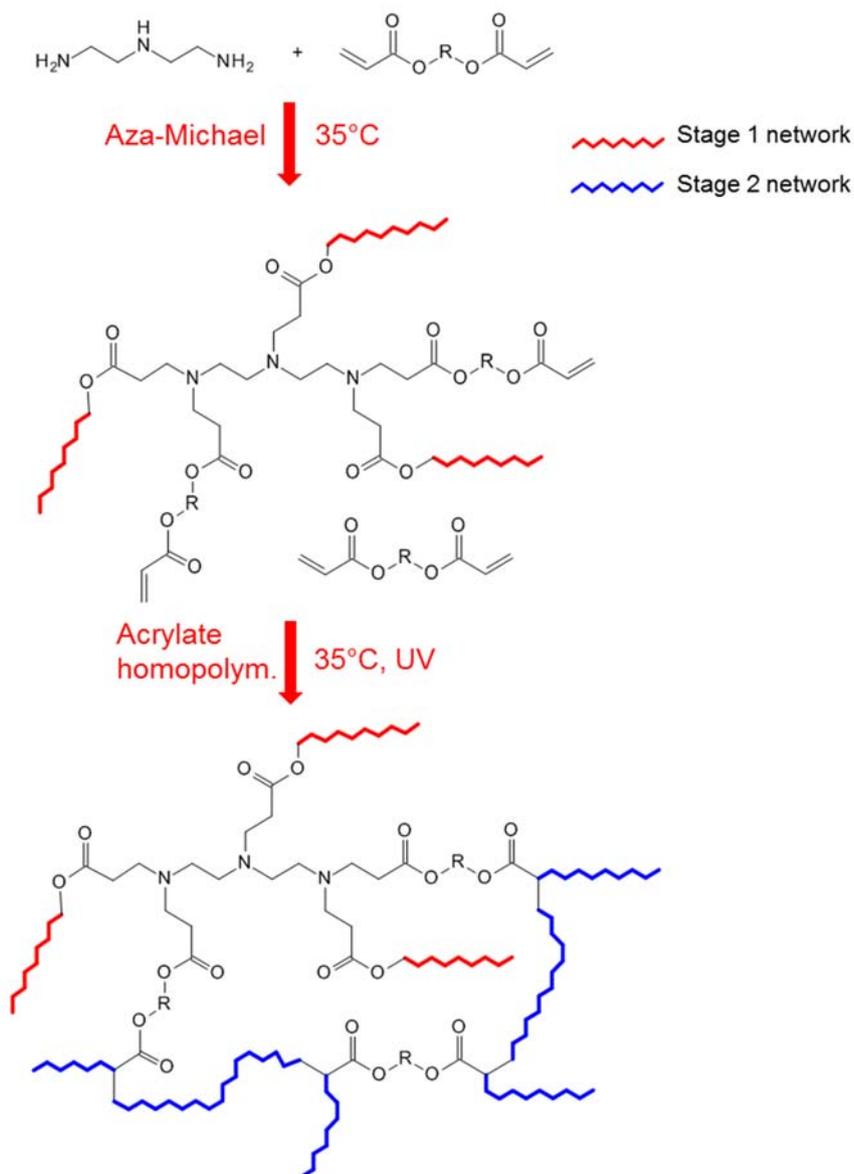
Figure 1.4 Wrinkle formation via photopatterning on a biaxially stretched specimen. Photolithography guides the alignment of the wrinkles perpendicular to the low stress regions of the thiol–ene elastomer. Corresponding photomasks are shown as inset. Reprinted (adapted) with permission from [93]. Copyright 2013 American Chemical Society.

Binici et al designed an interesting dual-curing system for spherically propagating polymerizations [94]. The idea is based on an amine-catalyzed Michael addition of trithiol to triacrylate, the latter being present in excess, followed by photopolymerization of remaining triacrylate to yield spherical gels.

Jian et al [95] designed a thiol-acrylate-epoxy ternary system where three different reactions occurred. The inclusion of a photobase generator (PBG) facilitated the simultaneous liberation of a strong base and the formation of radicals upon light irradiation. As a result, all three reactions took place concurrently: Thiol-acrylate Michael addition, radical thiol-acrylate (similar to radical thiol-ene), and base catalyzed thiol-epoxy. Due to the formation of radicals, some acrylate homopolymerization could not be discarded.

Matsushima et al [56] combined thiol-isocyanate, thiol-acrylate Michael and acrylate homopolymerization reactions to prepare materials with a ternary network structure. The first stage was the thiol-isocyanate coupling. Although the neat phosphine was not basic enough, the enolate anion formed by the reaction of the phosphine nucleophile with the acrylate successfully catalyzed the reaction. With slower kinetics, the thiol-acrylate Michael reaction was the second stage. The remaining excess acrylates were later homopolymerized using UV irradiation to yield the ultimate material. By changing the initial composition, a wide array of final properties could be achieved. Thiol-isocyanate coupling was also combined with methacrylate homopolymerization to fabricate well-defined surface topographies and functional geometric shapes [96]. The first curing stage was a base-catalyzed thiol-isocyanate click reaction, and the second stage was methacrylate UV homopolymerization facilitated by a photoinitiator and a photoabsorber.

Using amines as Michael donors in lieu of thiols has attracted attention in the recent years. Since amines act as both nucleophiles and bases, no added catalyst is necessary. The reaction of amines to electron deficient vinyl groups is defined as aza-Michael addition (See Section 1.2.1). Gonzalez et al [41] presented an efficient and eco-friendly procedure to cure off-stoichiometric amine-acrylate mixtures. Their dual-curing process consisted of a self-limiting aza-Michael reaction of multifunctional amines and acrylates, followed by a photoinitiated radical homopolymerization of excess acrylates (See **Scheme 1.16**). The intermediate materials after the first curing stage were storage stable, and their properties (such as their gelling state) could be tailored as a function of monomer feed ratio. The addition of tertiary amines to the formulations, or their formation during aza-Michael reaction also helped overcome the oxygen inhibition problem in acrylate homopolymerization. Similar to other systems formulated with acrylate excess, the mechanical properties improved significantly after the photocuring stage.



Scheme 1.16 A dual-curing system consisting of a click aza-Michael reaction carried out at near-ambient temperature, followed by photoinitiated acrylate homopolymerization.

Retailleau et al [97] also employed aza-Michael reaction in their dual-curing system based on off-stoichiometric amine-acrylate mixtures. The particularity in their work was that they could be able to post-consolidate their cured materials through a second aza-Michael reaction.

Interestingly, a homopolymerization process could be designed as a first curing stage as well. Lee et al [98] designed a thiol-allyl ether-methacrylate ternary system in which both step or chain-growth polymerizations took place. Upon UV irradiation, the formed thiyl radicals favored methacrylates rather than allyl ethers, since methacrylate double bonds have higher electron density. Furthermore, because vinyl radicals of methacrylates are more stable

(compared to acrylates) due to the methyl group, methacrylates underwent homopolymerization with chain transfer to thiol (at a lower rate than methacrylate homopolymerization). Only after a certain extent of methacrylate conversion that thiols were observed to start reacting with allyl ethers in a step growth fashion.

1.3.4. Combination of a click reaction with epoxy homopolymerization

Epoxy resin systems have remarkable features such as good adhesion to various substrates, superior physical and mechanical properties, and resistance to solvents and chemicals. As such, they are employed frequently in dual-curing systems. An epoxy excess in dual-curing formulations can be homopolymerized at a later stage to enhance final material properties such as crosslink density and elastic modulus. An interesting UV-thermal dual-curing system was developed by Sangermano et al [42]: Thiol-allyl-epoxy mixtures were first photocured (thiol-ene polymerization), then thermally treated to carry out epoxy homopolymerization. Since it was previously reported that the polysulfides that are formed by the thiol-ene reaction inhibited cationic epoxy polymerization [99], sequentiality was achieved. Once the UV-curing process is completed, the reaction mixture was heated above 100°C to initiate epoxy homopolymerization which was catalyzed by the alkylsulfonium salts formed in the first stage.

Thiol-ene/epoxy IPNs were prepared through a dual UV-thermal process [100]. In this system, the thiol-ene and epoxy homopolymerization took place concurrently. A penta-allylic triamine curing agent was first reacted with thiols to afford polysulfides, which inhibited cationic polymerization but catalyzed anionic polymerization of epoxides. This anionic reaction was initiated by the exothermic heat of the thiol-ene UV curing. It was observed that the final toughness of the materials was proportional to the amount of polysulfides formed. In a different paper [43], a thiol-ene/epoxy system was dual-cured via a similar procedure. The first stage was UV-initiated thiol-ene reaction between an allyl functional hyperbranched polyester and a trithiol to form a flexible thioether intermediate material, which acted as a cationic thermal initiator for the subsequent epoxy homopolymerization. The hyperbranched polyester helped achieve higher T_g s than neat formulations.

Recently, the dual-curing of an off-stoichiometric thiol-epoxy mixture was reported [5]. The procedure consisted of a click thiol-epoxy reaction catalyzed by a tertiary amine, followed by

anionic epoxy homopolymerization. As was documented by other researchers as well [53], the presence of proton donating thiol species throughout the first curing stage inhibited the anionic homopolymerization, thereby providing sequentiality. As a result, the intermediate materials had storage stability. By choosing different monomer feed ratios, intermediate properties could be controlled. As expected, the homopolymerization of the epoxy excess (i.e. enhanced thermomechanical properties greatly. The shape memory capabilities of these materials were documented in another paper [28].

Besides the monomer feed ratio, the structure and functionality of the thiol used were shown impact significantly the material properties in this type of dual-curing systems [101,102].

Similar to off-stoichiometric thiol-epoxy systems, one can formulate off-stoichiometric epoxy-amine systems [4,66,103] with the same motivation. As a matter of fact, off-stoichiometric epoxy-amine systems should be a promising research area since polyamines are the most common curing agents for epoxy resins [104].

1.3.5. Combining photopolymerizations with sol-gel process

Although they are not directly relevant to this thesis, it is worthwhile to mention hybrid organic-inorganic polymers that can be prepared via dual-curing procedures. Hybrid organic-inorganic formulations have some advantages over conventional resin systems such as improved scratch/abrasion resistance, thermal resistance, and optical properties [25]. The dual-curing procedure to fabricate these materials consists of a photoinitiated polymerization, followed by a thermal sol-gel reaction of alkoxyde precursors already present in the UV-curable formulation [105]. The use of photolabile species for temporal control over the process has also been documented for such dual-curing hybrid systems [106]. An excellent review on hybrid organic-inorganic coatings is available from the same author. For epoxy based hybrid sol-gel systems, the reader is directed to the review by Serra et al [107]. The organic part of the formulation can be based on similar click chemistries reviewed previously in this section. The final material properties depend on the type and feed ratio of organic monomers, initiator and coupling agent content, type and amount of inorganic precursors, amount of water for the sol-gel process, and curing conditions such as pH, and schedule of irradiation and thermal treatment [25].

Chapter 2

Research objective and scope

2. Research objective and scope

Inspired by the aforementioned approaches, in this Ph.D. project, dual-curing thermosets involving various chemistries were prepared and characterized. A common objective was to design truly sequential curing processes so that the materials were storage stable, at least after the first curing stage. The dual-curing systems were designed so as to obtain significantly improved physical and mechanical properties after complete cure. Although the majority of monomers used were clickable, some non-click reactions were also employed as long as they served to achieve the objectives mentioned.

The performance of different click (including copolymerizable monomer pairs thiol-acrylate/methacrylate, thiol-epoxy, amine-epoxy, amine-acrylate, acetoacetate-acrylate) and non-click (epoxy homopolymerization and acrylate/methacrylate homopolymerization) chemistries in dual-curing formulations were assessed. Intermediate and final materials were characterized with respect to a set of physical, mechanical and chemical properties. As it merited special focus due to a limited number of related publications, the kinetics of thiol-epoxy reaction was analyzed in and out of dual-curing context.

For reactive latency, we have developed a novel family of photobase generators (PBGs). The photolytic and thermal activation kinetics of these PBGs were studied. We have used differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) methods to monitor monomer conversions; thermomechanical analysis (TMA) (coupled with FTIR) for gel point measurements; thermogravimetric analysis (TGA) for thermal decomposition properties; DSC and dynamic mechanical analysis (DMA) for viscoelastic characterizations such as glass transition temperature (T_g) and alpha-relaxation temperature measurements; and proton nuclear magnetic resonance ($^1\text{H-NMR}$) for chemical characterization of our materials. Throughout the Ph.D. project, eight research articles were published in esteemed journals (all from Q1) in the area of polymer science. In the next section, we present the post-prints of those articles in chronological order. **Table 2.1** provides a timeline of these publications.

Table 2.1 Published articles during the PhD project

Article N°	Article title	Publish date
1	Sequential curing of amine-acrylate-methacrylate mixtures based on selective aza-Michael addition followed by radical photopolymerization	September 2016
2	Sequential curing of thiol-acetoacetate-acrylate thermosets by latent Michael addition reactions	February 2017
3	Latent curing of epoxy-thiol thermosets	March 2017
4	Analysis of the reaction mechanism of the thiol-epoxy addition initiated by nucleophilic tertiary amines	August 2017
5	Sequential dual curing by selective Michael addition and free radical polymerization of acetoacetate-acrylate-methacrylate mixtures	November 2017
6	Curing kinetics and characterization of dual-curable thiol-acrylate-epoxy thermosets with latent reactivity	November 2017
7	New allyl-functional catalytic comonomers for sequential thiol- Michael and radical thiol-ene reactions	January 2018
8	Preparation and characterization of dual-curable off-stoichiometric amine-epoxy thermosets with latent reactivity	May 2018

Chapter 3

Global discussion and conclusions

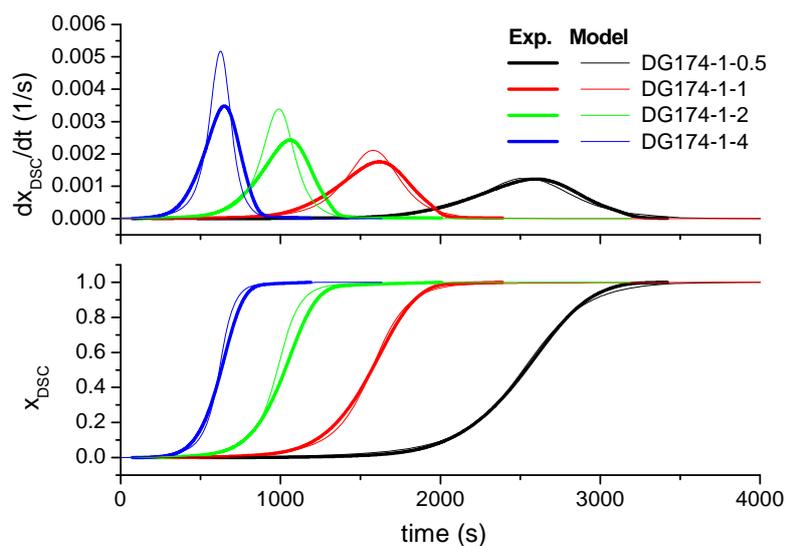
3. Global discussion and conclusions

In this PhD thesis, several approaches for the design of dual-curing formulations were investigated using a variety of clickable monomers and catalytic systems. In general, it was aimed to establish control over two aspects of dual-curing formulations: Curing reaction kinetics and material properties.

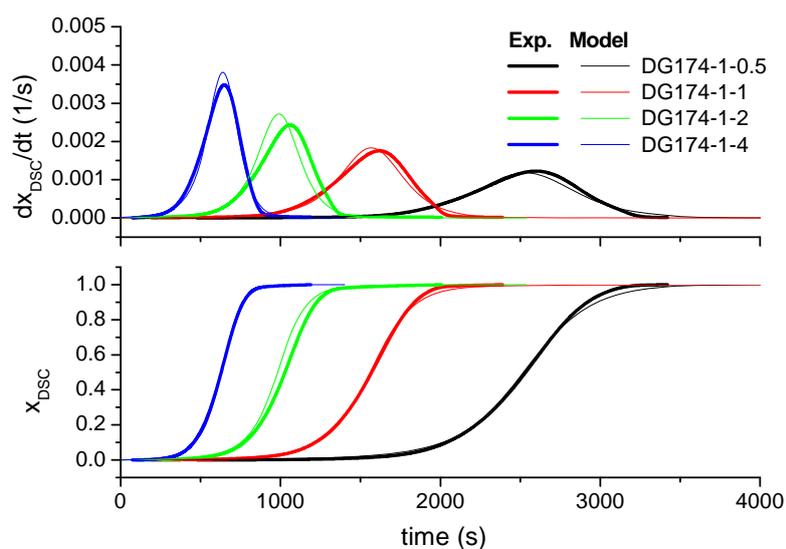
To study reaction kinetics, two methods of mathematical modeling were used: i) Phenological modeling (Articles 3 and 6), and ii) Mechanistic modeling (Article 4). The former method does not require knowledge about the reaction mechanisms. Experimental conversion data can be directly fitted to simple mathematical models and can be analyzed. Once the parameters of the model are determined, simulations can be run for extrapolated reaction conditions with acceptable accuracy. On the other hand, the latter method necessitates postulation of mechanistic hypotheses upon which differential rate expressions are written. Later, these expressions are tested against experimental data. Although this method provides more information about the reaction and therefore is more reliable for simulations, the regression procedure is more tedious.

Among the different click reactions used in dual-curing systems, the mechanism of thiol-epoxy reaction, especially the nucleophilic initiation mechanism, is relatively less studied. This motivated us for the kinetic studies carried out in articles 3, 4 and 6. In article 3, the model-free isoconversional methods confirmed the autocatalytic nature of the thiol-epoxy reaction catalyzed by the PBG: Activation energies were decreasing with conversion.

A Kamal autocatalytic kinetic model, which was also phenomenologically-based, represented the curing satisfactorily and facilitated accurate simulations at temperatures fairly outside of the experimental range. In article 4, we attempted to improve upon the mechanistic model proposed by Loureiro et al [52], by including the effect of thiol availability on initiation rate, and the formation of a non-catalytic ion-pair between an activated epoxy and thiolate. The quality of fit to experimental data improved significantly, reinforcing the ion-pair formation hypothesis (See **Figure 3.1**). As a further attempt to increase accuracy of the model, the ion-pair can be assumed a catalytic species as well.



(a)



(b)

Figure 3.1. Simple (a) vs. complex (b) kinetic model of thiol-epoxy click reaction. The inclusion of an ion-pair formation step in the reaction mechanism clearly improved the quality of fit and represented the effect of initiator content with higher accuracy. Note the peak reaction rates, especially of formulations with higher catalyst contents, significantly overestimated by the simple model. DG174 is epoxy resin with an equivalent weight of 174. Thiol part is Trimethylolpropane tris (3-mercaptopropionate). The rightmost numbers indicate phr of catalyst (1-methyl imidazole). Figure taken from article 4.

Another kinetics related result was obtained in article 5. The addition of methacrylate mixture diluted the reaction medium, reducing the reaction rate of the first curing stage. This was an indirect confirmation of the pseudo-first order dependence of acetoacetate-acrylate Michael addition kinetics on acrylate concentration as is documented in literature [32,34]. Without a doubt, our demonstration of these various kinetic methods for the analysis and control dual-curing systems is encouraging for future research on new formulations.

To obtain sequentiality in our curing reactions, we either exploited the intrinsic reaction kinetics and the selectivity of reactions, or employed latent catalysts. As an example to the former strategy, using methacrylates in Michael-type reactions in mixtures of acrylates and thiols (or amines for Aza-Michael) facilitated easy separation of the two curing steps. The pendant methyl group of a methacrylate reduces the electron deficiency of the vinyl bond, thus making them poor Michael acceptors. As a result, methacrylates could be incorporated into dual-curing polymer networks at different (usually later) stages, either through a heavily catalyzed Michael addition (see article 7), or homopolymerization (see articles 1 and 5). In **Figure 3.2**, the FTIR spectra of the dual-curing process of the acetoacetate-acrylate-methacrylate formulation (from article 5) is given. As can be seen, the first curing stage was selective towards acrylates. The same selectivity is observed with Michael donors such as acetoacetates. Compared to thiols, the deprotonation of an acetoacetate hydrogen is more difficult. Therefore, an acetoacetate will be left unreacted during reaction of thiols with a given Michael acceptor (See article 2).

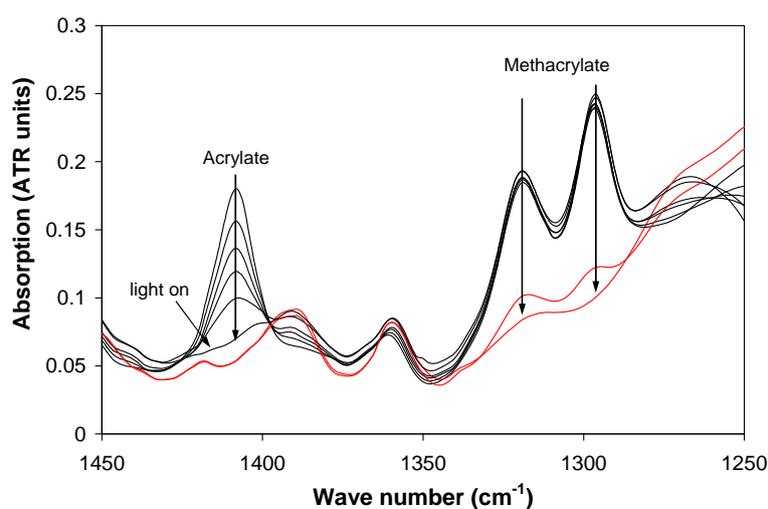


Figure 3.2 FTIR spectra obtained during dual-curing of acetoacetate-acrylate-methacrylate mixture. Black spectra were taken during acetoacetate-acrylate Michael reaction (Stage 1), red spectra were

taken during radical photopolymerization. The unchanging bands around 1300cm^{-1} suggest no methacrylate reaction was observed during stage 1. Figure taken from article 5.

We have prepared tetraphenyl borate salts of certain bases as photobase generators (PBGs) and used them in a number of dual-curing systems. We observed that reaction kinetics are governed not only by the strength of the liberated base, but also by the conditions of photobase activation, such as UV irradiation intensity or duration. We showed that these PBG salts are activated also by heating (See articles 3, 8, and **Figure 3.3**). The use of PBGs gave intermediate materials storage stabilities ranging from several days (article 6) to weeks (articles 2, 3, and 8). In some cases, vitrification of materials also contributed to storage stability (such as in article 8).

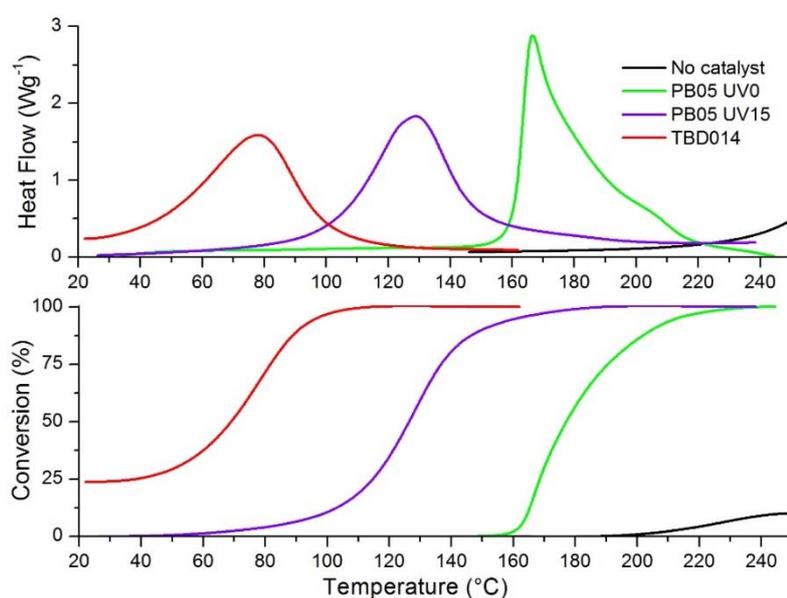


Figure 3.3 DSC conversions of thiol-epoxy reactions catalyzed differently. As can be seen, the reaction onset temperature decreases with the order non-catalyzed < thermally-activated PB < UV-activated PB < neat base (TBD). PB stands for photobase generator. Numbers after catalysts represent weight percentages based on total solids. UV irradiation was continued for 15 min. at an intensity of 36 mW/cm^2 . Figure taken from Article 3.

Material properties greatly varied over curing stages. In general, monomers with higher functionalities and wielding rigid structures (such as aromatic rings) resulted in significantly enhanced mechanical properties. However, in cases where mobility restrictions impeded complete conversions, less bulky and lower functional monomers were used as reactive diluents (such as HEMA in article 5) to ultimately improve viscoelastic properties (not through an increase in crosslink density, but by the introduction of more rigid structures into

the polymer network). Second stage homopolymerizations (of excess monomers) increased final crosslink density and T_g s several-fold. On the other hand, these stages yielded more heterogeneous polymer networks, typical of chain-wise polymerizations (see articles 1, 5, 8, and **Figure 3.4**).

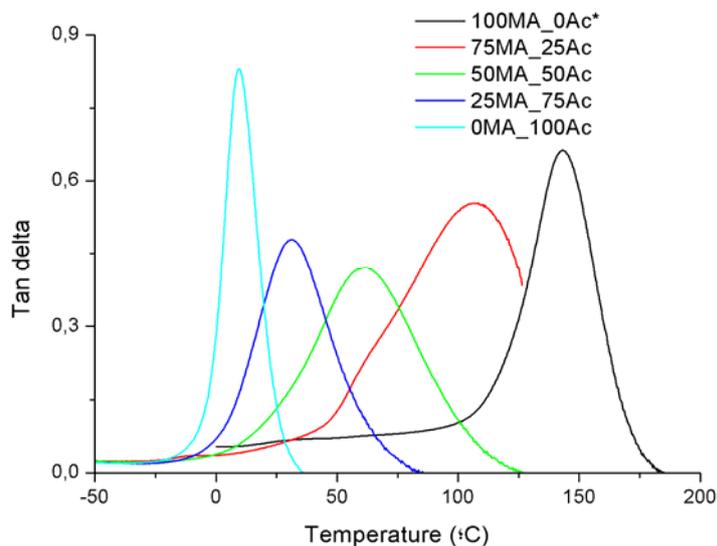


Figure 3.4 Tan delta curves of dual-cured amine-acrylate-methacrylate mixtures. α -relaxation temperatures and breadth of relaxations increase with increasing methacrylate (i.e. Stage 2 homopolymer network) content. Formulations are coded as xMA_yAc where x and y stand for weight percentages of poly(methacrylate) and poly(aminoester) networks, respectively. Broader relaxations of methacrylate-rich materials point to more heterogeneous polymer networks. Figure taken from article 1.

The possibility of catalytic comonomer preparation using click procedures was demonstrated in article 7. As this method provides almost complete freedom over the resulting monomer structures, it amplifies the achievable range of intermediate and final material properties. Furthermore, thiol-Michael reaction could be carried out at very different rates depending on the catalytic species involved. It was observed that the molecular structure of the catalyst (which governs steric hindrance effects on catalytic groups) has a greater influence (rather than catalyst concentration) on the overall reaction kinetics. When less hindered catalytic groups were employed, it was possible to react even methacrylates with thiols through fast Michael additions (See **Figure 3.5**)

As no added catalysts are necessary, high purity products can be obtained for demanding applications such as optical materials, given that the curing stages are of true click nature and no extractable material remains at the end of the process.

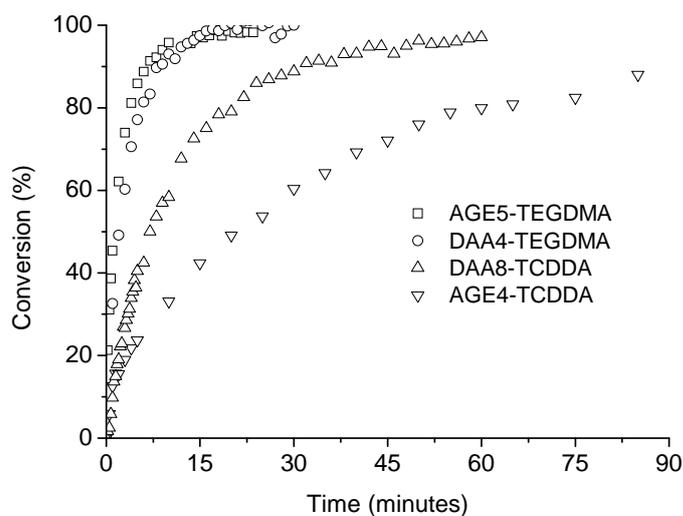


Figure 3.5 Michael reaction kinetics of tricyclo[5.2.1.0^{2,6}]decanedimethanol diacrylate (TCDDA) and triethylene glycol dimethacrylate (TEGDMA) with various allyl functional catalyst/comonomers. As catalyst/comonomers AGE5 and DAA4 wielded less sterically hindered tertiary amine groups (see article 7), they could react even with methacrylates at remarkably fast rates.

Interestingly, even though some procedures did not fit the “click” criteria exhaustively, no extractables were present in final materials (see article 1). This shows the robustness of dual-curing procedures: A click stage at some point during the process might offset some stages that are non-click, *per se*. The materials developed can be used in diverse applications ranging from soft coatings for delicate substrates (e.g. Article 7) and adhesives (e.g. non-gelled intermediate materials in Article 8), to rigid shape-memory materials (e.g. gelled intermediate materials in Article 8). A shape-memory material based on an off-stoichiometric epoxy-amine formulation is shown in **Figure 3.6**. The next logical step would be a more detailed characterization of these materials with regards to specific application scenarios. Such an effort would surely increase the likelihood of commercialization of these promising formulations.

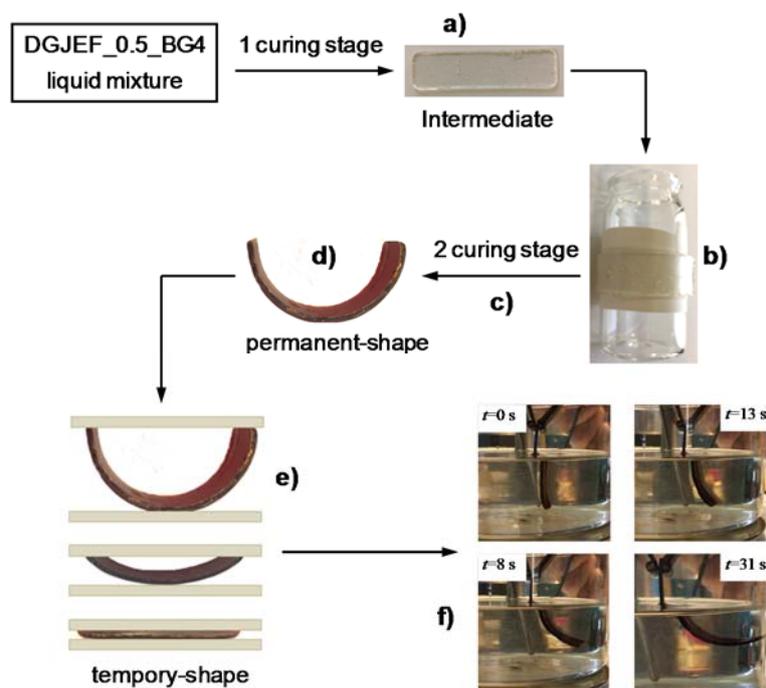


Figure 3.6 Preparation and testing of a shape memory polymer. The first stage amine-epoxy click reaction yields a conformable intermediate material (a). The rounded shape is fixed after homopolymerization of epoxy groups which were in excess in the original formulation (b-c-d). The temporary shape can be programmed by heating up to $T > T_g$, holding the shape, then cooling down to $T < T_g$ (e). Once heated above T_g , original shape is recovered (f). Figure taken from article 8.

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Articles published during the Ph.D. work

Article 1: Sequential curing of amine-acrylate-methacrylate mixtures based on selective aza-Michael addition followed by radical photopolymerization

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Article 2: Sequential Curing of Thiol-Acetoacetate-Acrylate Thermosets by latent Michael Addition Reactions

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Article 3: Latent curing of epoxy-thiol thermosets

Ali Osman Konuray*, Xavier Fernández-Francos, Xavier Ramis

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Article 4: Analysis of the reaction mechanism of the thiol–epoxy addition initiated by nucleophilic tertiary amines

Ali Osman Konuray, Xavier Fernández-Francos* and Xavier Ramis

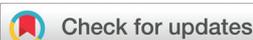
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Analysis of the reaction mechanism of the thiol–epoxy addition initiated by nucleophilic tertiary amines

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A kinetic model for thiol–epoxy crosslinking initiated by tertiary amines has been proposed. The kinetic model is based on mechanistic considerations and it features the effect of the initiator, hydroxyl content, and thiol–epoxy ratios. The results of the kinetic model have been compared with data from the curing of off-stoichiometric formulations of diglycidyl ether of bisphenol A (DGEBA) crosslinked with trimethylolpropane tris(3-mercaptopropionate) (S3) using 1-methylimidazole (1MI) as the initiator. The model has been validated by fitting the kinetic parameters to the experimental data under a variety of reaction conditions. In spite of the experimental uncertainty and model assumptions, the main features of the curing kinetics are correctly described and the reaction rates are quantitatively reproduced.

1 Introduction

Base-catalyzed thiol–epoxy polymerization is of industrial relevance in the area of adhesives, high performance coatings and composites.¹ A remarkable feature of thiol–epoxy condensation is that it can be categorized as a click reaction, which means that it is selective, leaves no by-products and it takes place quantitatively and under mild reactive conditions. Thus, it is possible to use it not only in conventional reactive formulations but also in dual-curable systems with a controlled curing sequence such as thiol–ene/thiol–epoxy,^{2–5} off-stoichiometric thiol–epoxy systems,⁶ or even in combination with inorganic network precursors in hybrid systems.⁷ Thiol–epoxy thermosets are highly transparent, which is favorable for their application as clearcoats⁸ and generally highly flexible,⁹ but this latter feature is also a drawback because their low T_g can limit their use in more temperature-demanding applications.¹⁰ In order to enhance the thermal–mechanical characteristics of thiol–epoxy, different strategies can be adopted, such as the use of more rigid and functional epoxy resins¹⁰ and the development of novel highly-functional thiol crosslinkers¹¹ in stoichiometric thiol–epoxy systems, or the use of excess epoxy in off-stoichiometric thiol–epoxy systems.⁶ Another severe drawback is the fact that the most commonly used catalysts for the thiol–epoxy addition, namely, basic tertiary amines are not latent and therefore, it makes difficult the handling and

control of the processing of thiol–epoxy formulations once prepared.^{2,9} Therefore, research efforts are directed towards the exploration of catalytic systems with thermal latency⁹ or the development of photolabile bases.^{7,8,12,13} Remarkably, some of these photolabile bases have been shown to be activated by both UV-light and temperature,¹⁴ which turns them into highly versatile catalytic systems. Another interesting research line is the use of tertiary amines with poor basicity but with nucleophilic characteristics^{6,15} that are not latent but with sufficiently slow activation and a strong auto-accelerating effect so as to permit safe formulation preparation and manipulation as well as complete curing at low temperature in short times.

The curing mechanism of the base-catalyzed thiol–epoxy condensation is assumed to be a simple nucleophilic addition between thiolate and epoxy groups.² In the presence of sufficiently strong bases, an acid–base proton exchange leads to the deprotonation of the thiol, producing a thiolate anion that is nucleophilic enough to attack the epoxy ring. The thiol–epoxy reaction is strongly autocatalytic due to the formation of hydroxyl groups that facilitate the ring-opening of the epoxy group.¹⁶ The reaction mechanism can become more complex in the presence of nucleophilic tertiary amine catalysts, such as benzyldimethylamine (BDMA) and 1-methylimidazole (1MI), which lead to a very slow initiation process followed by a strong autoacceleration up to the completion of the curing process.^{6,15} Loureiro *et al.* proposed a reaction mechanism to describe the curing kinetics of thiol–epoxy addition catalyzed by a tertiary amine, BDMA with poor basicity but a nucleophilic characteristic.¹⁵ In a recent study, we have described the dual-curing process of off-stoichiometric thiol–epoxy formu-

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lations containing excess epoxy groups.⁶ We observed that the thiol–epoxy reaction took place very quickly and with a sharp autocatalytic profile, followed at higher temperatures or longer curing times by a slower epoxy homopolymerization process. Although some of these kinetic features can be interpreted in terms of the proposed reaction mechanism,¹⁵ it should be modified in order to take into account properly the effect of initiation/termination reactions and the effect of the decreasing thiol group content.

The aim of this paper is to develop a consistent kinetic model, based on the consideration of the reaction mechanism, capable of capturing the kinetic behaviour during the curing of stoichiometric thiol–epoxy formulations and the first stage of the curing of off-stoichiometric thiol–epoxy formulations. The effect of the thiol–epoxy ratio and the catalyst content will be taken into consideration. The model will be validated experimentally using kinetic data obtained using differential scanning calorimetry.

2 Theoretical

A reaction scheme based on the model of Loureiro *et al.*¹⁵ is shown in Scheme 1, using 1MI as the initiator. In that work, the authors analyzed the curing process of stoichiometric thiol–epoxy formulations using a mechanism-based kinetic model and obtained a reasonable fitting under a wide range of temperatures, catalyst concentrations and curing histories. The active propagating species, the thiolate anion, was produced after nucleophilic addition of BDMA to the epoxy ring and subsequent proton exchange with a thiol group. The effect of the added catalytic hydroxyl groups on the reaction was also analyzed, but it was found that their effect was less important than that of the generated hydroxyl groups by the thiol–epoxy addition. The authors included the effect of termination reactions^{2,15} and used it to determine the amount of thiolate anions under pseudo-steady state conditions. However, this

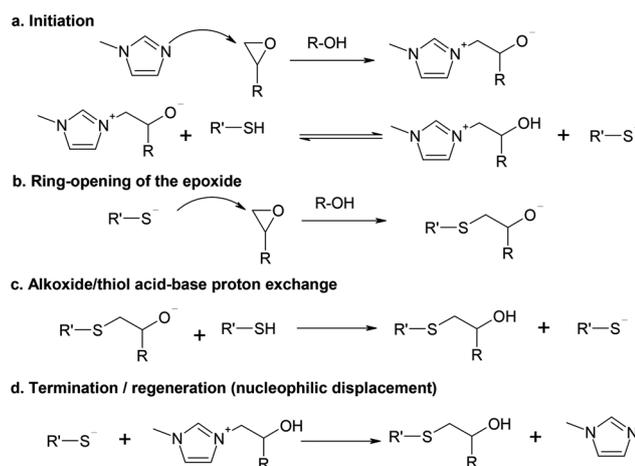
was an important shortcoming of their model because, eventually, the active thiolate species should be controlled by the available thiol in the reaction medium, not by the amount of epoxy and reaction products. In the work of Jin *et al.*¹⁶ one can also see that the catalytic effect of the added hydroxyl groups (*i.e.* coming from the epoxy oligomer itself) is less relevant than the autocatalytic effect of the hydroxyl groups generated in the course of the reaction.

In the general reaction scheme we propose that the initiation takes place by the nucleophilic attack of 1MI to the epoxy ring (Scheme 1a), leading to the formation of a zwitterion. Contrary to what is stated for common tertiary amines,¹⁷ the formation of epoxy–imidazole adducts, including zwitterionic species was convincingly argued by Heise and Martin.^{18,19} Indeed, epoxy–imidazole adducts are used as curing agents.²⁰ The nucleophilic addition of imidazoles to epoxy groups is catalyzed by proton donors,²¹ in a similar way to common epoxy–amine systems¹⁷ and nucleophilic addition to epoxy groups in general. This was also suggested by the autocatalytic character of the adduct formation between 2,4-unsubstituted imidazoles and epoxides.^{18,19} In fact, Rozenberg showed that the epoxy homopolymerization could not be initiated by tertiary amines in the absence of proton donors or other catalytic impurities.¹⁷

In the presence of thiol groups, a proton exchange would take place leading to the formation of a thiolate anion and a β -hydroxyimidazolium cation.¹⁵ The pK of the alcohol–alkoxide equilibrium is much higher than that of the thiol–thiolate equilibrium, and therefore, this exchange should be non-reversible from a practical point of view. However, the pK of the zwitterion system should be lower than that of a common alkoxide due to the stabilization caused by the electron withdrawing effect of the ammonium substituent and possible resonance within the imidazolium ring, in a similar way to the pK of the carboxylic acid proton in amino-acids. Nevertheless, depending on the relative acidity/basicity of the different species, this exchange might be considered almost non-reversible as well. Note that this β -hydroxyimidazolium cation should also have a catalytic effect on the nucleophilic addition to epoxy groups in the presence of both a positive charge and a hydroxyl group.

When the thiolate attack to the epoxy ring takes place (Scheme 1b), an alkoxide anion would be formed, but then fast proton transfer would take place from either a thiol group (Scheme 1c) or the β -hydroxyimidazolium cation, both with a lower pK than an alkoxide, to produce a β -hydroxythioether, the reaction product. The thiol/zwitterion equilibrium should lead to the formation of a thiolate anion that would propagate the reaction. The thiolate addition is also catalyzed by proton donors such as hydroxyl groups, resulting in a strongly autocatalyzed polymerization, as illustrated by Jin *et al.*¹⁶ This autocatalysis is explained by the fact that thiol groups have a negligible effect on proton donors²² and the reaction medium evolves from a thiol-rich environment to a hydroxyl-rich environment.

As the reaction proceeds, the increasing number of initiating species would also lead to an increasing rate of nucleo-



Scheme 1 Reaction mechanism of the thiol–epoxy reaction initiated by 1MI.

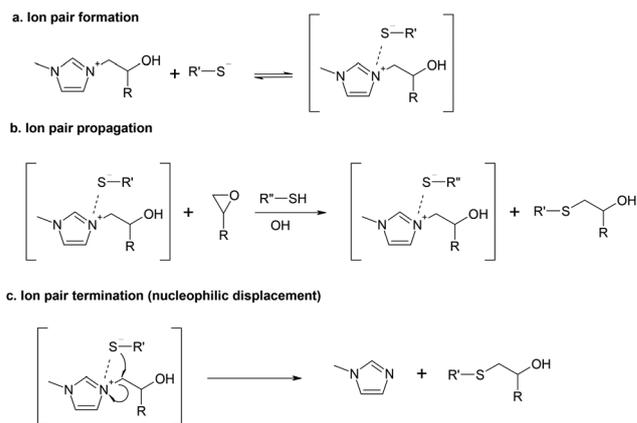


philic displacement of the initiator and regeneration (Scheme 1d). Thiolate anions are highly nucleophilic²³ and far less basic than alkoxide anions, and therefore, initiator regeneration by β -elimination as observed for the anionic homopolymerization of epoxides^{21,24,25} would not occur.

According to Scheme 1a, when thiol groups are depleted, the equilibrium would shift to the zwitterion form rather than to the thiolate form. If the equilibrium constant is high enough, this equilibrium would shift in a rather abrupt manner, thereby explaining the observed sharp decrease in the reaction rate upon reaching a complete thiol conversion in the off-stoichiometric thiol–epoxy formulations.⁶ In the absence of thiol groups, the initiation would continue in the presence of the remaining epoxy groups but it would produce only the zwitterionic active species. It should also be noted that, because this zwitterion should be less reactive than a common alkoxide, propagation of the epoxy homopolymerization would not take place just at the end of the thiol–epoxy addition, or else at a very slow rate in comparison.⁶ This is also supported by the previous results of Heise and Martin, reported on their study of epoxy systems catalyzed by imidazoles,^{18,19} who observed a clear separation between the epoxy-adduct formation and the epoxy homopolymerization, and stated that the adduct species formed was “dormant” before homopolymerization of the excess of epoxy groups started.

Some more mechanistic considerations can be made if we analyze a similar polymerization process, the nucleophile-catalyzed phenol–epoxy polymerization. The overall reaction mechanism^{23,26–29} is similar to that shown in Scheme 1. It is of particular relevance to the fact that, in off-stoichiometric phenol–epoxy formulations, the phenol–epoxy reaction takes place first, and once phenol groups are exhausted, homopolymerization of excess epoxy groups can take place,²³ like in thiol–epoxy systems.⁶ However, a fundamental difference is that the phenol–epoxy reaction is much slower due to the stability and lower nucleophilicity of the phenolate anion, making the separation between phenol–epoxy and epoxy homopolymerization less clear.^{23,26,28} In addition, the phenol–epoxy reaction is not generally autocatalytic (or only moderate due to the slow nucleophilic initiation step), and the reaction mechanism is usually analyzed in terms of the formation of stable ion pairs between the phenoxide and a mobile counterion that propagates the reaction.^{26–29}

Based on the above considerations, we wondered whether the formation of ion pairs is relevant in nucleophile-catalyzed thiol–epoxy reactions. We propose that some more reactions could be added to those already shown in Scheme 1. To begin with, Scheme 2a shows the hypothetical formation of an ion pair between the β -hydroxyimidazolium and the thiolate. We have illustrated this as an equilibrium because it is acknowledged that the formation and the activity of ion pairs are largely dependent on the possible solvent-ion and solvent-ion pair interactions and the ion concentration,³⁰ and the surrounding environment, with nucleophilic and electrophilic sites, should allow for the presence of “naked” or, rather, non-ion pair forming ions. The propagation of the reaction by this



Scheme 2 Alternative mechanism steps occurring in the thiol–epoxy reaction initiated by 1M1.

ion pair is illustrated in Scheme 2b, although it is unclear whether this nucleophilic addition should take place on epoxy rings activated by proton donors, like nucleophilic amine–epoxy addition, or else an internal activation with the β -hydroxyimidazolium cation takes place, in line with the mechanism proposed for amine-catalyzed phenol–epoxy reactions.²⁹ Finally, Scheme 2c shows a possible termination reaction by nucleophilic displacement within the ion pair.

The reactivity of ion pairs is complex but it is acknowledged that, in many cases, the presence of ion pairs decreases significantly the rate of ionic polymerization in comparison with free ion systems.³⁰ Rozenberg showed that alkali ions played a complex role in the anionic polymerization of epoxides.¹⁷ On the one hand, they could have a positive effect in the activation of the epoxy ring, like proton donors. However, their interaction with propagating alkoxide ions leading to the formation of ion pairs would decrease the propagation rate in comparison with the free alkoxide ions, an effect that was more relevant with increasing size of the alkali ion.¹⁷ Ooi *et al.*²⁴ tested the effect of tetramethyl ammonium chloride (TMAC) on the anionic homopolymerization of epoxides initiated by imidazoles,²⁴ but no effect on the reaction rate could be observed. Given the above considerations,^{17,30} the propagation of the reaction by this ion pair is supposed to be considerably slower than by the free thiolate anions, and therefore, it might be ruled out from a practical point of view.

The occurrence of the termination reaction proposed in Scheme 2c looks reasonable given the high nucleophilicity of the thiolate anion and the close presence of an electrophilic site within the ion pair, leading to the β -hydroxythioether reaction product and a regenerated imidazole. This reaction, from a kinetic point of view, would be unimolecular, in a similar way to what has been proposed for tertiary amine regeneration in other studies.^{31–34} In addition, if ion pairs are present in a significant amount in the course of the reaction, this termination mechanism would be presumably more frequent than the bimolecular termination reaction between free ions proposed in Scheme 1d.¹⁵



Taking into account all these considerations, different reaction mechanisms based on the reactions shown in Schemes 1 and 2 will be elaborated and their validity will be analyzed by considering their ability to reproduce the experimental results.

3 Materials and methods

3.1 Materials

Diglycidyl ether of bisphenol A (DGEBA) with an epoxy equivalent weight of 172–176 g per eq. (Aldrich), 184–190 g per eq. (Hexion) and 190–210 g per eq. (Huntsman) were dried at 80 °C under vacuum for 2 hours and stored in a desiccator prior to use. These three resins have been coded as DG174, DG187 and DG200, respectively, where the numbers indicate the assumed equivalent weight of the epoxy resin. Trimethylolpropane tris(3-mercaptopropionate) (S3) and 1-methylimidazole (1MI) from Sigma Aldrich were used as received.

A set of mixtures using DG174 as an epoxy resin and with different ratios r of thiol groups with respect to epoxy groups were prepared, adding 1 phr (parts per hundred of the total mixture) of 1MI with respect to the total mixture as catalyst. A different set of stoichiometric thiol–epoxy mixtures using DG174 was prepared, adding different proportions of 1MI. Finally, stoichiometric samples with 1 phr of 1MI and changing the epoxy resin were also prepared. The samples were quickly stirred using a spatula and analyzed immediately. Table 1 shows the compositions of the different formulations. The formulations have been coded as DGyyy- r - x where yyy is the epoxy equivalent weight of the epoxy resin, r is the thiol : epoxy equivalent ratio and x is the 1MI added in phr. It should be mentioned that the thiol equivalent weight was assumed to be the theoretical value of 132.85 g per eq. for the calculation of the composition, although the supplier reports a purity of 98% for this product.

3.2 Characterization techniques

A differential scanning calorimeter Mettler DSC821e calibrated with indium standards was used to study the isothermal

curing of the different formulations at 60 °C. Samples of ca. 5–10 mg were placed inside an aluminum pan with a pierced lid and were inserted into a preheated oven before analysis, under a nitrogen atmosphere.

The calorimetric degree of conversion was determined as $x = \Delta h / \Delta h_{\text{total}}$, where Δh is the reaction heat released up to a time t and Δh_{total} is the total reaction heat evolved. The calorimetric reaction rate was determined as $dx/dt = (dh/dt) / \Delta h_{\text{total}}$, where dh/dt is the heat flow. Taking into account the thiol–epoxy ratio r of the different formulations, an approximate conversion of epoxy groups, $x_{\text{e,DSC}}$, was calculated from the experimental DSC data as:

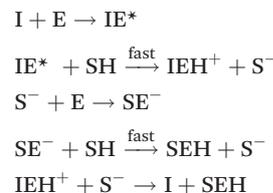
$$\begin{aligned} x_{\text{e,DSC}} &\approx r \cdot x & r < 1 \\ x_{\text{e,DSC}} &\approx x & r \geq 1 \end{aligned}$$

A rate of conversion of epoxy groups $dx_{\text{e,DSC}}/dt$ could also be estimated from the calorimetric data as:

$$\begin{aligned} \frac{dx_{\text{e,DSC}}}{dt} &\approx r \cdot \frac{dx}{dt} & r < 1 \\ \frac{dx_{\text{e,DSC}}}{dt} &\approx \frac{dx}{dt} & r \geq 1 \end{aligned}$$

3.3 Kinetic modelling

Basic model. Following the work of Loureiro *et al.*,¹⁵ a basic set of reactions based on the reaction mechanism in Scheme 1 has been defined:



where I is the initiator, E is the epoxy ring, IE* is the zwitterion formed after initiation, SH is a thiol group, IEH⁺ is the hydroxyl-ammonium cationic species formed by proton transfer from the thiol group, S[−] is the propagating thiolate anion, SE[−] is the alkoxide formed after thiolate addition, and SEH is the reaction product of the thiol–epoxy addition.

Table 1 Notation and composition of the formulations studied in this work, in weight fraction (wt%). The calculation of the initial concentration of epoxy groups (ee per kg), and hydroxyl groups coming from DGEBA (eqOH_{DG} per kg), the amount of initiator groups per epoxy equivalent (eq1MI per ee), and the thiol : epoxy molar ratio (r) is also included

Formulation	r	wt% 1MI	wt% DGEBA	wt% S3	ee per kg	eqOH _{DG} per kg	eq1MI per ee
DG174-1-1	1	0.99	56.18	42.83	3.227	0.0454	0.0375
DG174-0.75-1	0.75	0.99	62.99	36.02	3.618	0.0510	0.0334
DG174-0.5-1	0.5	0.99	71.68	27.33	4.118	0.0580	0.0293
DG174-0.25-1	0.25	0.99	83.16	15.85	4.778	0.0673	0.0253
DG174-1.33-1	1.33	0.99	49.06	49.95	2.820	0.0397	0.0428
DG174-2-1	2	0.99	39.21	59.80	2.252	0.0317	0.0536
DG174-4-1	4	0.99	24.42	74.59	1.404	0.0198	0.0860
DG174-1-0.5	1	0.50	56.45	43.05	3.243	0.0457	0.0187
DG174-1-2	1	1.96	55.63	42.41	3.195	0.0450	0.0748
DG174-1-4	1	3.85	54.55	41.60	3.134	0.0441	0.1497
DG187-1-1	1	0.99	57.89	41.12	3.095	0.1853	0.0390
DG200-1-1	1	0.99	59.49	39.52	2.975	0.3142	0.0406



The initiation step leading to the formation of the zwitterion IE^* and the thiolate addition to the epoxy ring can be catalyzed by proton donors, such as hydroxyl groups already present or formed in the course of the reaction.^{16,21}

Loureiro *et al.* modelled this catalytic effect by assuming the formation of an epoxy–hydroxyl equilibrium complex prior to the nucleophilic addition,¹⁵ following other studies.^{35,36} The effect of equilibrium complexes is a common issue in reacting systems such as epoxy–amine.^{17,37–40} However, hydroxyl-catalyzed nucleophilic addition of amines to epoxy groups is commonly modelled in a more simplified way by not considering the presence of such complexes: a trimolecular reaction between epoxy, amine and the catalytic hydroxyl group is assumed instead.^{41,42} Jin *et al.* modelled the base-catalyzed curing of thiol–epoxy formulations using phenomenological models and interpreted the fitted parameters quite convincingly assuming a simplified version of the catalyzed nucleophilic addition,¹⁶ like in epoxy–amine systems. This interpretation should be safe if the epoxy–hydroxyl equilibrium constant was low enough, leading to a reduced error.³⁶ However, in the present case the system is more complex since we have performed nucleophilic addition of both the initiator and the thiolate to the epoxy groups. The presence of catalytic impurities in the reagents as well as the absorption of some humidity from the environment during preparation could make it difficult to identify all the possible intermediate complexes. In such situations, the effect of impurities is taken into consideration in a simplified manner.¹⁷ Therefore, for the sake of simplicity, in the present model we assume that this somewhat inaccurate representation of the catalytic effect of hydroxyl groups provides a reasonable description of the effect.

Therefore, the basic reaction mechanism can be represented as follows in terms of rate equations (basic kinetic model):

$$\begin{aligned} \frac{d[\text{I}]}{dt} &= -k_i \cdot [\text{I}] \cdot [\text{E}] + k_t \cdot [\text{S}^-] \cdot [\text{IEH}^+] \\ \frac{d[\text{IE}]_{\text{total}}}{dt} &= -\frac{d[\text{I}]}{dt} \\ \frac{d[\text{E}]}{dt} &= -k_i \cdot [\text{I}] \cdot [\text{E}] - k_p \cdot [\text{S}^-] \cdot [\text{E}] \\ \frac{d[\text{SH}]_{\text{total}}}{dt} &= -k_p \cdot [\text{S}^-] \cdot [\text{E}] - k_t \cdot [\text{S}^-] \cdot [\text{IEH}^+] \\ \frac{d[\text{SEH}]}{dt} &= -\frac{d[\text{SH}]_{\text{total}}}{dt} \end{aligned}$$

Note that the total number of thiol/thiolate species is defined as $[\text{SH}]_{\text{total}} = [\text{SH}] + [\text{S}^-]$ and that the total amount of potentially active species is defined as $[\text{IE}]_{\text{total}} = [\text{IE}^*] + [\text{IEH}^+]$. In the course of the reaction, while $[\text{SH}]_{\text{total}} > [\text{IE}]_{\text{total}}$, the number of active propagating species is $[\text{S}^-] = [\text{IEH}^+] = [\text{IE}]_{\text{total}}$, and $[\text{IE}^*] \approx 0$. However, when the reaction reaches completion, it may be that $[\text{SH}]_{\text{total}} < [\text{IE}]_{\text{total}}$, so that $[\text{S}^-] = [\text{IEH}^+] = [\text{SH}]_{\text{total}}$ and $[\text{IE}^*] = [\text{IE}]_{\text{total}} - [\text{SH}]_{\text{total}}$.

In order to take into account the effect of the catalytic groups already coming from the reagents or hypothetical

impurities, as well as the formed hydroxyl groups by reaction, we have defined the initiation and propagation constants, k_i and k_p , as follows:

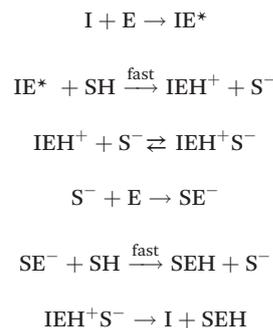
$$k_i = k_{i,\text{DG}} \cdot [\text{OH}]_{\text{DG}} + k_{i,\text{SH}} \cdot [\text{SH}]_0 + k_{i,\text{cat}} \cdot ([\text{SEH}] + [\text{IEH}^+])$$

$$k_p = k_{p,\text{DG}} \cdot [\text{OH}]_{\text{DG}} + k_{p,\text{SH}} \cdot [\text{SH}]_0 + k_{p,\text{cat}} \cdot ([\text{SEH}] + [\text{IEH}^+])$$

The different contributions to the initiation constant come from the presence of hydroxyl groups in the oligomeric structure of DGEBA, $[\text{OH}]_{\text{DG}}$, impurities contained in the thiol crosslinking agent that are assumed to be proportional to the initial concentration of thiol groups $[\text{SH}]_0$, and catalytic species formed in the course of the reaction, $[\text{SEH}] + [\text{IEH}^+]$. The contribution of the hydroxyl–thioether and the hydroxyl–ammonium cation should be different but, for the sake of simplicity, we have grouped them together.

It is quite common to model reaction kinetics using normalized concentrations rather than real concentrations,^{34,42} so that the normalized concentration of a species A can be calculated with respect to the initial concentration of epoxy groups, so that $a = [\text{A}]/[\text{E}]_0$. This makes it possible to define a set of kinetic reactions in terms of the normalized species, but the kinetic constants need to be redefined.^{34,42} The details of such transformations are shown in the Appendix.

Complex model. A complex kinetic model has also been defined on the basis of the additional mechanistic considerations in the presence of ion-pairs discussed in the preceding section, wherein the formation of an ion-pair is considered as shown in Scheme 2a. It is hypothesized that this ion-pair would not propagate the reaction (it should have a considerably lower reaction rate than free thiolate ions), so that that reaction shown in Scheme 2b is not included in the model. It is assumed that the termination reaction by an internal rearrangement of the ion-pair as shown in Scheme 2c takes place. For the sake of simplicity, the termination by the bimolecular mechanism shown in Scheme 1d is not taken into consideration. This kinetic model is represented by the following set of reactions:



where IEH^+S^- is the thiolate–hydroxylammonium complex ion-pair. Note that, from the kinetics point of view, the termination reaction should be regarded as a uni-molecular reaction. This reaction mechanism is represented by the following set of rate equations and an equilibrium:

$$\frac{d[\text{I}]}{dt} = -k_i \cdot [\text{I}] \cdot [\text{E}] + k_{t,\text{IP}} \cdot [\text{IEH}^+\text{S}^-]$$



$$\frac{d[\text{IE}]_{\text{total}}}{dt} = -\frac{d[\text{I}]}{dt}$$

$$\frac{d[\text{E}]}{dt} = -k_i \cdot [\text{I}] \cdot [\text{E}] - k_p \cdot [\text{S}^-] \cdot [\text{E}]$$

$$\frac{d[\text{SH}]_{\text{total}}}{dt} = -k_p \cdot [\text{S}^-] \cdot [\text{E}] - k_{t,\text{IP}} \cdot [\text{IEH}^+\text{S}^-]$$

$$\frac{d[\text{SEH}]}{dt} = -\frac{d[\text{SH}]_{\text{total}}}{dt}$$

$$k_{\text{eq,IP}} = \frac{[\text{IEH}^+\text{S}^-]}{[\text{S}^-] \cdot [\text{IEH}^+]}$$

In this set of reactions, we define:

$$[\text{IE}]_{\text{total}} = [\text{IE}^*] + [\text{IEH}^+] + [\text{IEH}^+\text{S}^-]$$

$$[\text{SH}]_{\text{total}} = [\text{SH}] + [\text{S}^-]_{\text{total}} = [\text{SH}] + [\text{S}^-] + [\text{IEH}^+\text{S}^-]$$

Also, one should consider that:

$$[\text{S}^-]_{\text{total}} = [\text{S}^-] + [\text{IEH}^+\text{S}^-] = [\text{IEH}^+] + [\text{IEH}^+\text{S}^-]$$

In the course of the reaction, while $[\text{SH}]_{\text{total}} > [\text{IE}]_{\text{total}}$, the number of active propagating species is $[\text{S}^-]_{\text{total}} = [\text{IE}]_{\text{total}}$ with $[\text{IE}^*] = 0$. When the reaction reaches completion, it may be that $[\text{SH}]_{\text{total}} < [\text{IE}]_{\text{total}}$, so that $[\text{S}^-]_{\text{total}} = [\text{SH}]_{\text{total}}$ and $[\text{IE}^*] = [\text{IE}]_{\text{total}} - [\text{SH}]_{\text{total}}$. The real amount of propagating thiolate and ion-pair species, $[\text{S}^-]$ and $[\text{IEH}^+\text{S}^-]$, are found by solving the equilibrium in any case.

In order to take into account the catalytic effect of the different species on the initiation and propagation rates, the initiation and propagation constants are defined exactly the same way as before. As in the previous model, the reaction kinetics is also analyzed making use of normalized concentrations of the different species (see Appendix).

Model-fitting of experimental data. The conversion of epoxy groups x_e can be defined as:

$$x_e = 1 - e$$

where e is the normalized concentration of epoxy groups (see the Appendix) and can take a value from 1 (no epoxy groups reacted) to 0 (completely reacted). Assuming that the heat evolved by the ring-opening of the epoxy group is similar in both the initiation and propagation, and in order to make comparison with experimental DSC results meaningful, one can calculate $x_{e,\text{DSC}}$ from the results of the kinetic model as:

$$x_{e,\text{DSC}} \approx r \cdot \frac{x_e}{x_{e,\text{max}}} \quad r < 1$$

$$x_{e,\text{DSC}} \approx \frac{x_e}{x_{e,\text{max}}} \quad r \geq 1$$

where $x_{e,\text{max}}$ is the maximum epoxy conversion calculated by the kinetic model. The rate $dx_{e,\text{DSC}}/dt$ can also be determined from the results of the kinetic model as:

$$\frac{dx_{e,\text{DSC}}}{dt} \approx r \cdot \frac{-de/dt}{x_{e,\text{max}}} \quad r < 1$$

$$\frac{dx_{e,\text{DSC}}}{dt} \approx \frac{-de/dt}{x_{e,\text{max}}} \quad r \geq 1$$

where de/dt is the normalized reaction rate of epoxy groups (see the Appendix).

The integration is performed simultaneously for all the compositions indicated in Table 1 and the kinetic constants and equilibrium constants, $k_{i,\text{DG}}$, $k_{i,\text{SH}}$, $k_{i,\text{cat}}$, $k_{p,\text{DG}}$, $k_{p,\text{SH}}$, $k_{p,\text{cat}}$, k_t , $k_{\text{eq,IP}}$ and $k_{t,\text{IP}}$ are fitted using a nonlinear regression procedure with the following minimization function:

$$\text{error} = \sum_i \sum_{x_{e,\text{DSC}}} |t_{x,i,\text{exp}} - t_{x,i,\text{mod}}|$$

where $t_{x,i,\text{exp}}$ is the experimental time and $t_{x,i,\text{mod}}$ is the time predicted by the kinetic model, for each experiment i , and at certain degrees of conversion $x_{e,\text{DSC}}$. The whole conversion curves are integrated in each iteration step, using a 4th order Runge–Kutta method. Approximate starting values for the different constants have been set by trial and error and visual comparison with experimental curves. The built-in GRG non-linear solver in the ExcelTM software has been used to fit the parameters.

4 Results and discussion

4.1 Experimental results

Fig. 1 shows the experimental rate curves that were obtained from the isothermal curing at 60 °C for all the formulations. If one compares these results with those reported by Jin *et al.*,¹⁶ some relevant differences between commonly used basic catalysts and nucleophilic catalysts can be highlighted. In base-

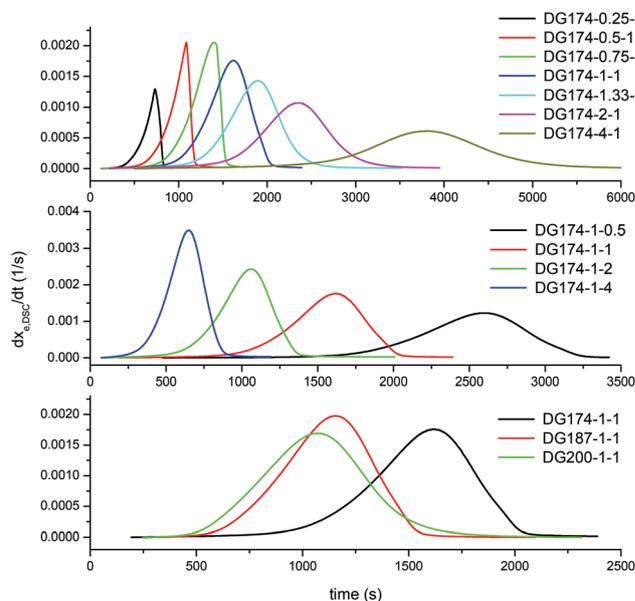


Fig. 1 Experimental rate curves illustrating the effect of the thiol-epoxy ratio (top graph), initiator content (middle graph) and epoxy equivalent weight (bottom graph).



catalyzed thiol–epoxy reactions, the reaction starts immediately after the reagents are mixed and, because of the strong autocatalysis of the reaction, it can become difficult to control. Note that in a recent study by Jin *et al.*¹⁶ the authors used DBU as the base catalyst in a concentration of just 0.17% with respect to the concentration of thiol groups. In contrast, Fig. 1 shows that the reaction onset is delayed using a nucleophilic initiator such as 1MI, as observed in the studies of Loureiro *et al.*¹⁵ and our recent study on dual-curable off-stoichiometric thiol–epoxy formulations.⁶ This may not be regarded as a truly latent behavior, but nevertheless it suggests it is safer to prepare and control their curing process using nucleophilic initiators rather than basic catalysts, which could be highly useful in terms of processing. This is a similar phenomenon to what has been reported for Michael addition reactions using specific nucleophilic catalysts.^{43,44}

A closer examination of Fig. 1 reveals a number of significant features of nucleophile-initiated thiol–epoxy reactions. In the top graph, the effect of the thiol–epoxy ratio r is illustrated. At lower thiol–epoxy ratios, the curve starts earlier because of the increasing concentration of epoxy groups and a subsequent enhancement in the rate of the initiation step, consisting of the nucleophilic addition of 1MI to the epoxy ring. An additional accelerating effect coming from the increasing concentration of the initial catalytic hydroxyl groups present in the formulation (see Table 1) is also expected. The formulations with thiol–epoxy ratios lower than 1 also show a strong autoacceleration just before a sharp decrease in the reaction rate that coincides with the exhaustion of the available thiol groups, in agreement with previously reported data.⁶ The formulations with a thiol–epoxy ratio higher than one show a slower activation and reaction rate due to the decrease in the concentration of the available epoxy groups and catalytic hydroxyl groups coming from the structure of DG174 (see Table 1). In all the formulations with $r < 1$, at the end of the reaction there remain unreacted epoxy groups, while at $r \geq 1$, a complete conversion of epoxy groups is achieved.

In the middle graph, the effect of the initiator content is shown for stoichiometric formulations using DG174 as epoxy resin. As expected, there is a clear trend of the decreasing reaction onset and increasing reaction rate with increasing initiator content. However, the effect is not apparently proportional to the initiator content (see Table 1). The bottom graph shows the effect of increasing the epoxy equivalent weight of the DGEBA and, with this, the content in catalytic hydroxyl groups coming from the oligomeric structure of DGEBA. The effect is apparently complex. It can be observed that increasing the epoxy equivalent weight leads to an earlier initiation of the reaction in spite of the decreasing concentration of epoxy groups in the formulation, because of the increasing concentration of oligomeric hydroxyl groups (see Table 1). The difference between the formulations containing DG187 and DG200 is not very significant, possibly because of this trade-off.

All these observations illustrate the complexity of the nucleophile-initiated thiol–epoxy addition. The basic and complex models, based on mechanistic considerations, are tested and their validity is discussed.

Table 2 Kinetic constants and error obtained after fitting of the experimental data to the different models

	Basic	Complex
$k_{i,DG}$ ($M^{-2} s^{-1}$)	5.725×10^{-4}	5.460×10^{-4}
$k_{i,SH}$ ($M^{-2} s^{-1}$)	1.729×10^{-6}	1.608×10^{-6}
$k_{i,cat}$ ($M^{-2} s^{-1}$)	1.962×10^{-3}	3.652×10^{-3}
$k_{p,DG}$ ($M^{-2} s^{-1}$)	3.712×10^{-4}	9.462×10^{-4}
$k_{p,SH}$ ($M^{-2} s^{-1}$)	7.727×10^{-5}	7.272×10^{-6}
$k_{p,cat}$ ($M^{-2} s^{-1}$)	2.386×10^{-2}	3.200×10^{-2}
k_t ($M^{-1} s^{-1}$)	3.712×10^{-2}	0
$k_{c,q,IP}$ (M^{-1})	0	13.41
$k_{t,IP}$ (s^{-1})	0	8.950×10^{-3}
Error (s)	60.5	50.2

4.2 Analysis of the kinetic models

First of all, we analyze the validity of the basic kinetic model inspired by the mechanism proposed by Loureiro *et al.*¹⁵ The fitted parameters are shown in Table 2. The experimental data and model predictions are compared in Fig. 2 for the effect of the thiol–epoxy ratio, in Fig. 3 for the effect of the catalyst content and in Fig. 4 for the effect of the epoxy equivalent weight. As can be seen in the figures, the model is capable of reproducing, at least from a qualitative point of view, the expected behaviour in terms of reaction rate and reaction onset: it includes both the effect of the nucleophilic initiation and the exhaustion of thiol groups in formulations with $r < 1$, and takes into consideration the autocatalytic behaviour of the reaction. The average error is 60.5 seconds, as seen in Table 2, although individual errors are quite substantial in some cases. The model produces an exceedingly high delay in the predicted reaction of formulations with $r < 1$ (Fig. 2) and overestimates the effect of the thiol–epoxy ratio r (Fig. 2) on the peak reaction rate. The effect of the catalyst content on the overall reaction time is well predicted, but it overestimates its effect on the peak reaction rate (Fig. 3). The kinetic model predicts quite well the effect of the epoxy equivalent weight (Fig. 4), but

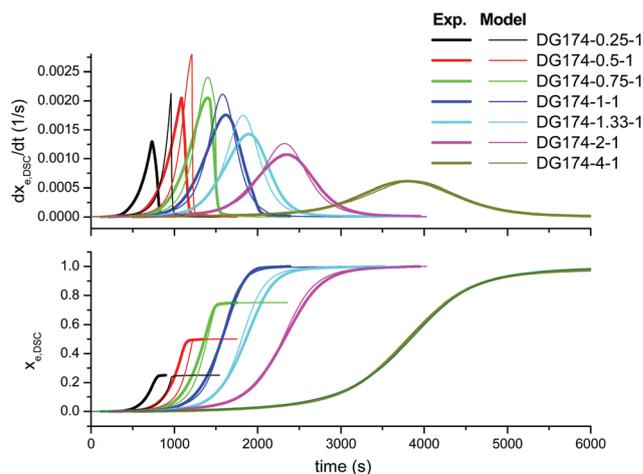


Fig. 2 Comparison between the predictions of the basic kinetic model and the experimental data, the effect of the thiol–epoxy ratio, using the parameters in Table 2.



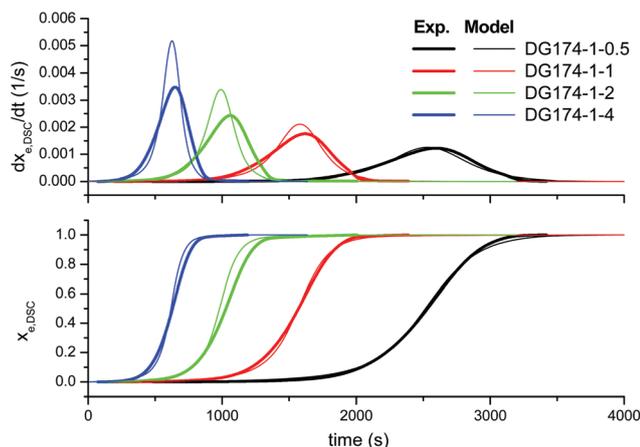


Fig. 3 Comparison between the predictions of the basic kinetic model and the experimental data, the effect of the initiator content, using the parameters in Table 2.

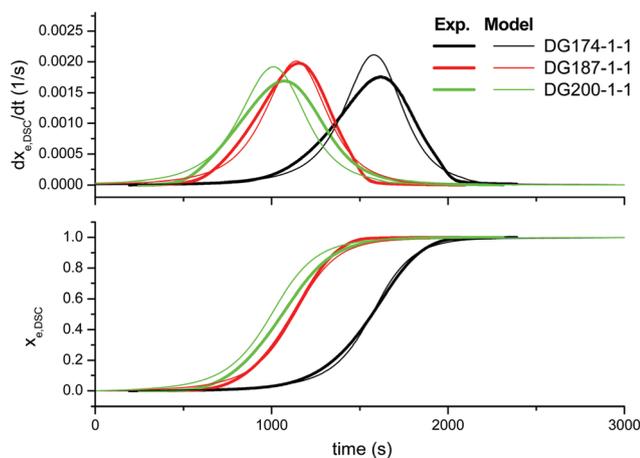


Fig. 4 Comparison between the predictions of the basic kinetic model and the experimental data, the effect of the DGEBA epoxy equivalent weight, using the parameters in Table 2.

the reaction rates are overestimated in the case of the DG174-1-1 and DG200-1-1 formulations. Although valid as a first approximation, this model does not accurately reproduce the shape of the different curing processes. Therefore, the underlying reaction mechanism must be different from that represented in this kinetic model.

In order to improve the quality of the fitting, the complex model, based on other mechanistic considerations, was tested. Fig. 5 shows the effect of the thiol-epoxy ratio, Fig. 6 shows the effect of the initiator content and Fig. 7 shows the effect of the epoxy equivalent weight. The fitted kinetic parameters and the error are shown in Table 2. The error of the adjustment is lower, only 50.2 seconds, and an inspection of the curves confirms that the quality of the fitting process is much better. Indeed, Fig. 5 shows that the effect of the thiol-epoxy ratio on the reaction rate is little overestimated, differences being most noticeable at the lowest thiol-epoxy ratios, 0.5 and, especially, 0.25. Although the model still predicts a slower initiation in these

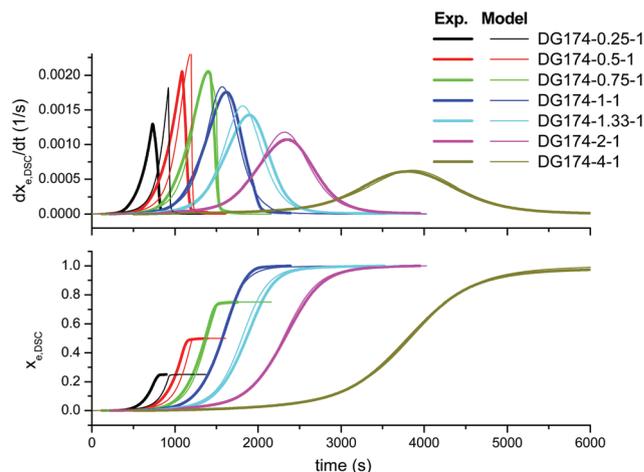


Fig. 5 Comparison between the predictions of the complex kinetic model and the experimental data, the effect of the thiol-epoxy ratio, using the parameters in Table 2.

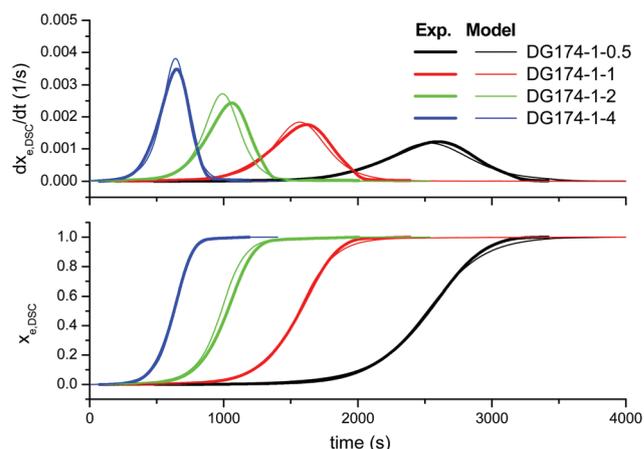


Fig. 6 Comparison between the predictions of the complex kinetic model and the experimental data, the effect of the initiator content, using the parameters in Table 2.

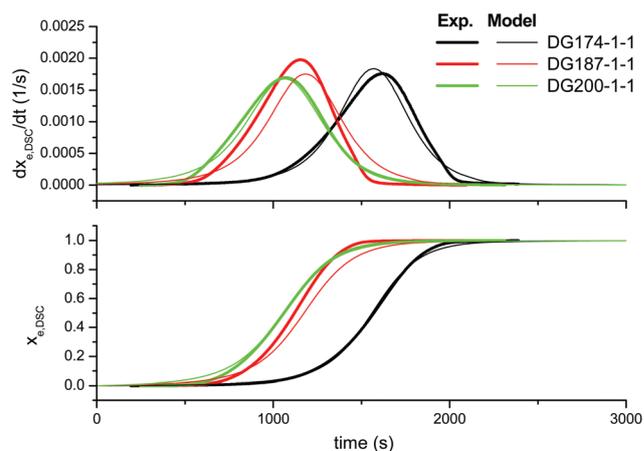


Fig. 7 Comparison between the predictions of the complex kinetic model and the experimental data, the effect of the DGEBA epoxy equivalent weight, using the parameters in Table 2.



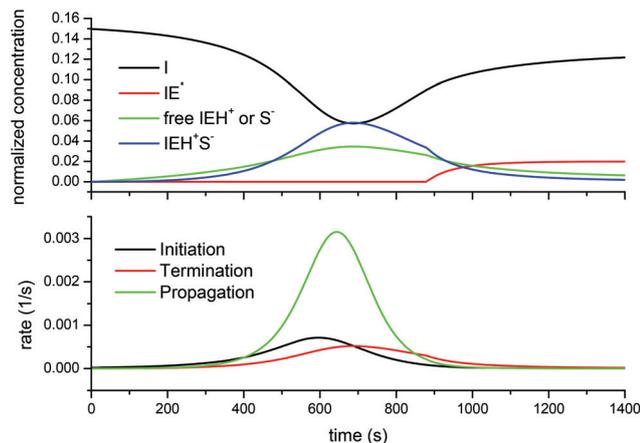


Fig. 9 Comparison of the normalized concentration of species I, IE^* , free IEH^+ or S^- and the IEH^+S^- ion-pair (top) and the rate of initiation, termination and propagation reactions (bottom) predicted by the complex model for the curing of the DG174-1-4 system.

active species promotes the formation of the ion-pair, to the detriment of the free thiolate anion propagating the reaction. Thus, it is no surprise that the ion-pair concentration becomes larger than the concentration of free thiolate. When Fig. 8 and 9 are compared, it can be observed that the maximum concentration of thiolate anions is slightly more than double when 4 phr of 1MI are used in comparison with 1 phr of 1MI. Another relevant difference between both figures is that the initiation rate contributes more heavily to the overall reaction rate in the presence of 4 phr of 1MI, which could be expected. At the end of the reaction process, as the thiol groups are exhausted, there is a non-negligible amount of the zwitterion formed.

Finally, Fig. 10 shows the evolution of the different species and rates for the off-stoichiometric DG174-0.5-1 formulation. The model predicts that, due to the exhaustion of thiol groups, the concentration of the free thiolate and ion-pair decreases sharply. However, because there is a significant excess of epoxy

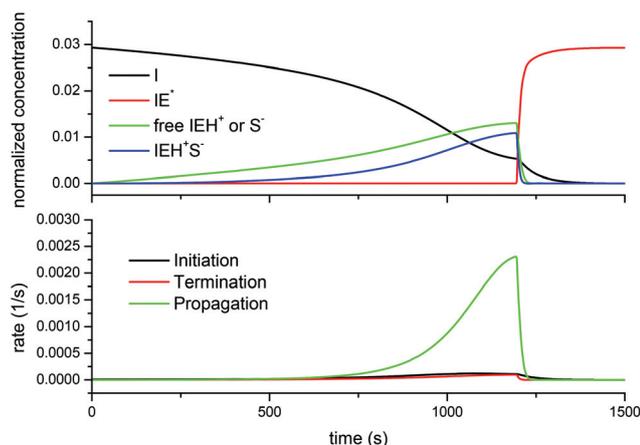


Fig. 10 Comparison of the normalized concentration of species I, IE^* , free IEH^+ or S^- and the IEH^+S^- ion-pair (top) and the rate of initiation, termination and propagation reactions (bottom) predicted by the complex model for the curing of the DG174-0.5-1 system.

groups, this takes place near the peak in the reaction rate, leading to a sharp decrease in the overall reaction rate altogether. At this point, the amount of the zwitterion starts to increase as well. However, because of the presence of the remaining epoxy groups and the high concentration of catalytic hydroxyl groups formed in the course of the reaction, the initiation continues at a fast rate and leads to a depletion of initiator species and the formation of the maximum possible amount of the zwitterion. This zwitterion is the species that would start the propagation of the epoxy homopolymerization, but this species would be more stable and less active than other alkoxide anions, as commented above. According to Heise and Martin, the adduct formation would reach completion before the homopolymerization process starts.^{18,19} According to the model, this species would be ready at the end of the thiol epoxy process, so that the homopolymerization process would eventually start if one waited for long enough or increased the temperature.⁶ It should be noted that for the curing of a formulation with excess thiol groups (results not shown), throughout the whole curing process and at the end of it there would not be any traces of this zwitterion species.

In the light of these results, it appears that the hypotheses behind the proposed complex kinetic model, involving the presence of the non-reactive ion-pair in the reaction medium, become quite realistic. The main features of the curing process and the rates and reaction onsets are well reproduced by the model. The effect of the composition on the reaction rate is also accounted for by the model. Indeed, if one compares the values of $k_{i,DG}$, $k_{i,SH}$, $k_{p,DG}$ and $k_{p,SH}$ as in Table 2, and considering the way these constants were defined (see section 3.3), it can be deduced that the effect of catalytic impurities in the thiol monomer (*i.e.* hydroxyl groups) on the initiation and propagation rate constants is indeed lower than that of the epoxy monomer, but not negligible. The values of $k_{i,cat}$ and $k_{p,cat}$ also indicate that the catalytic effect of the reaction product is significantly stronger, in agreement with the results of Loureiro *et al.*¹⁵ The model still overestimates the reaction onset in formulations with thiol-epoxy ratios lower than one, but this might be a consequence of both inaccuracies inherent to the reaction mechanism and experimental error caused by the fast initiation of these formulations. In any case, assuming that the distribution of reactive species produced by this model is right, it could be used to analyze the crosslinking process of stoichiometric or off-stoichiometric thiol-epoxy formulations, rather than relying only on ideal step-wise assumptions.⁶ In addition, the model could be extended to study the reaction processes of thiol-epoxy systems initiated by other nucleophilic tertiary amines,¹⁵ but obviously the values of the model constants would be different, especially those connected with the amine structure and reactivity such as the initiation and termination rate constants as well as the ion-pair equilibrium constant.

We acknowledge that the model has some inaccuracies and simplifications that might be addressed in future studies. Whether the termination is a unimolecular rearrangement of the ion-pair or a bimolecular reaction between free thiolate



and hydroxylammonium cation species makes no practical difference. We assumed that the propagation by means of the ion-pair species was negligible for the sake of simplicity, but one might consider some reactivity of the ion-pair towards propagation. The initiating mechanism based on the nucleophilic attack of the imidazole to the epoxy ring should be re-analyzed. Nucleophilic addition of amines to epoxy groups can be quite complex, as reported for epoxy-amine systems.^{35–38,40} The formation of multiple equilibrium complexes complicates significantly the apparently simple autocatalytic epoxy-amine addition. When several equilibrium complexes, some of which are active, are present at the same time, the real amount of active species is reduced and, if this effect is neglected, the reaction rate is overestimated.⁴⁰ A similar consequence could be expected for the initiation step between the imidazole and the epoxy ring. The initiation step in epoxy-imidazole systems is highly sensitive to the chemical environment, not only due to the presence of catalytic species^{17,21} but also to the formation of unreactive complexes in the presence of polyethers,⁴⁵ like in epoxy-amine systems.⁴⁰ Nevertheless, in the absence of more detailed experimental information (*i.e.* the individual determination of some rate or equilibrium constants), the inclusion of a larger number of fitting parameters would complicate the interpretation of the results. We already tested the effect of the epoxy-hydroxyl complexes, but we found that the complex equilibrium constant was very low (results not shown), so that our simplification of the catalytic effect could be considered as a safe one, in line with the results of Jin *et al.*¹⁶ and in agreement with the reasoning of Flammersheim,³⁶ although this might also be a side consequence of the mathematical fitting process. In multiple non-linear regression modelling of complex processes there could be more than one solution, given that the optimum point might be within a flat hollow rather than a deep valley of the solution space,³⁷ or else a number of local minima with a similar error could be easily found. In order to refine the proposed model, taking into account the above considerations, more experimental work should be carried out in order to investigate in more depth the effect of the chemical environment on the initiation step and the role of the ion-pair equilibrium complex, as well as the effect of temperature on the different kinetic parameters, so as to produce a more consistent model and a more meaningful set of kinetic parameters.

5 Conclusions

The thiol-epoxy addition reaction initiated by tertiary amines has been analyzed from theoretical and experimental points of view. DGEBA and S3 have been used as epoxy and thiol compounds, and 1MI has been used as the nucleophilic tertiary amine initiator. The effects of the thiol-epoxy ratio, epoxy equivalent weight and initiator content have been taken into consideration.

The reaction takes place earlier in formulations richer in epoxy monomers because of the initiation by the nucleophilic

attack of the tertiary amine to the epoxy group and the contribution of catalytic hydroxyl groups in the epoxy oligomer. The end of the reaction is sharp in formulations with excess of epoxy groups due to the exhaustion of thiol groups and transfer of the thiolate active species to a less active zwitterion species that would propagate the homopolymerization of the excess epoxy groups. Increasing the initiator content does not increase proportionally the propagation and initiation rates. The use of epoxy monomers with higher epoxy equivalent weights leads to faster reactions because of the catalytic effect of the hydroxylic epoxy oligomers, in spite of the reduced concentration of epoxy groups.

A kinetic model based on an approximate reaction mechanism for the thiol-epoxy reaction initiated by tertiary amines has been defined. This model satisfactorily reproduces all the phenomena associated with the curing process of stoichiometric and off-stoichiometric thiol-epoxy mixtures initiated by 1MI, and it is hypothesized it could be extended, with obviously different values of the parameters, to thiol-epoxy systems initiated by other nucleophilic tertiary amines. A complete validation of the model would require, however, the analysis of the effect of different curing temperatures under isothermal and nonisothermal reaction conditions, producing a more consistent and meaningful set of kinetic parameters.

One of the most remarkable features of the model is the assumption of the presence of a less-reactive ion-pair complex in equilibrium with free thiolate and cationic species, making it possible to predict correctly the effect of changing the initiator content and thiol-epoxy ratio on the reaction rate. However, the understanding of the exact role of the ion-pair in the reaction medium in terms of reactivity requires further investigation. The model also attempts, in a simplified way, to describe separately the catalytic effects of hydroxyl groups and other impurities present in the epoxy resin and in the thiol crosslinker, and the hydroxyl groups present in the reaction product. However, it is acknowledged that the model is not accurate enough in that respect. Among other issues, one should consider the formation of different active and non-active complexes depending on the presence of different catalytic or deactivating species. Proper elucidation of the initiation step, which is crucial for the understanding of the reactivity of these systems, remains therefore a pending task.

Conflicts of interest

There are no conflicts to declare.

Appendix

Basic kinetic model

In terms of the normalized concentration of the different species, the basic set of rate equations transforms into:

$$\frac{di}{dt} = -k'_i \cdot i \cdot e + k'_t \cdot s^- \cdot ieh^+$$



cases, the adjustment is significantly better. Fig. 6 shows that the effect of the catalyst content is now nicely predicted by the model. The effect of the epoxy equivalent weight is also quite well reproduced, as shown in Fig. 7, with some discrepancies in the case of the intermediate DG187-1-1 formulation.

An indirect confirmation of these results could be made from a comparison between the rate constants obtained and those found in the literature. Unfortunately, the adjustment procedure in the work of Loureiro *et al.*¹⁵ makes it difficult to compare their results with ours. Therefore, the only data we can use are from the work of Jin *et al.*¹⁶ These authors fitted the experimental data to a phenomenological Kamal model, with $dx/dt = (k_1 + k_2 \cdot x^m) \cdot (1 - x)^n$, and interpreted the parameters in terms of the reaction mechanism. For a stoichiometric formulation using a trifunctional thiol and an epoxy monomer of a low epoxy equivalent weight (180 g mol^{-1}), cured at $60 \text{ }^\circ\text{C}$ with $0.17 \text{ mol}\%$ of DBU, they obtained $k_1 = 0.77 \times 10^{-5} \text{ s}^{-1}$, $k_2 = 0.65 \times 10^{-3} \text{ s}^{-1}$, and $m = n = 1$. The values of the m and n parameters, which were about the same at all temperatures, were in excellent agreement with a base-catalyzed reaction mechanism, with the same assumptions that we made in this work concerning the activation of the epoxy ring by proton donors. Assuming that strong bases such as DBU produce the maximum amount of active species from the very beginning, and that an ion-pair such as the one in this work would not be formed (or present much weaker interactions), their value of k_2 should be equivalent to our value of $k_{p,cat} \cdot [E_0]^2 \cdot i$, for an equivalent thiol-epoxy formulation. The value of i should be the molar concentration of DBU the authors used in their work,¹⁶ $0.0017 \text{ mol DBU per mol of SH groups}$. The calculated value of $k'_{p,cat} \cdot i_0$ is equal to $0.75 \times 10^{-3} \text{ s}^{-1}$, only 15% higher than k_2 . While k_1 should be equivalent to $(k_{p,DG} \cdot oh_{DG} + k_{p,SH} \cdot sh_0) \cdot [E_0]^2 \cdot i$, our calculation yields a value of 10^{-6} s^{-1} , which is about 8 times lower. Comparison of k_2 with $k_{p,cat} \cdot [E_0]^2 \cdot i$ should be more reliable because of the strong autocatalytic component of the reaction, which is due to the generation of a hydroxyl group per each epoxy/thiol group reacted. However, comparison between k_1 and $(k_{p,DG} \cdot oh_{DG} + k_{p,SH} \cdot sh_0) \cdot [E_0]^2 \cdot i$ depends largely on the presence of catalytic impurities in the reaction medium, often coming from the use of industrial grade products. It should be considered that the results from our analysis are obtained from a numerical fitting of the data to a model with a significant number of parameters, which may involve uncertainties stemming from the numerical method. Added uncertainty comes from the fact that the reaction starts by nucleophilic attack of 1MI to the epoxy ring, which is highly sensitive to catalytic groups and impurities present in the system, and this might conceal the effect of such impurities on the propagation rate.

At this point, it is also good to analyze the distribution of the relevant species (other than epoxy and thiol groups) in the course of the reaction, and the contribution of the different rates of initiation, propagation and termination to the overall reaction rate.

Fig. 8 shows the situation for the DG174-1-1 formulation. It is noteworthy that, as the reaction starts, the growing concentration of free thiolate anions does not start the reaction

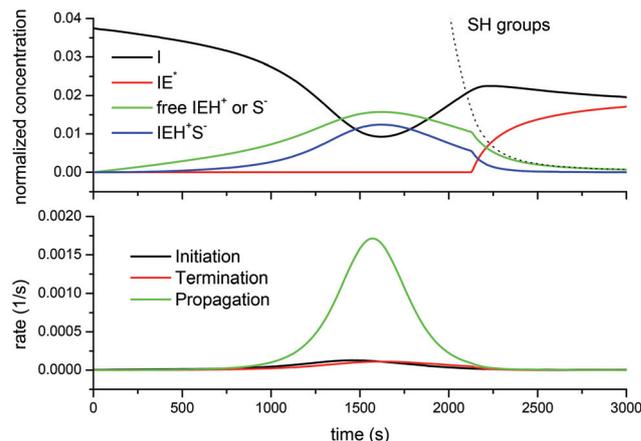


Fig. 8 Comparison of the normalized concentration of species I, IE^* , free IEH^+ or S^- and the IEH^+S^- ion-pair (top) and the rate of initiation, termination and propagation reactions (bottom) predicted by the complex model for the curing of the DG174-1-1 system.

immediately. When the propagation rate starts to increase, an increase in the concentration of active species is noted, but this is offset by the formation of the ion-pair, which moderates the amount of free thiolate propagating the reaction. The amount of active species reaches a maximum around the maximum propagation rate because the decreasing concentration of the epoxy groups and initiator I leads to a decreasing initiation rate. At this point, about 75% of the initiator has been converted into IEH^+ species (free and ion-pair). In consequence, the concentration of the free initiator starts to increase again. A change in the trend is observed once the concentration of the thiol groups falls below a certain threshold, so that the amount of active species is no longer controlled by the total reacted initiator but by the availability of the thiol groups to produce free thiolate anions. At this point, the concentration of the inactive (or rather less active) zwitterion IE^* , which was 0 (or nearly) because of the presence of a sufficient amount of thiol groups leading to a fast proton transfer to produce thiolates, starts to increase as well. The absence of the zwitterion IE^* , in addition to its low reactivity, justifies the absence of epoxy homopolymerization, so that in the presence of thiol groups only the thiol-epoxy addition takes place. At the end of the process a significant amount of the unreacted initiator I remains, which is in good agreement with the experimental results of Loureiro *et al.*,¹⁵ who showed that, at the end of the thiol-epoxy addition, there was a significant amount of the unreacted initiator in the SEC traces of the reaction product. Throughout the curing process the contribution of the initiation and termination reactions to the reaction rate is very small in comparison with the propagation, due to the small concentration of the initiator and active species available.

Fig. 9 shows the same results but for the DG174-1-4 system, with four times more catalyst. The shape of the curves is pretty much the same as in the previous case, but there is a relevant difference in the relative contribution of the free IEH^+ or thiolate species and the ion-pair. The larger concentration of total



$$\frac{die_{\text{total}}}{dt} = -\frac{di}{dt}$$

$$\frac{de}{dt} = -k'_i \cdot i \cdot e - k'_p \cdot s^- \cdot e$$

$$\frac{dsh_{\text{total}}}{dt} = -k'_p \cdot s^- \cdot e - k'_t \cdot s^- \cdot ieh^+$$

$$\frac{dseh}{dt} = k'_p \cdot s^- \cdot e + k'_t \cdot s^- \cdot ieh^+$$

where

$$sh_{\text{total}} = sh + s^-$$

$$ie_{\text{total}} = ie^* + ieh^+$$

The number of propagating species is calculated as:

$$sh_{\text{total}} > ie_{\text{total}} \Rightarrow \begin{cases} s^- = ie_{\text{total}} \\ ie^* = 0 \end{cases}$$

$$sh_{\text{total}} < ie_{\text{total}} \Rightarrow \begin{cases} s^- = sh_{\text{total}} \\ ie^* = ie_{\text{total}} - sh_{\text{total}} \end{cases}$$

Because of the normalization process, the kinetic and equilibrium constants are now expressed as:

$$k'_i = (k_{i,\text{DG}} \cdot oh_{\text{DG}} + k_{i,\text{SH}} \cdot sh_0 + k_{i,\text{cat}} \cdot (seh + ieh^+)) \cdot [E]_0^2$$

$$k'_p = (k_{p,\text{DG}} \cdot oh_{\text{DG}} + k_{p,\text{SH}} \cdot sh_0 + k_{p,\text{cat}} \cdot (seh + ieh^+)) \cdot [E]_0^2$$

$$k'_t = k_t \cdot [E]_0$$

An implicit assumption here is that the volume changes during curing are negligible. If one were to consider the volume changes, the expressions should be modified in a convenient way.³⁴

Complex kinetic model

In terms of normalized concentrations, the rate and equilibrium expressions of the complex model take the following form:

$$\frac{di}{dt} = -k'_i \cdot i \cdot e + k'_{t,\text{IP}} \cdot ieh^+ s^-$$

$$\frac{die_{\text{total}}}{dt} = -\frac{di}{dt}$$

$$\frac{de}{dt} = -k'_i \cdot i \cdot e - k'_p \cdot s^- \cdot e$$

$$\frac{dsh_{\text{total}}}{dt} = -k'_p \cdot s^- \cdot e - k'_{t,\text{IP}} \cdot ieh^+ s^-$$

$$\frac{dseh}{dt} = -\frac{dsh_{\text{total}}}{dt}$$

$$k'_{\text{eq,IP}} = \frac{ie^+ s^-}{s^- \cdot ieh^+} = \frac{ie^+ s^-}{(s^-)^2}$$

In this set of reactions, we define:

$$ie_{\text{total}} = ie^* + ieh^+ + ieh^+ s^-$$

$$sh_{\text{total}} = sh + s^-_{\text{total}} = sh + s^- + ieh^+ s^-$$

One should also consider that:

$$s^-_{\text{total}} = s^- + ieh^+ s^- = ieh^+ + ieh^+ s^-$$

The number of potentially active species is determined as:

$$sh_{\text{total}} > ie_{\text{total}} \Rightarrow \begin{cases} s^-_{\text{total}} = ie_{\text{total}} \\ ie^* = 0 \end{cases}$$

$$sh_{\text{total}} < ie_{\text{total}} \Rightarrow \begin{cases} s^-_{\text{total}} = sh_{\text{total}} \\ ie^* = ie_{\text{total}} - sh_{\text{total}} \end{cases}$$

Having determined s^-_{total} , the ion-pair equilibrium is solved as:

$$k'_{\text{eq,IP}} = \frac{ie^+ s^-}{(s^-)^2} = \frac{ie^+ s^-}{(s^-_{\text{total}} - ieh^+ s^-)^2}$$

The normalized propagation and initiation constants k'_i and k'_p are defined in the same way as in the basic model. The equilibrium and termination constants of the ion-pair are defined as:

$$k'_{\text{eq,IP}} = k_{\text{eq,IP}} \cdot [E]_0$$

$$k'_{t,\text{IP}} = k_{t,\text{IP}}$$

Initial concentration of reactive species

Taking into account the weight fraction of each component specified in Table 1, the initial concentrations of the epoxy and initiator groups were calculated as:

$$[E]_0 = \frac{w_{\text{DG}}}{\text{eq}_{\text{DG}}} \cdot \rho \quad [I]_0 = \frac{w_{\text{MI}}}{\text{eq}_{\text{MI}}} \cdot \rho$$

where w_{DG} and w_{MI} are the weight fractions of the epoxy monomer and initiator in the mixture (the values in Table 1 divided by 100), and eq_{MI} is the equivalent weight of 1MI and assumed to be 82 g mol⁻¹. The density ρ has been estimated from the composition of the formulations and the density of the pure compounds at room temperature assuming the additivity of volumes and correcting the density to the curing temperature using the approximation of Van Krevelen for oligomers or polymers above their glass transition temperature.^{34,46}

With $[E]_0$ and $[I]_0$, one can determine the initial normalized concentrations for the integration of the rate equations:

$$e_0 = 1 \quad sh_0 = sh_{\text{total},0} = r \cdot f_{\text{SH}} \quad i_0 = [I]_0/[E]_0 \quad ie_{\text{total},0} = 0 \quad seh_0 = 0$$

In the expression for the normalized initial concentration of thiol groups sh_0 , r is the theoretical thiol-epoxy ratio used for the calculation of the mixture composition, and f_{SH} represents the purity of the thiol monomer and takes a value of 1 for a perfectly pure reagent, but in this case takes a value of 0.98 according to the product specifications.



The initial amount of hydroxyl groups coming from DGEBA, oh_{DG} is approximately calculated from the epoxy equivalent weight, eq_{DG} , as:

$$oh_{DG} = \frac{1}{2} \cdot \frac{2 \cdot eq_{DG} - 340}{284}$$

The initial concentration of all the other species in the basic or complex models is initially equal to 0.

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Article 5: Sequential dual curing by selective Michael addition and free radical polymerization of acetoacetate-acrylate-methacrylate mixtures

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