DÉVELOPPEMENT DE NOUVEAUX PRODUITS ÉPOXY BIOSOURCÉS À BASE DE DIOXYDE DE LIMONÈNE

par

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SUMMARY

Nowadays, polymers are used in various parts of life, and it can be said that polymers have become an integral part of the industry. Epoxy monomers have several three-membered rings consisting of an oxygen atom joined by single bonds to two adjacent carbon atoms. Epoxy polymers are one of the most widely used polymers in various sectors such as automobiles, coatings, semiconductor encapsulants, paints, adhesives, and aerospace. They possess interesting properties such as dimensional stability, chemical resistance, dimensional stability, excellent mechanical strength, and toughness. Epoxy monomers usually have at least two epoxide functions, while the compounds with one functional epoxide are used as reactive diluents.[1]

Diglycidyl ether bisphenol A (DGEBA) was introduced in the 1940s as the first commercial epoxy monomer. Gradually, epoxy polymers have become a significant category of industrial polymers, and the global demand for epoxy polymers has increased over time. DGEBA results from the reaction between bisphenol A (BPA) and epichlorohydrin (ECH). Nowadays, many efforts are being made to replace DGEBA by a biobased source because it is petroleum-based and based on BPA which is toxic.

Many bio-materials have been presented in the literature as a replacement to DGEBA. However, most of them are functionalized with ECH which is a toxic molecule, too.[1,2]

Among all biomaterials, limonene dioxide (LDO) can be an interesting candidate. First of all, ECH is not used to functionalize this molecule. Also, this molecule originates from limonene, which is an extract from the orange peel. LDO is constituted by a mixture of four stereoisomers that do not react in the same way. This study attempts to synthesize a new epoxy polymer using LDO as epoxy monomer. Several epoxy monomers and two different curing agents were used in a new LDO based formulation, and were compared with industrial formulations containing DGEBA.[3]

When preparing an epoxy polymer, the time it takes to transform the liquid mixture to solid polymer (reaction time) is a critical factor to control. Various catalysts have been proposed to reduce this reaction time. These catalysts must be soluble in the epoxy monomer or curing agent, must withstand environmental conditions and must not be expensive due to the widespread use of the epoxy polymer. Even though many catalysts have been reported for ring-opening of epoxides in solution, only a small number of catalysts is useful for the curing of epoxy, especially in the presence of amines.[4,5]

The first chapter of this thesis consists in a presentation of the essential theoretical notions in the field of epoxy polymer.

Chapter 2 presents an article on the use of LDO, as an alternative to BADGE. Different samples containing various amounts of epoxy monomers were prepared. The resulting samples were characterized by different tests such as swelling test, Dynamic Mechanical Analysis (DMA), and tensile test. The results are presented in an article form, which has been submitted to the journal Polymer.

Chapter 3 presents an article showing that lanthanide dodecyl sulfates ($LnDS_x$) effectively catalyze reaction of amines with epoxy functions. It was demonstrated that the new catalysts could be synthesized from the reaction between lanthanide salts with sodium dodecyl sulfate. Catalysts were characterized by different techniques such as Nuclear Magnetic Resonance (NMR), Fourier-Transform Infrared Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

The results of these analyses are presented in an article form, which will be submitted to Chemical Communications.

Keywords: Limonene dioxide, Biobased epoxy, Diglycidyl ether bisphenol A (DGEBA)

SOMMAIRE

De nos jours, les polymères sont utilisés dans diverses parties de la vie, et on peut dire que les polymères sont devenus une partie intégrante de l'industrie. Les monomères époxy ont plusieurs cycles à trois chaînons constitués d'un atome d'oxygène lié par des liaisons simples à deux atomes de carbone adjacents. Les polymères époxy sont l'un des polymères les plus largement utilisés dans divers secteurs tels que l'automobile, les revêtements, les encapsulants semi-conducteurs, les peintures, les adhésifs et l'aérospatiale. Ils possèdent des propriétés intéressantes telles que la stabilité dimensionnelle, la résistance chimique, une excellente résistance mécanique et la ténacité. Les monomères époxy ont généralement au moins deux fonctions époxyde, tandis que les composés à un époxyde fonctionnel sont utilisés comme diluants réactifs.[1]

Le diglycidyl éther bisphénol A (DGEBA) a été introduit dans les années 1940 en tant que premiers monomères époxy commerciaux. Peu à peu, les polymères époxy sont devenus une catégorie importante de polymères industriels, et la demande mondiale de polymères époxy a augmenté au fil du temps. Les monomères DGEBA résultent de la réaction entre le bisphénol A (BPA) et l'épichlorhydrine (ECH). De nos jours, de nombreux efforts sont faits pour remplacer le DGEBA par une source biosourcée car il est à base de pétrole et à base de BPA qui est toxique.

De nombreux biomatériaux ont été présentés dans la littérature en remplacement du DGEBA. Cependant, la plupart d'entre eux sont fonctionnalisés avec ECH qui est également une molécule toxique.[1,2]

Parmi tous les biomatériaux, le dioxyde de limonène (LDO) peut être un candidat intéressant. Tout d'abord, ECH n'est pas utilisée pour fonctionnaliser cette molécule. En outre, cette molécule provient du limonène, qui est un extrait de la peau d'orange. Le LDO est constitué d'un mélange de quatre stéréoisomères qui ne réagissent pas de la même manière. Cette étude tente de synthétiser un nouveau polymère époxy en utilisant le LDO comme monomère époxy. Plusieurs monomères époxy et deux agents de durcissement différents ont été utilisés dans une nouvelle formulation à base de LDO, et ont été comparés à une formulation industrielle contenant du DGEBA.[3]

Lors de la préparation d'un polymère époxy, le temps nécessaire pour passer du mélange liquide au polymère solide (temps de réaction) est un facteur critique à contrôler. Divers catalyseurs ont été proposés pour réduire le temps de réaction. Ces catalyseurs doivent être solubles dans le monomère époxy ou l'agent de durcissement, doivent résister aux conditions environnementales et ne doivent pas être coûteux en raison de l'utilisation répandue du polymère époxy. Même si de nombreux catalyseurs ont été rapportés pour l'ouverture du cycle d'époxydes en solution, et un petit nombre de catalyseurs sont utiles pour le durcissement de l'époxy, en particulier en présence d'amines.[4,5]

Le premier chapitre de cette thèse consiste en une présentation des notions théoriques essentielles dans le domaine des polymères époxy.

Le chapitre 2 présente un article sur l'utilisation de LDO, comme alternative à BADGE. Différents échantillons contenant diverses quantités de monomères époxy ont été préparés. Les échantillons résultants ont été caractérisés par différents tests tels que le test de gonflement, l'analyse mécanique dynamique (DMA) et le test de traction. Les résultats sont présentés sous forme d'article, qui a été soumis à la revue Polymer.

Le chapitre 3 présente un article montrant que les dodécyl sulfates de lanthanide (LnDSx) catalysent efficacement la réaction des amines à fonctions époxy. Il a été démontré que les nouveaux catalyseurs pouvaient être synthétisés à partir de la réaction entre des sels de lanthanide et du dodécyl sulfate de sodium. Les catalyseurs ont été caractérisés par différentes techniques telles que la résonance magnétique nucléaire (RMN), la spectroscopie infrarouge à transformée de Fourier (FTIR), la spectroscopie photoélectronique à rayons X (XPS), la spectrométrie de masse à plasma à couplage inductif (ICP-MS). Les résultats de ces analyses sont présentés sous forme d'article, qui sera soumis à Chemical Communications.

Mots clés : Dioxyde de limonène, époxy biosourcé, éther diglycidylique bisphénol A (DGEBA)

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ABREVIATIONS LIST

AFM	Atomic force microscopy
BPA	Bisphenol A
DMA	Dynamic mechanical analysis
DGBEF	Bisphenol F Epoxy monomers
DGEBA	Diglycidyl ether bisphenol A
DSC	Differential scanning calorimetry
E’	Storage modulus
E’’	Loss modulus
ECH	epichlorohydrin
EEW	Epoxy Equivalent Weight
EVO	Epoxidized vegetable oil
f	Functional group in molecule
f_{avg}	average functionality
GP	Gel Point
LDO	Limonene dioxide
M_c	Molecular weight between cross-linked
M_w	Average molecular weight
SEM	Scanning electron microscopy
$\tan\delta$	Dissipation factor
TEM	Transmission electron microscopy
TETA	triethylenetetramine
TGA	Thermal gravimetric analysis
δ	Solubility parameter

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$f_{avg} = \frac{\sum N_i f_i}{\sum N_i}$ [1.1] ………..10

$P_c = \frac{2}{f_{avg}}$ [1.2] ………..10

$\alpha_{gel} = \frac{1}{\sqrt{r_m(f_A - 1)(f_E - 1)}}$ [1.3] ………...10

$EEW = \frac{M_W}{f}$ [1.4] ………..11

$\alpha = \frac{\Delta H_t}{\Delta H_{total}}$ [1.5] ………...30

$\frac{d\alpha}{dt} = \frac{1}{\Delta H_{total}}\left(\frac{dH}{dt}\right)$ [1.6] ………..30

$\frac{d\alpha}{dt} = K(1 - \alpha)^n$ [1.7] ………..31

$K = Aexp(\frac{-\Delta E_a}{RT})$ [1.8] ………..31

$\frac{d\alpha}{dt} = K\alpha^m(1 - \alpha)^n$ [1.9] ………..31

$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1 - \alpha)^n$ [1.10] ………..31

Swelling (%) $= \frac{W_s - W_d}{W_d} \cdot 100$ [1.11] ………. 36

$X_{solubility}$ (%) $= \frac{W_{d0}}{W_d} \cdot 100$ [1.12] ………..36

$M_c = \frac{\rho qRT}{E'}$ [1.13] ……….37

INTRODUCTION

Nowadays, polymers have become an essential part of human life that they have penetrated in all aspects of it, including clothing, food, packaging, buildings, etc. Polymers have different properties which originate from their molecular structure, so they are classified as linear chain, branched, and networked polymers.[6] Thermosets are a class of synthetic polymer that molecular chains are connected by cross-links, creating a network of three-dimensional bonds. Epoxy is one of the most popular thermoset polymers. It is made by combining two parts; the epoxy monomers that include prepolymer molecules containing more than one epoxide group and the curing agents or hardeners.[7] Epoxy polymers are used in a wide range of applications because of their designable properties such as reasonable prices, high strength, impressive electrical insulation, negligible shrinkage, chemical and solvent stability, ease of processing, and excellent adhesion to many substrates. They are applied in many fields such as coatings, electrical/electronic laminates, adhesives, aerospace, flooring, and paving applications.[8]

1.1. Motivation and significance

The properties of epoxy polymer are particularly affected by the choice of hardener and epoxy monomer.[9] Most epoxy monomers on the market are based on petroleum. The concern for global warming and the inconstancy of oil prices is pushing businesses to move toward a sustainable economy.

Nowadays, BADGE is the most commonly used monomer in epoxy formulation.[1] It is obtained by combining BPA with epichlorohydrin, ECH. BPA is derived from petrochemical resources and it is harmful for the human body. BPA affects hormonal activity, which can increase cancerous tumors, and birth defects.[10]

In developed countries such as Canada or France, they are thinking of replacing this compound with less hazardous substances. But unfortunately, BADGE is the most used epoxy monomer and it is predicted to grow more in the future. Also, ECH, used in BADGE synthesis, is highly toxic and is known to cause cancer in the human body.[10–12]

1.2. Objectives

Various research types in academia and industry have been devoted to the search for non-toxic ecosystem-based alternatives for the synthesis of significant epoxy polymers. For example, researchers have investigated vanillin, vegetable oils such as soy, corn, rosemary, and eugenol. Millions of tonnes of citrus waste worldwide every year, can be used to produce limonene. Limonene can be epoxidized by various methods to produce limonene oxide and LDO. These molecules can be then used to synthesize bio-epoxy monomers (Figure 1).[3,13,14]

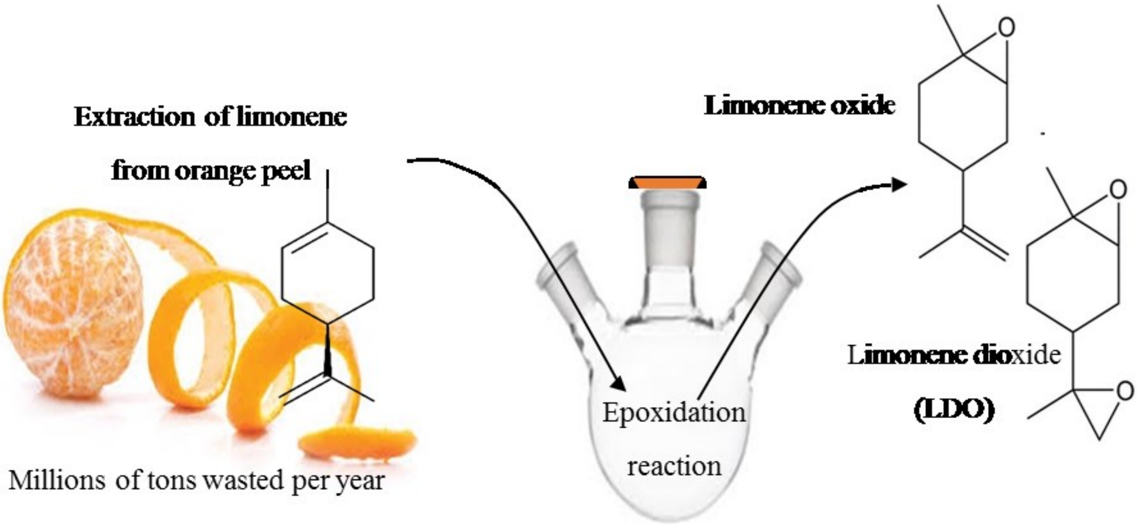


Figure 1. Limonene oxide and LDO from orange peel.

Limonene appears to be an interesting candidate amongst potential bio-based molecules. First, unlike the other biomolecule, it can be epoxidized without using ECH. Second, it is based on an already generated food-waste.[3]

The goal of my research is to develop an epoxy formulation with higher biobased content and comparable properties with its petroleum-based counterparts. In this project, LDO was used as epoxy monomers for bio-based epoxy polymer synthesis. Several hardeners have been selected that react with LDO. Also, two or three epoxy monomers have been added to improve the formulation. After synthesise, the samples are compared, and their properties are investigated.

One major issue with biobased epoxy monomers, and in particular with LDO, is their slow reaction time. Therefore, many catalysts have been proposed to decrease the epoxy reaction time. However, none are efficient with LDO. In this work, I propose a novel family of catalysts that is particularly appropriate to cure epoxy polymer based on LDO monomers (Figure 2).

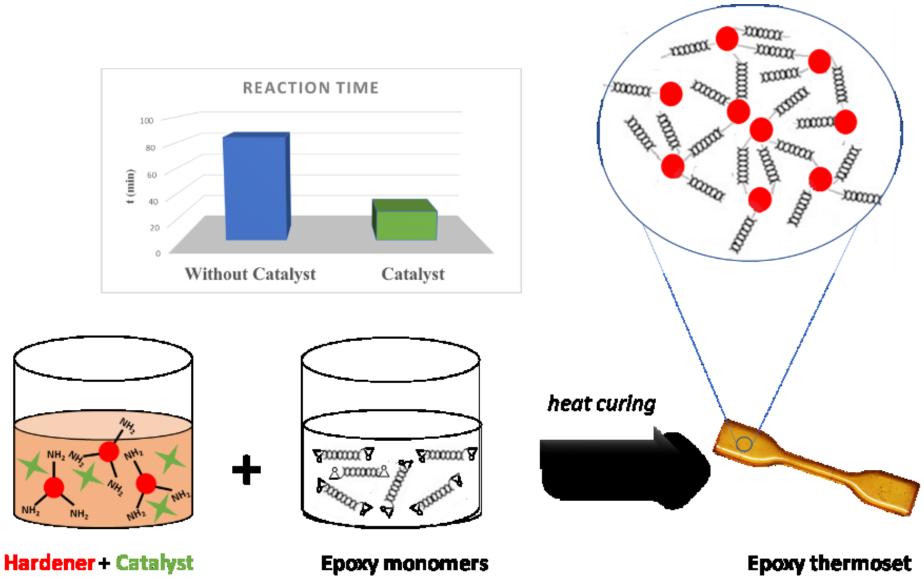


Figure 2. Effect of catalyst on epoxy reaction time.

CHAPTER 1. KNOWLEDGE OF EPOXY POLYMERS AND FACTORS AFFECTING THEIR PROPERTIES

1.1. Polymers classification

Polymers are made by repeating a small monomer unit to form a chain. By knowing the monomers and their order, we can understand the properties of polymers. The properties of polymers depend on many factors, including the chemical structure of polymer chains and the way monomers are connected (for instance, linear, branched, or networked polymers). In general, polymers are divided into three categories in terms of application: thermoplastics, thermosets, and elastomers.[6]

1.1.1 Thermoplastics

Polymers that can melt and be reused almost indefinitely are known as thermoplastics. In a thermoplastic, the molecules are held together by relatively weak intermolecular forces, so due to heat exposure, the material softens and returns to its original state after cooling. Thermoplastics can be melted and solidified several times without significant damage. Many linear and slightly branched polymers are thermoplastic at ambient temperature. Thermoplastics are below the melting point (T_m) or below the glass transition point (T_g) at ambient temperature. Vehicle bumpers and credit cards are examples of thermoplastics.[15]

1.1.2 Elastomers

Elastomers are rubbery polymers that can easily be extended to several times their original dimensions. If force is applied, they return to their original position after being pulled or compressed. Elastomers are obtained by vulcanization that causes cross-linking of polymer chains. High molecular weight between cross-links leads to elastomeric behavior. In other words, elastomers are cross-linked but have a low density of cross-links. At ambient temperature, elastomers are above Tg.[6]

1.1.3 Thermosets

Thermosets are polymers that solidify or "sets" irreversibly when heated. Therefore, reheating does not change their shape. Thermosets are typically three-dimensional networked polymers derived from low molecular weight liquid monomers. Polymer chains in thermosets have a high density of cross-links. The cross-links limit the movement of the chains and contribute to obtaining a rigid material. Thermoset is cured and solidified using curing methods such as heat or radiation. Figure 3 illustrates how molecules become cross-linked. The curing process is irreversible because covalent chemical bonds are formed inside the sample. Epoxy polymers, phenolic polymers, polyurethanes, acrylics, alkyds, furans, polyimides, vinyl esters, and unsaturated polyesters are typical examples of thermosets on the market.[16] During the cure, a transition from a liquid to solid (infinite viscosity) occurs at the gel point. The gel point (GP) corresponds to the percolation threshold, that is to say, to the stage at which at least one infinitely long chain is formed. Past the GP, the reaction continues to proceed, leading to a network that is more and more cross-linked.[17,18]

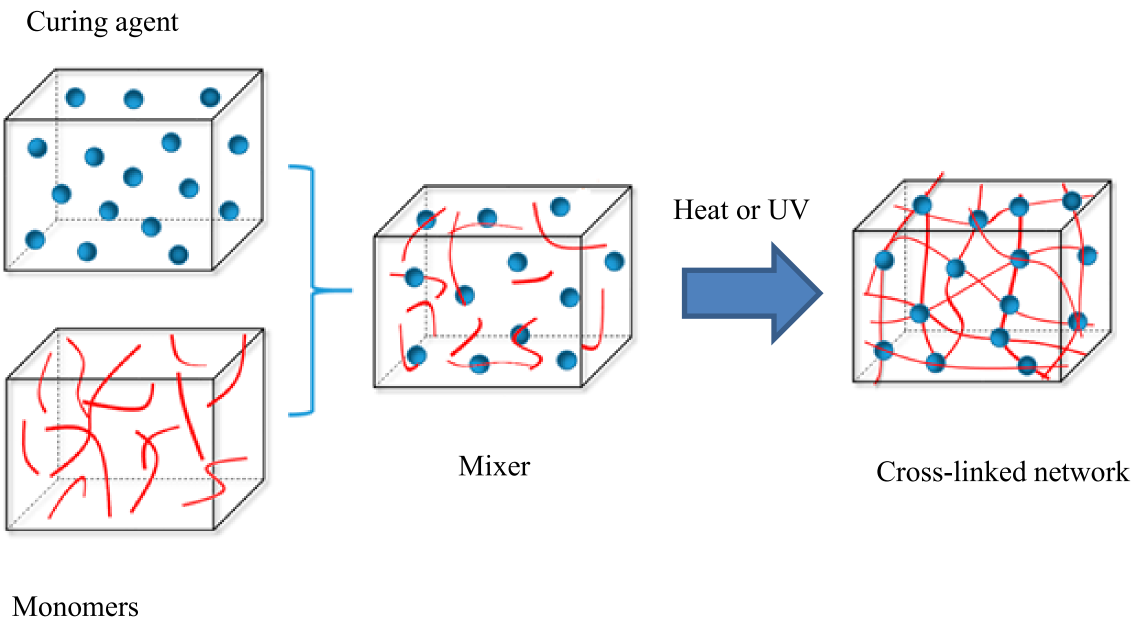


Figure 3. Stages of thermoset formation.[19]

1.2. History of epoxy polymers

Epoxy polymers are one of the most common and widely used thermosets today. In the early 1900s, it was discovered that an epoxide is formed by the reaction between olefins and peroxybenzoic acid. In the mid-1930s, a high-molecular-weight polymer was obtained by reacting polyamines with epoxide compounds resulting from the reaction of ECH with BPA. Finally, the first industrial epoxy polymer entered the market in 1940.[9]

Epoxy polymers are known for their outstanding chemical resistance. In the 1970s, the production and marketing of epoxy vinyl ester polymers thrived due to improved corrosion resistance properties and organic solvents. With the growth of the structural composites market, epoxy vinyl ester polymer composites have found environmental usage applications. Growing demands for aerospace and defense applications in the composite sectors in the 1980s led to the improvement of high-performance multifunctional epoxy polymers based on complex amine and phenolic structures.

Epoxy monomers naturally contain at least two epoxide groups represented by a three-membered ring containing of two carbon atoms and one oxygen atom (Figure 4). The epoxide ring strain causes these epoxy monomers to be highly reactive. These rings are opened by reaction with the second compound, which is the hardener or curing agent. As a result, a cross-linked polymer with high-molecular-weight is formed.[3,20]

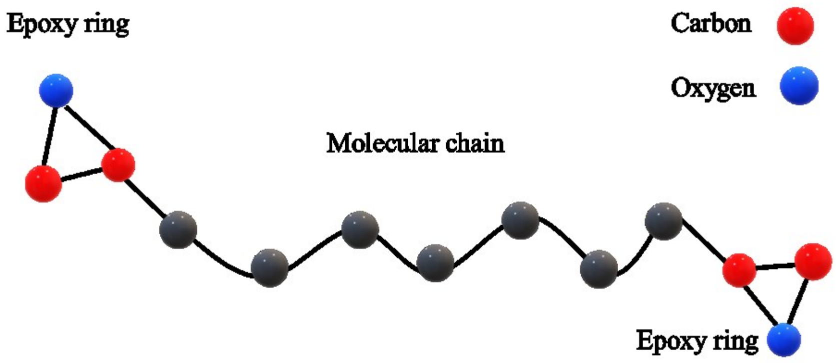


Figure 4. Epoxy monomer structure.

1.2.1 Applications of epoxy polymers

For two reasons, the applications of epoxy-based materials are wide such as automotive, paintings, coatings and flooring, insulation materials, adhesives, composites, and constructions (Figure 5). First, their properties can vary with the choice of epoxy monomers and curing agents. The chemical structure of epoxy allows the production of various polymers with very different properties. Second, epoxy are generally known for their adhesion, chemical and heat resistance, solvent resistance, excellent mechanical properties, and excellent electrical resistance compared to most other polymers.[2]

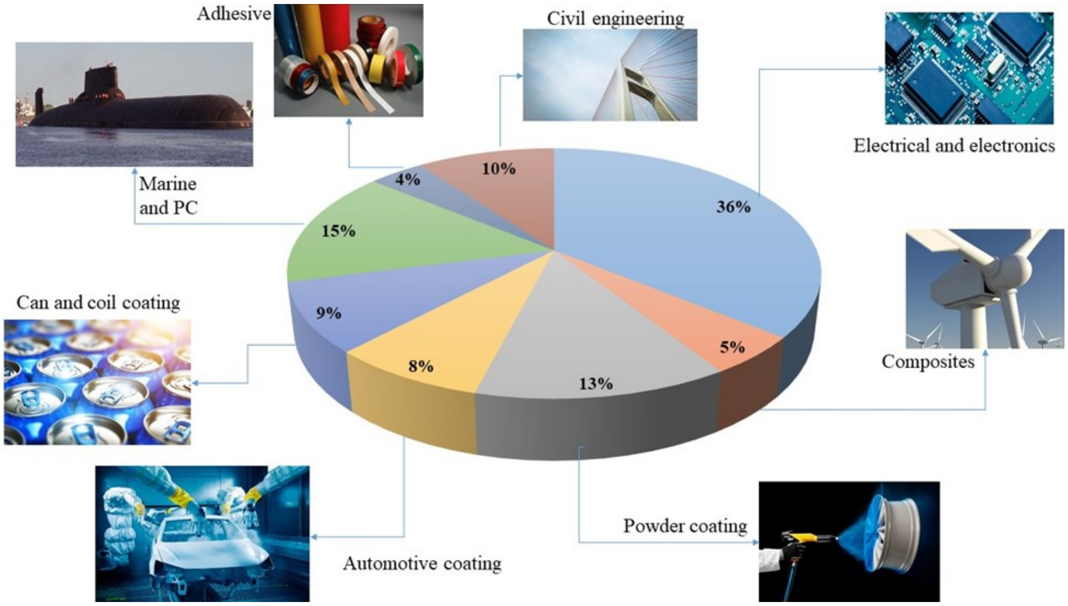


Figure 5. Global epoxy polymer applications.[8]

For further clarification, epoxy polymers are often used for coating metal cans and containers to prevent corrosion, especially when a metal container is in contact with acidic foods. Also, due to the mechanical and corrosion resistance and excellent adhesion to many substrates, epoxy polymers can be applied for decorative flooring and paving.[21] In general, epoxy polymers have made significant progress in adhesives because they have high adhesive properties and reasonable cost. Thus, they are used in the aerospace industry, automobiles, boats, skis, snowboards, and other applications.[22,23] In brief, epoxy polymers are being used more and more, and this upward trend is expected to continues. The growing demand for epoxy polymers in the European market is illustrated in Figure 6.

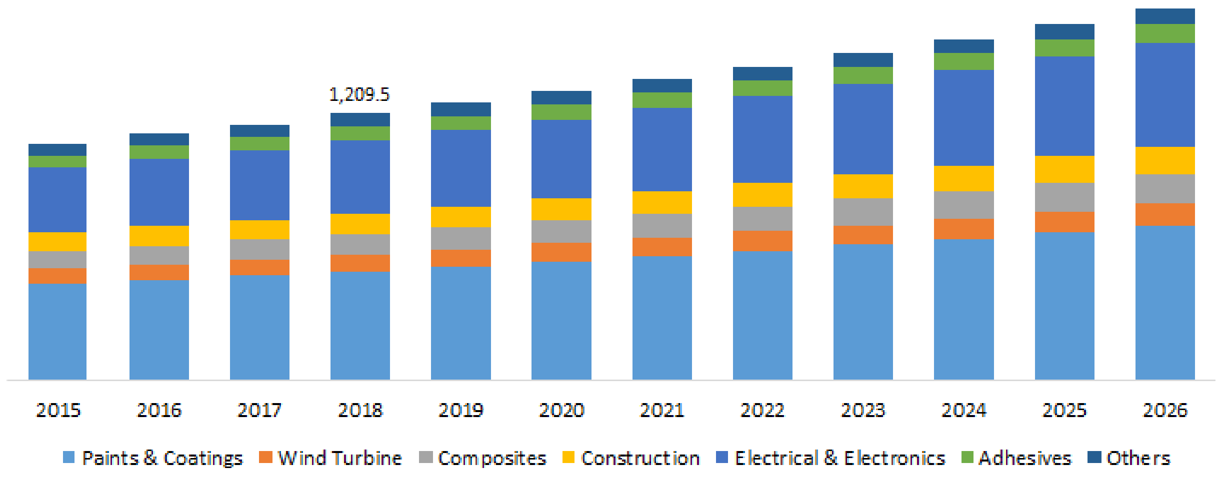


Figure 6. Europe epoxy polymers market between 2015-2026 and application.[24]

1.2.2 Epoxy cure process

Epoxy monomers have more than one epoxide group. They can react with themselves or can react with curing agents (hardeners). In this work, only the latter is considered.[9,25]

Depending on the curing temperature, the desired T_g, or the final mechanical properties, many curing agents are used.

The epoxy curing system is usually carried out by a particular process, such as heat curing, room temperature curing, photo-curing. Generally, epoxy polymers are cured by the heat curing method because the achieved epoxy polymer exhibits better thermomechanical properties. Heat curing contains two steps; pre-curing at a lower temperature and post-curing at a higher temperature.[7,26]

The synthesis of thermosetting polymer begins with monomers that react with each other or with the appropriate curing agent to create branched structures leads to an increase in viscosity. One of the basic features of thermoset preparation is this sol-gel transformation. Viscosity increases to infinity at gelation, and an insoluble fraction (the gel fraction) is created in the system after gelation. In the high conversion of functional groups, the sol fraction vanishes, and the final thermosetting polymer is formed. Gelation in thermosetting polymers is not a reversible process. The system is converted from a gel into a glass when vitrification occurs. For this purpose, the study and interpretation of the various curing and kinetic evolution states are crucial to achieving the optimum level of efficiency in the final material. Time-temperature-transformation (TTT) diagrams are often used to capture the possible curing state. In TTT diagram, the time to gelatin and vitrification is plotted as a function of isothermal cure temperature (Figure 7).

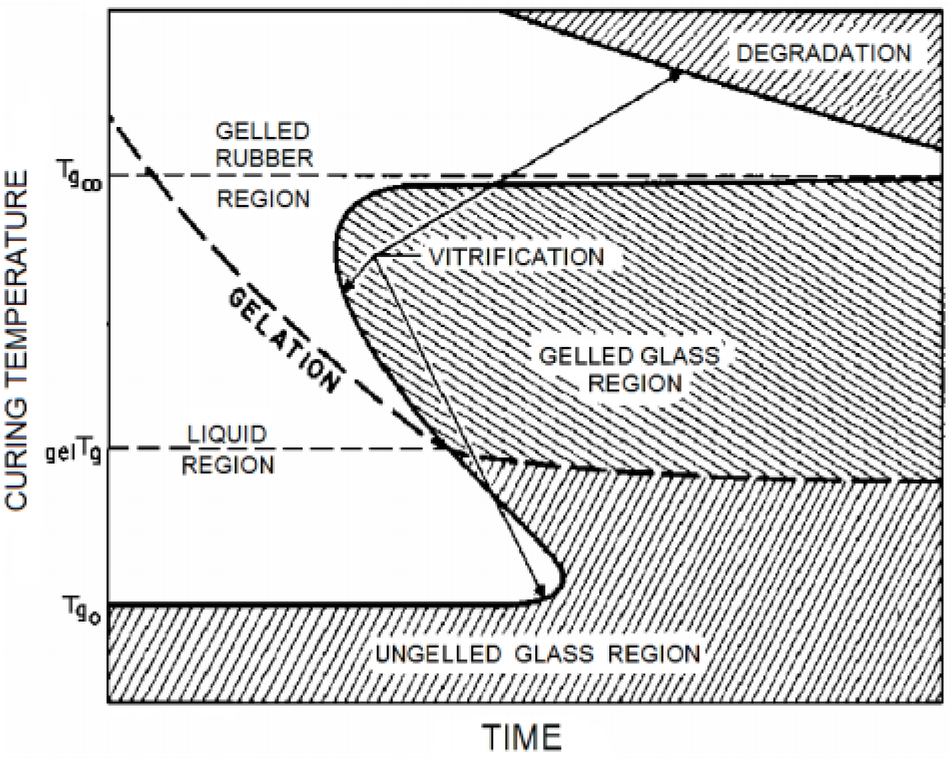


Figure 7. Time-temperature-transformation diagram (TTT).[27]

GP and start of vitrification are the two main characteristics of TTT diagram. The beginning of vitrification occurs when the glass-transition temperature surpasses the curing temperature. Ideally, a suitable thermosetting system for structural applications will cure until all monomers in the network are reacted. The S-shaped vitrification curve and the gelation curve divide the time-temperature plot into four stages, which are liquid, gelled rubber, ungelled glass, and gelled glass.[27,28]

1.2.2.1 *Gelation (theoretical)*

Gelation can be described in a chemical cross-linking system as the moment when the average molecular weight approaches infinity. Two well-known theories related to GP were proposed by Carothers[29] and Flory.[30]

The relationship between the degree of reaction at GP and the average functionality (f_{avg}) of the polymerization system was defined by Carothers. For different types of monomer molecules, the average functionality is defined as the average number of functional groups per monomer molecule:[15]

$$f_{avg} = \frac{\sum N_i f_i}{\sum N_i} \qquad [1.1]$$

Where N_i is the number of molecules of monomer i with functionality f_i. The critical extent of reaction P_c at GP can be obtained:[15]

$$P_c = \frac{2}{f_{avg}} \qquad [1.2]$$

Equation [1.2] can be used to measure the extent of reaction required by its average functionality to achieve the onset of gelling in a mixture of reactive monomers. Experimentally, it is found that P_c is lower than the value predicted by equation [1.2].

α_{gel} is degree of conversion at gel time, according to Flory's gelation theory. α_{gel} depends only on the functionality and stoichiometric ratio of the epoxy systems and it does not depend on the reaction temperature and other experimental conditions. According to this theory, there are two main assumptions. First, all functional groups in monomers react the same way and are independent of the monomers' size, and second, there are no intramolecular connections. The theoretical value of GP conversion degree for the epoxy amine system is given by:

$$\alpha_{gel} = \frac{1}{\sqrt{r_m(f_A - 1)(f_E - 1)}} \qquad [1.3]$$

Where f_A and f_E are the functionalities of amine and epoxy reactants, respectively, and r_m is their molar or stoichiometric ratio.[31] Experimentally, it is found that the Flory's gelation theory underestimates the gel point.

The Carothers equation can only be used in stoichiometric mixtures but for non-stoichiometric ratios, the Flory equation provides more accurate results.

1.3. Epoxy monomers

Commercial epoxy monomers can be produced in three different methods such as ECH etherification, double-bond oxidation, and glycidyl methacrylate etherification which is responsible for the production of more than 90% of commercial epoxy. Epoxy Equivalent Weight (EEW) is an essential feature to characterize epoxy monomers. Based on EEW, the required amount of the curing agent can be calculated. In other words, EEW can be used to determine the stoichiometry between curing agents and epoxy monomers.[26] EEW is a ratio of the molecule weight of a monomer to the number of epoxide groups, which can be calculated as follow:

$$EEW = \frac{M_W}{f} \qquad [1.4]$$

Some of the known epoxy monomers are:

- Bisphenol A epoxy monomer
- Bisphenol F epoxy monomer
- Epoxy phenol novolac monomer
- Cycloaliphatic epoxy monomer

1.3.1 Bisphenol A epoxy monomer (DGEBA)

The first epoxy monomer to be discovered was DGEBA, obtained by a reaction between BPA and ECH. DGEBA still the most widely used monomer nowadays. DGEBA can represent a wide range of properties by varying the number of repeating units in its structure (Figure 8). Aromatic and hydroxyl groups in the backbone improve thermal resistance and provide good adhesion to the epoxy polymer.[1,9]

BPA is derived from petrochemical sources and has a negative impact on human bodies. It is an endocrine disruptor and can increase cancerous tumors, birth defects, and other growth disorders in human body.[10]

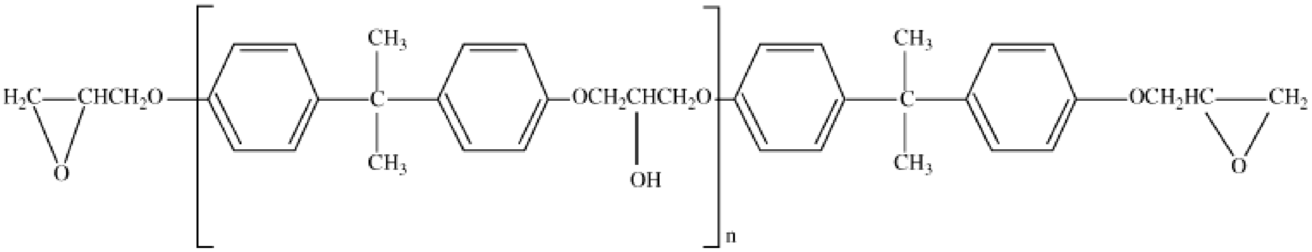


Figure 8. Chemical structure of DGEBA.[7]

1.3.2 Bisphenol F epoxy monomer (DGBEF)

The chemical structures of DGBEF and DGEBA are similar, except that in the DGBEF structure, the carbon between the two aromatic groups is attached to the hydrogen (H) atoms instead of methyl groups in DGEBA.

Consequently, Bisphenol F has a lower molecular weight and viscosity than BPA. Bisphenol F is used as the reactive diluent and has no significant effect on the cured properties.[1,9]

1.3.3 Epoxy phenol novolac monomer

Epoxy phenol novolac can be classified as a multifunction epoxy monomer produced by reacting between a phenolic novolac monomer with ECH. The chemical structure of the novolac epoxy monomer is shown in Figure 9. Due to the high number of epoxide functions in this molecule, a highly cross-linked density polymer can be achieved. This feature can improve solvent, chemical, and thermal resistances.[1,9]

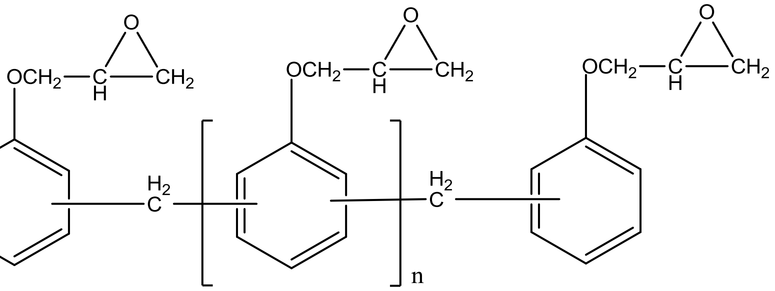


Figure 9. Chemical structure of novolac epoxy monomer.[9]

1.3.4 Cycloaliphatic epoxy monomer

Figure 10 shows the structure of the most classical cycloaliphatic epoxy monomers mentioned previously. Due to the absence of chromophores, these monomers are principally used in UV-curing formulation. The obtained polymer shows a variety of properties including, outstanding UV stability, strong thermal stability, excellent environmental and electrical properties.[1,9] Table 1 shows the classification of epoxy monomers and their properties.

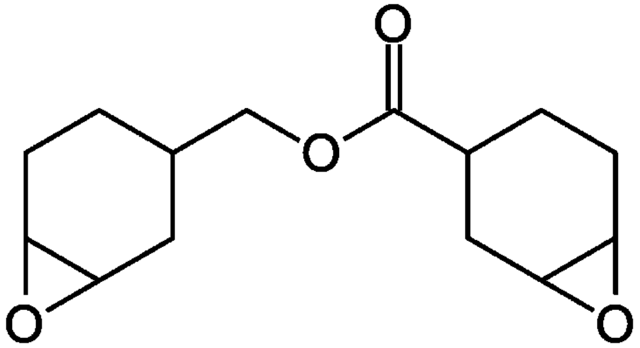


Figure 10. Chemical structure of cycloaliphatic epoxy.[7]

Table 1. Classification of epoxy monomers.[32]

Chemical class	Physical form	Reactive sites	EEW (g/eq)	Viscosity (cP)	Applications
Bisphenol A	Liquid, solid	2	174–500	5,000–20,000	General
Bisphenol F	Liquid	2	165–190	2,000–7,000	High fillers
Novolac	semisolid, solid	2-5	150–280	20,000-50,000	High thermal resistance
Cycloaliphatic	Liquid	2	131 - 143	250–450	UV curing

1.4. Curring agents

Epoxy monomers can react and form cross-linked networks with a wide range of chemical materials called curing agents. The curing agent also can be called hardeners, curatives, co-reactants, co-polymers. There are infinite ways to formulate epoxy monomers and hardeners to control properties such as T_g, pot life, cure kinetics, gel time, physical form, system stability, mechanical performance, viscosity, chemical resistance, and cost. Some of the curing agents are listed as bellow:[9]

- Amines
- Amine adducts
- Cyanoethylated amines
- Ketimines
- Polyoxyalkylene amines
- Cycloaliphatic amines
- Aromatic amines
- Polyamides
- Amido amines
- Dicyandiamides
- Polyester co-polymers
- Phenolic co-polymers
- Melamine and urea formaldehyde co-polymer monomers
- Phosphate flame retardants
- Ultraviolet and electron beam curing of epoxy monomers
- Mannich bases
- Mannich-based adducts
- Anhydrides
- Carboxylic acid

1.4.1 Amine functional curing agents

Generally, most epoxy curing agents are based on amines. The functionality of the amine is calculated by the number of hydrogen atoms in the amine molecule. Thus, the primary amine ($-NH_2$) and the secondary amine (-NH-) can react with two epoxide functions and one epoxide function, respectively (Figure 11). Tertiary amine has no active hydrogen, so it cannot react directly with the epoxy monomers, but it can act as a catalyst. Besides, tertiary amine accelerates the cure of primary and secondary amine with epoxy monomers.[33]

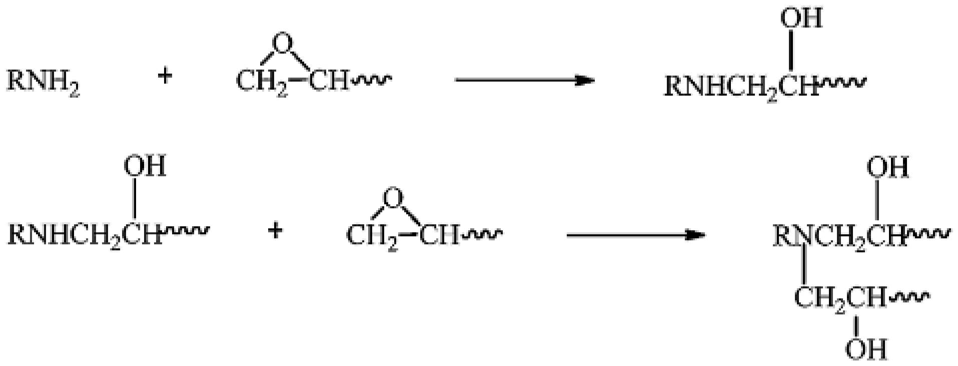


Figure 11. The reaction of amines with an epoxy monomer.[7]

1.4.2 Anhydrides

Anhydrides are another type of epoxy curing agent, that are produced in various forms. The presence of a tertiary amines as a catalyst is essential for epoxy-anhydride systems. The reaction process between an anhydride as a curing agent and an epoxide group is complex. Initially, the anhydride reacts with the secondary alcohols from the epoxy backbone or other alcohols (aliphatic) to form a half-ester containing carboxylic acid. Then, the carboxylic acid group can react to open an epoxide ring that forms another hydroxyl. The reaction continues as shown in Figure 12.[7,9]

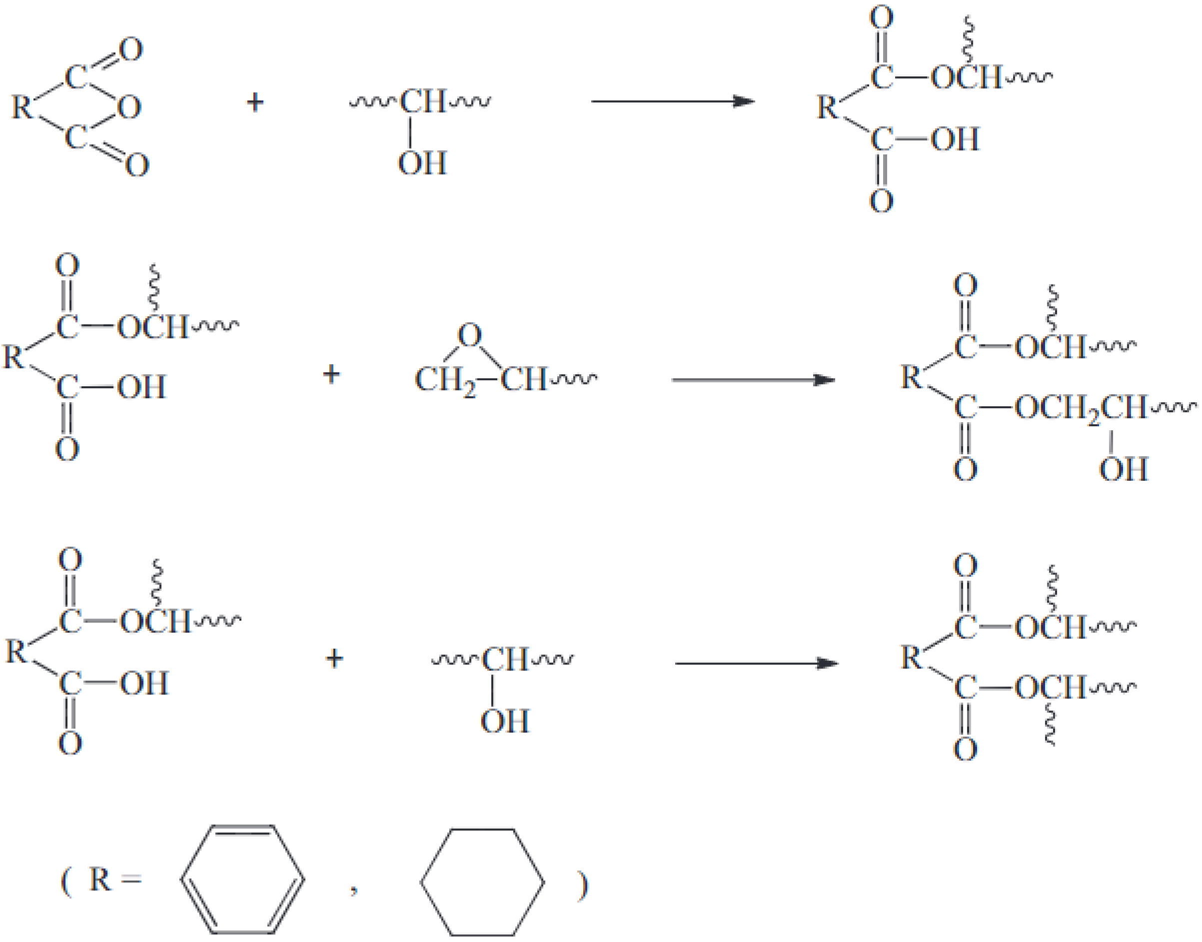


Figure 12. The mechanism of reaction between anhydrides and epoxy monomers in the presence of a tertiary amine.[7]

1.4.3 Carboxylic acid cure agents

Carboxylic acids are another class of curing agent that are used in epoxy technology. Epoxy reaction with carboxylic acids requires a catalyst and high temperatures to have an acceptable reaction rate. Because carboxylic acids have lower nucleophilicity than amines, both base and acid catalysis have been applied in these reactions. Still, base-catalyzed is usually preferred because the initiation of the competing homopolymerization of epoxy polymerrs is more limited in that case.[34] Figure 13 illustrates the base-catalyzed curing mechanism with a carboxylic acid.[26]

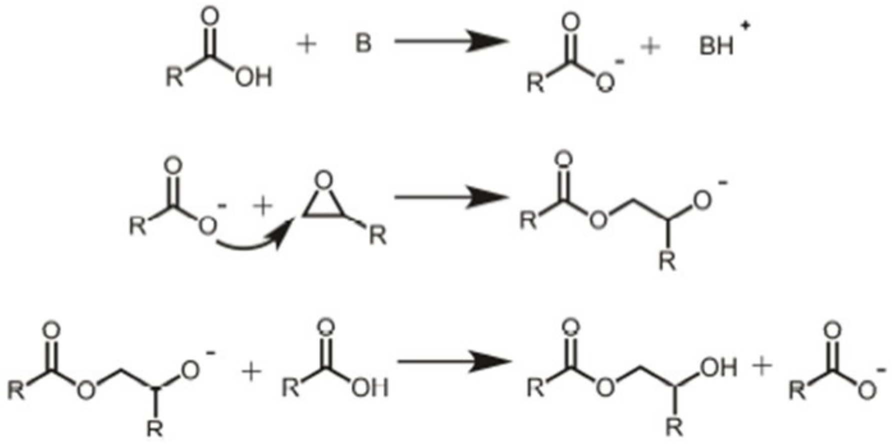


Figure 13. The mechanisms for the curing of an epoxy monomer with carboxylic acids under base-catalyzed conditions.[35]

Triphenylphosphine and ethyltriphosphonium iodide (ETPI) are widely used to catalyze the carboxylic acid/epoxy monomer reactions.[35]

Table 2. Curing agents for epoxy monomers.[9]

Type	Advantage	Disadvantage	Application
Aliphatic amines and adducts	cure in room temperature	toxic; moisture sensitive	flooring; adhesives
Polyamides	low toxicity	expensive	adhesives
Anhydrides	good mechanical and thermal properties	cure at high temperature	composites
Phenol-formaldehyde, novolacs	good chemical resistance	weak ultraviolet stability	electrical laminates
Phenol-formaldehyde resols	excellent chemical resistance	fragile	coating for can
Urea-formaldehyde	reasonable price	Curing in high temperature	coating
Melamine-formaldehyde	good hardness	curing in high temperature	oven paints

Cycloaliphatic amines	low toxicity	slower reactivity; high costs	industrial coatings
Aromatic amines	good resistance in moisture	long time to cure	composites
Dicyandiamide	electrical properties	low compatibility with epoxy monomers	coatings
Carboxylic-terminated polyesters	high mechanical properties	low chemical resistance	powder covering

1.5. Bio-based epoxy monomers

Most of the epoxy monomers on the market are petroleum-based, and their stockpiles have been significantly reduced. Furthermore, a better understanding of the climate and growing environmental and health concerns have pushed forward the use of renewable resources. Therefore, in recent years, research has been conducted on the partial or complete replacement of epoxy monomers such as DGEBA by renewable monomers.[3,36] Bio-based epoxy monomers are currently derived from several bio-based feedstock[37], including vegetable oils, lignin, tannins, cardanol, terpene, and carbohydrates, are summarized below.

1.5.1 Vegetable oil-based monomers

Vegetable oils, such as linseed oil, soybean oil, and castor oil, appears to be excellent raw materials for thermosetting polymers. Epoxidation of various vegetable oils, which are fatty acid esters of glycerol, is one of the most popular ways for producing bio-based epoxy monomers in the chemical industry.[38–40] The preparation of this oil is a solvent-free process, which occurs with high conversion and selection, as reported by Kim and Sharma.[41]

Many applications of oil-based epoxy monomers are used in the non-engineering field because the mechanical performance of oil-based epoxy monomers is low. Oil-based epoxy monomers are used in coatings and adhesives or as reactive diluents to minimize the viscosity of petroleum-based epoxy monomers.[42]

Epoxidized vegetable oil (EVO) in epoxy systems was investigated by Miyagawa and et al.[43] It was observed that EVO could increase the toughness and decrease the T_g of epoxy polymers compared to those epoxy polymers synthesized with DGEBF and DGEBA.[43–46] Epoxidized structures of soybean oil and castor oil are shown in Figure 14.[7]

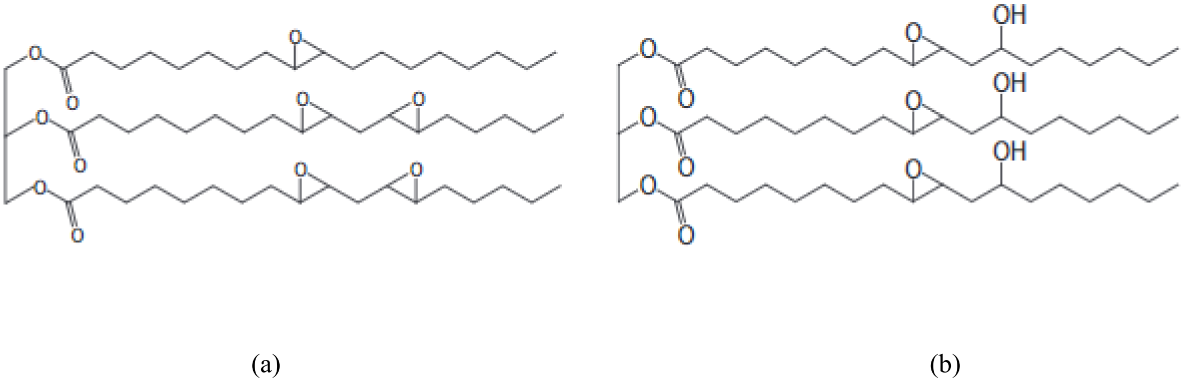


Figure 14. (a) Epoxidized soybean oil, (b) Epoxidized castor oil.[7]

1.5.2 Lignin-based monomers

Wood is composed of three primary components: 1) cellulose, skeleton; 2) hemicellulose, matrix; 3) lignin which is a substance that holds cells together and ties them together and imparts stiffness to cell walls. Lignin is the second most abundant macromolecule in nature after cellulose. This substance is usually considered waste. Aliphatic and phenolic hydroxyl groups are two parts of lignin, which can be used to synthesize bio-based polymers.[47]

Epoxy monomers based on industrial lignin have been described in the literature[47], and most of them involve pre-treatment before epoxidation reaction because lignin has a highly branched and irregular structure (Figure 15). Treatments are such as chemical, biochemical and physical processes. The chemical structure and lignin properties depend on the type of treatment.[48]

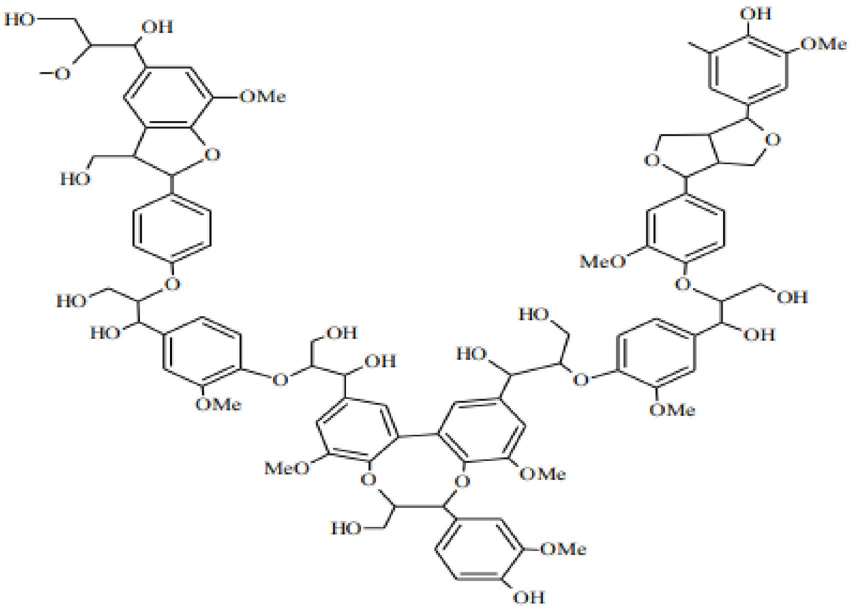


Figure 15. A fraction of lignin model structure.

Lignin has an irregular structure, so some attempts have been made to break down lignin into beneficial chemical compounds such as vanillin. As shown in Figure 16, there are three ways to synthesis vanillin-based epoxy monomers, which all present good thermal resistance.[49–51]

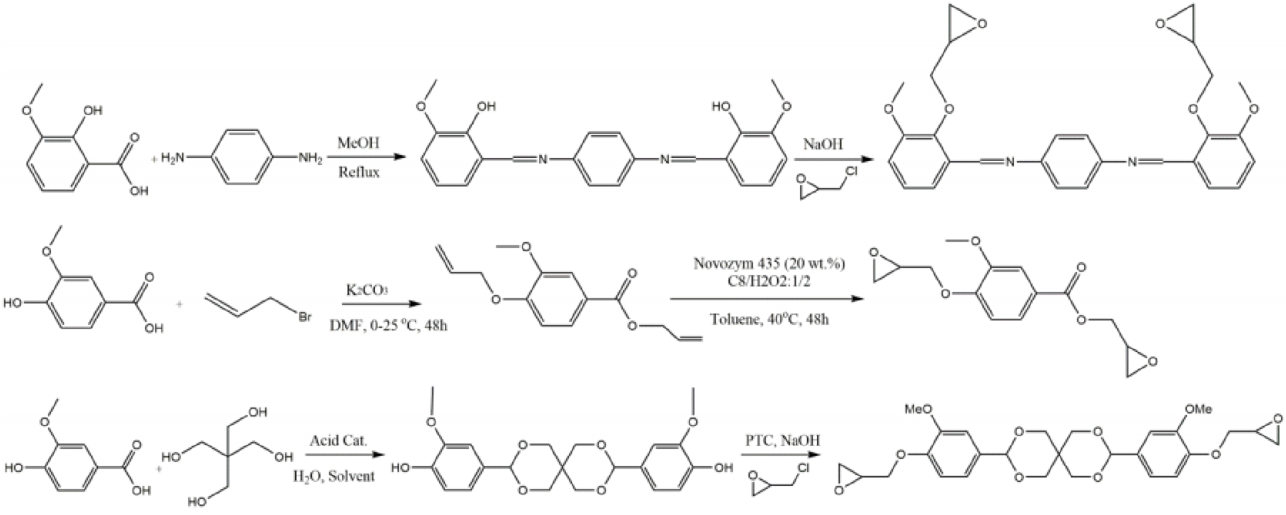


Figure 16. Three ways of synthesizing vanillin-based epoxy monomers.[52]

Feng and Chen[53] mixed lignin-based epoxy monomers and DGEBA in different percentages, and samples were cured using triethylenetetramine (TETA) as a hardener. It was found that samples made with lignin-based epoxy monomers have more adhesive shear strength than the samples devoid of such monomers.

1.5.3 Tannin- and cardanol-based monomers

Gallic acid, catechin, curcumin, resveratrol, green tea tannins, and cardanol can be categorized as polyphenol compounds. Gallic acid can be epoxidized with ECH. Other methods for the epoxidation of gallic acids, such as the use of a two-step synthesis involving the allylation of OH groups, were reported.[54]
Curcumin and resveratrol have been studied in the hopes of developing new biobased epoxy monomers.[55]
Tannins are water-soluble phenolic compounds, that are stored by plants as a product. Epoxy monomers were synthesized by ECH reaction with green tea extracts.[56,57]
Green tea tannins have five different chemical structures, namely, epicatechin (EC), catechin (CT), epigallocatechin (EGC), epicatechin gallate, and epigallocatechin gallate (EGCG). Green tea-based epoxy polymers have an interesting T_g. However, their mechanical properties have not been reported.[58]
Cardanol is obtained in large amounts by vacuum distillation of cashew nut shell liquid. In the presence of NaOH, cardanol monoglycidyl ether reacted with ECH in the phenolic OH group leads to a monoepoxide that can be used as a reactive plasticizer. Cardanol and BPA in different molar compositions were mixed and then cross-linked with a polyamine. The obtained polymer showed less rigidity due to epoxied cardanol act as a reactive plasticizer.[58,59]

1.5.4 Carbohydrate-based monomers

Due to the presence of highly reactive hydroxyl group(s) in carbohydrates, a wide range of monomers can be synthesized, making them suitable for developing various polymer groups.[60–63]
Compared to those coming from the petrochemical feedstock, carbohydrate-based products usually exhibit lower toxicity and greater vulnerability to biodegradation. Carbohydrate-based materials include cellulose and starch. Various epoxidizing reagents such as hydrogen peroxide and ECH have been used to epoxidize starch and cellulose.[64–66]
One of the most well-known and available sources of starch is corn that can be converted to sugars, fuels, or new chemicals such as isosorbide (Figure 17). The epoxy polymer was synthesized with isosorbide-

based epoxy monomers, improved some properties such as impact strength and tensile compare with a commercial epoxy polymer. Hence, isosorbide-based epoxy monomers can be substituted for DGEBA. Still, expanded research is needed to promote their hydrolytic stability.[67]

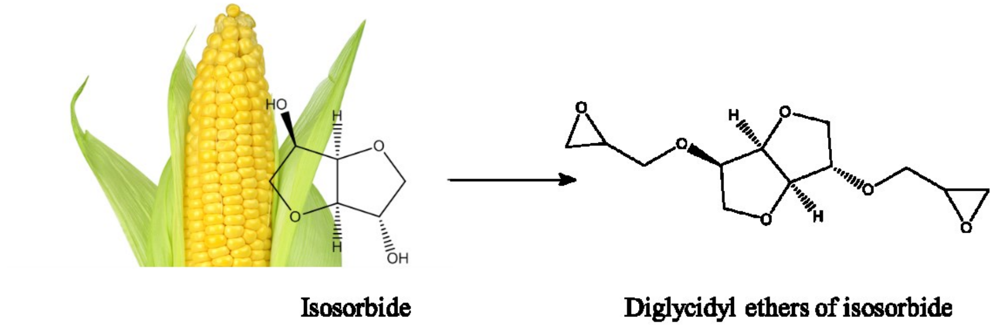


Figure 17. Producing bio-epoxy monomer from corn.

1.5.5 Terpene-based monomers

One of the most important groups of bio-sourced materials is constituted of rosin acids, terpenoids, and terpenes. Rosin acids contain approximately 90% of abietic acid and its isomers. They are obtained from a pine tree. Due to the presence of aromatic structure in rosin acids, it is a rigid molecule. It is also a strong candidate for the preparation of rigid and highly cross-linked epoxy polymers.[68]

Liu et al.[69] prepared trifunctional abietic acid epoxy monomers and obtained a completely bio-based epoxy polymer with comparable mechanical properties to the benchmark DGEBA using anhydrides as a curing agent.

Mantzaridis et al.[70] have synthesized numerous functional epoxy monomers from rosin acids. The properties of the obtained epoxy polymer when it was synthesized with DGEBA were studied in terms of T_g. It was concluded that the lowest values of T_g were attributed to the polymer containing 40% of rosin-based monomer (Figure 18).

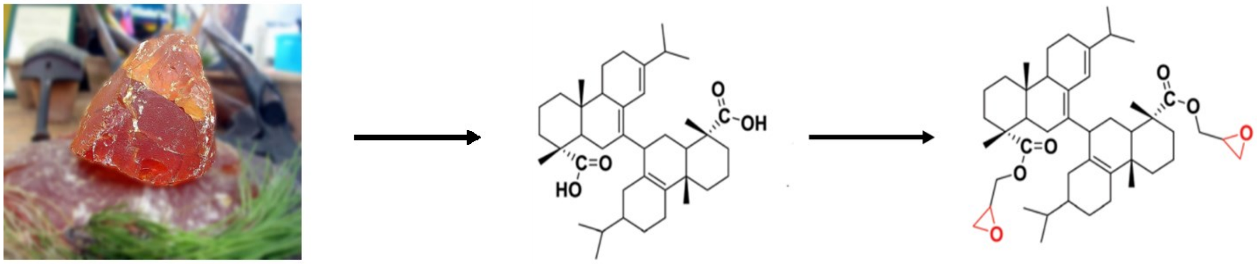


Figure 18. Synthesis bio epoxy monomer from rosin acids.

1.5.6 Limonene-based epoxy

Among all terpenes, one of the most well-established ones is limonene, which is a cyclic diterpene containing carbon-carbon double bonds. Limonene oxide and can be obtained by epoxidation of the double bond. These products are commercially available (Figure 19).[3]

Globally, 88 million tonnes of citrus are produced each year, including oranges and lemons. Approximately 50 percent of oranges and lemons are refined into marmalade or juice, creating an approximated 40 million tonnes of citrus waste which is a significant global waste.[13,71,72]

Figure 19. Structure of limonene, limonene oxide, and LDO.

1.6. Formulation of epoxy systems

Developing the right epoxy formulation is the most critical step to achieve a three-dimensional cross-linked network. Several steps must be considered to attain a successful epoxy formulation with the desired properties for the specific application. First of all, each epoxy monomer should react with the right and proper curing agent. Secondly, the stoichiometric ratio of the epoxide functionality/curing agent should be calculated. Also, if the reaction needs to have a catalyst/accelerator, it should be considered. Afterward, curing and post-curing processes and their conditions should be determined.[1,73,74]

1.6.1 Relationship between the structure and properties of the cured epoxy polymer

Properties of cured epoxy vary with cross-link density, monomer structure, and curing method.[1,75,76] For example, the epoxy polymers which are cross-linked with dicarboxylic anhydrides produce polyesters that have a little resistance to moisture but a high resistance to oxidation.[77] It is the opposite with cross-linked amine epoxy that is very weak against oxidation, but resistant to saponification. Many factors such as cross-link density, type of curing agents, and epoxy monomers can be controlled by curing temperature and process.[77,78]

1.6.2 Epoxy cure chemistry

Curing of the epoxy monomers occurs in three steps. First, monomers grow linearly and molecular weight increases. At the second step, the chains start branching. Finally, an insoluble continuous three-dimensional network is formed if the adequate amount of these branches interconnect and GP is reached. There is a certain amount of extractable monomers in the insoluble gel network that has not bonded with the network, which is referred to as the sol fraction. At the end of the reaction, most of the residual sol part is connected to the network. The rate of the chemical reaction can be controlled kinetically when the glass transition is lower than the cure temperature. When the network forms, GP temperature of the system rises, and finally, T_g reaches the cure temperature. The curing reaction continues slowly under these conditions since the reaction rate is restricted by the rate of diffusion of the un-reacted monomers, an experience known as vitrification. Chemical reaction rates can be insignificant when an epoxy curing reaction has achieved vitrification, which leads to having a high soluble fraction. The unreacted monomers can have a negative impact on the final properties of the cured polymer, so a second cure known as a post-cure is typically used to minimize sol fraction and have a complete cure. The cure of epoxy polymers can proceed with three main chemical mechanisms, which are as follow:[26,79,80]

1. Nucleophilic addition.
2. Cationic polymerization.

3. Anionic polymerization.

These processes are shown in Figure 20.

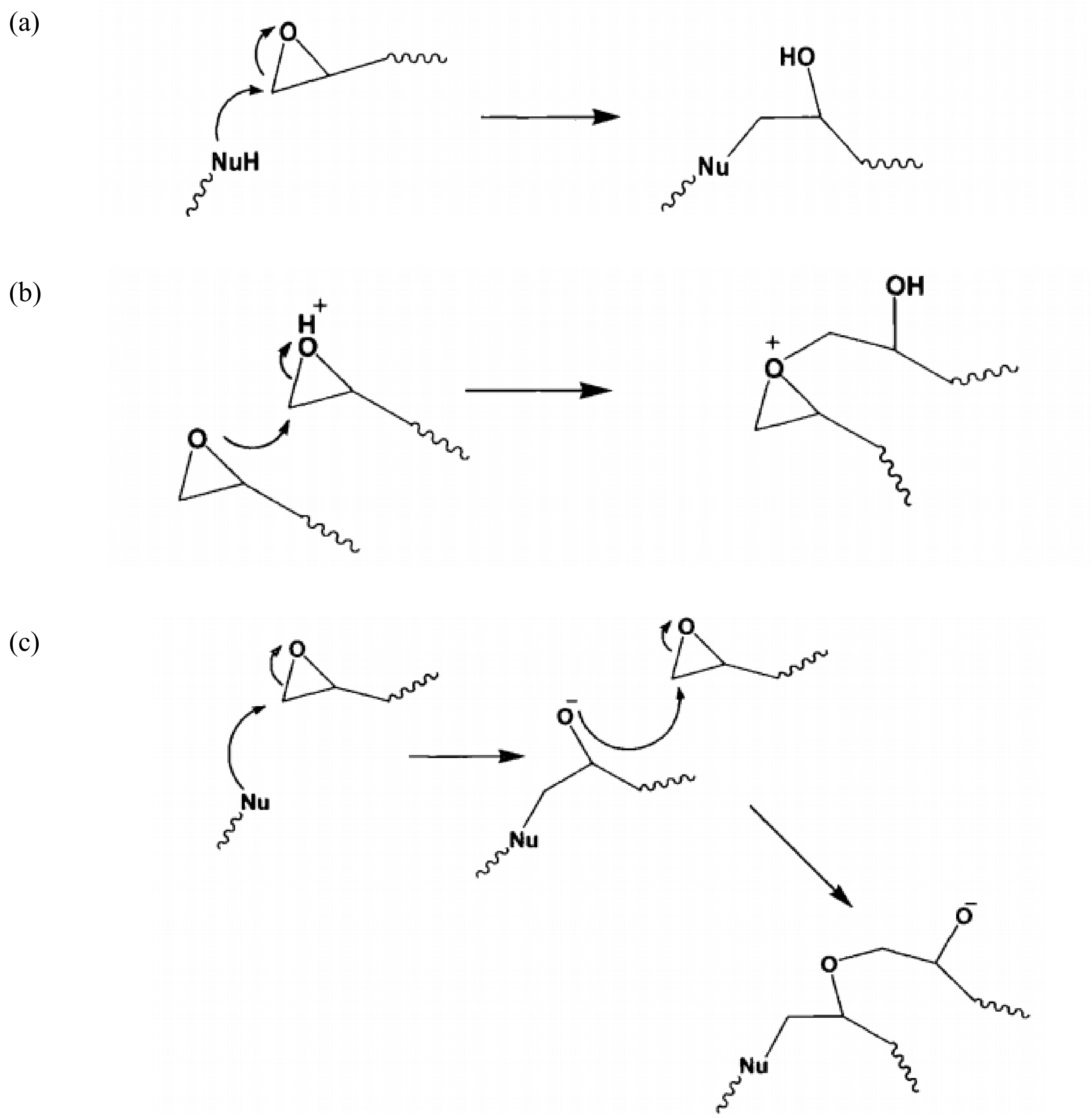


Figure 20. Reaction mechanism of epoxy monomers via (a) nucleophilic addition of an active hydrogen nucleophile. (b) cationic polymerisation. (c) anionic polymerization.[80]

1.6.3 Epoxy monomer/curing agent stoichiometric ratios

The stoichiometric ratio of epoxy monomer/curing agent has an influential factor in network configuration and efficiency.[1,81] Theoretically, one equimolar of epoxide functionality and hardener should react together to obtain a cross-linked thermoset.[81,82]

Excess amine in the epoxy system can act as chain-stoppers, leading to a decrease in cross-linking. Therefore, the obtained polymer can be slightly tougher but more vulnerable to moisture and chemicals. In formulas containing anhydrides, owing to substantial epoxy homopolymerization, less curing agents are usually used.[1,83–85]

1.7. Catalytic cure

A group of compounds that can enhance the rate of a reaction without interfering with the process is known as catalysts or accelerators. The choice of catalyst and catalyst amount are two important factors in the epoxy curing reaction. Several factors such as cost, toxicity, solubility, processing effects, final characteristics, regulatory issues, and ease of use must be taken into account to select a catalyst.[86] Lewis bases have a pair of nonbonding electrons that attacks electrophilic, whereas a Lewis base is an electron-pair donor. Typically, nucleophilic catalysts can be used with acidic curing agents to reduce the gel time.[87] For example, tertiary amines are used to catalyze the anionic homopolymerization of epoxy via the formation of a zwitterionic alkoxide group (Figure 21). This alkoxide attacks another epoxide leading to the formation of another alkoxide with glycidyl ether monomer. This reaction happens at the ends of the monomers, leading to a cross-linked polymer. Anionic initiators cannot be used to cure cycloaliphatic epoxy.[88]

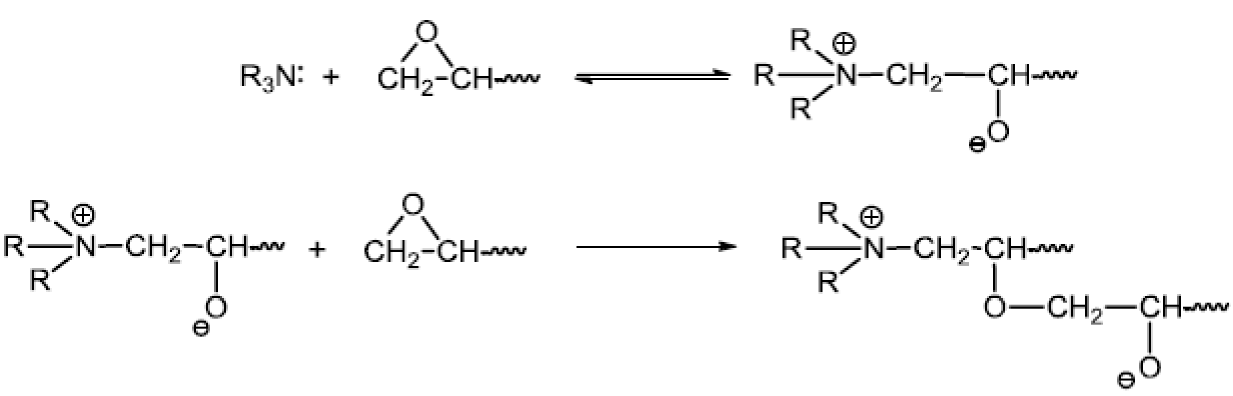


Figure 21. The curing mechanism reaction of epoxy monomers with tertiary amines.[88]

1.7.1 Lewis acids

There is an empty outer orbital in Lewis acid catalysts can gel epoxy monomers within minutes. Also, the curing process is slowed by the complexation of the Lewis acids with amines.[86,89] The first Lewis-acid catalyst was reported by Kobayashi in 1991.[90]

Metal ions have one or two empty orbitals and may behave like Lewis acids. Lewis acids such as boron trifluoride (BF_3) are a substance that accepts a pair of electrons. They are electron attracting and attack places with high electron densities, such as epoxide ring-opening reaction. BF_3 and epoxy monomers can react together very fast and form a cross-linked network. Boron trihalide (BX_3) is a Lewis acid and it has been found that it can improve amine reactions.[91] It is possible to achieve an acceptable pot life using these complexes because the temperature needs to be increased to cleave the complex between BF_3 and the amin. The choice of halide and amine can control the reaction. Besides, the choice of amine affects other properties such as moisture sensitivity and solubility in the polymer. Mono ethylamine-borontrifluoride ($BF_3 \cdot NH_2C_2H_5$) is the most common complex. It is a crystalline substance that cures epoxy monomers at 80–100 ºC.[92] The mechanism reaction is shown in Figure 22.[88]

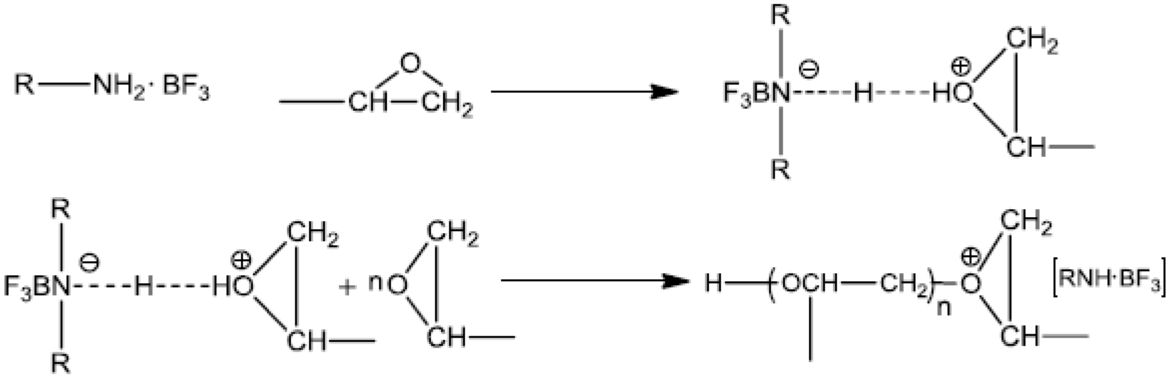


Figure 22. The mechanism of epoxy monomers curing with BF_3 amine complexes.[88]

Lanthanides are strong Lewis acids, so they have a significant effect on carbonyl oxygen. Lanthanide salts in combination with an electron-withdrawing group such as triflates have strong Lewis-acid reactivity. Lanthanide triflates such as samarium(III) triflate ($Sm(OTf)_3$), ytterbium(III) triflate ($Yb(OTf)_3$), or lanthanum(III) triflate ($La(OTf)_3$) was proposed as cationic epoxy catalysts in the literature.[93] Lanthanide triflates are cheap, easy to handle, stable in water and air, low toxicity, and heat stable.[90] Yb^{3+} has higher hardness and Lewis acidity than other lanthanide cations. So, $Yb(OTf)_3$ as a catalyst can allow the curing reaction to being performed at a low temperature.[94] Besides, materials obtained using $La(OTf)_3$ have a lower T_g than those obtained with $Yb(OTf)_3$.[35] Benzyl ammonium, benzyl sulfonium, and benzyl phosphonium salts are other thermal cationic catalyst.[88,95]

1.7.2 Lewis bases

In Lewis bases, there is an unshared electron pair or outer orbital that can react with low electron density regions. This type of catalyst can be used as nucleophilic catalytic curing agents for primary amines, polyamides, and amidoamine, or as a catalyst for anhydrides. The most commonly used nucleophilic catalysts are tertiary amines and imidazoles.[96,97]

1.8. Characterization of epoxy curing and cured networks

Since thermoset polymers form a cross-linked network after curing, they are insoluble in solvents. Therefore, because of that insolubility, they are more challenging to analyze. Various techniques are used to characterize epoxy and obtain information about functional groups, conversion, thermal, physical, and mechanical properties.

Thermal analysis of polymers such as Thermal Gravimetric Analysis (TGA), DSC, DMA can be used to investigate the thermal properties and to examine the curing process, degree of cure, and T_g.[98]

Epoxy polymers are widely used in the adhesive industry, so surface characteristics such as dynamic contact angle and surface tension play an important role. They also need to be analyzed using microscopic techniques such as Scanning Electron Microscopy (SEM),[99] Transmission Electron Microscopy (TEM), and Atomic Force Microscopy (AFM).[100]

Due to their high density of cross-linking, epoxy polymers have high mechanical properties, but they are fragile and have low impact tolerance. The tensile test is a standard measure used to examine elongation at break, resistance in failure, tensile stress, young modulus.[101,102] To better identify epoxy and its functions, methods such as swelling,[103] functional groups titration, FTIR,[104] or NMR spectroscopy have been used.

1.8.1 Cure kinetics

Understanding the curing process and the relationship between the structure and property of the cross-linked epoxy polymers can help have economic products and optimize physical properties. Various experimental techniques, including ultrasound, X-ray analysis, NMR, DSC, dielectric and infrared spectroscopy, etc., are required to understand the reaction kinetics and the characteristics of the microscopic engineering structure.[105,106]

1.8.1.1 Kinetic characterization using DSC

Usually, the kinetics of the cured reaction of thermosets are investigated by applying DSC. Generally, the aim of kinetic analysis of a curing thermostat is to estimate the reaction rate or Tg for a temperature-time contour by creating a kinetic model. In this regard, DSC has been used as a useful tool for evaluating rate of conversion and estimating related kinetic parameters.

DSC measurements of thermoset reactions are divided into two tests, isothermal tests, and non-isothermal tests. The rate of released energy at a constant temperature is calculated in the isothermal test, and the degree of the reaction is estimated by equation [1,5].[106–108] The key assumption of this method of study is that the total heat of the reaction can be precisely evaluated and that all reactions have the same total enthalpy.

$$\alpha = \frac{\Delta H_t}{\Delta H_{total}} \qquad [1,5]$$

Where ΔH_t is the total heat evolved up to time t, ΔH_{total} is the total heat released during a complete reaction, and α is the degree of conversion.

The reaction heat is monitored through a linearly rising temperature scan in non-isothermal scanning experiments. These analyses include the derivation of kinetic data from phase integrals of the rate curve and the derivation of a relationship from exotherm maxima at different heating speeds for kinetic parameters.[109,110]

1.8.1.2 Cure kinetic models

The monomers can be converted into a highly cross-linked three-dimensional macromolecule, resulting from the curing process in thermostats. In general, the curing degree, α, indicates the rate of chemical reaction of the curing polymer, usually defined as equation [1,5].[111] For an uncured polymer, $\alpha = 0$, while for a fully cured polymer, $\alpha=1$.

The curing rate is proportional to the heat generation rate, and can be given as follows:

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_{total}}\left(\frac{dH}{dt}\right) \qquad [1,6]$$

A number of models for cure kinetics have been proposed to describe the curing mechanism of various systems. The simplest one is the equation of the nth order rate:

$$\frac{d\alpha}{dt} = K(1-\alpha)^n \qquad [1,7]$$

$$K = Aexp(\frac{-\Delta E_a}{RT}) \qquad [1,8]$$

Where K, which is an Arrhenius temperature function, is the reaction rate constant, A is the pre-exponential constant or Arrhenius frequency factor and n is the reaction order. ΔE_a is the activation energy, R is the universal gas constant, and T is the absolute temperature.

Table 3 summarizes the models presented in the literature to explain the chemical kinetics of thermoset cures.[110–113]

Table 3. Kinetic models for the thermoset cure chemical kinetic.[114]

Model	Equation	Equation no.
Nth order reaction	$\frac{d\alpha}{dt} = K(1-\alpha)^n$	[1,7]
Autocatalytic reaction	$\frac{d\alpha}{dt} = K\alpha^m(1-\alpha)^n$	[1,9]
Nth order + autocatalytic reaction	$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1-\alpha)^n$	[1,10]
Arrhenius dependence of rate constant	$K = Aexp(\frac{-\Delta E_a}{RT})$	[1,8]

Where:

α = calorimetric conversion,

$\frac{d\alpha}{dt}$ = reaction rate,

m, n = reaction orders,

T = absolute temperature,

R = universal gas constant,

E = activation energy.

1.8.2 Gel-timer test

When epoxy monomers start to cure with hardener, they change from a liquid to a solid. It can be considered that gelation is the first emergence of a cross-linked network. During the reaction, the viscosity of the liquid increases until it reaches GP. Before GP, the liquid polymer is known as sol because it dissolves in a good solvent. After GP, a rigid polymer is considered a gel because it swells only in a good solvent. However, the unconnected molecules (sol fraction) are still in the gel part. Figure 23 shows a schematic of the epoxy reaction as follows (a) monomers and hardener, (b) Linear/branched oligomers, (c) Sol/gel transition, (d) 3D network.[115]

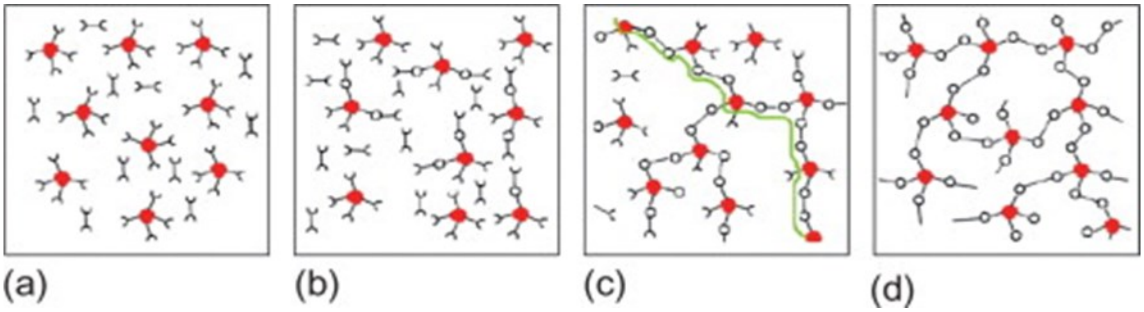


Figure 23. Schematic of epoxy reaction.[115]

One of GP measurement methods is the gel timer test, which determines the formation time of the gel part. Other tests can be offered to find GP, such as rheology and DMA. The viscosity in GP is infinite, while the modulus is still zero because the stress in a deformed critical gel can still be completely relaxed (Figure 24).[116]

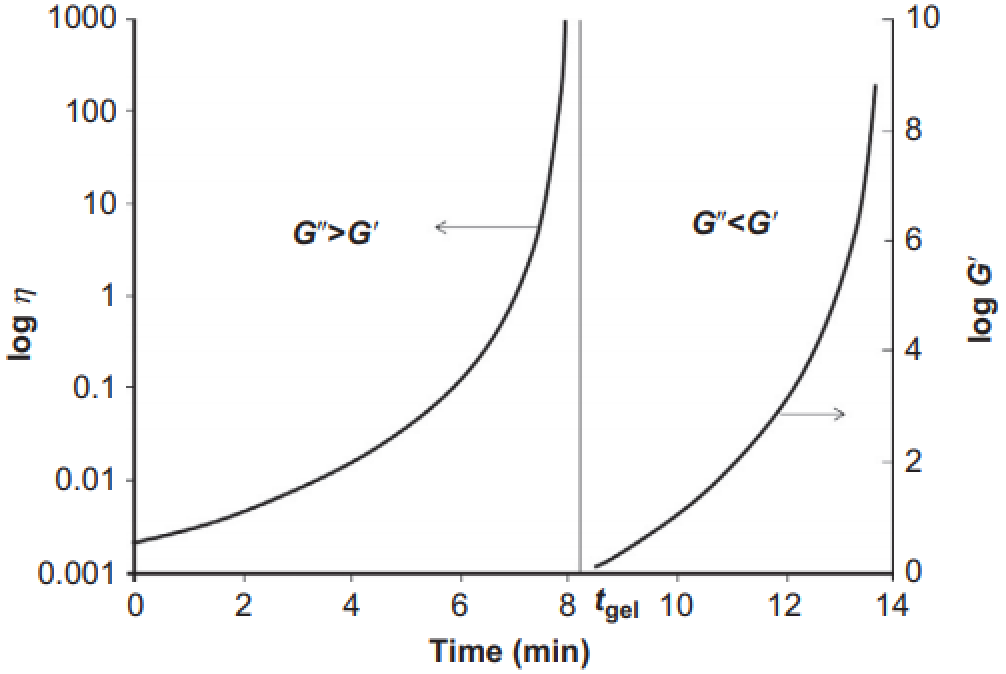


Figure 24. Modulus and viscosity changes during of a thermoset during cross-linking.[115]

1.9. Characterizing cross-linked networks

Structural parameters such as the cross-link density, chain distribution, the completeness of the network, and the number of polymer chains not joined to the network can affect cross-linked structures. Figure 25 presents the different forms of the cross-linked network configurations in thermoset polymers that can be considered by numbers of functions, intramolecular loops, etc. Research approaches for network architectures include:

1) Alteration in T_g.
2) Chemical methods.
3) Elastic moduli in rubber state.
4) Swelling solvents.
5) Creep above T_g.
6) Chemical methods.
7) Mechanical damping.

By knowing the concentration of the curing agent and assuming the reaction to be complete, the average molecular weight of M_c can be obtained which estimates the molecular weight between the cross-links in the polymer.[117]

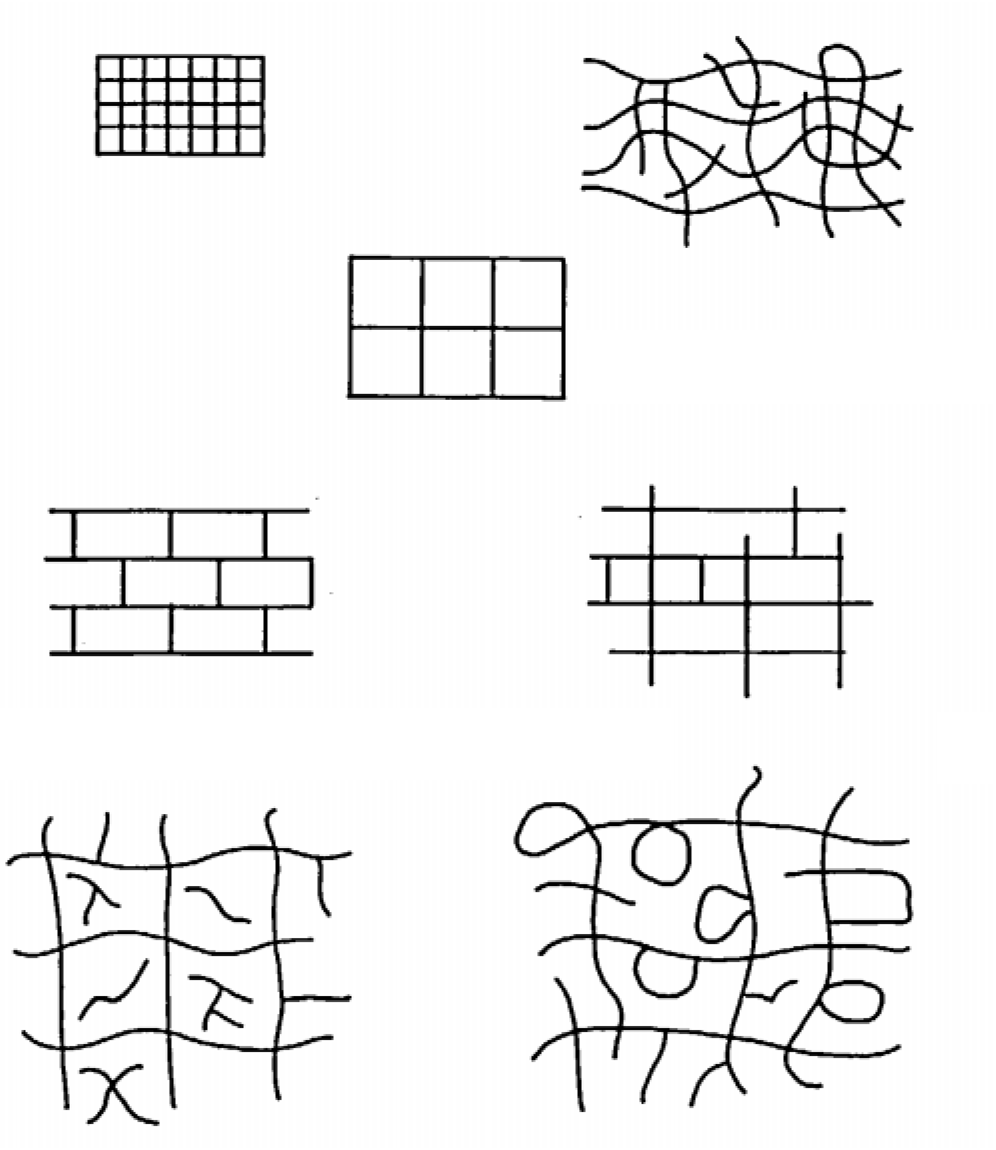


Figure 25. Different shapes of the cross-linked network configurations.[117]

1.9.1 Swelling test

In a good solvent, the polymer coils expand, but in a poor solvent, the polymer coils shrink. A linear polymer dissolves in a good solvent, but when the polymer becomes cross-linked, it swells in the solvent.[118,119]

As shown in Figure 26, the solubility parameter (δ) for the polymer and the solvent must be close to each other to reach maximum swelling in the cross-linked polymer. The networked polymer (1) has more swelling than the networked polymer (2), it shows a lower cross-link density. So a highly cross-linked polymer shows low amount of swelling and has a low Mc value.[120]

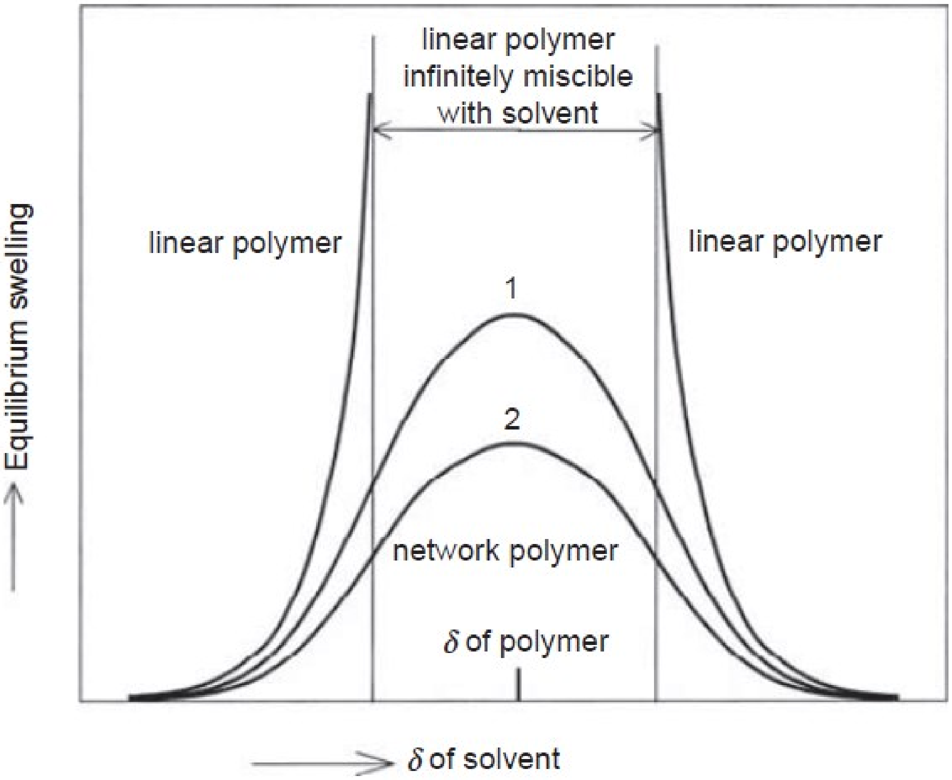


Figure 26. Swelling in equilibrium as a function of the solvent solubility parameter for a linear and cross-linked polymer. The density of the cross-link of 2 is greater than that of 1.[120]

Swelling measurement provides three types of data:

- Sol fraction is the amount of polymer that is not attached to the network.
- Degree of swelling of the gel fraction.
- Comparison of average molecular weight between cross-links by amount of swelling.

The swelling percentage and soluble fraction can be calculated as follows:

$$\text{Swelling}\ (\%) = \frac{W_s - W_d}{W_d} \cdot 100 \qquad [1.11]$$

$$X_{\text{solubility}}\ (\%) = \frac{W_{d0}}{W_d} \cdot 100 \qquad [1.12]$$

Where;

W_d: the weight of the polymer (before swelling).

W_s: the weight of the polymer (after swelling).

W_{d0}: the weight of solved polymer.

1.9.2 Impact of cross-linking on mechanical properties

A cured polymer mechanical properties can be used to evaluate the degree of curing.[121] DMA is a thermal analysis technique that analyzes the material properties when they deform under periodic stress and is used to measure the following parameters:

- Storage modulus (E', G').
- Loss modulus (E", G").
- Tan δ
- Glass transition
- M_c
- Creep and stress relaxation
- Gelation and vitrification

Storage modulus is a measure of elastic response of a material which relates to the stress stored in the material as mechanical energy. Loss modulus is a measure of viscous response of a material signifies the stress dissipated as heat. Tan δ shows damping or energy dissipation in the sample. Polymers have three regions that include the glassy, transition, and rubbery regain. The density of cross-links does not significantly affect stage modulus below Tg. However, above Tg, more cross-linked density cross-linked samples exhibit higher stage modulus (Figure 27).[122]

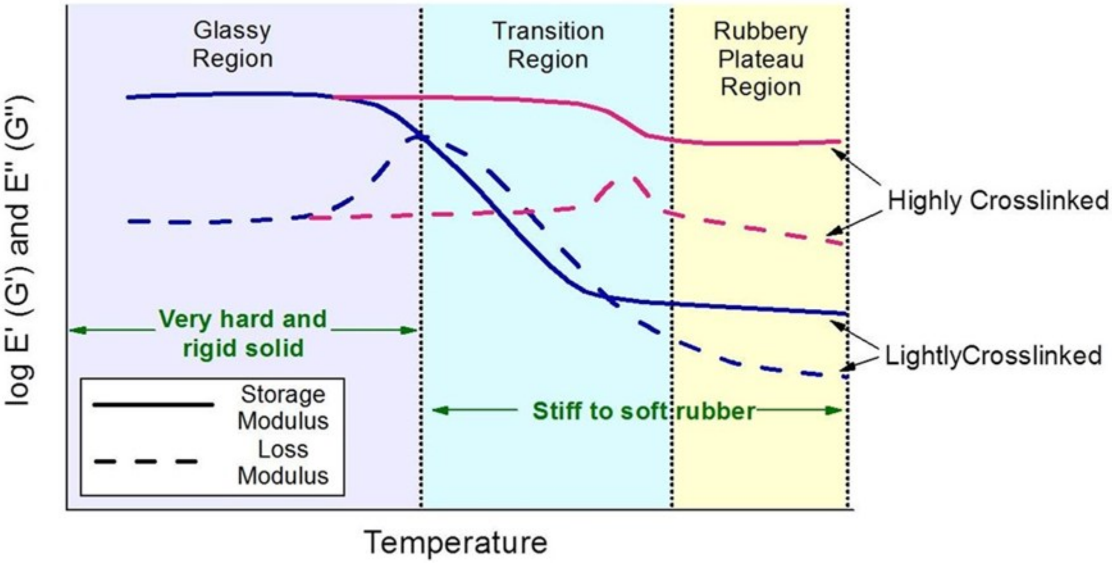


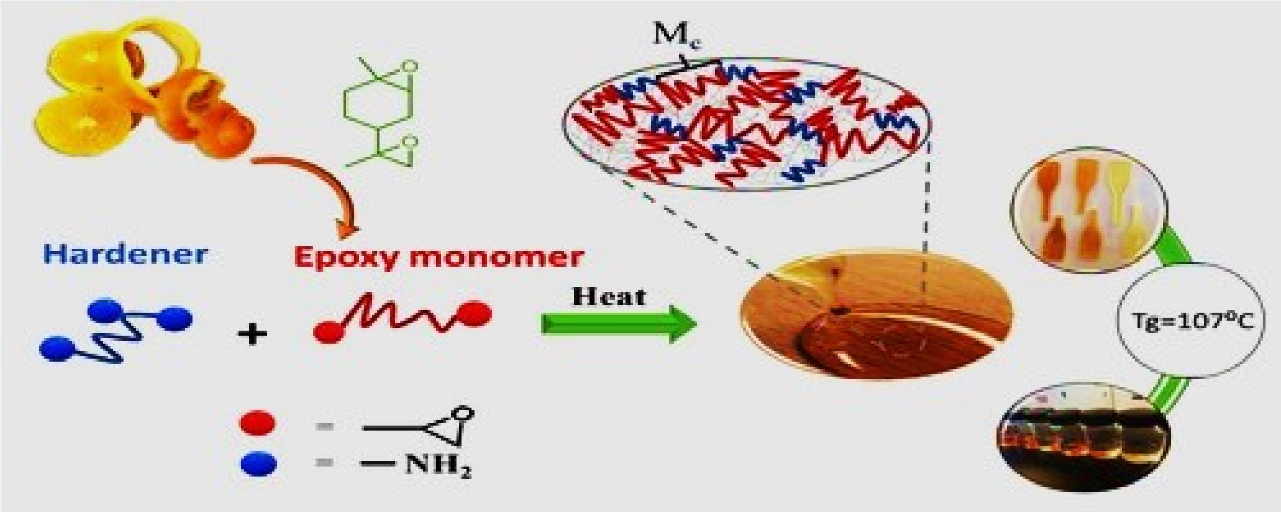
Figure 27. The effect of increasing the cross-linked on the modulus and T_g.[122]

Thus, the average molar mass between cross-links can be calculated using DMA data as follows:

$$M_c = \frac{\rho q R T}{E'} \qquad [1.13]$$

Where M_c is the number average molar mass between cross-links, q is the forward factor (usually equal to 1), ρ is the density at temperature T (K), E’ is the storage modulus in the rubber region at temperature T, and R is the universal gas constant.[123]

CHAPITRE 2. CAN LIMONENE DIOXIDE, A BIOBASED EPOXY MONOMER, BE USED AS REPLACEMENT OF BISPHENOL A DIGLYCIDYL ETHER?



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2.1. About the Project

This chapter presents an article on the use of limonene dioxide (LDO) as a partial replacement to diglycidyl ether bisphenol A (BADGE). Different samples were prepared that included various amounts of different epoxy monomers. Also, two hardeners were examined, polyethylene amine and Epikure. Then samples were characterized by different tests such as swelling test, Dynamic Mechanical Analysis (DMA), and tensile test. These analyses were used to investigate molecular weight between cross-linked, chemical resistance, and mechanical properties. The results are presented in the article form which has been submitted to the journal Polymer.

This research study was conducted at the University of Sherbrooke under the supervision of Professor Claverie in collaboration with SOPREMA CANADA. Professors Claverie, Louis Schutz, and I studied the concept and design. I synthesized the different formulations and investigated the swilling test for two solvents. I prepared appropriate samples for DMA test, and tensile test. I analyzed the results of these tests. Louise Schutz worked on the DSC characterization. Mégane Clerget carried out DMA test and tensile test. I wrote the first draft. Professor Claverie reviewed and edited the drafts. All members reviewed the final version of the article.

2.2. Abstract

Epoxy resins are widely employed for applications such as adhesives, composite materials and protective coatings. Recently, there has been a surge of interest for the development bio-based epoxy monomers as potential replacement to bisphenol A diglycidyl ether (BADGE). An interesting candidate is limonene dioxide (LDO), a bis-epoxide derived from the terpene limonene. However, its use has been curtailed by its low reactivity which often prevents the formation of robust crosslinked networks. In this work, we unravel epoxy formulations based on LDO which offer thermomechanical properties that are equivalent to those of BADGE. Thus, five groups of hardeners and epoxy monomers were used to generate several formulations that were characterized by swelling tests, dynamic mechanical analysis (DMA), and tensile tests.

Keywords : Biobased epoxy resin; Limonene dioxide (LDO); Bisphenol A (BSA); Thermomechanical properties,

2.3. Introduction

Thermosetting polymers are materials that undergo an irreversible transition from a liquid state to a highly crosslinked solid state during a curing step.[1] Epoxy resins occupy a prominent position among thermosetting materials because of their low costs, their tunable properties and the vast choice of monomers and crosslinkers that can be employed.[2] Furthermore, these resins exhibit desirable properties such as adhesion to various substrates, high strength, low shrinkage, effective electrical insulation, as well as chemical and solvent resistance. Taking advantage of such properties, they are often used as barrier coatings, electrical/electronic laminates, adhesives, flooring and paving applications, or in the fabrication of composites.[1,2] All epoxy resins are obtained by curing an epoxy monomer (that is to say a difunctional epoxide) with a hardener or curing agent chosen among a variety of compounds, including amines, anhydrides, alcohol or carboxylic acids.[3]

Bisphenol A diglycidyl ether (BADGE) is the most popular epoxy monomer used for the preparation of epoxy polymers. It is a liquid or paste, thus simplifying the formulation of epoxy resins. It has an Epoxy Equivalent Weight (EEW) as low as 170 g/eq which results in the formation of a highly crosslinked network. Importantly, it is an inexpensive epoxy monomer. However, this petrochemical is based on bisphenol A, which is widely recognized as an endocrine disruptor.[4-6] Concerns for the potential toxicity of BADGE as well as for the use of fossil fuels have prompted many researchers to look for non-toxic replacements issued from renewable resources.[7,8] For example, bio-based epoxy resins derived from vanillin,[9] eugenol,[10-12] rosin acid,[9,13] vegetable oil,[14-18] isosorbide,[19-21] and furan[22] have recently been reported.

Limonene is a terpene containing two Alkene functionalities that can be easily epoxidized to yield limonene dioxide (LDO, Figure 1). Every year, between 50 million and 75 million Kg of citrus peels are produced,[1] containing in average 1.3%wt of limonene.[23] Thus, limonene is readily accessible from waste food, in quantities that are sufficient to be used for several main-stream applications of epoxy resins. Recently, green epoxidation methods, including catalytic oxidation with O_2 have been developed.[24,25] Thus, the preparation of LDO does not require toxic epichlorohydrin and occurs with an atom economy of 100%, making LDO a biobased epoxy monomer with a potential zero-carbon footprint that originates from the valorization of waste food. Furthermore, LDO, an epoxide monomer with a calculated EEW value of 84 g/eq, is expected to yield highly crosslinked resins that should be thermally and chemically stable due to the aliphatic nature of the LDO structure. However, to our knowledge, the use of LDO as epoxy monomer has not been reported. Several reasons have been advanced to explain the fact that LDO is not suitable as epoxy monomer. Sotto *et al*.[26] highlights that LDO is in fact a mixture of four stereoisomers, with only the so called *trans* 1,2 epoxides which can be ring-opened by an amine or other nucleophile. Indeed, in order to be ring-opened, the two *cis* isomers need to pass through a high-energy twist-boat transition state whereas the two *trans* isomers adopt a low-energy half-chair conformation. In another report, Crivello *et al*.[27] have shown that LDO readily rearrange into ketones in the presence of Lewis-acids, making it an unsuitable monomer for a cationic ring-opening mechanism. Thus, LDO is unable to react as a difunctional epoxy monomer, in either anionic or cationic mechanisms. Here, we demonstrate in this study that under suitable conditions, LDO can be used as a biobased alternative to BADGE, leading to cured epoxy with comparable thermomechanical properties. For this purpose, LDO was used in conjunction with trimethylolpropane triglycidyl ether (TMPTE) and a small amount of multivalent epoxy monomer that we recently described, polynorbornene epoxy (PNBE-epoxy).[28] In this case, we were able to form highly crosslinked epoxy resins with mechanical properties and T_g that are equivalent to those of BADGE resins. Thus, this works demonstrates that, when suitably formulated, LDO could be used to form epoxy resins with properties that are equivalent to those of common industrial epoxy resins.

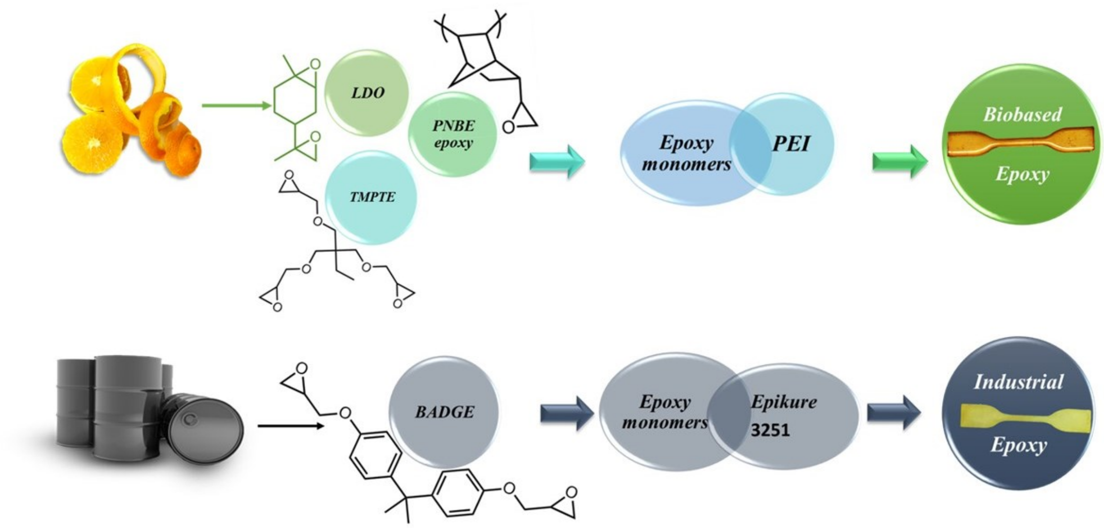

Figure 1. Preparation of epoxy resins using biobased limonene dioxide (LDO, top) and BADGE (bottom)

2.4. Experimental

2.4.1 Materials

Diglycidyl ether of bisphenol A (BADGE) with an epoxy equivalent weight 170 g. eq^{-1}, polyethylenimine branched (PEI), average molecular weight 800 g.mol^{-1}, trimethylolpropane triglycidyl ether (TMPTE) were supplied from Sigma Aldrich as a commercial epoxy monomer. Limonene dioxide (LDO), mixture of *cis* and *trans* isomers and Epikure 3251 as an oligomeric modified Mannich base hardener with an amine value of 76 g. eq^{-1} were respectively acquired from Symrise and Hexion company. Polynorbornene epoxy, PNBE-epoxy, was prepared based on reference.[28]

2.4.2 Sample preparation

The epoxy samples were prepared by mixing hardener and epoxy monomers in amounts that are consigned in Table 1. Conversions from mol% to wt% was performed by multiplying by the respective EEW and amines values. Hardeners and epoxy monomers were mixed completely with a glass rod until a homogeneous mixture was obtained. Then the mixtures were poured aluminum molds with a radius of 2 cm and the molds were degassed under vacuum for approximately 5 min at a pressure of 6.6 kPa. Afterward, they were cured in an oven for 3 hours at 120 °C. In order to ensure that curing was complete, these objects were post-cured at 150°C for 4 hours. After each curing step, the samples were allowed to cool slowly to room temperature leading to samples which were rigid and self-standing except for the Epikure3251 / LDO samples.

Table 1. Composition of the various samples evaluated in this study.

NO	Samples	Amine / Epoxy function mol.%
1	PEI / LDO	40 / 60
2	PEI / BADGE	40 / 60
3	PEI / TMPTE / LDO	40 / 30 / 30
4	PEI / PNBE-epoxy / TMPTE / LDO	40 / 2 / 29 / 29
5	Epikure3251 / LDO	50 / 50
6	Epikure3251 / BADGE	50 / 50
7	Epikure3251 / TMPTE / LDO	50 / 35 / 15
8	Epikure3251 / PNBE-epoxy / TMPTE / LDO	50 / 2 / 35 / 13

2.5. Characterization and measurements

2.5.1 Swelling ratio and insoluble fraction determination

The cured epoxy resins were cut into coupons with size approximately 1 cm x 1 cm squares with 2mm thickness, were weighed (mass w_d), and were immersed in methanol or water for 48h. The swollen samples were removed from the solvent, patted-dry to absorb the solvent in surface, and weighed (mass w_s). The solvent part then left in a vacuum oven at a pressure of 6.6 kPa for 24 hours and weighed again (mass w_{do}). The swelling percentage and soluble fraction were calculated as follows:

$$\text{Swelling } (\%) = \frac{w_s - w_d}{w_d} \cdot 100 \qquad (1)$$

$$X_{\text{solubility}} \ (\%) = \frac{w_{do}}{w_d} \cdot 100 \qquad (2)$$

2.5.2 Dynamic mechanical analysis

The temperature dependencies of the viscoelastic properties (loss modulus, E’’, storage modulus, E’ and mechanical loss tangent, tan (δ) of the cured resins were evaluated by dynamic mechanical analysis (DMA) in shear strain mode using a frequency of 1 Hz on a Physica MCR 301 Anton Paar instrument. After sample sheets were cured, they were cut in plates of size 50 mm × 10 mm × 1 mm. The samples were tested in triplicata over a temperature range from ambient temperature 30 to 200°C with a heating rate of 2°C/min. The glass-transition temperature (T_g) was assigned as a temperature where the loss factor was maximum. The average molar mass between crosslinks was calculated using DMA data as follows:[29]

$$M_c = \frac{\rho q R T}{E'} \tag{3}$$

Where M_c is the number average molar mass between crosslinks (g/mole), q is the front factor (usually equal to 1), ρ is the density at temperature T (K), E' is the storage modulus in the rubbery region at temperature T, and R is the universal gas constant.

2.5.3 Tensile tests

Tensile tests of epoxy resins were performed on a Universal Testing Machine Model 5966 Instron with a load cell of 5 kN at a crosshead speed of 5 mm/min and the gauge length of 59 mm in accordance to ASTM D412. Samples sheets were cured at 120 °C for 3h. While they were still hot, a dumbbell-shaped puncher was used to cut them into the form of dumbbells. After they reached room temperature, the resulting dumbbell-shaped samples were cured again at 150 °C for 4h.

2.6. Results and discussion

2.6.1 Swelling Test

LDO is constituted of four isomers, two *trans* isomers (where the exocyclic isomer is trans to the methyl group) and two *cis* ones. Since the endocyclic epoxide of the *cis* stereoisomers are less reactive toward ring opening to amines,[26] the *cis* isomers are considered in this study as monofunctional epoxy monomers (the exocyclic epoxide is reactive but not the endocyclic one). As the LDO mixture contains equimolar amounts of the four isomers,[26] an average functionality of 1.5 was determined for LDO (two bifunctional isomers, two monofunctional ones), leading to an average EEW of 112 g. eq^{-1}. Resulting from this average EEW of 1.5, curing of LDO with Epikure3251as hardener (sample 5) led to brittle samples that are fully soluble in methanol, and therefore that are not crosslinked. By contrast, curing of BADGE with Epikure3251 (sample 6) leads to a crosslinked (insoluble) resin which will be used as benchmark for our study. This experiment confirms that LDO is indeed not a difunctional monomer, as insufficient crosslinking occurred. Furthermore, it indicates that methanol is a good solvent for the polymer formed upon reacting LDO with Epikure3251. In fact, samples prepared by curing LDO with a variety of difunctional amines (such as Epikure3251, isophorone diamine or ethylene diamine) were always found to be fully soluble in methanol. Thus, methanol was selected in subsequent swelling tests as it is able to fully dissolve uncrosslinked polymer chains in partially crosslinked samples. Water was also used to perform swelling tests, due to the importance of water uptake from an applicative point of view. When LDO is used in conjunction with TMPTE, a trifunctional epoxy monomer, a crosslinked network is obtained (no soluble fraction), but significant swelling indicates that the crosslink density is low (Table 2). By adding PNBE-epoxy, a multifunctional epoxy monomer, swelling decreases, resulting from a higher crosslink density. It should be mentioned that the swelling values in methanol of the BADGE containing samples cannot be compared because methanol is not a good solvent of resins containing BADGE. Using PEI as crosslinker yields similar results: the resin is insoluble once TMPTE and PNBE-epoxy are used in conjunction with LDO. In the presence of PEI and TMPTE, the resin becomes more hydrophilic, as shown by a higher swelling in water. It also indicates that the crosslink density of the PEI / TMPTE / LDO samples is most likely lower than for PEI / BADGE samples.

Table 2. Swelling in methanol and water and percentage of the soluble fraction.

Samples	**Methanol**		**Water**	
(Amine / Epoxy function) mol.%	Swelling (%)	$X_{solubility}$ (%)	Swelling (%)	$X_{solubility}$ (%)
Epikure3251 / BADGE	4	0.3	1	0.3
Epikure3251/ TMPTE / LDO	67	0	3	0.2
Epikure3251 / PNBE-epoxy / TMPTE / LDO	56	4	2	0.4
PEI / BADGE	0	0.2	1	0.3
PEI / TMPTE / LDO	39	2	22	0.8
PEI / PNBE-epoxy / TMPTE / LDO	7	0.6	10	1.6

2.6.2 Dynamic mechanical analysis

Table 3 exhibits the storage modulus (E'), loss modulus (E''), tanδ and molecular weight between crosslinks, M_c, as obtained from dynamic mechanical tests for samples hardened with Epikure3251 and PEI.

The glass transition temperature (T_g) was measured when tanδ reached a maximum and M_c was estimated by using Eq 3.[30] The Epikure3251 / BADGE sample exhibits the typical behaviour of an epoxy resin, with a storage modulus greater than 1 GPa at room temperature, and a T_g around 85°C. The molecular weight between crosslinks, M_c, calculated from the value of the loss modulus in the rubbery plateau, should be taken as an indication of the crosslink density. Switching BADGE by LDO / TMPTE results in lower T_g and lower storage modulus which can be explained by the flexibility of the TMPTE unit which is usually used as reactive diluent rather than constitutive monomer.[31] The high value of M_c can be explained by the fact that due to the LDO functionality of 1.5, in average two LDO units are found in between crosslinks. By adding PNBE-epoxy, a highly rigid multifunctional polymer containing epoxide groups, the storage modulus and T_g increase and concomitantly, M_c decreases.

Similar conclusions can be drawn for the system PEI / BADGE. The hardener PEI having a low molecular weight between primary and secondary amines, the value of M_c is comparatively lower than with Epikure3251.

Remarkably, the values of the PEI / PNBE-epoxy/ TMPTE / LDO sample are comparable to those of Epikure3251 / BADGE.

Table 3. Storage modulus, loss modulus, T_g and M_c for samples with PEI and Epikure3251 as a hardener.

Samples	**Storage modulus (MPa)[1]**	**Loss modulus (MPa)[1]**	**T_g (°C)**	**M_c ($g.mol^{-1}$)**
Epikure3251 / BADGE	1330±30	19±1	95	460
Epikure3251/ TMPTE / LDO	840±20	47±2	62	2240
Epikure3251 / PNBE-epoxy / TMPTE / LDO	1010±20	47±3	65	1580
PEI / BADGE	510±20	13±3	151	290
PEI / LDO	930±30	24±3	81	810
PEI / TMPTE / LDO	1040±40	25±4	101	470
PEI / PNBE-epoxy / TMPTE / LDO	1220±40	35±4	107	370

1. At 30 °C.

Figure 2 a and b respectively show the storage modulus (E') and tan(δ) vs temperature for the various samples. Although PEI / BADGE has the highest Tg, it also has the lowest storage modulus, which can be explained by the flexibility of the PEI chain. By comparison, the presence of LDO with PEI results in higher storage modulus. The samples containing Epikure3251 have two tan(δ) peaks. We surmise that this behavior can be explained by a microphase separation phenomenon between the epoxy phase and the oligomeric Mannich base hardener (Epikure3251).[32] By contrast, samples with PEI as a hardener for which all curves have a single tanδ peak, form homogeneous networks.

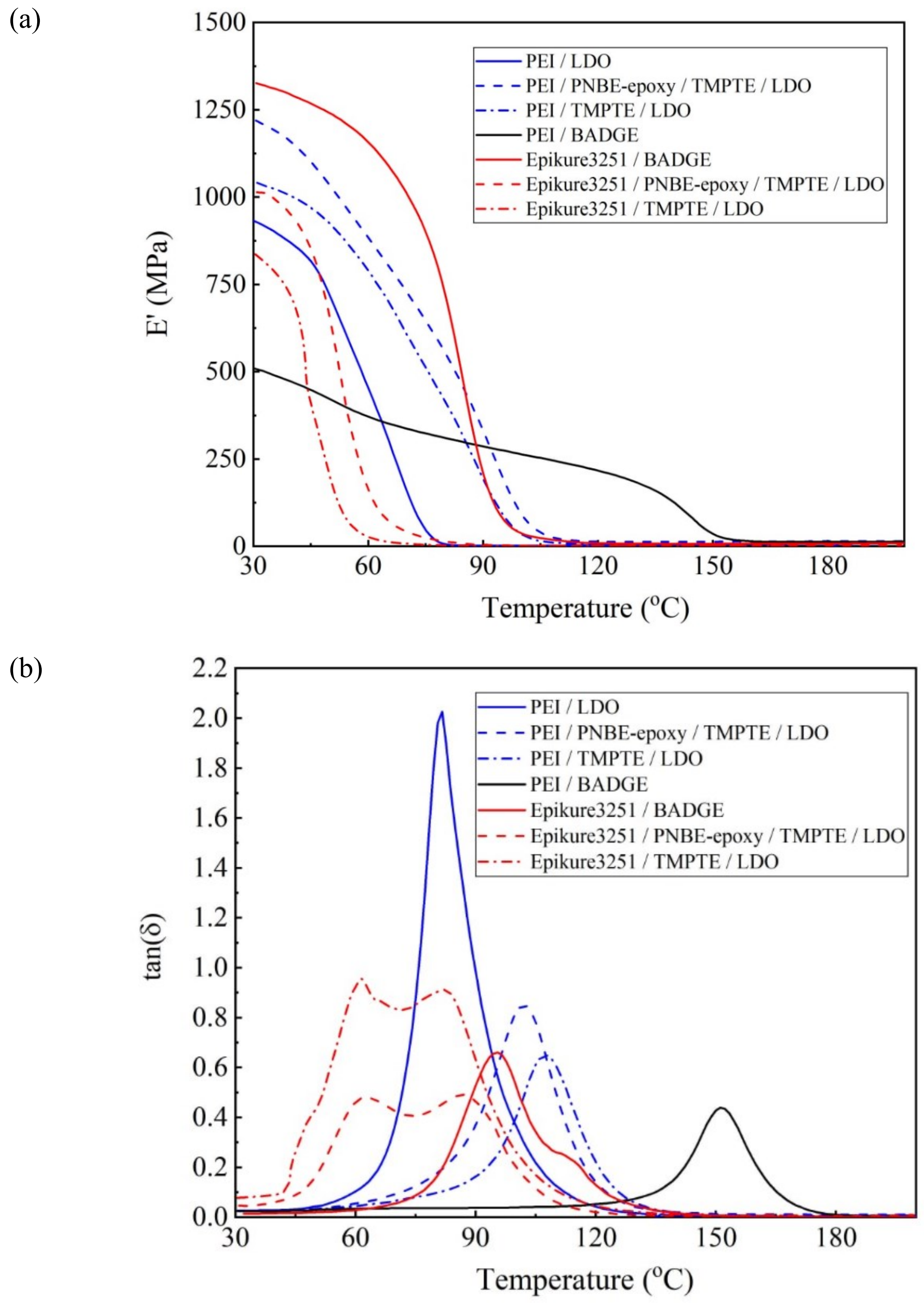

Figure 2. DMA results for samples (a) storage modulus as a function of temperature (b) tan(δ) as a function of temperature.

2.6.3 Tensile Tests

Table 4 shows the tensile properties of samples prepared with two different hardeners; The Young moduli of the samples prepared with BADGE or LDO/TMPTE using either Epikure3251 as hardeners are comparable (2.3 +/- 0.1 GPa). Remarkably, for samples hardened by PEI, the Young moduli of samples containing LDO are higher than those prepared with BADGE. In fact, the sample PEI / PNBE-epoxy / TMPTE has tensile properties (Table 4) which are similar to those of Epikure3251 / BADGE. Interestingly, the inclusion of TMPTE and of PNBE-epoxy within the formulations result in an improvement of elongation at break as well as tensile strength, rendering the corresponding materials both more ductile and tougher.

Table 4. Young Moduli, Ultimate tensile strength, Elongation at break for samples with Epikure3251 and PEI as hardeners (triplicate experiments).

Samples	Young Modulus (GPa)	Ultimate strength (MPa)	Elongation at break (%)
PEI / LDO	1.7±0.4	16.8±3	1±0.07
PEI / TMPTE / LDO	1.9±0.2	34.5±3.2	2±0.3
PEI / PNBE-epoxy / TMPTE / LDO	2.2±0.1	37.5±3	3.6±0.9
Epikure3251 / TMPTE / LDO	2.3±0.1	24.7±5.4	1.1±0.3
Epikure3251 / PNBE-epoxy / TMPT-E /LDO	2.2±0.25	29.9±5	1.4±0.4
Epikure3251 / BADGE	2.3±0.1	66.5±7	3.7±1

2.7. Conclusion

In this paper, we assessed the possibility of using limonene dioxide (LDO) as bio-based replacement for BADGE in epoxy resin formulations. Samples were investigated and compared with a commercial benchmark sample formed with Epikure3251 and BADGE. Interestingly, the results indicate that it is possible to formulate epoxy resins based on LDO with thermomechanical properties that are equivalent to those of the benchmark system, either in terms of water uptake, or in terms of thermomechanical properties (DMA) and finally in terms of mechanical testing. Although literature hinted that LDO should not be a suitable epoxy monomer, these results demonstrate that when properly formulated, biobased LDO can be considered as a valid replacement for the petroleum-based BADGE. Considering that the catalytic epoxidation of limonene using oxygen as oxidant has recently been reported,[25] the elaboration of carbon-neutral epoxy resins should become feasible in the future.

2.8. References

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CHAPITRE 3. LANTHANIDE DODECYL SULFATES, A POTENT FAMILY OF CATALYSTS FOR THE PREPARATION OF BIOBASED EPOXY THERMOSETS

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3.1 About the Project

This chapter presents an article showing that lanthanide dodecyl sulfates ($LnDS_x$) effectively catalyze the reaction of amines with epoxides. This catalytic effect can be observed, especially in the cross-linking reactions of LDO with amines. It was demonstrated that new catalysts can be synthesized from the reaction between lanthanide salts with sodium dodecyl sulfate. Catalysts were characterized by different techniques such as nuclear magnetic resonance (NMR), Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), inductively coupled plasma mass spectrometry (ICP-MS). The activity of this family of catalysts was assessed by measuring the gel-time and drying-time of several epoxy formulations.

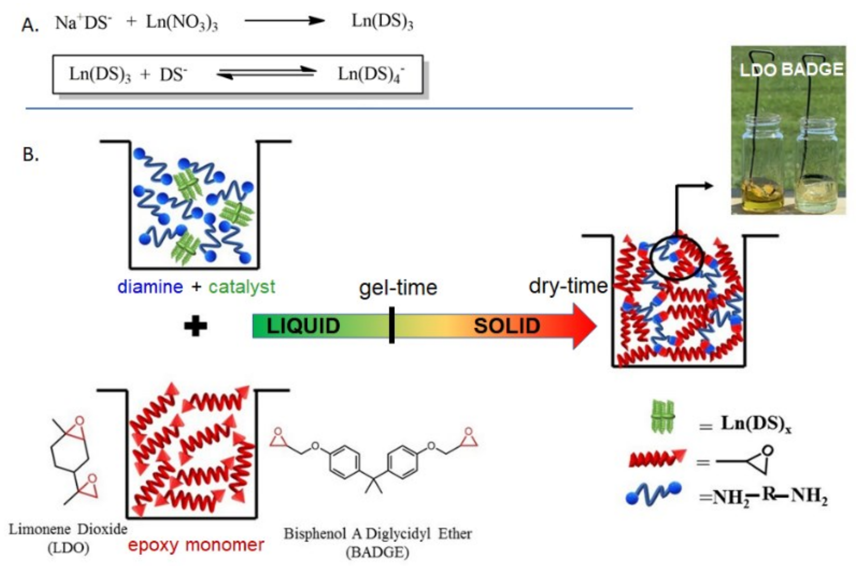
The results of these analyses are presented in an article form which has been submitted to Chemical Communications. It is shown in the article that the lanthanum-based catalyst, $LaDS_x$, is the most active of all lanthanides.

This research study was conducted at the University of Sherbrooke under the supervision of Professor Claverie in collaboration with SOPREMA CANADA. Professors Claverie, Louis Schutz, and I studied the concept and design. I synthesized the catalysts and tested the gel timer, IR, and drying time. Louise Schutz and I worked on the DSC results to test the activation energy of each catalyst. Louise Schutz characterized the catalyst. Louise Schutz and I wrote the first draft. Professor Claverie reviewed and edited the drafts. All members reviewed the final version of the article.

3.2 Scientific article

Lanthanide dodecyl sulfates, $LnDS_x$, are remarkably effective to catalyze the reaction of diepoxides with diamines in the liquid and solid states, a key reaction in the formation of epoxy thermosets. Among all lanthanides, the lanthanum complex $LaNa(DS)_4(H2O)_2$ is the most active, allowing a decrease of 60 kJ/mol of the activation energy between polyethylene imine and limonene dioxide, a biobased epoxy monomer.

Thermosetting materials are a broad class of materials that find countless applications in all technological domains. Among them, epoxy thermosets are the most popular and widely used.[1] Fundamentally, an epoxy thermoset stems from the solvent-free ring-opening of epoxide moieties belonging to an epoxy monomer by a variety of nucleophiles (amines, alcohols, carboxylates or thiols) which are borne by the cross-linker. The rate at which this ring-opening reaction occurs is a key parameter which controls the time it takes for the liquid to phase-transition to the solid state (so-called gel time) and the time for the solid to be hard and fully crosslinked (so-called dry time). To accelerate this reaction, epoxy thermosets are formulated with various catalysts or accelerators which must be soluble in either the epoxy monomer and/or the crosslinker (no solvent), be tolerant to all sorts of environmental conditions and be widely available and inexpensive considering the massive scale at which epoxy are produced. Despite the plethora of catalysts that have been reported in literature for the ring-opening of epoxides in solution,[2] only a handful satisfy the requirements cited above.[3] Alcohols such has nonylphenol derivatives, tertiary amines such as 1,4-diazabicyclo[2.2.2]octane, substituted ureas and imidazoles are often used to catalyze the nucleophilic addition of amines in an epoxy thermoset.[4] In many instances, the slow rate of reaction, resulting in long gel-times and drying-time curtail the application of epoxy formulations. This limitation is particularly stringent with bio-based epoxy monomers, which are often less reactive than their petroleum-based counterparts,[5,6] either because of a greater steric hindrance, or because of the absence of an oxygen in beta position. resulting in long gel-times and drying-time curtail the application of epoxy formulations. This limitation is particularly stringent with bio-based epoxy monomers, which are often less reactive than their petroleum-based counterparts,[5,6] either because of a greater steric hindrance, or because of the absence of an oxygen in beta position.



Scheme 1 A. $Ln(DS)_x$ catalysts composed of $Ln(DS)_3$ and $Ln(DS)_4^-$ (counter ion Na^+ or H^+, DS^- = dodecyl sulfate). B. Formation of the epoxy thermoset catalyzed by $Ln(DS)_x$, with an industrial formulation (BADGE + Epikure 3251) or a biobased one (LDO + polyethylene imine, PEI) and representative pictures of the hardened samples.

Such oxygen atom is known to act as a directing group for the formation of a H-bond between the alcohol (catalyst)[7] and the epoxide group, leading to a stabilization of the transition state. For example, the biobased monomer limonene dioxide (LDO) (scheme 1), which contains a 2,2-disubstituted epoxide and trisubstituted epoxide is a known example of epoxide monomer which reacts excessively slowly with any classical catalyst.[8,9] In the past 30 years, Lewis-acids surfactant catalysts (LACS), a class of compounds introduced by Kobayashi[10–13] were explored for a variety of organic reactions whereby the LACS acts both as a water-tolerant Lewis acid and a surfactant. Among the catalysts explored, only few example used lanthanides as metal cation such as La,[12] Ce,[14] Sm,[15] Dy,[15] Yb[13,15] for reactions such as allylation of benzaldehyde, aldol reaction and preparation of quinoleine. The organo-soluble and amphiphilic nature of LACS motivated us to assess their reactivity for the cross-linking of epoxy monomers with amines in the solid-state.

In this communication, we demonstrate that lanthanide dodecyl sulfates ($LnDS_x$) efficiently catalyse the reaction of amines with epoxides in the solid state, leading to gel-times and drying-times that are shorter than those obtained with all conventional aforementioned catalysts (Scheme 1). Using two test formulations, one industrial one, based on diglycidyl ether of bisphenol A (DGEBA), the other one based on biobased LDO, we demonstrate that the lanthanum based catalyst, $LaDS_x$, is the most active of all lanthanides, resulting in a large decrease of the activation energy for the reaction between the epoxide and the amine in the solid state. Due to their high oxophilicity, $LnDS_x$ catalysts are highly potent Lewis acids catalysts that are uniquely able to activate an epoxide group in the presence of amines making them highly potent catalysts for the preparation of epoxy thermosets.

The $Ln(DS)_x$ complexes result from the precipitation of water soluble lanthanide nitrate in the presence of NaDS (Scheme 1). This simple procedure was tested for all lanthanides, excepted radioactive Tc and expensive Dy, and found to be quantitative in all cases, leading to a powder which was isolated by filtration (see ESI for experimental procedure). Although litterature systematically reports that these complexes with three sulfates per metal, there are, to our knowledge, no spectroscopic evidence in support of such stoechiometry. Careful elemental analysis performed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Table S4) or Inductively Coupled Plasma Mass Spetrometry (ICP-MS) (table S5) indicate that the stoechiometry is actually comprised between 2.5 and 4. Analysis by X-ray Photoelectric Spectroscopy (XPS) indicates that the complexes contain Ln, C, O, N and H (the latter one not be detected by XPS). No major amount of Na is incorporated in the complex, ecepted in the case of Lu. The value of the Ln:DS^- ratio depends on the concentrations of $Ln(NO_3)_3$ and NaDS, indicating that there exists an equilibrium between $Ln(DS)_3$ and $Ln(DS)_4^-$ (Scheme 1). As a result, $Ln(DS)_x$ is an amorphous solid with stoechiometry x close to 4 for La and Ce (the lanthanides with the largest ionic radius), and x varying between 3 and 4 for the other ones. The precise stoechiometry of the diamagnetic La complex was also confirmed by ^1H NMR (Figure S12).

In order to further examine the structure of these $Ln(DS)_x$ complexes, single-crystals of $NaLa(DS)_4.(H2O)_2$ were grown from a reaction performed in the presence of an excess of NaDS (Figure 1). In this structure, all La atoms are in a dodecahedral eight-coordination environment, with six sulfates and two water molecules coordinating (Figure S13).[16,17] All the sulfate groups are bridging between two La atoms or between La and Na, but none of them are chelating. The absence of η^3-SO_2^- coordination mode can be explained by the large ionic radius of the La atom (130 pm). The eight La-O distances are comprised between 2.42 and 2.50 Å (Figure S13), which is commensurate, yet slightly smaller, than the average La-O bond of 2.50-2.55 Å found in eight-coordinated La(III) complexes.[18,19]

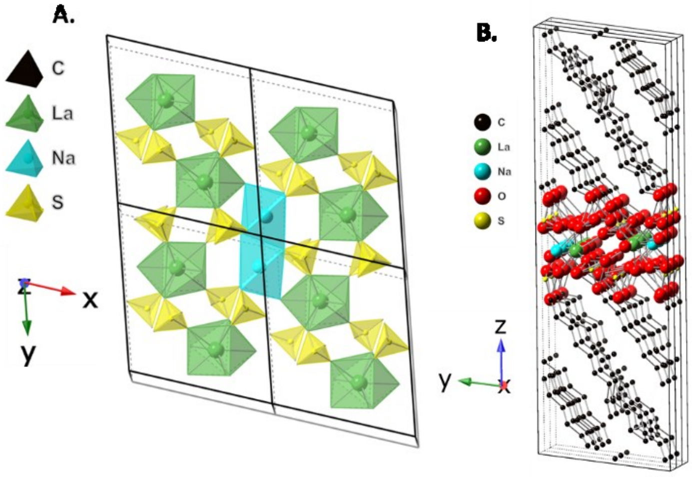


Figure 1. Crystal structure of LaNa(DS)$_4$(H2O)$_2$. A. Polyhedral representation of the La, N and S environments. B. View of the crystal lattice from the (100) direction

Each unit cell contains in its 001 plane two La atoms which are decorated by the long alkyl chains at a 60^o angle with the 001 plane. Thus, the complex adopts a lamellar structure of thickness 3.16 nm, where all sulfates and metallic atoms are located in the center of the lamella and are shielded from the external environment by the lipophilic $C_{12}H_{25}$ chains.

All Ln(DS)$_x$ complexes were found to be soluble in a variety of diamines used as cross-linkers for the preparation of epoxy polymers. In this study, the results are shown for polyethylene imine (PEI) and for Epikure 3251, an oligomeric modified aliphatic amine of proprietary structure. Notably, Epikure 3251 (labelled Epikure), which is already formulated with a series of additives, was selected in order to assess the compatibility of the Ln(DS)$_x$ with the variety of additives that are used industrially. Figure 2 illustrates the effect of the Ln(DS)$_x$ catalysts on the so called gel-time, which is the time it takes for the thermosetting formulation to transition from liquid to solid. All Ln(DS)$_x$ significantly decrease the gel-time, with La(DS)$_x$ being the most effective catalyst. In our hands, the La(DS)$_x$ catalyst was found to be more effective than all assessed commercial catalysts (Table S6) when using identical amounts. Remarkably, the gel-time, which is a characteristic reaction time, was found to be inversely proportional to the concentration of Ln(DS)$_x$ (Table S7, Figure S14), which is indicative of a first-order dependency of the reaction rate with catalyst concentration, an advantage in terms of formulation as the gel-time can be simply dialled in by adjusting the amount of catalyst. At gel-time, the sample reaches the solid-state, which means that the gel-time is characteristic of a kinetics occurring in the liquid state. Another characteristic time is the drying time which is the time required for the sample to be fully hardened, a time which is representative of the kinetics in the solid state. Remarkably, the La(DS)$_x$ catalyst is also able to significantly decrease the drying time (Table S8), with drying of the BADGE-Epikure formulation being dried in 1 hour with 2 wt% of La(DS)$_x$ instead of 2 hours. Thus, the catalysts are also efficient in the solid state. In the time-temperature-transformation (TTT) isothermal cure diagram developed by Gillham et al,[20] the La(DS)$_x$ operates in the lower section of the S curve: the reaction is chemically controlled and vitrification occurs only at high conversion.

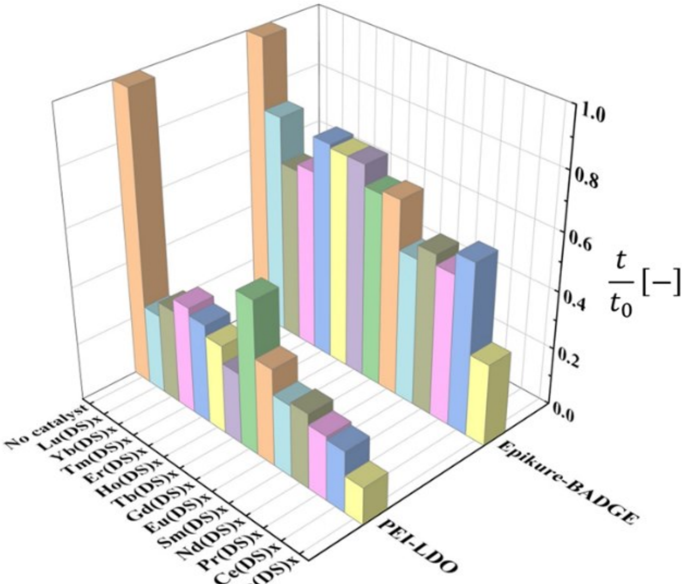


Figure 2. Effect of the Ln(DS)$_x$ catalyst (2 wt%) on the gel-time (transition liquid to solid) for two formulations. The gel-time is normalized by the corresponding gel-time measured in the absence of catalyst (84 minutes for Epikure-BADGE, 48 hours for PEI-LDO).

In order to further clarify the catalytic effect of La(DS)$_x$ on the hardening of the biobased LDO with PEI, the reaction kinetics was monitored by differential scanning calorimetry (DSC, Figure 3). As shown in Figure 3a for a DSC experiment performed at 2^{o}C/min, the reaction proceeds between 100 and 200^{o}C with a maximum heat released at 151 and 139^{o}C respectively in the absence and presence of catalyst, indicating that the reaction occurs at lower temperature when catalyzed. A more precise kinetics analysis was performed by measuring the instantaneous heat flow as measured by DSC, q(t), under isothermal conditions. The heat flow is related to the conversion, x, via:

$$q(t) = \Delta H \, \square \, \frac{dx}{dt} \tag{1}$$

where ΔH is the reaction enthalpy obtained by integration of the heat flow. Thus, using equation (1), it is possible to assess dx/dt, and by integration, x. The reaction kinetics was modeled using a modified so-called Kamal model,[21,22] which includes a non auto-catalytic pathway (kinetic rate constant k_1, order n_1) and an auto-catalytic pathway (kinetic rate constant k_2, orders n_2 and m_2):

$$\frac{dx}{dt} = k_1 (1-x)^{n_1} + k_2 x^{m_2} (1-x)^{n_2} \tag{2}$$

When an epoxide is ring-opened by an amine, the reaction is expected to proceed in a bimolecular fashion ($n_1 = 2$). The product of this reaction is an alcohol which can activate the epoxide group via the formation of a H-bond, thus explaining the presence of an autocatalytic pathway. Non-linear fitting of the dx/dt curves over t was used to extract the values of all kinetic parameters (Table S6 and Figures S15-S19). For the LDO/PEI system, the rate constants for the non auto-catalytic pathway were more than one order of magnitude smaller than those of the auto-catalytic pathway. For this latter one, the apparent activation energy (Figure 3b) of the reaction performed with 2% $La(DS)_x$ is 53 kJ/mol whereas it is 112 kJ/mol in the absence of catalyst. Other lanthanides were found to have activation energy slightly higher than $La(DS)_x$ (54-60 kJ/mol), which in good agreement with the gel-time results which show that $La(DS)_x$ is the most active catalyst (Figure 2) in the lanthanide series. Several other catalysts were also prepared, using sodium dodecyl benzene sulfonate (NaDBS), sodium phenolate (NaOPh) as starting material instead of NaDS. The resulting La complexes were found to catalyze the reaction, albeit less efficiently than $La(DS)_x$ (Table S10-S11).

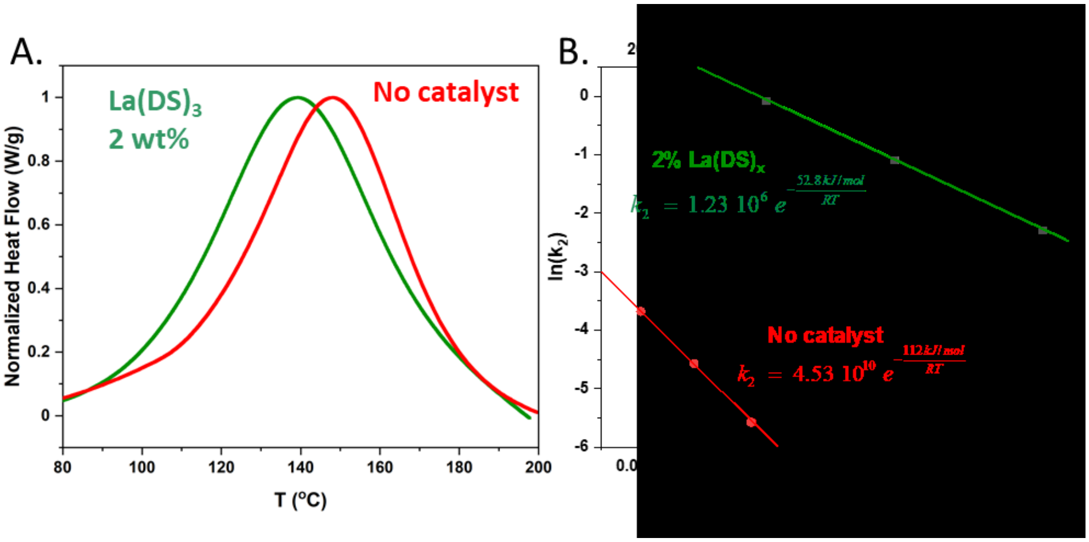


Figure 3. A. DSC thermogram at 2 °C/min of equimolar biobased LDO + PEI. B. Arrhenius plot for the reaction performed with and without catalyst.

These experiments indicate that $Ln(DS)_x$, and particularly $La(DS)_x$, is remarkably efficient to catalyze the formation of epoxy polymers with amines. Although the nucleophilic attack of epoxides is known to be activated by Lewis acids, such strategy usually fails in the presence of amines due to the formation of a Lewis adduct between the amine and the Lewis acidic catalyst. Lanthanides are the most oxophilic elements known, and they will preferably bind to hard oxygen-containing moieties.[23] Of all lanthanides, the most active one is La, followed by the early ones (Ce, Pr, Nd and Sm). Several factors could explain this trend. The $La(DS)_x$ complex was found to be eight-coordinated (Figure 1), but heavier elements which are smaller due to lanthanide contraction, tend to favor lower coordination numbers, and therefore, less coordination sites to activate the epoxide. Furthermore, for heavier elements, the Ln-O distances are smaller, and the resulting complexes are therefore more stable and less labile. Using Fourier Transform InfraRed (FTIR) spectroscopy, the vibrations characteristic of S-O was monitored (Table S12). In NaDS, two vibrations are observed at 1218 cm^{-1} and 1081 cm^{-1}. These bands are respectively assigned to asymetric and symetric stretching SO_2^- vibrations (see Figure S20). In $Ln(DS)_x$ complexes, each of these vibrations is doubled, one of which remains unchanged whereas the other one varies with the nature of the lanthanide ion (Table S12). Thus, the vibrations which remain unchanged correspond to the sulfate groups that are coordinated to Na^+ whereas the other ones correspond to sulfate groups coordinated to $Ln^{3+.}$ The progression from the lowest to highest wavenumber of the symetric stretching is La < Ce < Pr < Nd < Er < Eu < Tm < Yb < Ho < Lu < Gd which corresponds well to the catalytic activity for LDO polymerization: La > Ce > Pr > Nd > Sm > Tb > Lu > Ho > Yb > Eu > Er > Tm > Gd (Table S13). Rankings performed with asymetric stretching vibrations or with catalytic activity for DGEBA polymerization are also similar. The SO_2 stretching wavenumbers increase with the mass of the lanthanide (with the exception of Gd, the central lanthanide which is ranked last), therefore mass effects cannot explain the wavenumber ranking. Rather, the ranking reflects the fact that SO_2-Ln bond strength increases from La to Lu. The lower catalytic activity of the Gd complex and higher wavenumber is an illustration of the so-called gadolinium break,[24] which is a discontinuity in many properties for this central lanthanide atom. The fact that the highest catalytic activity is observed with La^{3+} therefore correlates with its larger size, which results in a longer and weaker SO_2-La bond, as shown by a lower SO_2 wavenumber. For subsequent lanthanides, as their size decreases (due to lanthanide contraction), the SO_2-Ln bond becomes shorter and stronger, resulting in metal atoms which are less oxophilic and more tightly bonded to the sulfate ligands, thus making them less prone to activate the epoxide toward nucleophilic attack.

In this communication, we have demonstrated that $Ln(DS)_x$, and among them $La(DS)_4^-$ (counter-ion H^+ or Na^+) is a highly-efficient catalyst for the formation of epoxy thermosets, largely surpassing the activity of conventional commercial catalysts. Due to their activity, these catalysts allow the formation of epoxy polymers based on LDO, a biobased monomer which has remarkably low activity due to its high steric hindrance and the absence of β-oxygen group.[9] Since biobased epoxy monomers often suffer from a lower reactivity than conventional monomers such as BADGE, we envision that $La(DS)_x$ will be highly valuable for the development of biobased epoxy formulations.

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3.4 Electronic Supplementary Information

Materials and methods

Limonene dioxide (LDO) was purchased from the company Symrise Chemical. Epikure 3251 was purchased from the Hexion company. All lanthanide nitrates were purchased from the Strem company. All other chemicals were purchased from Sigma Aldrich. Fourier Transformed Infrared spectroscopy (FTIR) were acquired on a Bomem MB104 spectrometer, using a Golden Gate attenuated total reflectance (ATR) module from Specac. Spectra were recorded between 4000 and 600 cm^{-1} with a resolution of 2 cm^{-1} using an average of 64 measurements in the final spectrum. Nuclear Magnetic Resonance (NMR) spectra were acquired on an Avance Neo 400 MHz spectrometer at ambient temperature using anhydrous benzene as internal standard.

Synthesis of the catalysts

Amounts used for each synthesis are consigned in Table S1. A representative procedure is described for cerium. In a 125 mL Erlenmeyer loaded with a magnetic stirred bar, 0.996 g of sodium dodecyl sulfate were dissolved in 37.5 mL of deionized water at room temperature. Another aqueous solution was prepared by dissolving 0.500 g of Cerium (III) nitrate hexahydrate in 12.5 mL of deionized water, and then added into the Erlenmeyer while stirring. After 3 min of stirring, the solid formed was recovered by Büchner filtration over a paper filter and washed 3 times with 25 mL of deionized water. The solid was then dried in a vacuum oven (50 Torr, 60°C) for 24 hours, giving 1.036 g of a white powder (Yield > 95%).

Table S1. Amounts used for each syntheses.

Lanthanide used	SDS (g)	$Ln(NO_3)_3$ (g)	$Ln(DS)_x$ (g)	Aspect of the solid
La	0.999	0.500	1.055	White
Pr	0.994	0.500	1.037	Greenish
Nd	0.987	0.500	1.036	Pale magenta
Sm	0.973	0.500	1.008	Ivory
Eu	0.970	0.500	1.025	White
Gd	0.961	0.500	1.019	White
Tb	0.955	0.500	0.962	White
Ho	0.981	0.500	0.996	Pale Orange
Er	0.976	0.500	1.017	Pink
Tm	0.934	0.500	0.974	White
Yb	0.963	0.500	1.019	White
Lu	0.922	0.500	1.005	White

Measurement of gel-time

First, the catalyst and cross-linker were mixed inside a 20 mL vial using an ultrasonic bath with slight heating. Then the epoxy monomer was added to the mixture. Immediately after, the vial was thermostated in a water or sand bath in order to absorb the reaction heat and the mixture was continuously stirred by a wire stirrer (Figure S1) and the gel-time corresponds to the time it takes for the wire to stop stirring. The various formulations used for gel-time measurements are detailed in Table S2 and S3.

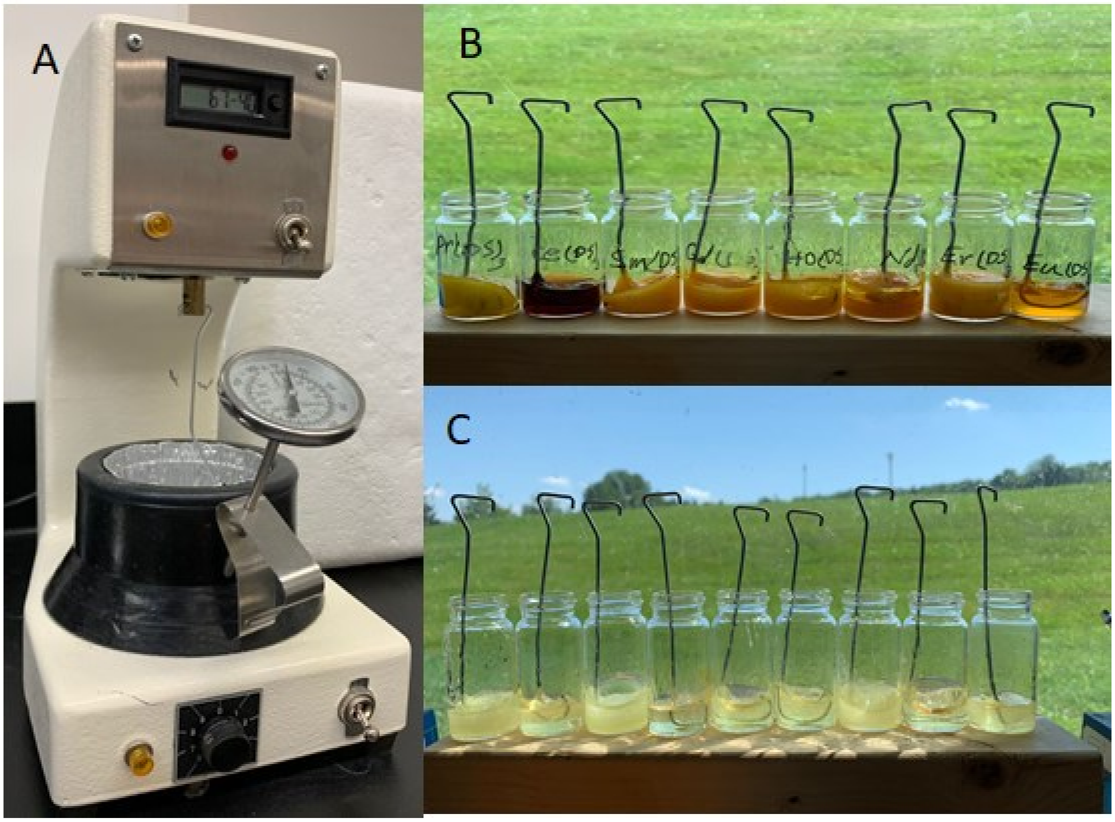


Figure S1.28 A. gel-time measurement setup. B. Various solid LDO-PEI formulations. C. Various solid DGEBA-Epikure formulations.

Table S2. Gel-time for formulations based on BADGE (the reference gel-time for the uncatalyzed reaction was 84 min).

Dodecyl sulfates catalysts	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
Mass of BADGE (g)	3.40												
Mass of Epikure 3251 (g)	1.52												
Mass of catalyst (g)	0.10												
Gel-time (min)[a]	24	50	44	47	43	57	56	62	62	63	53	51	64

Table S3. Gel-time for formulations based on LDO (the reference gel-time for the uncatalyzed reaction was 48 hours).

Dodecyl sulfates catalysts	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Ho	Er	Tm	Yb	Lu
Mass of LDO (g)	3.00												
Mass of Polyethylenimine (g)	2.00												
Mass of catalyst (g)	0.92												
Gel-stime (h)[a]	6	10	11	12	12	16	25	12	15	16	18	15	13

Measurement of the drying time

This procedure was adapted from ASTM D5895. In a 20 mL vial, the catalyst La(DS)$_x$ (0.1 g) was dissolved in Epikure 3251 (3.04g). Then, BADGE (6.81 g) was then added into the vial and quickly mixed with a glass rod for 1 min. The resulting viscous mixture was poured over a glass plate and spread with a universal blade applicator (GARDCO company) set at a nominal 10 mils thickness (250 micrometers). Every 15 min, the film was gently scratch with a needle, and the film was declared dry when the needle did not leave any mark on the film.

X-ray PhotoElectron Spectroscopy (XPS)

Analyses were performed on a Physical Electronics XPS PHI 5600-ci instrument equipped with an Al anode (1486.6 eV) at 300 W in survey mode, using the charge compensation mode. High resolution analyses were performed at an incident angle of 45 ^{o} on a surface of 0.5 mm^2. High resolution spectra were performed on C$_{1s}$, O$_{1s}$ and S$_{2p}$ using 30, 30 et 60 scans respectively.

Inductive Coupled Plasma (ICP)

ICP-MS measurements were performed on a X series II instrument from ThermoFisher Instrument equipped with a Elemental Scientific PC^3 Peltier spray chamber. The nebulizer gaz flow was set at 0.98 L/min, the forward power at 1400 W, the cooling gas at 13 L/min, the auxiliary gas at 0.8 L/min. For each run, 100 sweeps with dwell times of 10 ms were performed. The monitored isotopes were ^{45}Sc, ^{89}Y, ^{139}La, ^{140}Ce, ^{141}Pr, ^{143}Nd, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{155}Gd, ^{157}Gd, ^{159}Tb, ^{161}Dy, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{167}Er, ^{169}Tm,

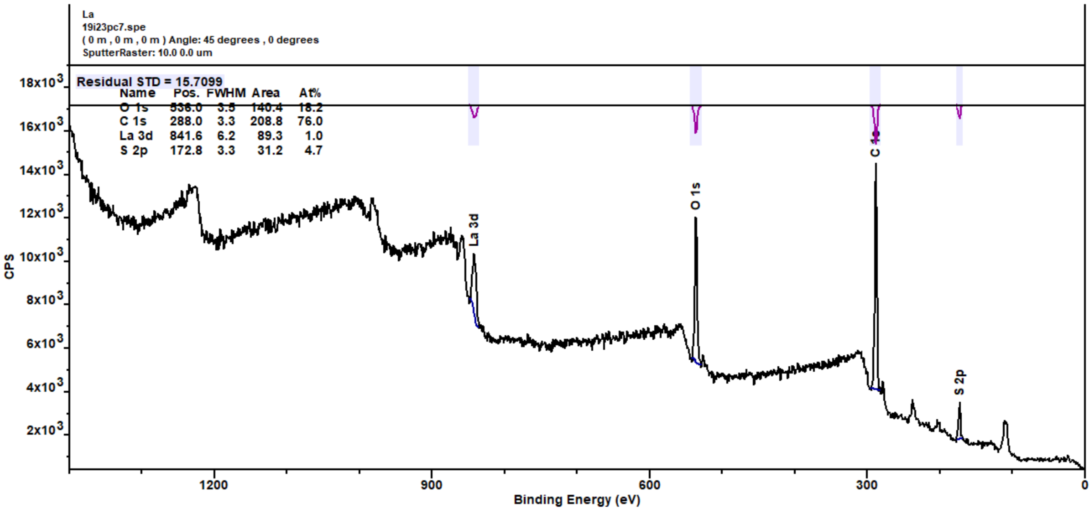
^{172}Yb and ^{175}Lu using ^{103}Rh as internal standard. ICP-OES measurements were performed an Agilent Technology 5100 ICP-OES instrument. The instrument was calibrated for S, Ce, Pr, Nd, La, Y, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, using ICP-OES standards purchased at Sigma-Aldrich. Samples (analysed both by ICP-MS and ICP-OES) were prepared by dissolving a known amount of catalyst (approx. 10 mg) in 2 mL of of HNO_3 (*Tracecert*® grade) for 4 h at 65°C. Then, 2 mL of HNO_3 were added to this solution for a second heating step of 2h at 85°C in order to ensure complete dissolution. All sample were analysed as a triplicate

Single Crystal X-ray Diffraction

A needle-like specimen of $C_{48}H_{96}LaNaO_{18}S_4$ of approximate dimensions 0.22 mm x 0.100 mm x 2.12 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker Kappa APEX II DUO CCD system equipped with a TRIUMPH curved-crystal monochromator and a Mo fine-focus tube (l= 0.71073 Å). Data collections have been carried out at nine different temperatures – 100 °C. The lattice parameters were obtained by least-squares fit to the optimized setting angles of the entire set of collected reflections.

Differential Scanning Calorimetry

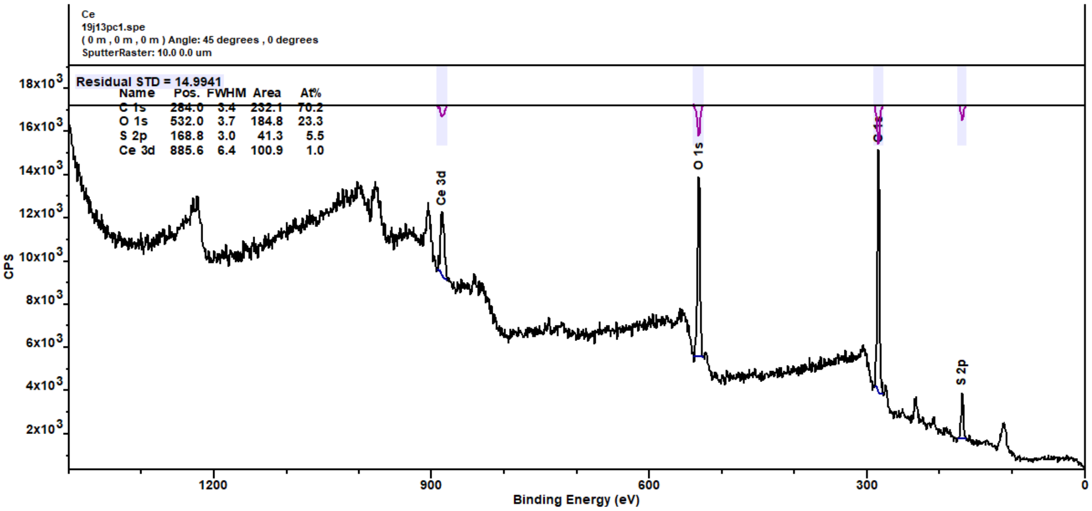
Differential Scanning Calorimetry (DSC) measurements were performed on a DSC 7 from Mettler-Toledo under nitrogen flux of 20mL/min equipped with an autosampler and a cooler. For each formulation, a sample containing the appropriate mixture of LDO and hardener was vigorously mixed using a vortex for 2 min. The resulting homogeneous and viscous liquid was then immediately placed in a DSC pan, which was hermetically sealed. The sample was then placed on the autosampler and was introduced in the oven which was pre-heated at the requested temperature.


La
19i23pc7.spe
(0 m , 0 m , 0 m) Angle: 45 degrees , 0 degrees
SputterRaster: 10.0 0.0 um

Residual STD = 15.7099

Name	Pos.	FWHM	Area	At%
O 1s	536.0	3.5	140.4	18.2
C 1s	288.0	3.3	208.8	76.0
La 3d	841.6	6.2	89.3	1.0
S 2p	172.8	3.3	31.2	4.7

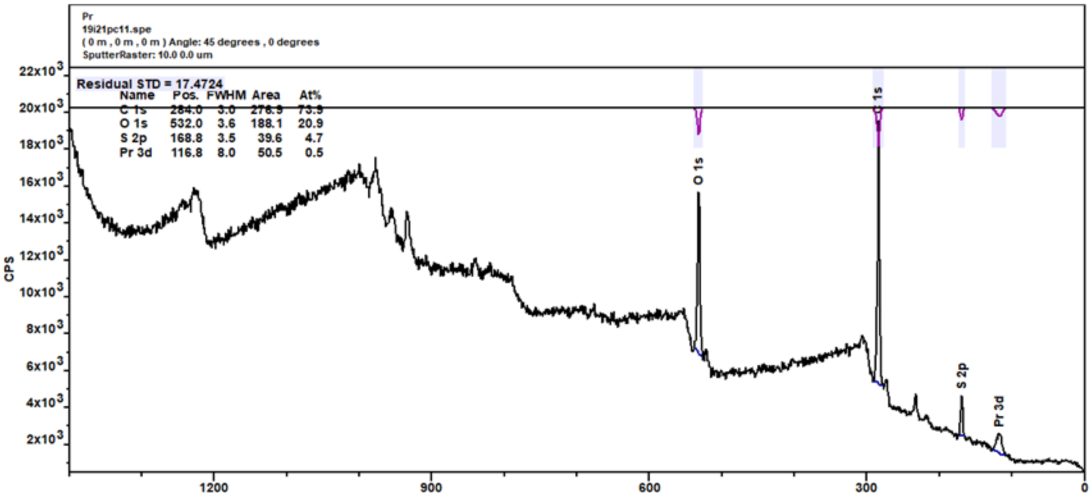
Figure S29. XPS – Survey mode for La(DS)$_x$ catalyst.


Ce
19j13pc1.spe
(0 m , 0 m , 0 m) Angle: 45 degrees , 0 degrees
SputterRaster: 10.0 0.0 um

Residual STD = 14.9941

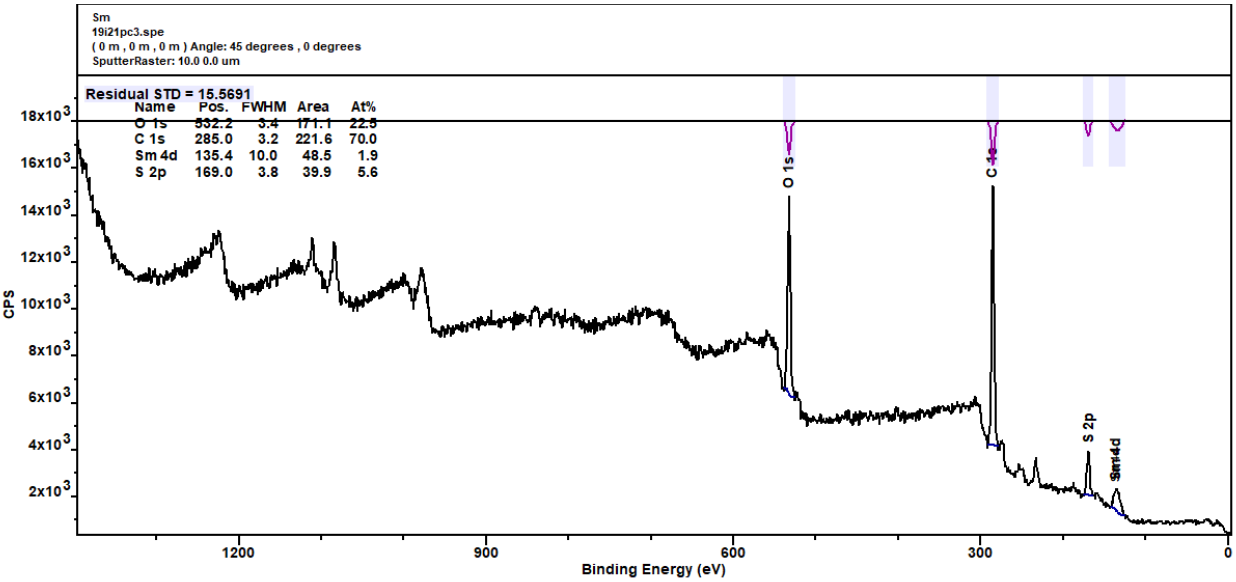
Name	Pos.	FWHM	Area	At%
C 1s	284.0	3.4	232.1	70.2
O 1s	532.0	3.7	184.8	23.3
S 2p	168.8	3.0	41.3	5.5
Ce 3d	885.6	6.4	100.9	1.0

Figure S30. XPS – Survey mode for Ce(DS)$_x$ catalyst.



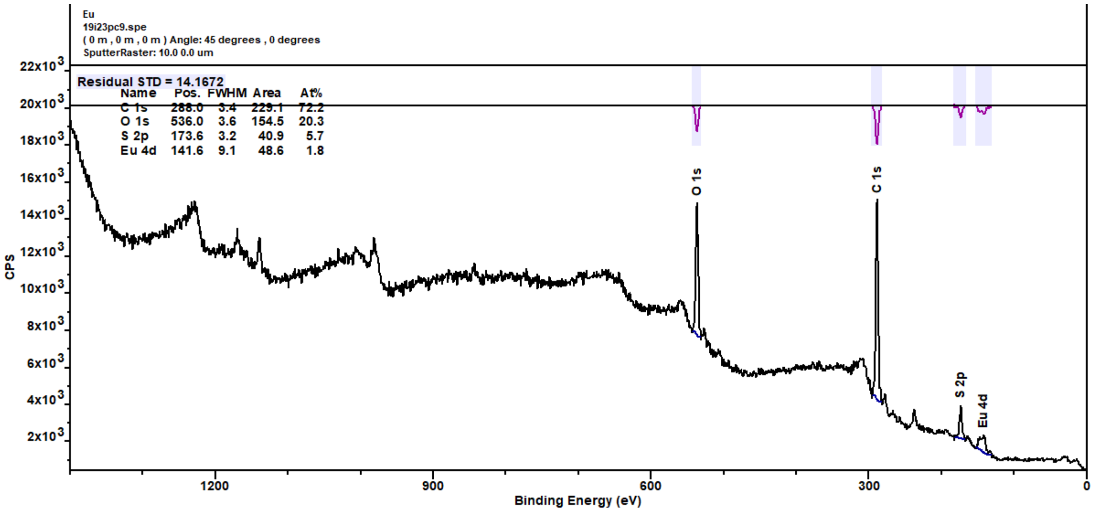
Name	Pos.	FWHM	Area	At%
C 1s	284.0	3.0	276.9	73.9
O 1s	532.0	3.6	188.1	20.9
S 2p	168.8	3.5	39.6	4.7
Pr 3d	116.8	8.0	50.5	0.5

Figure S4. XPS – Survey mode for Pr(DS)$_x$ catalyst.



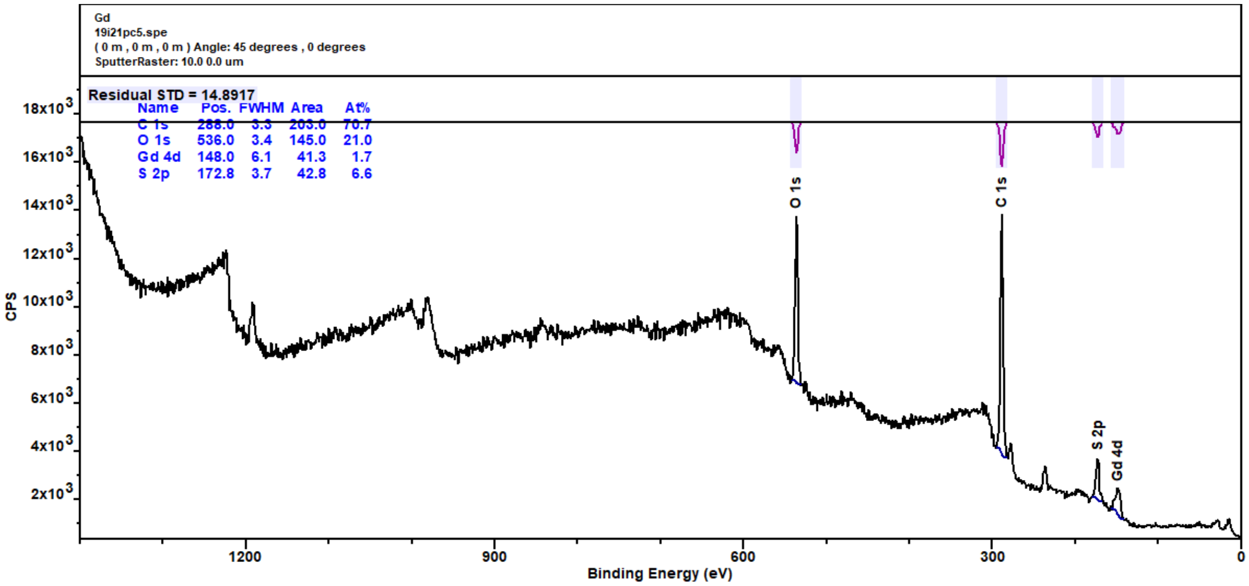
Name	Pos.	FWHM	Area	At%
O 1s	532.2	3.4	171.1	22.5
C 1s	285.0	3.2	221.6	70.0
Sm 4d	135.4	10.0	48.5	1.9
S 2p	169.0	3.8	39.9	5.6

Figure S5. XPS – Survey mode for Sm(DS)$_x$ catalyst.



Name	Pos.	FWHM	Area	At%
C 1s	288.0	3.4	229.1	72.2
O 1s	536.0	3.6	154.5	20.3
S 2p	173.6	3.2	40.9	5.7
Eu 4d	141.6	9.1	48.6	1.8

Figure S6. XPS – Survey mode for Eu(DS)$_x$ catalyst.



Name	Pos.	FWHM	Area	At%
C 1s	288.0	3.3	203.0	70.7
O 1s	536.0	3.4	145.0	21.0
Gd 4d	148.0	6.1	41.3	1.7
S 2p	172.8	3.7	42.8	6.6

Figure S7. XPS – Survey mode for Gd(DS)$_x$ catalyst.

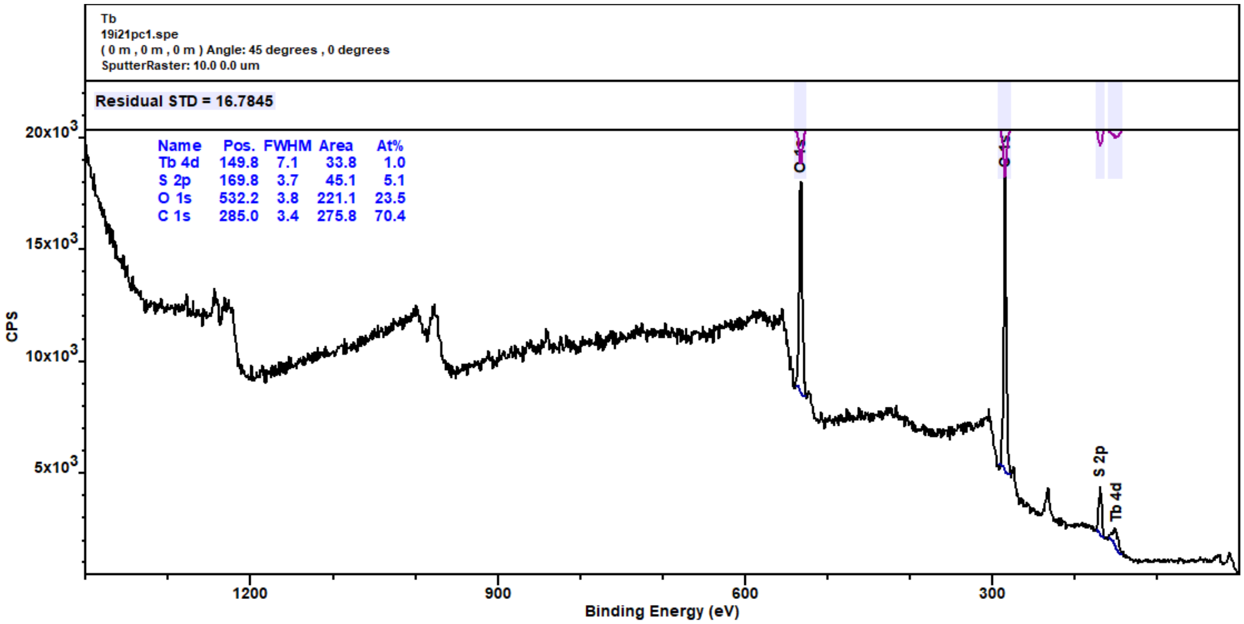


Figure S8. XPS – Survey mode for Tb(DS)$_x$ catalyst.

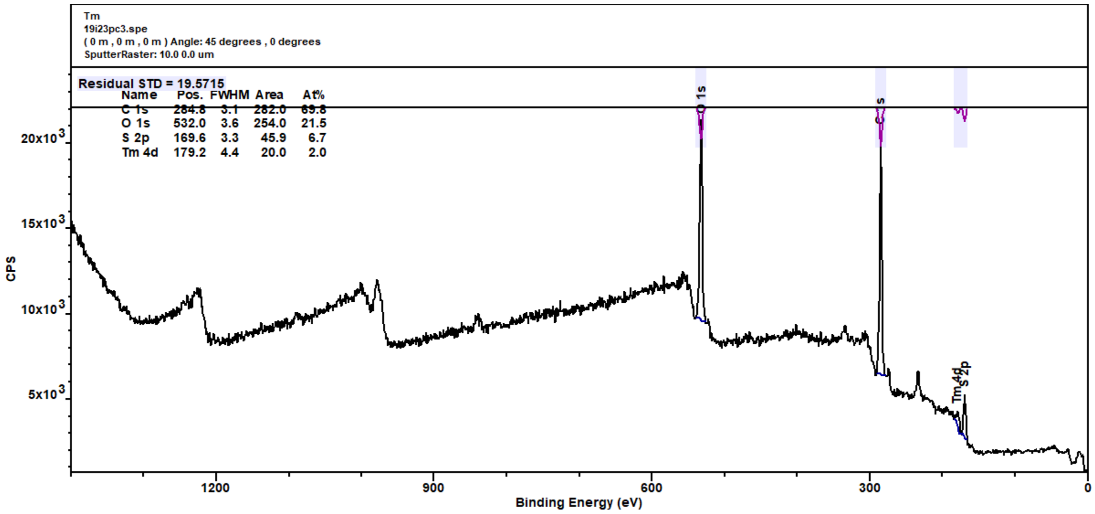
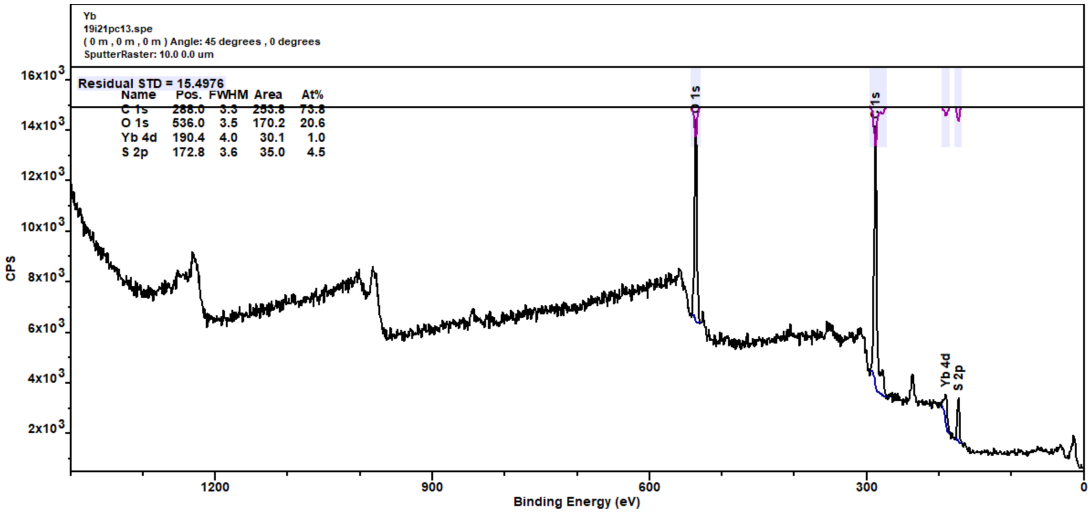


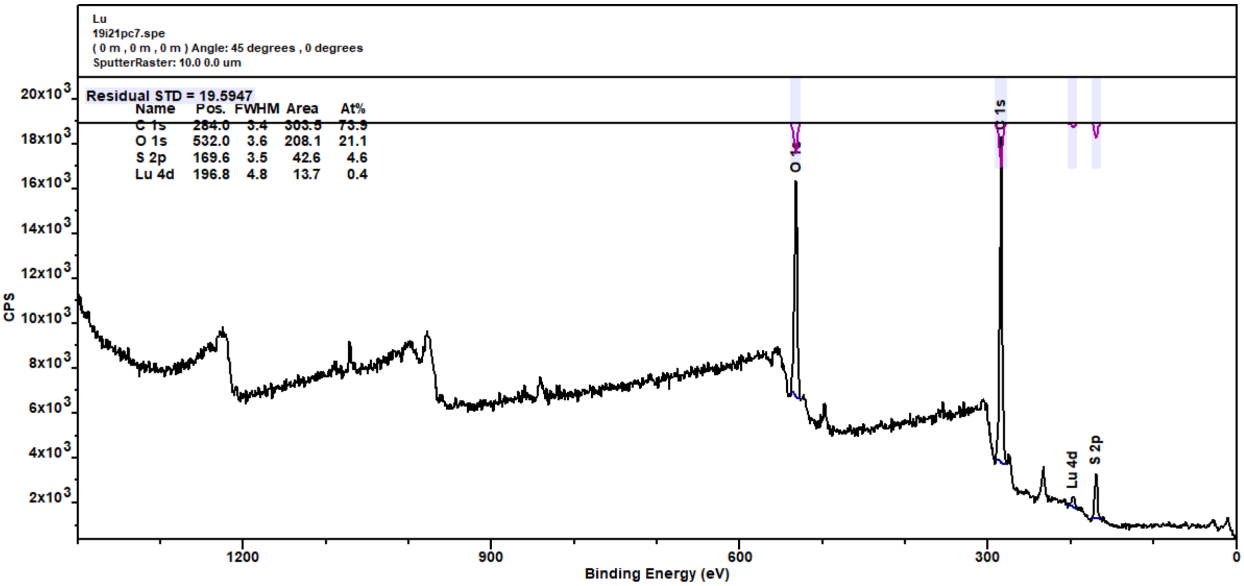
Figure S9. XPS – Survey mode for Tm(DS)$_x$ catalyst.


Yb
19i21pc13.spe
(0 m , 0 m , 0 m) Angle: 45 degrees , 0 degrees
SputterRaster: 10.0 0.0 um

Residual STD = 15.4976

Name	Pos.	FWHM	Area	At%
C 1s	288.0	3.3	253.8	73.8
O 1s	536.0	3.5	170.2	20.6
Yb 4d	190.4	4.0	30.1	1.0
S 2p	172.8	3.6	35.0	4.5

Figure S10. XPS – Survey mode for Yb(DS)$_x$ catalyst.


Lu
19i21pc7.spe
(0 m , 0 m , 0 m) Angle: 45 degrees , 0 degrees
SputterRaster: 10.0 0.0 um

Residual STD = 19.5947

Name	Pos.	FWHM	Area	At%
C 1s	284.0	3.4	303.5	73.9
O 1s	532.0	3.6	208.1	21.1
S 2p	169.6	3.5	42.6	4.6
Lu 4d	196.8	4.8	13.7	0.4

Figure S11. XPS – Survey mode for Lu(DS)$_x$ catalyst.

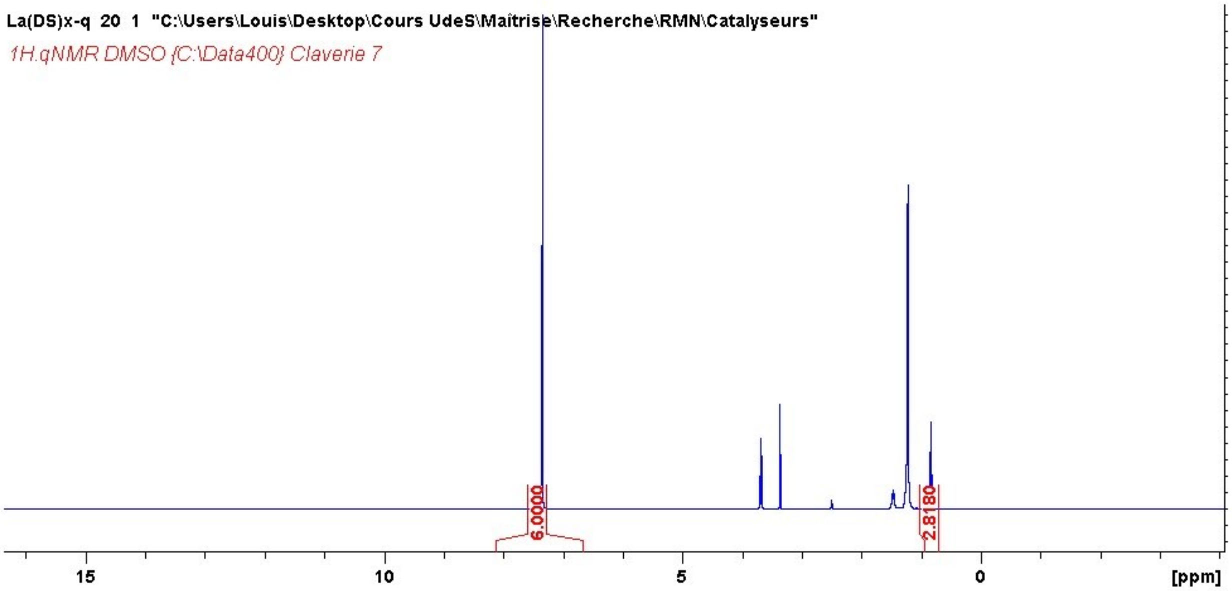


Figure S12. ^{1}H NMR (400MHz, DMSO-d6) of La(DS)$_x$ and benzene as internal standard.

In a clean NMR tube, 48.36 mg of La(DS)$_x$ catalyst and 12.58 mg of benzene (0.161 mmol) were added to 0.5 mL of DMSO-D6. From the benzene integral, it was found that an integral of 1 corresponds to 0.161 mmol of protons. The CH$_3$ signal of La(DS)$_x$ has an integral of 2.818. Thus, there are 0.151 mmol of CH$_3$ groups.

The molecular weight of La(DS)$_x$ is 138 + 265 x + (2-x) 18 (considering that the La(DS)$_x$ is hydrated and is octa-coordinated). Thus,

$$\frac{x}{138+265x+18\cdot(2-x)} = \frac{0.151}{48.36}$$

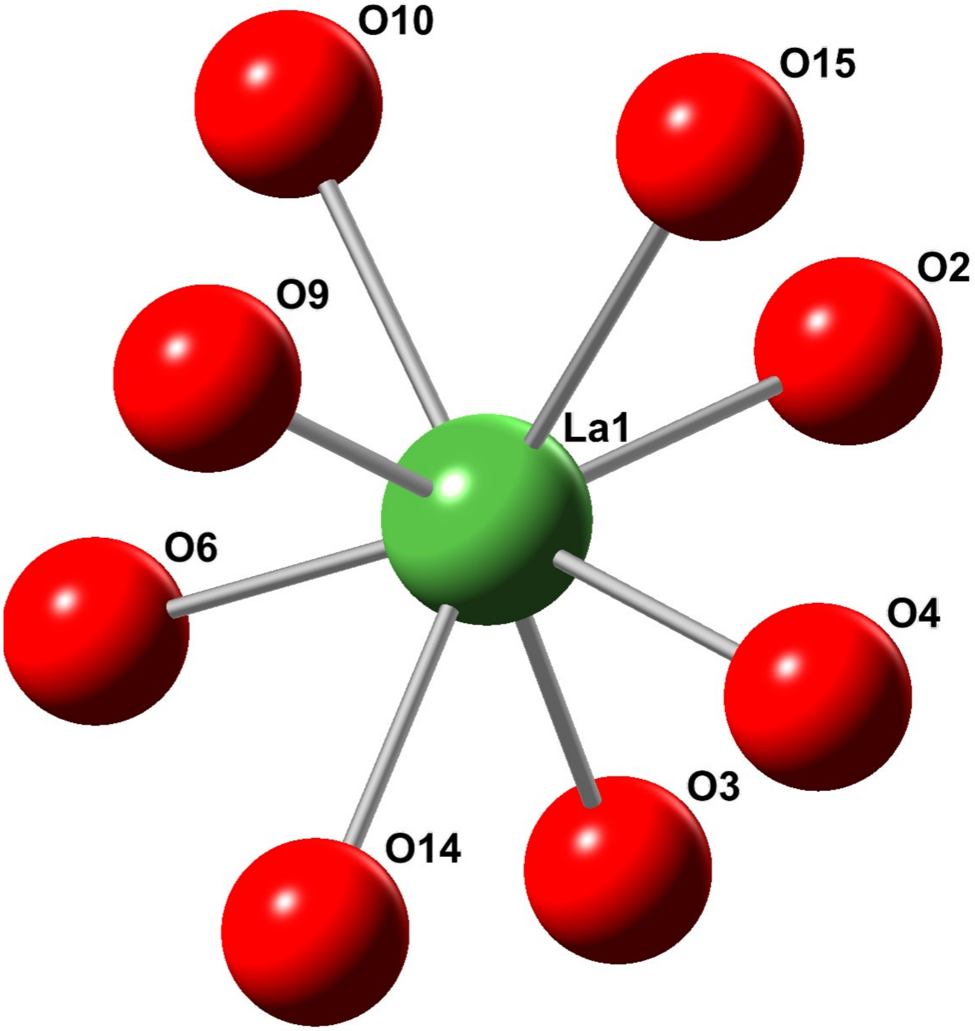
This leads to x = 3.85 (Not taking hydration water in the hydration sphere leads to x = 2.5)

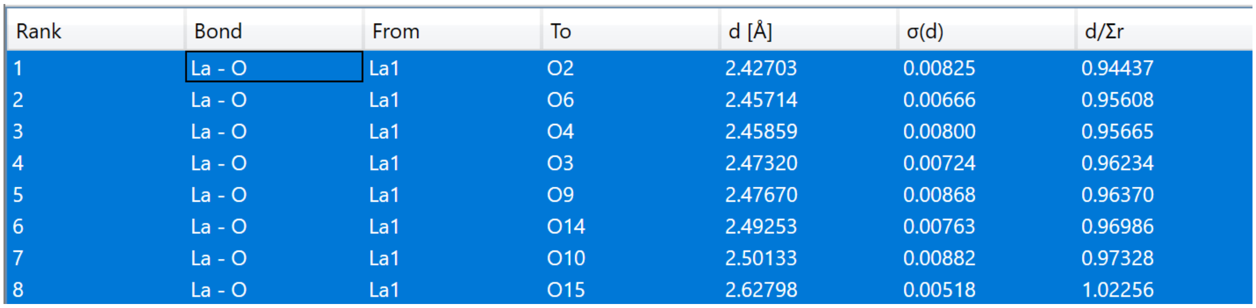
Table S4. Summary of the ICP-MS results.

Compounds	**% Lanthanide exp**	**Value of x in $La(DS)_xNa_{x-3}(H_2O)_{x-2}$**
$Ce(DS)_x$	10.78 ± 0,50	4.1
$Pr(DS)_x$	10.26 ± 0,12	4.3
$Nd(DS)_x$	11.41 ± 1,04	40
$Sm(DS)_x$	13.63 ± 0,21	4.4
$Eu(DS)_x$	12.02 ± 0,68	3.4
$Gd(DS)_x$	13.60 ± 1,12	4.0
$Tb(DS)_x$	13.13 ± 1,10	3.8
$Ho(DS)_x$	12.80 ± 0,86	4.0
$Er(DS)_x$	13.24 ± 0,43	3.9
$Tm(DS)_x$	14.84 ± 1,49	3.5
$Yb(DS)_x$	15.63 ± 0,48	3.3
$Lu(DS)_x$	11.21 ± 0,63	4.5

Table S5. Summary of the ICP-OES results.

Compounds	**S/Ln**	**Standard Deviation**
La(DS)x	3.8	0.3
Ce(DS)3	3.7	0.2
Pr(DS)3	3.2	0.1
Nd(DS)3	3.2	0.1
Sm(DS)3	3.1	0.3
Eu(DS)3	2.8	0.3
Gd(DS)3	3.0	0.1
Tb(DS)3	3.8	0.7
Ho(DS)3	3.7	0.7
Er(DS)3	3.6	0.1
Tm(DS)3	2.9	0.2
Yb(DS)3	2.3	0.6
Lu(DS)3	3.4	0.8





Rank	Bond	From	To	d [Å]	σ(d)	d/Σr
1	La - O	La1	O2	2.42703	0.00825	0.94437
2	La - O	La1	O6	2.45714	0.00666	0.95608
3	La - O	La1	O4	2.45859	0.00800	0.95665
4	La - O	La1	O3	2.47320	0.00724	0.96234
5	La - O	La1	O9	2.47670	0.00868	0.96370
6	La - O	La1	O14	2.49253	0.00763	0.96986
7	La - O	La1	O10	2.50133	0.00882	0.97328
8	La - O	La1	O15	2.62798	0.00518	1.02256

Figure S13. Environment of the La atom in the crystal cell and corresponding bond distances. Atoms O14 and O15 belong to water molecules whereas all other oxygen atoms belong to sulfates.

Table S6. Gel-time of an equimolar formulation of Epikure 3251 and BADGE containing 2 wt% of a catalyst.

Catalyst (2%wt)	Gel-time (min)
Without catalyst	84
Benzyl alcohol	67
Nonylphenol	61
Triethanolamine	60
DMP-30	52
La $(DS)_3$	24

Table S7. Effect of the concentration of La$(DS)_x$ (equimolar formulation of Epikure 3251 and BADGE).

Catalyst La $(DS)_3$ (%wt)	Gel-time (min)
0	86
0.5	63
1	42
2	25
3	19

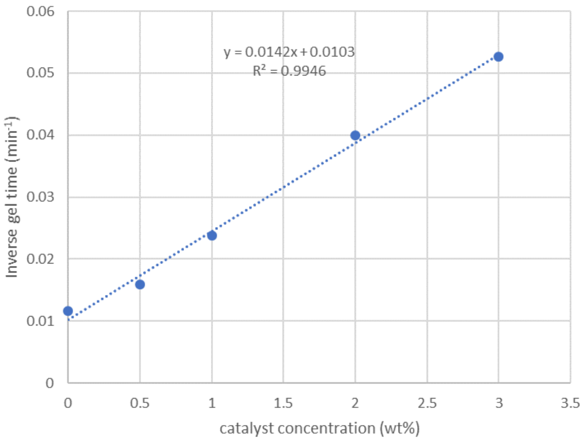


Figure S14. Inverse of the gel time vs La(DS)$_x$ catalyst concentration (equimolar formulation of Epikure 3251 and BADGE).

Table S8. The effect of percent La (DS)$_3$ in Epicure/BADGE (50/50 mol.%) formulation on Drying time and dissolution mode.

Catalyst La (DS)$_3$ (%wt)	Dry time (min)
0	120
1	90
2	60

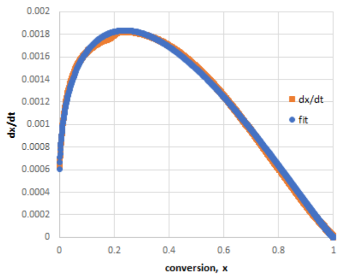
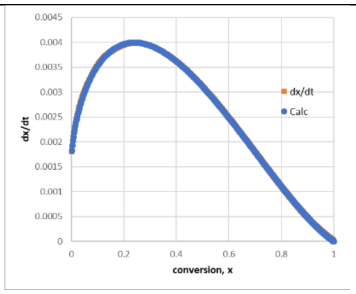
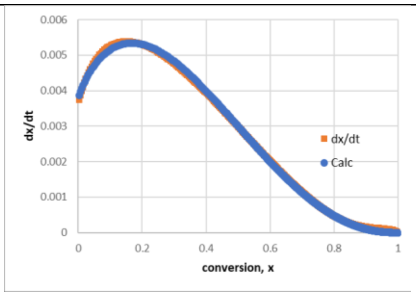
T = 173 °C	***T = 188 °C***	***T = 203 °C***
		

Figure S15. Experimental and fitted curve dx/dt vs conversion (x) at 173°C, 188 °C *and 203* °C *(LDO:PEI = 60:40 wt%, no catalyst)*.

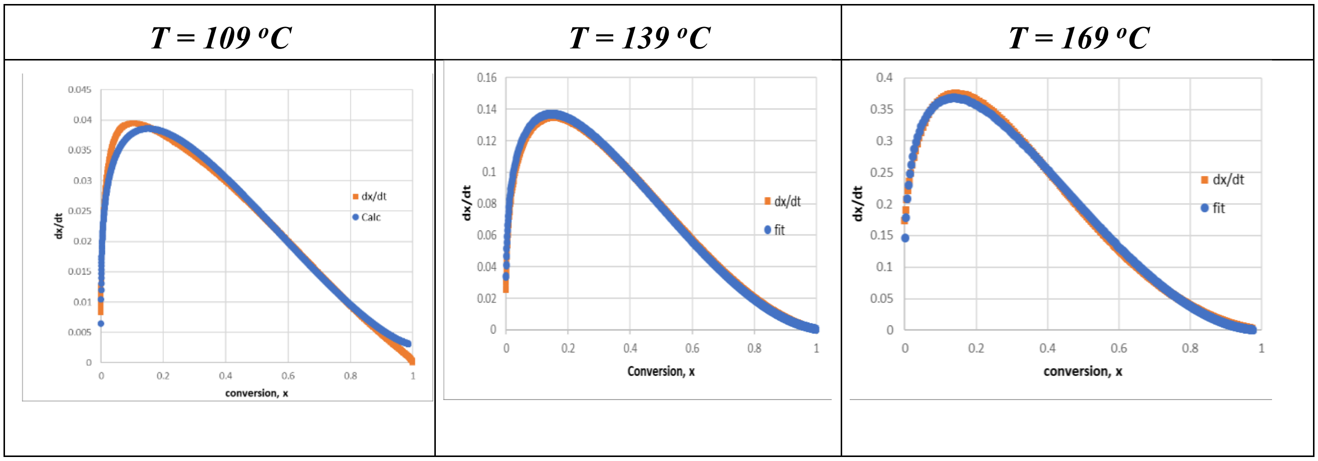


Figure S16. Experimental and fitted curve dx/dt vs conversion (x) at 109^{o}C, 139 ^{o}C *and 169* ^{o}C *(LDO:PEI = 60:40 wt%, 2 wt% of La(DS)x).*

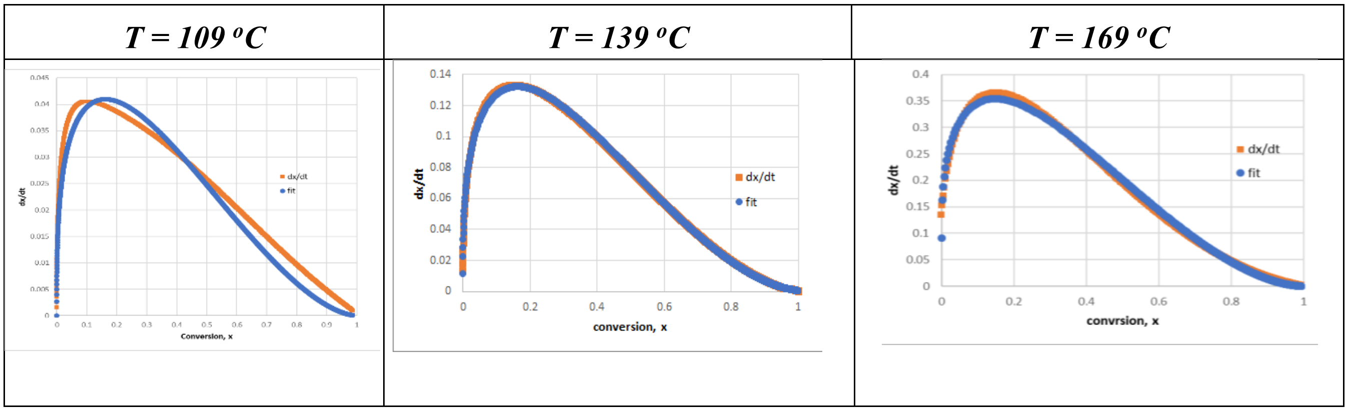


Figure S17. Experimental and fitted curve dx/dt vs conversion (x) at 109^{o}C, 139 ^{o}C *and 169* ^{o}C *(LDO:PEI = 60:40 wt%, 2 wt% of Pr(DS)$_x$).*

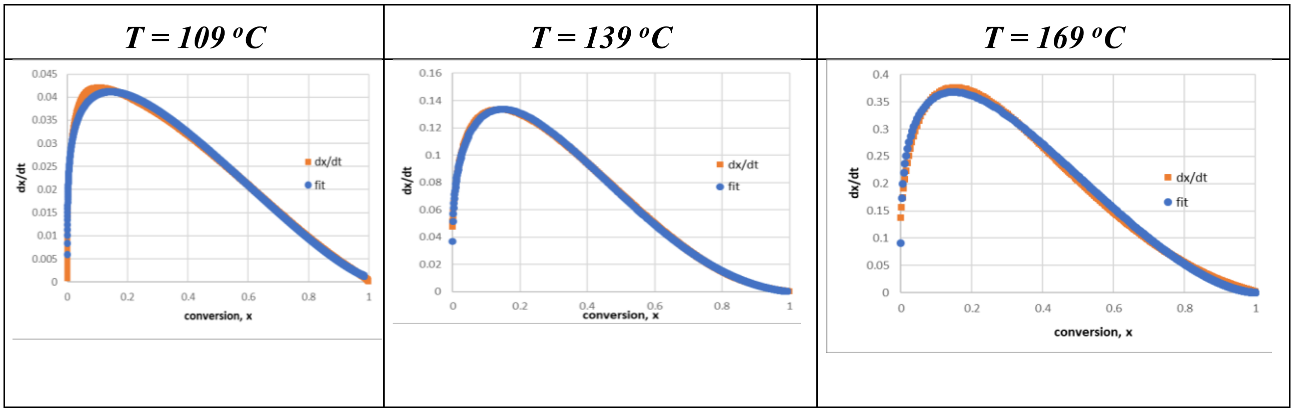


Figure S18. Experimental and fitted curve dx/dt vs conversion (x) at 109^{o}C, 139 ^{o}C *and 169* ^{o}C *(LDO:PEI = 60:40 wt%, 2 wt% of Gd(DS)$_x$).*

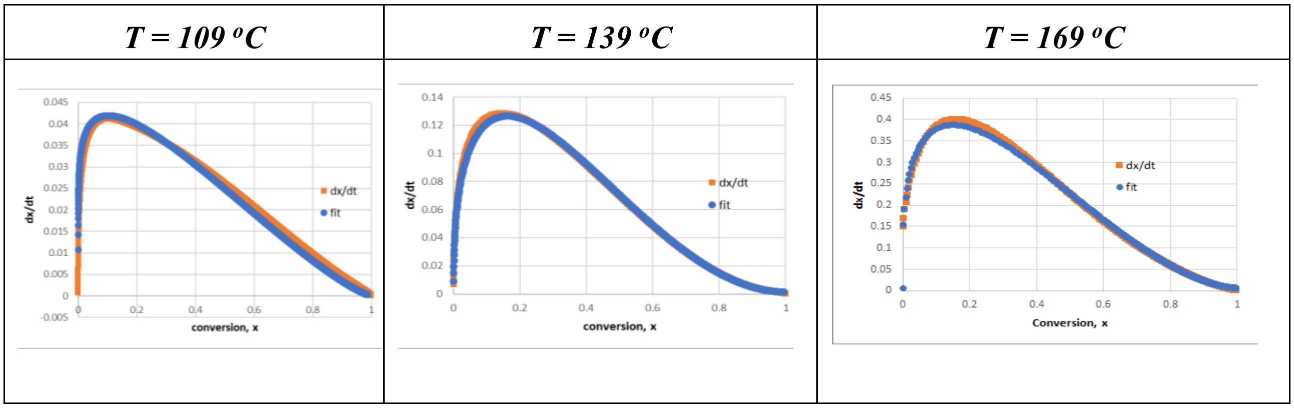


Figure S31 Experimental and fitted curve dx/dt vs conversion (x) at 109°C, 139 °C *and 169* °C *(LDO:PEI = 60:40 wt%, 2 wt% of Eu(DS)$_x$).*

Table S9. Fit parameters corresponding to kinetic curves S13-S17

No catalyst

Parameter	T = 173 °C	T = 188 °C	T = 203 °C
k_1	0.00045	0.0016	0.0037
m_1	1.12	0.84	3.42
k_2	0.0037	0.010	0.025
m_2	0.43	0.630	0.89
n_2	1.12	1.60	2.36

2% La(DS)$_x$

Parameter	T = 109 °C	T = 139 °C	T = 169 °C
k_1	0	0.0078	0.087
m_1	1.83	0.51	3.27
k_2	0.099	0.33	0.91
m_2	0.33	0.35	0.39
n_2	1.69	1.82	1.92

2% Pr(DS)$_x$

Parameter	T = 109 °C	T = 139 °C	T = 169 °C
k_1	0.00023	0.0032	0.091
m_1	0.90	0.35	3.26
k_2	0.076	0.33	0.87
m_2	0.23	0.35	0.41
n_2	1.43	1.78	1.78

2% Gd(DS)$_x$

Parameter	T = 109 °C	T = 139 °C	T = 169 °C
k_1	0.0015	0.037	0.090
m_1	0.086	1.07	3.27
k_2	0.076	0.34	0.87
m_2	0.23	0.44	0.39
n_2	1.36	2.23	1.70

2% Eu(DS)$_x$

Parameter	T = 109 °C	T = 139 °C	T = 169 °C
k_1	0.00060	0.0014	0.0066
m_1	0.68	0.0028	0.0029
k_2	0.067	0.36	0.89
m_2	0.15	0.38	0.30
n_2	1.30	1.98	1.71

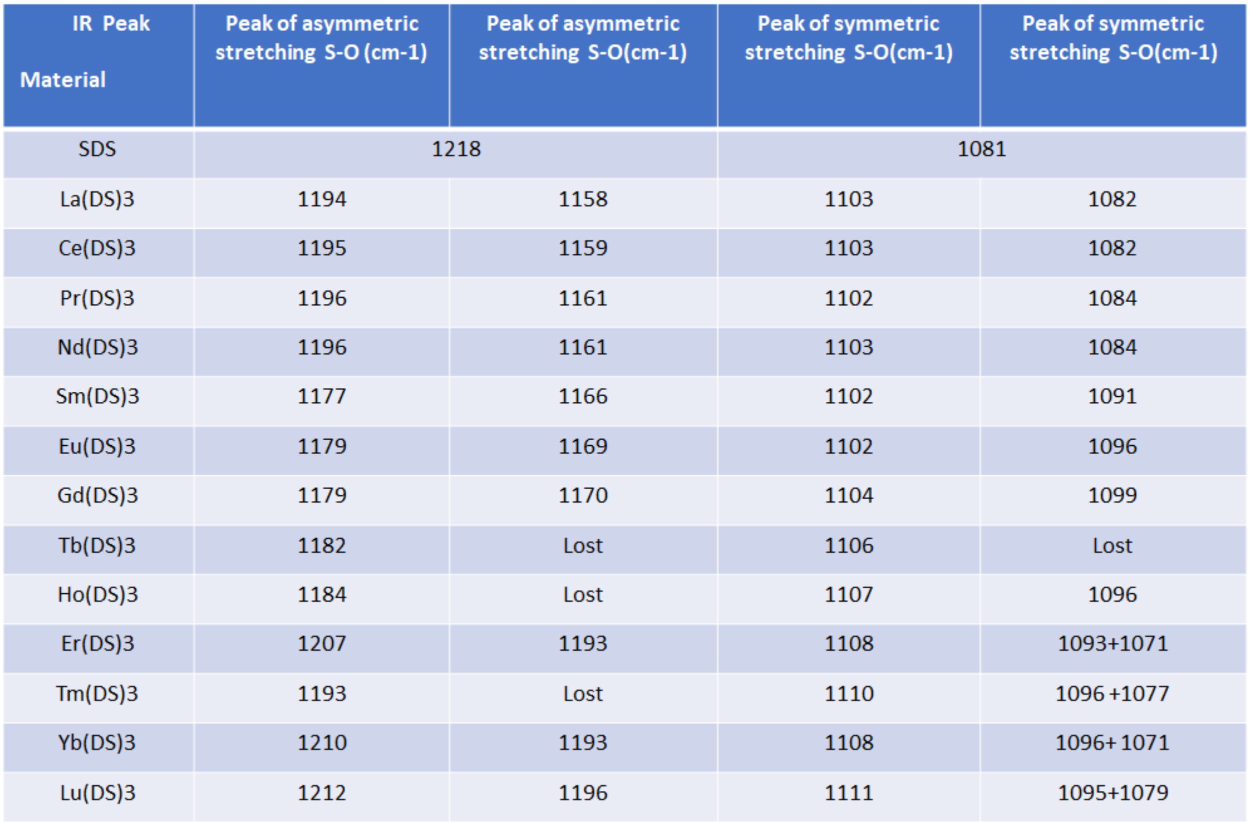
Table S10. Comparison of the gel-time for various catalysts, La(DS)$_x$, La(OPh)$_x$ and La(DBS)$_x$.

Formulations	Gel-time of La (DBS)$_x$	Gel-time of La (phenolate)$_x$	Gel-time of La (DS)$_x$	Without catalyst
LDO-PEI (60/40 wt%)	39h	42h	33h	>48h
BADGE-Epikure (50/50 mol.%)	43min	55min	24min	84min

Table S11. Influence of the alkali-metal.

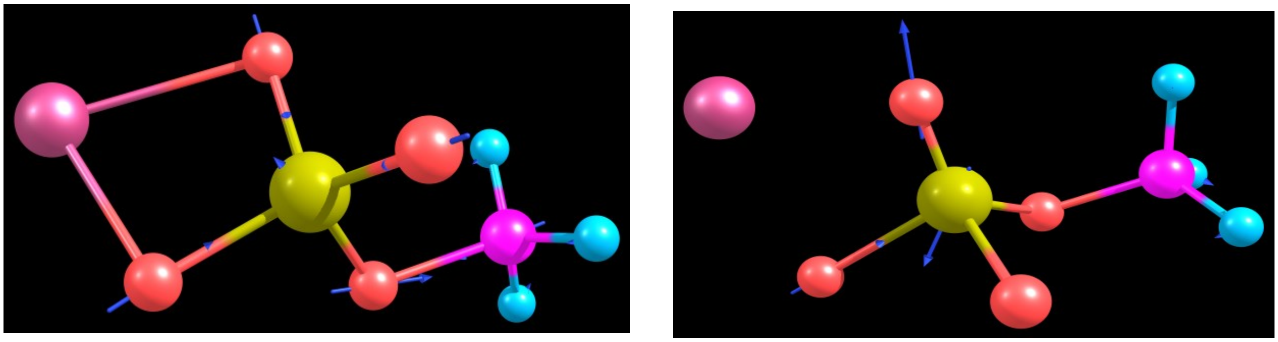
Reactants	Gel-time (min)
Lithium dodecyl sulfate + La (NO3)$_3$ · 6H_2O	27
Sodium dodecyl sulfate + La (NO3)$_3$ · 6H_2O	28
Potassium dodecyl sulfate + La (NO3)$_3$ · 6H_2O	30

Table S12. Wavenumbers of the S-O vibrations in Ln(DS)$_x$ complexes.



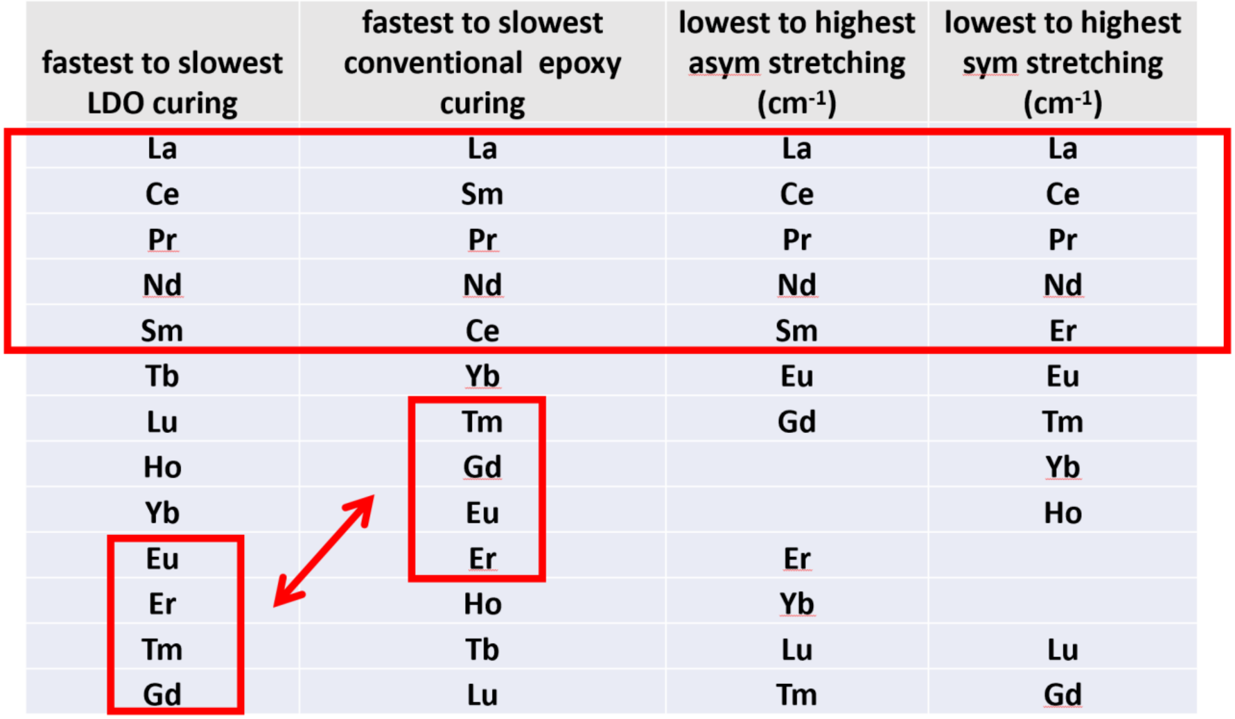
IR Peak Material	Peak of asymmetric stretching S-O (cm-1)	Peak of asymmetric stretching S-O(cm-1)	Peak of symmetric stretching S-O(cm-1)	Peak of symmetric stretching S-O(cm-1)
SDS	1218		1081	
La(DS)3	1194	1158	1103	1082
Ce(DS)3	1195	1159	1103	1082
Pr(DS)3	1196	1161	1102	1084
Nd(DS)3	1196	1161	1103	1084
Sm(DS)3	1177	1166	1102	1091
Eu(DS)3	1179	1169	1102	1096
Gd(DS)3	1179	1170	1104	1099
Tb(DS)3	1182	Lost	1106	Lost
Ho(DS)3	1184	Lost	1107	1096
Er(DS)3	1207	1193	1108	1093+1071
Tm(DS)3	1193	Lost	1110	1096 +1077
Yb(DS)3	1210	1193	1108	1096+ 1071
Lu(DS)3	1212	1196	1111	1095+1079

Figure S20. Calculated vibrations for $\mathrm{NaSO4CH_3}$ at 1076 cm^{-1} and 1225 cm^{-1} (the vectors indicate the direction of displacement).



The molecule was optimized using the def2tzvpp basis set and the MO6 DFT method.

Table S13. Comparison of catalytic activity and SO_2 stretching wavenumber.



fastest to slowest LDO curing	fastest to slowest conventional epoxy curing	lowest to highest asym stretching (cm^{-1})	lowest to highest sym stretching (cm^{-1})
La	La	La	La
Ce	Sm	Ce	Ce
Pr	Pr	Pr	Pr
Nd	Nd	Nd	Nd
Sm	Ce	Sm	Er
Tb	Yb	Eu	Eu
Lu	Tm	Gd	Tm
Ho	Gd		Yb
Yb	Eu		Ho
Eu	Er	Er	
Er	Ho	Yb	
Tm	Tb	Lu	Lu
Gd	Lu	Tm	Gd

GENERAL CONCLUSION

The first objective of this study was to replace a DGEBA monomer with LDO and to produce a new bio-epoxy. Limonene has four isomers that react differently together, so it shows less reactivity in thermosetting epoxy. Until now, LDO has never been applied as an only epoxy monomer in the epoxy thermoset. However, it has already been available in the industry as a solvent and has many advantages. For instance, its epoxidation occurs without using ECH that is a toxic molecule, and it is also extracted from citrus waste. All of these reasons introduce the LDO as an attractive candidate for the synthesis of a biobased epoxy polymer.

For biobased epoxy polymer synthesis, LDO was studied as an epoxy monomer with PEI as a selected hardener and Epikure as an industrial hardener. Then swelling tests were performed to examine the crosslinked density. The results showed that LDO cannot be cross-linked with Epikure because it dissolved in the solvent. However, LDO and PEI became cross-linked but not as much as expected for an epoxy thermoset polymer. It means that the LDO-PEI sample had a high amount of swelling, so other epoxy monomers that have more functions applied to improve cross-linked density while cured with PEI and Epikure. A new epoxy formulation with LDO in absence of DGEBA was obtained, which indicated an acceptable swelling amount compare to the sample with DGEBA (industrial sample).

Other tests such as DMA and tensile tests were performed to examine samples in terms of thermal and mechanical properties. The results for the samples with Epikure as a hardener in DMA confirmed two phases, highly cross-linked and less cross-linked, that belongs to regain without and with LDO, respectively. Otherwise, DMA results show homogenous cross-linked networks, and higher T_g for samples containing PEI.

Tensile tests showed that LDO made samples to be more brittle than the industrial sample. Finally, a biobased epoxy formulation was achieved that partially contained LDO and had comparable properties with the industrial sample.

The second objective of this study was to find a new and effective catalyst that is based on the reaction between lanthanides with sodium dodecyl sulfate. It is demonstrated that lanthanide dodecyl sulfates ($LnDS_x$) efficiently catalyze the reaction of amines with epoxides. Two formulations were tested, one with LDO and another one with DGEBA, which are corresponded to biobased and industrial epoxy monomer, respectively. Among all lanthanide dodecyl sulfates, $LaDS_x$ exhibited the most activity by presenting a considerable reduction of the activation energy for the reaction between the epoxide and the amine. Also, $LaDS_x$ had a significant effect on the reaction time of LDO even though LDO showed low reactivity compared to DGEBA.

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