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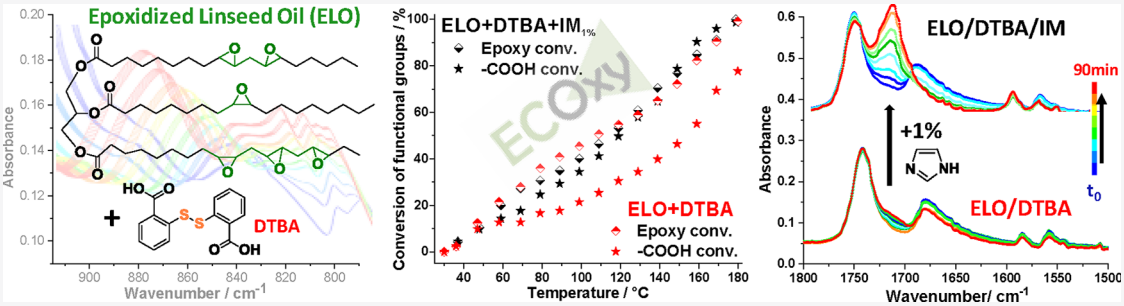

ABSTRACT: In a sustainable development context, epoxidized vegetable oils (EVO) have unlimited and promising future prospects as renewable and environmentally friendly feedstock. The only drawback to their use is their low and non-selective reactivity compared to the aromatic epoxides. Properly, a small optimized amount of "true" initiators can overcome this issue and also beneficially serve in properties such as glass transition, modulus, strength, elongation at break, and chemical resistance. This paper presents efforts to understand and identify the initiator's effect to more accurately predict how to select a good initiator on EVO/dicarboxylic acid systems. A new bio-based reprocessable epoxy resin was prepared from epoxidized linseed oil (ELO) and 2,2′-dithiodibenzoic acid (DTBA). The evolution of the chemical structures and the reactions' mechanisms have been systematically studied by *in situ* Fourier transform infrared (FT-IR) and nuclear magnetic resonance (NMR) spectroscopies and differential scanning calorimetry (DSC). A screening of 10 initiators was performed for the ELO/DTBA cross-linking reaction. The influence of the initiator's structure, basicity, and nucleophilicity was assessed and ranked in terms of the kinetic response including the epoxy−acid reaction rate and the percentage of functional group consumption. An excellent effect achieved by imidazole as an initiator was demonstrated. An attempt has been proposed to corroborate the experimental values with the results of quantum chemistry calculations.

INTRODUCTION

Bio-based epoxy resins featuring ecological and environmental advantages toward sustainable development are gaining academic and commercial interest. The use of vegetable oils as starting materials is one of the most feasible strategies and cost-competitive approaches because of their universal availability, advantageous costs, and biodegradability.[1−6] The epoxy thermosets are obtained during the cross-linking reactions in the presence of curing agents such as amines, anhydrides, acids, thiols, polyols, etc. Among them, carboxylic acids are the second most popular hardeners for epoxy resins after the amines due to their relatively low price, raw-material widespread availability, and good flexibility and weatherability properties of their resulted materials.[7] The epoxy−acid reactions have been widely studied for several years.[8−11] However, the overall complete mechanism has not been described because of its complexity by the number of side reactions. The main reaction is the nucleophilic addition of the carboxylic acid to the epoxy groups, giving rise to the formation of a β-hydroxyl ester (reaction 1, Scheme 1).

Scheme 1. Reactions Occurring in an Epoxide−Acid system Under Non-catalyzed Conditions[13−16]

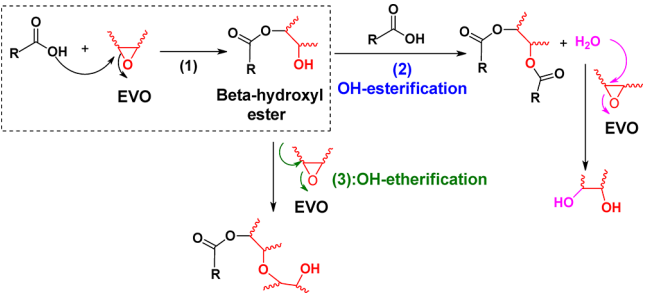

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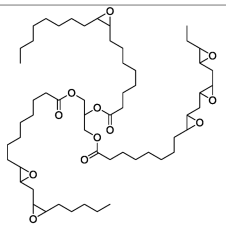
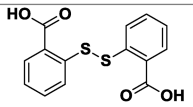
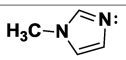
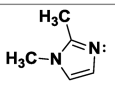
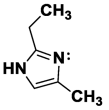
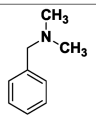
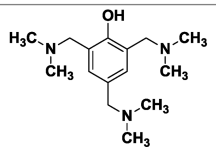
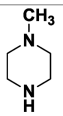
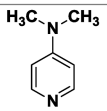
Table 1. Characteristics of the Epoxy Monomer, Hardener, and 10 Initiators[35−41]

Acronym	Structure and name	Name	Melting Point [°C]	pKa	Function
ELO		Epoxidized linseed oil	-	-	Epoxy monomer
DTBA		2,2'-Dithiodibenzoic acid	287-290	5.02[35]	Hardener
IM		Imidazole	89-91	6.95[36]	Initiator Donor-acceptor
1-MI		1-Methylimidazole	-60	7.21[36]	Initiator Acceptor
2-MI		2- Methylimidazole	145	7.85[36]	Initiator Donor-Acceptor
1,2-DMI		1,2-Dimethylimidazole	37 - 39	8.21[36]	Initiator Acceptor
2E4MI		2-Ethyl 4-Methylimidazole	47 - 54	8.68[36]	Initiator Donor-Acceptor
DMBA		N, N-Dimethylbenzyl-amine	43 - 45	8.97[37]	Initiator Acceptor
DMP30		2,4,6-Tris(dimethylamino-methyl)phenol	< -20	8.41[38] 9.12 9.75	Initiator Donor-Acceptor
1-MP		1-Methylpiperazine	-6	9.14[39]	Initiator Donor-Acceptor
TBD		1,5,7-Triazabicyclo[4.4.0] dec-5-ene	125-130	14.5[40]	Initiator Donor-Acceptor
DMAP		Dimethylaminopyrid-ine	108 - 110	9.2[41]	Initiator Acceptor

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Nevertheless, secondary reactions can occur such as (i) OH-esterification reactions between the residual −COOH groups and −OH groups generated by the main reaction or (ii) OH etherification of the epoxide with secondary alcohols by nucleophilic addition[9,12] (reactions 2 and 3, Scheme 1).

Consequently, the topology of the generated network is deeply affected by the occurrence of these secondary reactions (2 and 3). Indeed, these reactions will affect the polymer architecture by introducing branching points, implying the increase of the network cross-linking density and thus having a strong impact on the final properties. To diminish or avoid the occurrence of these secondary reactions, a small amount of Lewis bases could be employed, which act as initiators often named "catalytic" curing agents in the literature.

Some studies on the curing of epoxidized vegetable oil (EVO) with dicarboxylic acids (DCA) have been reported. In 2012, Supanchaiyamat et al.[15] described the synthesis of thermosetting resins from epoxidized linseed oil (ELO) in combination with a bio-derived diacid cross-linker (Pripol 1009) in the presence of different catalysts including triethylamine (TEA), 1-methylimidazole (1-MI), 2-methylimidazole (2-MI), 1,8 diazabicyclo[5.4.0]undec-7-ene (DBU), and 4-dimethylaminopyridine (DMAP). The authors demonstrated that the thermomechanical properties of the prepared materials were significantly influenced by the type of the catalyst. They showed that these properties could be improved, e.g., the tensile strength improved by up to 545% in the presence of DMAP. Additionally, in 2015, Ding et al.[11] stated the effect of the diacid's chain length: aliphatic from C6 to C18 of ELO-derived epoxy in the presence of DMAP. The authors showed that a shorter diacid's chain conducts better reactivity toward the epoxide groups and the use of DMAP as a catalyst efficiently accelerates the curing rate and reduces the activation energy of the reaction. These results were confirmed by Zeng et al.[17] when they studied the curing reaction of epoxidized soybean oil (ESO) with bio-based aliphatic dicarboxylic acids. All authors agreed that the properties of epoxy thermosets strongly depend not only on the chemical nature of the epoxy−hardener couple but also on that of the initiators. However, the comprehension on the initiator's mechanism and its effect on curing reactions step by step was not precisely discussed in the literature. For example, the influence of the initiator's structure is still unexplained, such as the substituents and electronic density effects. Moreover, these studies were limited to the case of aliphatic diacids. To our knowledge, very few studies report the curing of EVO with aromatic dicarboxylic acids (ArDCA).

Materials' end of life and aspects in circular economy are very important when developing materials. Bio-based epoxy vitrimers have attracted great attention as the most efficient strategy to confer reprocessability to a thermoset by incorporating exchangeable chemical bonds into the polymer network.[18,19] Several dynamic covalent reactions have been developed such as carboxylate transesterifications,[20−22] transalkylation of triazolium salts,[23] olefin metathesis,[24] disulfide exchange,[18,25] etc. Distinguished from the others, the disulfide dynamic S−S bond was used to produce reversible reactions in which the exchange can be activated at moderate temperature without any catalyst or initiator.[25−28] Rekondo et al.[29] developed a new poly(urea−urethane) thermoset elastomer with aromatic disulfide amine. The prepared material presents near quantitative self-healing efficiency at room temperature without the need for any external intervention such as heat or light. Implementing this approach to develop novel thermosets from vegetable oils, 2,2′ dithiodibenzoic acid (DTBA) was particularly selected in this study as an aromatic hardener for the curing of ELO. The reprocessability of the ELO/DTBA copolymers will be discussed in further work. Epoxidized linseed oil (ELO) was chosen due to its availability in the market and high functionality in epoxy groups.

The main objective of the study is to understand and identify the initiator's chemical and structural effect on the cross-linking process of the ELO/DTBA system. The purpose is focused on nitrogen Lewis bases as initiators with two main goals: (1) to prove the initiator's ability to activate and accelerate selective epoxy−diacid cross-linking and (2) to rank the chemical reactivity of 10 selected initiators (Table 1) then infer the initiator's structure on ELO/DTBA copolymerization. Imidazole was initially selected as a reference because of its high reactivity and relatively low cost.[11,30−33] Various percentages of IM were studied to optimize the reactivity. An equimolar amount of epoxide versus carboxylic functions was used.[34]

RESULTS AND DISCUSSION

Effect of the Initiator on ELO/DTBA Curing Kinetics. *Effect of Imidazole on ELO/DTBA Copolymerization.* The curing behavior of the ELO/DTBA mixture was first investigated using dynamic DSC analysis in the presence of different amounts of the initiator (Figure 1). The analysis of the data is given in Table 2.

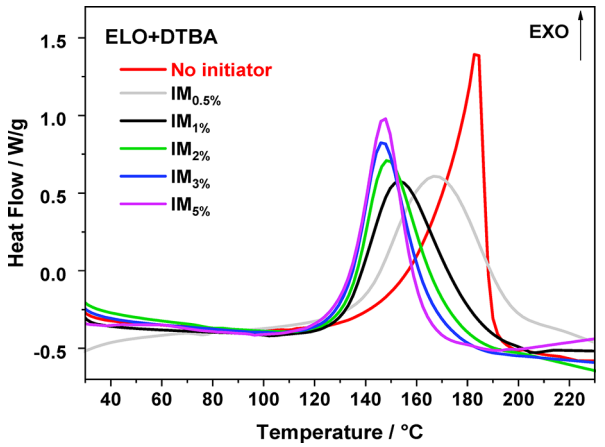

Figure 1. Dynamic DSC thermograms for ELO/DTBA mixtures with different percentages of imidazole as an initiator during heating at 10 °C·min^{-1}.

Table 2. Reactivity Study of the ELO/DTBA Mixture in the Presence of Different Ratios of IM and Dynamic DSC Results

ELO/DTBA	T_{on} (°C)	T_{peak} (°C)	T_{end} (°C)	ΔT (°C)	ΔH (J·g^{-1})	T_g (°C)[a]
no initiator	167	184	189	22	248	13
$IM_{0.5\%}$	138	168	199	61	234	45
$IM_{1\%}$	130	154	184	54	214	76
$IM_{2\%}$	132	149	173	41	190	80
$IM_{3\%}$	131	147	166	35	189	83
$IM_{5\%}$	129	146	160	31	190	84

[a] T_g values were measured on the cured thermosets.

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Macromolecules XXXX, XXX, XXX−XXX

The DSC scans in Figure 1 show a single exothermal event of the ELO/DTBA curing. The obtained results show that the reaction's peak is shifted gradually to a lower temperature while increasing the IM concentration: T_{peak} = 184 °C without IM versus 146 °C for $IM_{5\%}$. Concerning the onset temperature of the reaction, we can observe the same trend. By adding 0.5% initiator, T_{on} decreased significantly with 29 °C from 167 to 138 °C, while the maximum of the peak decreases with 16 °C from 184 °C (system without IM) to 168 °C. By increasing the IM concentration from 0.5 to 1 wt %, T_{on} decreases to 130 °C and the exothermic peak narrowed to the range of 130−184 °C. It should be noticed that, among all studied systems, ELO/DTBA without an initiator formulation exhibits the highest enthalpy value (248 $J{\cdot}g^{-1}$ vs 214 $J{\cdot}g^{-1}$ for $IM_{1\%}$) together with a shorter interval of the reaction. Comparing the shape of the DSC curve corresponding to the cross-linking of this system (Figure 1) with that of all the reactions initiated by IM, it is evident that the mechanisms are not the same. First, ELO/DTBA without the initiator system has the highest onset reaction temperature, 167 versus 138 °C for the system with 0.5% IM, together with the highest peak of reaction temperature, 184 versus 168 °C for the system with 0.5% IM. Then, this exotherm peak is not symmetrical with the first half peak (T < 172 °C) having a lower slope than that of the second half (T ≈ 183 °C). All these data are signs of the occurrence of mostly random ELO/DTBA copolymerization accompanied by secondary reactions (homopolymerization and etherification) that currently occur at so high temperatures. As already reported in the literature[42] and our previous work,[43] epoxy/dicarboxylic acid copolymerization is not selective without an initiator. Therefore, we can assume that the ELO/DTBA non-initiated reactions occur by a complex and random mechanism of copolymerization, ELO homopolymerization, etherification, etc. This assumption could explain the highest reaction enthalpy and peculiar curve shape.

A noticeable change in the material's properties is observed when the initiator is added since T_g increases from 13 °C for ELO/DTBA/No-initiator to 45 °C with only 0.5% IM in the curing system. This result is probably correlated to better selectivity of the copolymerization reaction, a more ordered network structure, and finally a higher density of the cross-links.

These data represent an experimental proof that the addition of an initiator provides an efficient way to lower the curing activation energy and avoid the occurrence of secondary reactions. It suggests that a higher initiator concentration will produce a greater extent of initiated chains and consequently a faster propagation rate of copolymerization. Similar results were reported by Such et al.[44] when they studied the curing of DGEBA in the presence of 1-MI and by Chow et al.[45,46] and Fringant et al.[47] for the curing of EVO/anhydride systems. Nevertheless, for the ELO/DTBA curing system, all the formulations with IM wt % ≥ 1 gave similar values of T_{on}, as shown in Table 2. We should highlight that by increasing to 1, 2, 3, and 5% the initiator content, the reaction temperature peak decreases, together with the temperature interval and reaction enthalpy. Again, this result is a clear evidence of the initiator's effect on the reaction's mechanism and kinetics.

Considering enthalpies of reaction values corroborated with the onset temperature of the reaction, it appears that the system with 1 wt % initiator is the optimal. This ratio represents a good compromise between the lower IM amount (0.5%) that requires longer curing times at higher temperature and a larger interval of the reaction and the higher IM amount (5%) that allows faster curing times and therefore is difficult to control during mixture preparation. This trend is confirmed by the thermal properties of the obtained thermoset: by changing the initiator's percentage, the T_g changes from 13 °C (without an initiator) to 84 °C when the polymerization was done with 5 wt % IM. According to Fringant et al.,[47] a second exothermic peak at higher temperature after the completion of the main reaction was attributed to epoxide homopolymerization for ESO/anhydride systems. Interestingly, for all of our systems with or without an initiator, only one exotherm peak was detected in the region of 120 to 200 °C as shown in Figure 1. However, the DSC experiments give information about the reaction's evolution but not about its nature. In order to evaluate the functional group's evolution and corroborate it with previous DSC considerations, *in situ* FT-IR spectroscopy was chosen to estimate the cross-linking kinetics because of its robustness, rapidity, and sensitivity. The FT-IR spectra were registered each minute during heating from 30 to 180 °C at a 10 $°C{\cdot}min^{-1}$ heating rate.

The FT-IR spectra illustrated in Figure 2 provide direct experimental evidence of the consumption of starting reactants and product formation. The spectra show clearly a complete consumption of ELO's epoxide groups at the end of the curing process. This was confirmed by the disappearance of the characteristic absorption peaks of epoxy groups, oxirane C−O twin bands at 823 and 847 cm^{-1} (Figure 2 B).[1,11,48,49]

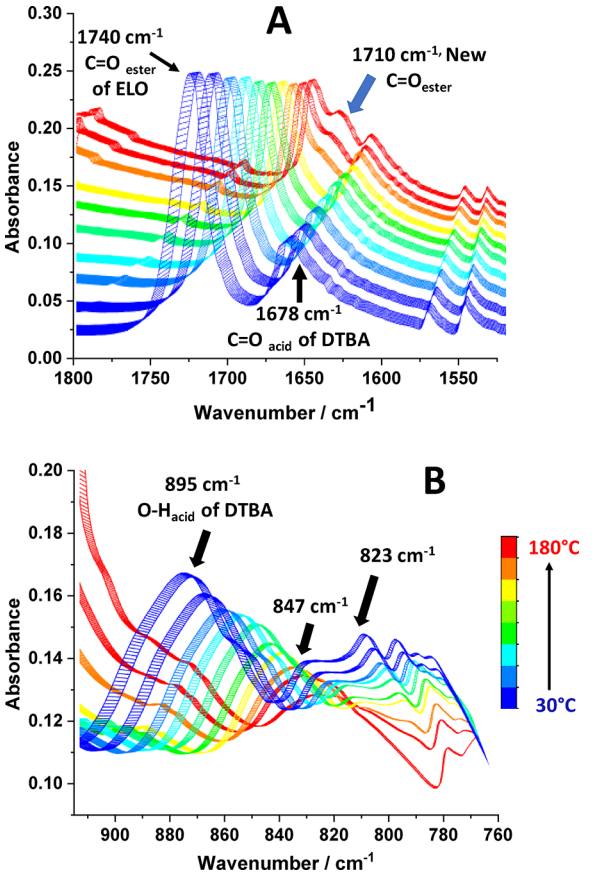

Figure 2. Evolution of FT-IR spectra of the ELO/DTBA mixture during heating from 30 to 180 °C at 10 $°C{\cdot}min^{-1}$. (A) Zoomed-in region of 1800−1525 cm^{-1}; (B) zoomed-in region of 915−760 cm^{-1}.

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Macromolecules XXXX, XXX, XXX−XXX

The decrease of broad peaks at approximately 1678 and 895 cm^{-1} is assigned to the conversion of free carboxylic groups of DTBA followed by the generation of a new ester absorption band at approximately 1710 cm^{-1} (Figure 2A, "New C═O_{ester}") indicating the ring opening of epoxy groups by the acid groups during the curing. At t = 0 min at 30 °C, the same intensity of the peak at 1740 cm^{-1} could be observed for both systems with and without an initiator. However, the intensity of −C═O stretching of DTBA at 1678 cm^{-1} is not the same; this peak seems to spread out in the presence of imidazole. These findings could be attributed to the interaction between IM and DTBA during the pre-mixing stage[50] (Figure S16). The evolution of imidazole signals was difficult to detect in this experiment due to its low concentration in the reactive mixture. The extent of the reaction was determined by the peak area in the region of 823 cm^{-1} for epoxy groups and in the region of 895 cm^{-1} for carboxylic groups in reference to the peak at 1586 cm^{-1}, which corresponds to C═C stretching of the DTBA aromatic ring (Figure 2). A comparison of reactants' FT-IR spectra including ELO, DTBA, and each initiator was performed. These data enabled us to verify that the addition of DTBA as well as the initiator in the ELO matrix does not cover the functional bands used for the conversion calculation. The conversion of functional groups is given by eq S1, Supporting Information. The corresponding results are presented in Figure 3.

For the formulation without an initiator, the cross-linking of ELO with DTBA was not selective, being accompanied by secondary reactions. A faster consumption of epoxy groups versus carboxylic groups was observed (Figure 3). At the end of the experiment, no trace of epoxide absorption remained in the FT-IR spectra. On the contrary, only ∼78% of −COOH groups were consumed confirmed by the presence of two peaks, the C═O_{acid} band at 1678 cm^{-1} and the O−H band of carboxylic acid at 895 cm^{-1}. Interestingly, by adding 1% IM, both epoxy and −COOH functions are consumed at the same rate (Figure 3A). The disappearance at the same reaction rate of −COOH absorption at 895 and 1678 cm^{-1} together with that of epoxide at 823 and 847 cm^{-1} accompanied by the appearance and increases in intensity of C═O_{ester} at 1710 cm^{-1} is proof that epoxy−acid esterifications occurred via a copolymerization reaction.

^{1}H NMR spectral measurements were also performed in the same thermodynamic curing conditions. The chemical shifts and the corresponding peak assignments of starting materials, including ELO and DTBA, are listed in the Supporting Information. The conversions of epoxy groups were calculated by integrating the signals in the 2.70−3.30 ppm range, which corresponds to the evolving *cis*-epoxy proton signal (H_g) in the reference of glyceryl methine at 5.18 ppm. The ^{1}H NMR spectrum of the ELO/DTBA/IM mixture shows the appearance of characteristic proton signals from the ring opening of the epoxy moiety in the range of 3.10−4.20 ppm corresponding to CH(OH) protons. The total reaction of all epoxide groups was confirmed by the total disappearance of the signals at 2.70−3.30 ppm and between 1.88 and 1.55 ppm, corresponding to the protons of the oxirane ring (H_g) and those of $-CH_2$ in the α-position of epoxides. The assignment of protons in the α-position of a hydroxyl group formed during cross-linking was partially overlapped in the region of methylene hydrogens from the glyceride moiety (−CH−CH_2−O−) located at 4.00−4.40 ppm. The presence of correlation signals in 2D ^{1}H−^{13}C HSQC NMR (Figure S19, Supporting Information) between signals located at 76.3 and 73.4 ppm and proton signals in the range of 3.10−4.20 ppm proves the formation of hydroxyl groups by the generation of a secondary alcohol. The calculations obtained via NMR analyses (Figure 3B) corroborate very well with the FT-IR results (Figure 3A) showing that the ELO/DTBA copolymerization was not selective and the epoxy group conversion occurs faster in the absence of an IM initiator.

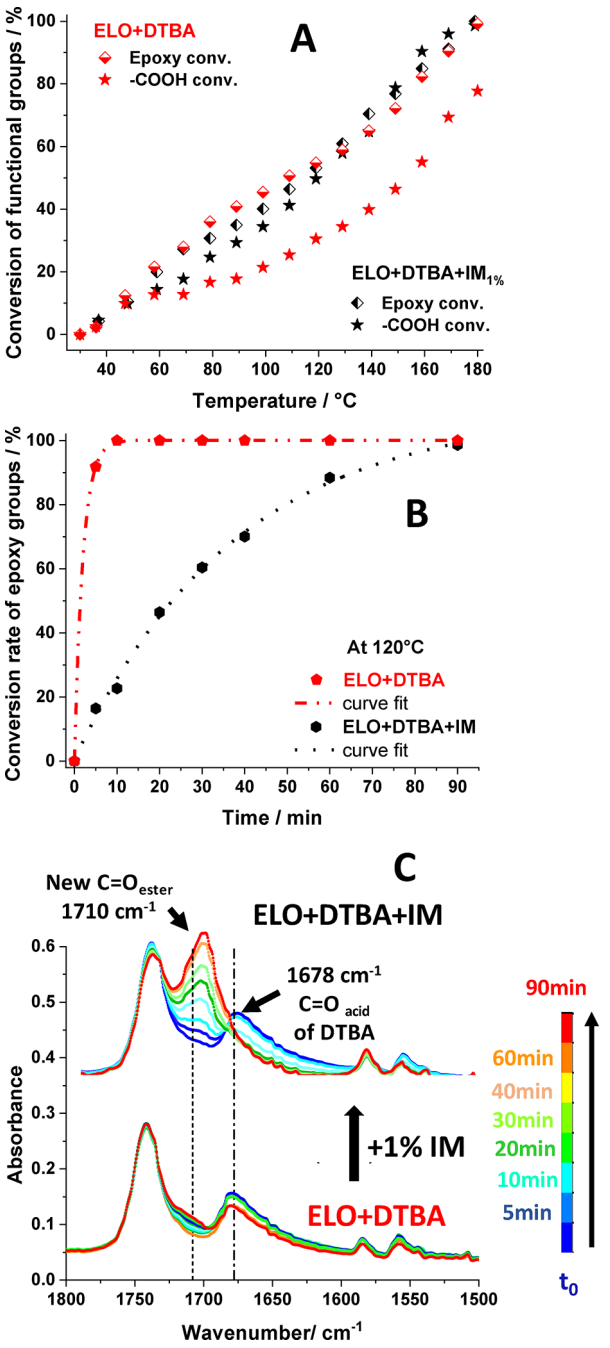

Figure 3. (A) Conversion (%) of epoxy and carboxylic acid groups during heating from 30 to 180 °C at 10 °C·min^{-1} calculated by FT-IR analyses. (B) Curves of conversion of epoxy functions on time determined by ^{1}H NMR analyses. (C) Isothermal FT-IR spectra during heating at 120 °C for 90 min of the ELO/DTBA mixture with (top) and without (bottom) imidazole.

At 120 °C, the consumption of the epoxy group was quasi-complete after 10 min of the reaction, compared to only ∼23%

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Macromolecules XXXX, XXX, XXX−XXX

when IM is present (Figure 3B). This result was again corroborated with the isothermal FT-IR analyses at 120 °C during 90 min (Figure 3C) in the systems with and without IM. The obtained data show that, in the absence of IM, a very low quantity of DTBA was converted by cross-linking with the epoxides, even after 90 min of heating at 120 °C. In contrast, a total disappearance of carboxylic signals was observed after 30 min when IM is added to ELO/DTBA (Figure 3 C). It should be noted that the NMR experiments were carried out in DMSO-d_6 as solvent. Consequently, DMSO could alter the reaction kinetics by solvent interactions and also by lowering the quantity of reactant collisions in diluted reactive media. In fact, under solvent conditions without an initiator, DTBA could become extremely active versus the epoxy reactions considered as auto-acid-catalyzed. The oxygen atom on the oxirane ring is thus protonated and stabilized by an inductive effect from the most substituted (most electron-rich) carbon atom. This renders the tertiary carbon atom more electrophile, therefore susceptible to a random nucleophilic attack by several mild nucleophiles present in the medium reaction such as carboxylic acid, hydroxyl product, etc. As a consequence, it induces a loss of control and non-selective reactions. All above results prove clearly that, in the presence of IM as an initiator, the reaction is accelerated and the main cross-linking epoxy−acid reaction (reaction 1) is dominant, while etherification and condensation−esterification (reaction 2 and 3) are negligible.

Influence of the Initiator's Chemical Structure on the Epoxy−Diacid Copolymerization Kinetics. The epoxy−diacid copolymerization depends strongly on the presence of the initiator in the reactive mixture. The subsequent objective of this study was to investigate the influence of the initiator's chemical structure on the reactivity of the ELO/DTBA system. For this purpose, we selected three groups of nitrogen Lewis base initiators: (1) the first group contains DMBA and DMP30, tertiary amine types known as frequently used initiators; (2) the second group comprises the heterocyclic nitrogen initiators (DMAP, IM, 1-MP, and TBD); and finally, (3) the last group focus on imidazole and its derivatives. The kinetic studies of the ELO/DTBA copolymerization performed in the presence of 1 wt % initiator were done by *in situ* FT-IR spectroscopy and DSC experiments.

Effect of Tertiary Amines Including DMBA and DMP30. The effect of two tertiary amines as initiators was first evaluated by DSC analysis. Figure 4A illustrates a similar effect on curing obtained by DMBA and DMP30. Comparable exothermal events occur in both systems in the temperature region of 145−200 °C, indicating an effective activation of ELO/DTBA copolymerization by tertiary amines. It is noted that the T_{peak} shows a slight downtrend with increasing basicity: DMBA < DMP30 (176 °C for DMP30 and 178 °C for DMBA).

Figure 4B shows the consumption of functional groups obtained by *in situ* FT-IR analyses. It can be seen that the conversion trend of epoxides with the temperature is divided into two domains. At temperatures of <110 ° C, the consumption of epoxy groups is fast, and it increases in the initiators' order: DMP30 < DMBA. The curing reaction starts at a lower temperature for the ELO/DTBA/DMBA system. At temperatures of >110 °C, this order is inversed; the ELO/DTBA/DMP30 system became more reactive, i.e., the conversion of epoxy functions is higher. This observation is supported by the DSC results presented in Figure 4A. It explains why the T_{on} value of the ELO/DTBA/DMBA system

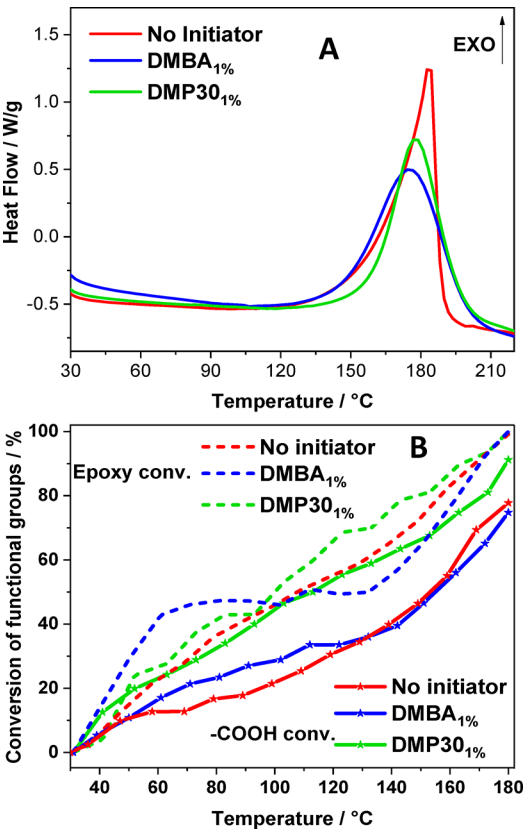

Figure 4. Investigation of ELO/DTBA/tertiary amine reactivities by (A) DSC analysis. (B) Conversion (%) of epoxy and −COOH groups obtained by FT-IR analysis.

is lower compared to ELO/DTBA/DMP30 (145 °C vs 158 °C, respectively).

In fact, in the case of the DMP30 structure, the three $-N(CH_3)_2$ substituents are strong electron donor groups, and the −OH group has also an electron-donating character. The conjugation effect of these groups makes the electrostatic charge on the −N position more negative than that of the DMBA (−0.739 vs −0.542, Figure 5A). These electronic effects lead to an increased nucleophilic strength and basicity of the DMP30, therefore intensifying its ability to accelerate the cross-linking reaction. This attribution was observed and confirmed by both of DSC and FT-IR analyses. However, at the same time, DMP30 can also be considered as a phenol

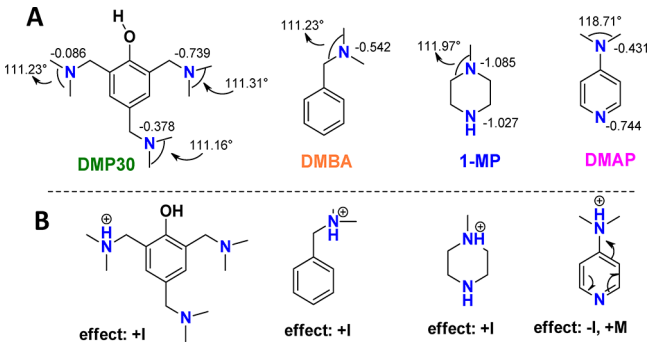

Figure 5. (A) Electronic charges of DMP30, DMBA, 1-MP, and DMAP. (B) Stabilization effect of different initiators on the transition state.

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Macromolecules XXXX, XXX, XXX−XXX

derivative, so it could also react with the epoxides or with the −COOH of the mixture, acting as a cross-linker. On the other hand, the presence of −OH in the *ortho* position can introduce an electrostatic hindrance effect, thus a restrain of the reactivity. This could explain the lower conversion rate of epoxy in the presence of DMP30 in the first steps of curing (<50%), compared to the DMBA initiator (Figure 5B). For both systems, a total conversion of epoxy groups is observed at the end of the reaction at ∼180 °C, while the signals attributed to carboxylic groups of DTBA at 1678 and 895 cm^{-1} remain present (∼25% −COOH of DTBA remained in the case of DMBA and ∼10% for DMP30).

Effect of N-Heterocyclic Initiators Including DMAP, IM, 1-MP, and TBD. The aim of this study is to discuss the effect of *N*-heterocyclic initiators on ELO/DTBA curing. Again, DSC and *in situ* FT-IR investigations were performed during curing of these systems and the results are illustrated in Figure 6.

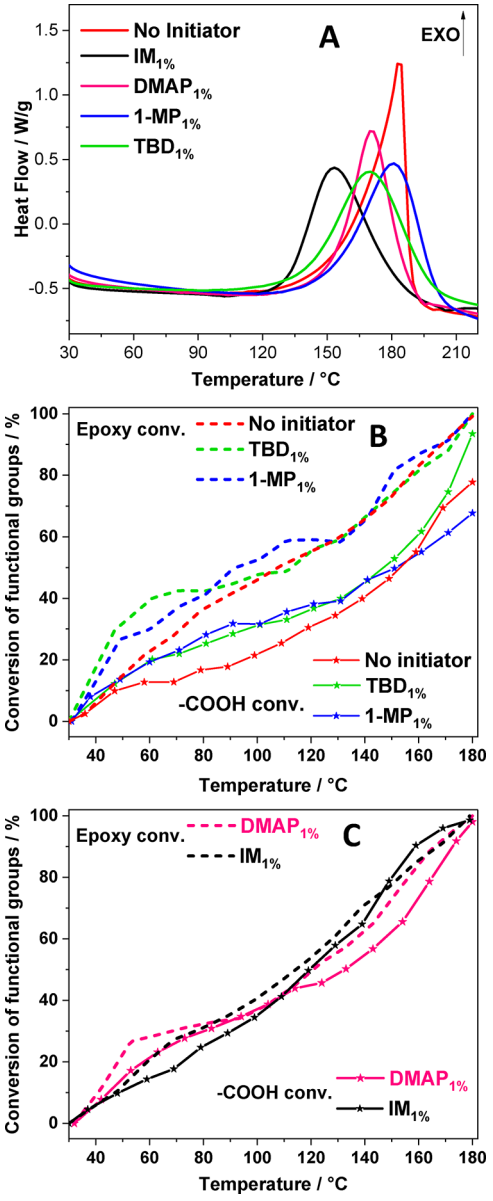
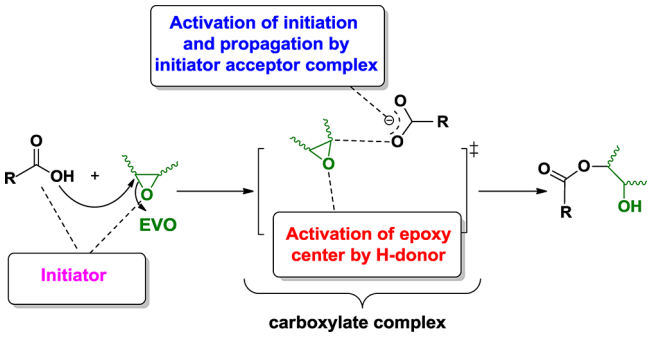


Figure 6. ELO/DTBA reactivity in the presence of *N*-heterocyclic initiators: (A) DSC analysis. (B, C) Conversion (%) of epoxy and −COOH groups obtained by FT-IR analysis.

These results show that the addition of *N*-heterocyclic initiators accelerate the ELO/DTBA reaction in the order 1-MP < TBD < DMAP ≤ IM. Among these four initiators, 1-MP is the weakest initiator not only in terms of kinetics curing behavior but also in terms of the ELO/DTBA selectivity reaction.

Compared to the DMBA tertiary amine initiator, the formulation with 1 wt % 1-MP presents a similar effect: no selective cross-linking was achieved, and only 68% of carboxylic acid groups were converted while 100% of epoxy groups were already reacted. This effect could be associated to the bifunctional nature of 1-MP since it is considered as also a tertiary amine compound. Therefore, it indicates that, in the same reaction conditions, the tertiary amines are less powerful to promote selectively the epoxy−acid cross-linking compared with the IM as an initiator even if it has a higher basicity (higher pK_a). It suggests that the amine-base initiator's concept is limited in EVO/DA systems[10,51] and a complex mechanism should be considered. We can hypothesize that this effect is first related to the lower nucleophilicity of the tertiary amines and, second, to the nitrogen's positive charge stability in the transition state of carboxylate complexes, which is more stable in the DMAP, TBD, and IM structures by resonance effects. Moreover, the addition of 1 wt % TBD (very strong base, $pK_a \approx 14.5$[40]) increases as expected with the ELO/DTBA reactivity, which is higher in terms of epoxy consumption. A high reaction rate is observed from the first minutes of reactions (at low temperature) as shown in Figure 6B. However, compared to IM or DMAP, no selective copolymerization epoxy-COOH was achieved, i.e., the consumption of epoxy groups is extra faster than that of −COOH groups (Figure 6B). Once again, this is proof that EVO/DA reactivity does not follow the basicity of initiators. More parameters must be considered and discussed such as nucleophilicity, electronic effects, and nucleophilic−electrophilic interactions, as proposed in Scheme 2.

Scheme 2. Proposed Mechanism Showing the Initiator's Influence on the EVO/DA Interaction



In the case of DMAP, the FT-IR results demonstrate that it is one of the efficient initiators for accelerating the curing rate of ELO/DTBA, confirmed by DSC results (Figure 6A) in which T_{on} decreased from 167 °C (without an initiator) to 150 °C with a shorter interval reaction (ΔT < 40 °C) and lower enthalpy value (ΔH = 206 $J \cdot g^{-1}$ vs 214 $J \cdot g^{-1}$ for IM and 248 $J \cdot g^{-1}$ for the system without an initiator). This observation is in the same trend with the reported results by Zeng et al.[17] who studied the curing behavior of ESO with aliphatic DA. Compared to the IM reference initiator, the ELO/DTBA cross-linking is faster in the presence of DMAP in the first

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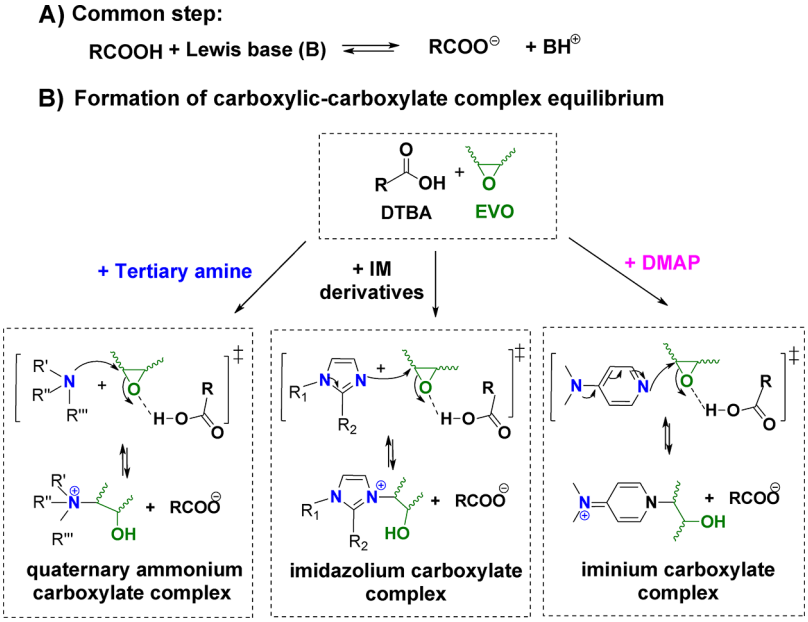
Scheme 3. Proposed Mechanism for the ELO/DTBA Reaction in the Presence of Three Types of Initiators



steps of the reaction; more epoxide groups were converted. However, at higher curing temperatures (≥120 °C), a higher reactivity for the IM system is observed (Figure 6C). This consideration was confirmed by a kinetic study monitored by ^{1}H NMR analyses and isothermal FT-IR at 120 °C (Figures S20 and S21). This result could be explained by the fact that, in the initial stage, the DMAP reacts as an organic base to transform the −COOH into $-COO^{-}$ (same result as for all Lewis base initiators). In the same time, the DMAP is a strong nucleophile,[11] stronger than IM.[52] Therefore, it can exert the epoxide ring opening by nucleophilic addition, leading more rapidly to the formation of a carboxylate complex (Scheme 2). However, it should be noticed that the key step to control the selectivity of epoxy−acid propagation is the carboxylic−carboxylate complex equilibrium (Scheme 3, process B) instead of the carboxylate $RCOO^{-}$ (Scheme 3, process A). A proposed mechanism for the ELO/DTBA reaction in the presence of three types of initiators is presented in Scheme 3.

To confirm our previous observations that the initiators could attack the activated epoxy rings and validate the initiation mechanism proposed in Scheme 3, a mixture of ELO and the initiator (1%, w/w) in the absence of a hardener was followed by isothermal *in situ* FT-IR experiments at 120 °C for 90 min. The product obtained after the FT-IR experiment was recuperated, dissolved in $CDCl_3$, and then analyzed by ^{1}H and ^{13}C NMR. These analyses demonstrate that the three initiators (IM, tertiary amine, and DMAP) attack the epoxy rings but with a very low rate considering that the percentage of the initiator was only 1 wt % in the mixture (Figures S13−S15). All the obtained results indicate that the Lewis base initiators react as a base catalyst and nucleophilic catalyst in the transition state. For the ELO/DTBA system, the nucleophilicity of the initiator could play a more important role; the nucleophilicity order of initiators varies: tertiary amine < IM ≤ DMAP. This attribution could be associated to a steric hindrance of the triglyceride chains, present on ELO's structure. Comparing the three kinds of initiators, the copolymerization of ELO/DTBA is more efficient in the order tertiary amine < DMAP ≤ IM due to the stabilization of "reactive" intermediate carboxylic−carboxylate complexes that initiate and promote selectively the copolymerization reaction.

Effect of Electro-donating Substituents on the IM Initiator and Their Derivatives. In the previous sections, we highlighted that, among the three kinds of initiators, IM is one of the most efficient and the initiator's nucleophilicity could play a more important role for ELO/DTBA curing in terms of kinetics and reaction selectivity. Now, the question arises on the influence of substituent groups on the imidazole ring on its activity on the epoxy−acid reaction. To answer this question, four imidazole derivatives including 1-MI, 1,2-DMI, 2-MI, and 2E4MI were selected and divided into two categories: 1-N- and 2-N-substituted. To give insights to this aspect, DSC and FT-IR studies of the ELO/DTBA copolymerization in the presence of 1 wt % initiator were done. In fact, imidazole has an amphoteric structure, behaving as an acid as well as a base.[53] As an acid, the pK_a of imidazole is ∼14.5, making it less acidic than carboxylic acids, phenols, and imides but slightly more acidic than alcohols. The acidic proton is located on position 1 (Figure 7).

As a base, the pK_a is ∼7, making imidazole approximately 60 times more basic than pyridine. These properties are explained by the electronic resonance interactions. In the IM derivative

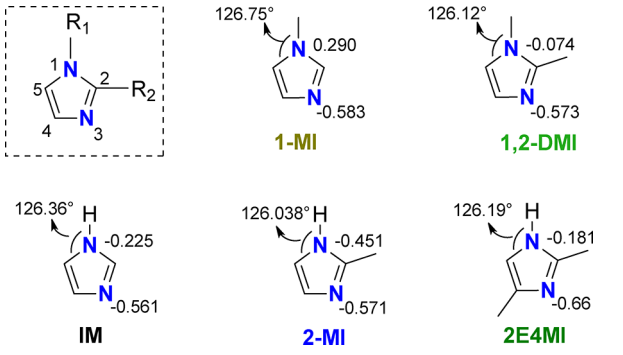


Figure 7. Electronic charges on imidazole and its derivatives IM, 1-MI, 2-MI, 1.2-DMI, and 2E4MI.

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structure, the alkyl substituents are expected to exhibit an electro-donating effect that should increase the electronic charge on the N atom, thus making it a stronger nucleophile. According to quantum chemistry calculations (Figure 7), the electrostatic charge on 3-N of IM is approximately −0.561, which is the less negative, compared to that of 2-MI (−0.571), 1.2-MI (−0.573), 1-MI (−0.583), and 2E4MI (−0.66). Therefore, it is obviously less nucleophilic, and consequently, we can estimate that the conversion rate of the epoxides in the presence of substituted IM could occur faster, compared to IM.

Contrarily, an opposite behavior was detected by FT-IR analyses that show that the ELO/DTBA/IM displays the higher reactivity in terms of the highest conversion rate of epoxy groups (Figures 8 and 9) and of the highest formation of

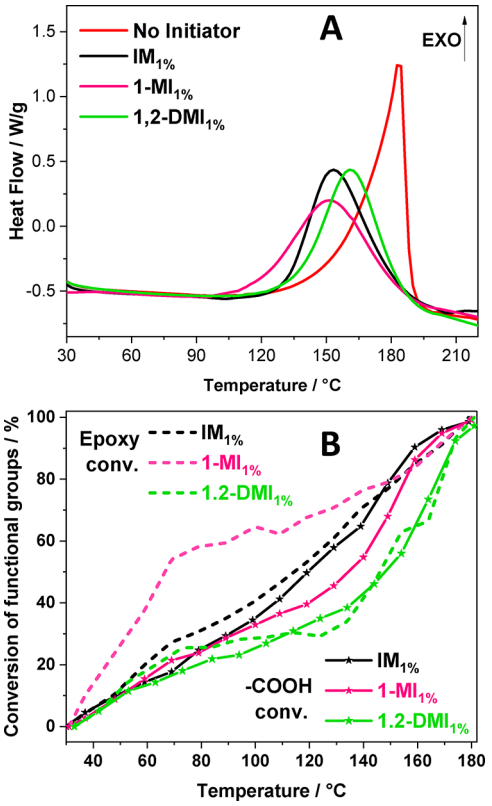

Figure 8. Comparison of ELO/DTBA reactivities with IM and 1-N substituted IM derivatives by (A) DSC analysis. (B) Conversion of epoxy and carboxylic acid groups calculated by FT-IR analysis.

a new ester linkage. The DSC results confirm this result (Table S2, Supporting Information). Apart from the 1-MI system, the reaction occurs at a lower temperature (T_{on} of ∼117 °C vs 130 °C for IM) but with a larger temperature interval (Figure 8A). An extra fast consumption of epoxy versus −COOH functions was observed (Figure 8B). It indicates that 1-MI activates strongly the epoxide conversion at a lower temperature, nevertheless provoking secondary reactions (OH etherification) instead of selective copolymerization. Ooi et al.[44] also reported that 1-MI is a more efficient curing agent for DGEBA polymerization via OH etherification, compared to 2-MI.

When IM is substituted in position 2 (namely, 2-N-substituted IM), the reactivity of ELO/DTBA decreases significantly, but the reaction is more selective compared to 1-N-substituted IM (Figure 9). A similar effect was observed

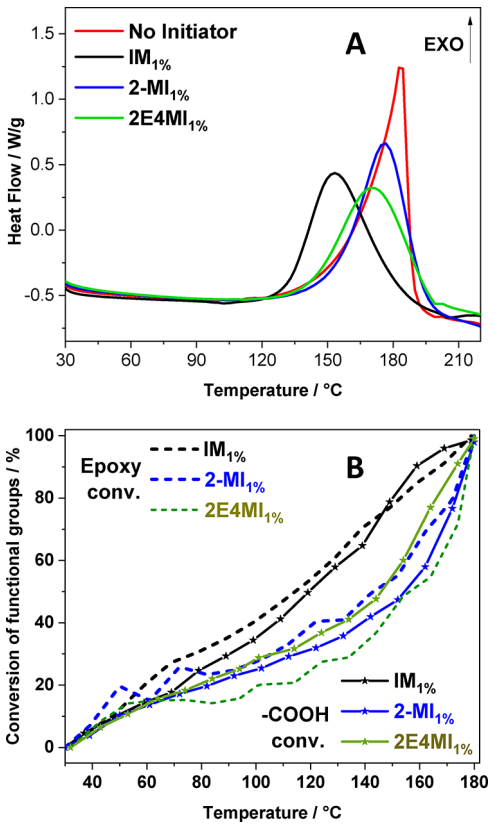

Figure 9. Comparison of ELO/DTBA reactivities with IM and 2-N-substituted IM derivatives by (A) DSC analysis. (B) Conversion of epoxy and carboxylic acid groups calculated by FT-IR analysis.

for 2-MI, 1,2-DMI, and 2E4MI. In fact, the 2-N substituents on IM raise the steric hindrance compared to 1-N-substituted IM. This reflects that, for the ELO/DTBA system, the electronic hindrance effect became more important therefore restraining the formation of "reactive" carboxylate complexes at the first steps. As a result, the attack on active epoxy sites became slower and more difficult. The DSC analysis of ELO homopolymerization in the presence of 1 wt % imidazole initiator supports this observation. As resumed in Table S5, the ELO homopolymerization in the presence of 2-N-substituted IM occurs with lower enthalpies, higher T_{peak} values, and broader intervals of reactions, compared to the same reaction initiated by 1-N-substituted IM.

Proposed ELO/DTBA/IM Copolymerization Mechanism. NMR experiments gave the opportunity to monitor the structural changes on the initiator but especially on the ELO/DTBA/IM interactions. The N-H proton signal of imidazole located at about δ = 12 ppm is shifted at a higher frequency in the mixture DTBA+IM (Figure 10A) and suggests an effect of self-association through hydrogen bonding. It could be noticed that the formation of hydrogen bonds provoke some shifts to a higher frequency (higher ppm) due to deshielding.[54] In the case of the ELO/DTBA/IM mixture (Figure 10C), no signal at 12 ppm was detected by ^{1}H NMR, a result that could come from the formation of a hydrogen-bonding complex implying both reactants (ELO and DTBA) in a transition state, therefore reducing the exchange rate of the proton and leading to the disappearance into the baseline of the NH signal.

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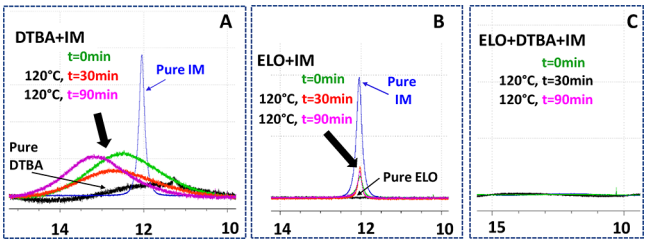


Figure 10. ^{1}H NMR analyses. Imidazole proton's peak in different mixtures: (A) DTBA+IM, (B) ELO + IM, and (C) ELO + DTBA +IM in DMSO-d_6 at 120 °C, [ELO] = 0.05 M and [DTBA] = 0.14 M.

Simultaneously, a new peak at approximately 8.7 ppm (Figure 11) was detected but with a very low amplitude and

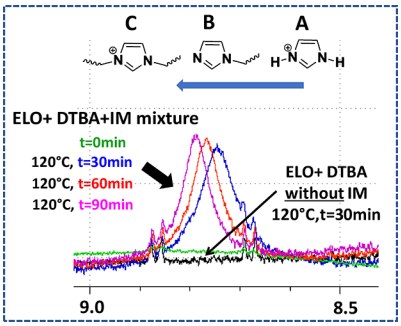


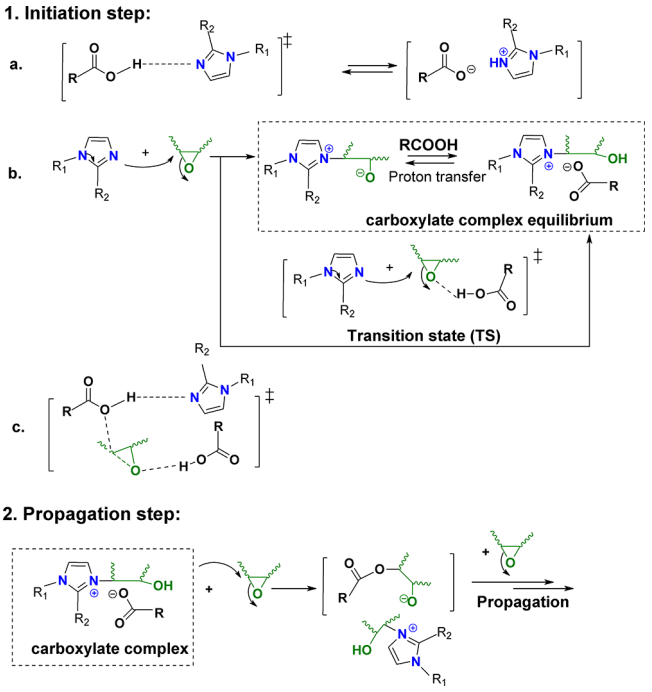
Figure 11. Zoomed-in ^{1}H NMR spectra in the region of 9.0−8.5 ppm of ELO/DTBA/IM mixture at 120 °C at different times, showing the appearance of new peaks attributed to protons of the imidazolium ring at approximately 8.7 ppm.

shifted to a higher frequency with time. This new peak could be attributed to the formation of imidazolium rings[55] (Figure 11A−C), suggesting an attack of IM on the epoxy ring. Indeed, this attribution was reported by Khaligh et al.[55] who identified novel chemical structures of a sulfo-imidazolium zwitterionic-type salt basis with the help of 2D NMR analyses. As presented in Figure S12, the ELO homopolymerization was also studied in the presence of IM in DMSO conditions at 160 °C for 4 h. The obtained results indicate that a part of IM forms hydrogen bonding with the reactants and the other part attacks the epoxy ring.[31,56] Due to the steric effects on internal and terminal oxirane of EVO, the attack of IM on these epoxy rings occurs in a more difficult manner, and consequently, small changes in the epoxy region were detected by ^{1}H NMR analyses (Figure S11). We can hypothesize that 120 °C is a too low temperature to overcome the energetic barrier, so the intermolecular hydrogen interactions could be predominantly established compared with the IM attack and epoxy ring-opening DMSO conditions.

The previous considerations in combination with these NMR results confirm that the ELO/DTBA copolymerization's activation and selectivity are strongly dependent on the initiation step. The presence of IM as an initiator helps us to achieve stabilization of the transition state via hydrogen bonding implied with both epoxy and acid comonomers. At the same time, IM reinforces the nucleophilicity of DTBA. In fact, the initiation step of ELO/DTBA/IM copolymerization is highly sensitive to all the chemical environments, i.e., not only to the presence of the initiator species but also to the formation of reactive complexes in the transition state. We can hypothesize that the mechanism of initiation involves simultaneous two processes, implying IM:

(i) the deprotonation of the carboxylic acid into a carboxylate anion (COO^-) due to the basicity of IM (Scheme 4a)

Scheme 4. Proposed Mechanism of Initiation and Propagation on the ELO/DTBA/IM Copolymerization System



(ii) in parallel, more dominantly, IM's attack to the epoxy ring, a reaction activated by a H-donor of DTBA, leading to the formation of carboxylate complexes via hydrogen bonding in the transition state (Scheme 4b).

In fact, the pK_a of the alcohol−alkoxide equilibrium ($R'O^-$/$R'OH$) (~17)[57] is much higher than that of carboxylic−carboxylate equilibrium due to the stabilization caused by resonance with the carboxylate anion. Therefore, the alkoxide anion is a very strong base. In the presence of a "good initiator", this "active" alkoxide could be rapidly quenched by a weak acidic proton present in the system via a transfer non-reversible reaction, therefore impeding a ring-opening polymerization via etherification (side reaction), and in consequence, ELO/DTBA copolymerization becomes more selective. A proposed mechanism concerning the initiation step of curing is proposed in Scheme 4. Indeed, imidazole is bidentate with higher possibility to form hydrogen bonding with both reactants (ELO and DTBA) compared to other IM derivatives, therefore enhancing the formation of a carboxylate complex. It could be considered as a moderate α-donor and weak π-acceptor. The addition of an alkyl group could reduce the "degree of freedom" of the imidazole ring, causing an unstable carboxylate complex since it cannot be stabilized by the loss of a proton. Moreover, as an alkyl group is present at position N-2, it enhances the steric hindrance with nitrogen's ion pair and therefore impending the nucleophilicity of the initiator (process b, Scheme 4). Consequently, the propaga-

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tion, initiated by the activated carboxylate complex could be inhibited.

CONCLUSIONS

This study highlights the significant influence of the initiators' nature on the ELO/DTBA copolymerization. In the reaction systems without an initiator, the curing occurs randomly, promoted by hydrogen donation of DTBA diacid functions. Therefore, DTBA reacts as a self-promoter initiator to form hydroxyl functions. The formed −OH groups can accelerate the curing by formation of hydrogen bonds with the epoxide's functions in the same way as the acid curing agents, thus provoking numerous etherification side reactions.

By adding Lewis bases as initiators in the ELO/DTBA system, the nucleophile attack of the epoxy ring by the acid function becomes selective and dominant. Three important parameters of initiators' nature should be considered including basicity, nucleophilicity, and steric hindrance. At the beginning of ELO/DTBA reactions, two consecutive initiation stages could occur. For base catalysts, the use of strong bases could lead to a fast generation of carboxylate anions. Therefore, the reactions could start rapidly after the reagents mix, but it would cause difficulties to control its rate and particularly its selectivity. In consequence, the strong base initiators are not as selective as those less. For nucleophilic catalysts, the initiator is consumed in the quaternization stage with activated oxirane by the DTBA to form an equilibrium with the "reactive" carboxylate anion, called a "carboxylate complex", which is the true initiator of ELO/DTBA copolymerization. Then, this complex leads to selective propagation of copolymerization by a nucleophile attack on the activated oxirane ring. It is important to note that steric hindrance plays an important role during the formation of carboxylate complexes due to the triglyceride and pendant chains on EVO's structure. Therefore, the available and initiator's centers should be well controlled.

Comparing ELO/DTBA copolymerization by using three kinds of initiators, we found that the more efficient are IM and DMAP. Very interestingly, in the presence of IM, a low increase in conversion is observed in the first step of the reaction. However, after this induction period, the reaction takes place at a very fast rate following an autocatalytic mechanism. Benefiting from this advantage, IM could be considered the best initiator candidate for ELO/DTBA copolymerization. It achieves appropriately the induction period needed in commercial formulations considering workability purposes as well as a fast cure rate. The excellent thermomechanical properties and reprocessability abilities correlated to the type of the initiator of these thermosets will be presented in a future paper.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.9b02700.

Experimental details (PDF)

AUTHOR INFORMATION

Corresponding Author

Alice Mija − *Université Côte d'Azur, Institut de Chimie de Nice, 06108 Nice, France;* orcid.org/0000-0001-5208-5956; Email: Alice.Mija@unice.fr

Authors

Thi-Nguyet Tran − *Université Côte d'Azur, Institut de Chimie de Nice, 06108 Nice, France*

Chiara Di Mauro − *Université Côte d'Azur, Institut de Chimie de Nice, 06108 Nice, France*

Alain Graillot − *Specific Polymers, 34160 Castries, France*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.macromol.9b02700

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

EVO epoxidized vegetable oil; ELO epoxidized linseed oil; DCA dicarboxylic acids; ArDCA aromatic dicarboxylic acids; DTBA 2,2′-dithiodibenzoic acid; IM imidazole; 1-MI 1-methyl imidazole; 2-MI 2-methyl imidazole; 1,2-DMI 1,2-dimethyl-imidazole; 1-MP 1-methyl-piperazine; 2E4MI 2-ethyl-4-methyl-imidazole; DMBA *N*,*N*′-dimethyl benzamine; DMAP dimethylaminopyridine; DMP30 2,4,6-Tris-(dimethylaminomethyl)phenol; TBD 1,5,7-triazabicyclo-[4.4.0]dec-5-ene; FT-IR Fourier transform infrared spectroscopy; NMR nuclear magnetic resonance spectroscopy; DSC differential scanning calorimetry; vs versus

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