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Lightweight Rigid Foams from Highly Reactive Epoxy Resins derived from Vegetable Oil for Automotive Applications

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ABSTRACT

For the two last decades, the reduction of fuel consumption and CO₂ emissions is a topic of first importance in automotive industry. Among the possible technical approaches, the reduction of the vehicles weight seems to be a promising solution. This option can be achieved by the growing use of lightweight structures based on rigid foams. However, most of the commercial materials are oil-based and sometimes involve harmful chemical compounds. Moreover, some products that require long time processes are inadequate for fulfilling automotive cadence. In this paper, we investigated the development of new generation of highly reactive epoxy foams. These materials were obtained by mixing epoxidized plant oil-derivates with a cycloaliphatic amine hardener (isophorone diamine IPDA) and a harmless foaming agent (sodium bicarbonate NaHCO₃ named SB). The chemical composition of the reactive mixture was optimized by adding several chemical additives acting as “exothermicity regulators” (ER) in order to control more particularly the exothermicity of the curing reaction. Their efficiency in the consumption of the heat excess released during cross-linking was explored. Kinetic rheological analyses, DSC and TGA experiments were used to tune the dosing of each chemical component in the reactive formulation. They made it possible the production of foams in a few minutes (< 3 min) with an ultimate glass transition temperature close to 48 °C and apparent density of about 0.17 g cm⁻³.

KEY WORDS. Bio-based polymer, blowing agent, DSC, epoxy resin, rheology, rigid foam.

INTRODUCTION

For many years now, human activity is identified as being responsible of a significant increase of the production of greenhouse gases including carbon dioxide. Then, several environmental rules were voted to limit and even reduce this problem. Within this context, numerous researches are supported in academic and industrial communities to reduce fuel consumption by automotive vehicles and consequently their CO₂ emission. Since almost 75% of the fuel consumption is directly related to the mass of vehicles, one of the most promising solutions consists in developing lightweight structures based on rigid foams [1]. A great majority of commercial polymeric foams are oil-based. But, this situation is rather perfectible. On one hand, the materials derived from thermoplastic matrices (polystyrene, polyolefinics...) are inadequate for structural applications due to their creep behaviour. On the other, foams produced from thermoset polymers are often based on harmful chemical compounds such as bisphenol A in the case of DiGlycidyl Ether of Bisphenol A (DGEBA) epoxy resin or isocyanate compounds in the case of polyurethane formulations. Anyway, all these polymeric systems do not represent sustainable technical solutions, as petroleum is a depleting resource. Then, the definition and optimization of foams derived from biomass seems to be worthy research field. But, this topic must be conducted by keeping in mind that automotive industry mostly requires highly reactive systems compatible to high cadence production lines.

The study of bio-based foams has been discussed in the literature since the 1990s [2-4]. Some authors investigated the use of starch in order to replace industrial foams produced from petrochemistry [3, 5-8]. Starch is present in many plant products (corn, potato, wheat, rice...) and is easy to be extracted. Both low price and relative abundance support its industrial development. Unfortunately, foams made from pure starch are brittle and sensitive to moisture and water. Then, different studies used natural fibres as fillers to increase the mechanical performances of starch. For example, Lawton et al. [9] used aspen fibres to

reinforce baked cornstarch foams. Soykeabkaew *et al.* [6] studied composite starch foams reinforced with cellulose fibres (jute and flax fibres). Bergeret *et al.* [10] also incorporated natural fibres produced from raw materials (coconut, cotton, hemp, sugarcane) in starch-based formulations before foam production by melt extrusion. The addition of lignocellulosic fibres extended the use of this class of foams in food industry in various packaging functions. Nevertheless, even with the use of reinforcing agent, the mechanical properties and moisture resistance of these cellular materials are clearly insufficient for fulfilling structural functions.

Special attention was paid to thermosetting foams because they were likely to present higher mechanical properties. In particular, Pizzi and co-workers investigated tannin-based foams in order to replace synthetic phenol-formaldehyde materials [11-16]. Tannins are multifunctional aromatic compounds obtained by water extraction from wood or trees bark such as mimosa, quebracho or pine. They can be considered as polyphenolic compounds. After mixing with furfuryl alcohol and formaldehyde, they allowed the production of rigid foams. In a first approach, these compositions can be considered as a promising solution for substituting petro-sourced phenolic foams in various applications due to their high content in renewable raw materials. However, formaldehyde [17-20] and in a lower extent furfuryl alcohol [21, 22] are suspected to be toxic and even carcinogenic for humans.

Many other studies explored the possibility of developing polyurethane foams from biomass using the reaction between polyols and diisocyanates. Indeed, it is well known that carbon dioxide gas is generated from a side reaction between water (present in the atmosphere or present in the formulation) and di-isocyanate monomers and acts as a blowing agent. By varying the nature of the polyol and isocyanate components, foams could be produced with a wide range of properties [23]. Within this context, several authors investigated the chemical modification of vegetable oils such as linseed, rapeseed, sunflower, soybean [24-30] or animal oils [31] for the production of polyols. Other vegetable resources such as cardanol extracted from cashew nut shell were also used with the same purpose [32]. Some

formulations also comprised vegetable fibres in order to increase the final level of the mechanical properties [33-36]. Many bio-based foams displayed physicochemical performances comparable to that characteristic of petroleum-based foams. However, their initial chemical composition remains toxic because of the residual presence of isocyanate such as methylene diphenyl 4,4'-diisocyanate (MDI) that is classified “R20/R36/37/38” in European rules [37, 38]. Indeed, this compound is often in excess, up to 30% [24, 26, 29, 33-35] and even 50% [32] to insure short reaction times or complete consumption of the polyol.

Vegetable oils can also be cured with styrene after maleination [39] or acrylation [40]. By incorporating in the formulation a reactive blowing agent, it is possible to produce thermosetting foams. But, once more, the curing agent (styrene) is highly toxic.

Considering all these reasons, other classes of bio-based thermoset formulations must be developed to expect sustainable applications of polymeric foams in industry and particularly in automotive segment. Then, different elements must be considered: i) the use of less toxic chemical compounds must be preferred; ii) the reactivity of the initial mixtures must be high enough to allow the foam production in short processing times. Indeed, to expect potential application in automotive industry, the time for the foaming process can not exceed 3 minutes to maintain high production rates [41]; iii) the ultimate thermomechanical properties must be compatible with a structural use for temperature ranging from 50 to 120 °C; iv) the method has to make it possible the production of foams with density lower than 0.2 g/cm³. The industrial partner defined all these technical specifications and the manufacturing conditions were driven by economical aspects.

In this research, we investigated the ability to produce epoxy foams partially based on renewable resources. Actually, different molecular platforms from biomass can be used to produce epoxy prepolymers. Unsaturated vegetable oils are probably one of the most studied building blocks due to their relative abundance and low production cost. Moreover, the unsaturations initially present along the fatty chains can be modified into oxirane groups

using peracid method or enzymatic way. Epoxidized vegetable oils (EVO) can react with traditional epoxy curing agents (such as anhydride, amines, amides) to produce thermosetting materials [42-45]. But, it is well established now that whatever the curing agent, EVO are much less reactive than classical epoxy prepolymers produced from petrochemistry. Then, some authors proposed to combine EVO with DiGlycidyl Ether of Bisphenol A (DGEBA) to produce more reactive formulations. Nevertheless, this solution reduces the “green carbon content” in the resin. A preferable approach, developed in our laboratory, consisted in mixing EVO with epoxidized glycerol EG [46]. This latter molecule is derived from glycerol that can be produced from the hydrolysis or trans-esterification of vegetable oils. It presents the advantage to be much more reactive than EVO due to the position of its oxirane units that are more accessible to hardeners units. But, it cannot be cured alone with a polyamine hardener because the corresponding crosslinking reaction is quite excessive and provokes the thermal degradation of the sample [47]. Inversely, mixed with EVO in variable proportions, it allows the production of ternary formulations “EVO-EG-hardener” with versatile properties. In particular, highly reactive formulations leading to rigid materials can be obtained using either polyamine or anhydride as hardener. Up to now, the possible application of this kind of bio-derived resin as basis for polymeric foams was not investigated. This topic will be discussed in this paper.

The formulations used in this research contains two different epoxy compounds namely, epoxidized linseed oil (ELO) and epoxidized glycerol (EG). ELO was chosen between other EVO because it derives from linseed oil that is rich in linoleic and linolenic acids that contain two and three unsaturations, respectively (Table 1). After the epoxidation step, ELO contains an average number of 5.8 epoxy groups per triglyceride [42]. Isophorone diamine (IPDA) was selected as curing agent. Characterized by a cycloaliphatic structure, it presents a reactivity that is intermediate between that characteristic of aliphatic amines and aromatic amines, respectively. Moreover, IPDA permits the production of cured epoxy

materials with higher performances compared to aliphatic amines while its toxicity is lower than aromatic amines [45, 48, 49]. Indeed, IPDA is not suspected of carcinogenic effects [50, 51].

The manufacture of a foam using a thermoset polymeric formulation is only possible if a gas is simultaneously emitted during the crosslinking reaction. In the particular case of epoxy systems, some curing agents can also be used as a possible source of gas. Dogan et al. [52] explored the reaction between malonic acid and epoxidized soybean oil (ESO). Malonic acid is a difunctional carboxylic acid and can be used as hardener of the epoxy prepolymer. But, unlike other dicarboxylic acids, malonic acid and its monoester formed during the curing process can also decarboxylate upon heating. This latter reaction produces CO_2 that is valuable as foaming agent. Unfortunately, both crosslinking and decarboxylation reactions are monitored by specific kinetic. Then, the foaming process is difficult to be mastered and the excessive reaction time does not make easier its scaling up to full production. The use of an amine hardener in place of a diacid usually allows the production of a cured epoxy polymer with shorter times but is not accompanied by any gas emission. Then, a foaming agent must be added to the initial formulation to obtain, through a chemical or physical process, the gas necessary for the expansion of the material during the curing step. Its exact nature plays a dominant role in the final performances of cellular materials such as density, microstructure and morphology [53]. Different types of foaming agents are typically known. A first one is based upon the use of a liquid that will permit the cells development during its vaporization step. A second method employs a gas initially dissolved in the resin and that escapes from the resin formulation in the form of micro-bubbles as the pressure is reduced. Another one bases itself on a chemical agent that decomposes or reacts to form a gas under heating or after contact with another chemical compound.

As our study aims to develop lightweight rigid foams from highly reactive bio-based polymeric formulations, we have chosen to focus on the use of a harmless foaming agent able

to act in a very short time (about 3 minutes) in particular for possible use in automotive industry. To control the excessive exothermicity of the curing reaction, several chemical additives were also added to the initial reactive formulation to act as “exothermicity regulators” (ER) through endothermic transformations during the curing step.

Experimental

Material

Epoxidized linseed oil (ELO) with 5.8 epoxy groups per triglyceride, molecular weight of 974 g mol^{-1} was kindly offered by ARD (France). Epoxidized glycerol (EG) with 3 epoxy groups per molecule, molecular weight of 260 g mol^{-1} was a generous gift from Nagase ChemteX (Japan). The curing agent, isophorone diamine (IPDA), with a molecular weight of 170 g/mol was supplied by BASF. Sodium bicarbonate (NaHCO_3 named SB), was used as harmless foaming agent and was purchased from Sigma Aldrich. The “exothermicity regulators” (ER) were chosen in mineral compounds family. Due to industrial confidentiality, their exact composition cannot be specified here. Their action is based on an endothermic dehydration reaction that is thermally activated and that produces itself above a temperature specific of each compound. All chemicals were used as received *i.e.* without any purification step. The chemical structure of ELO, EG and IPDA are presented in Figure 1.

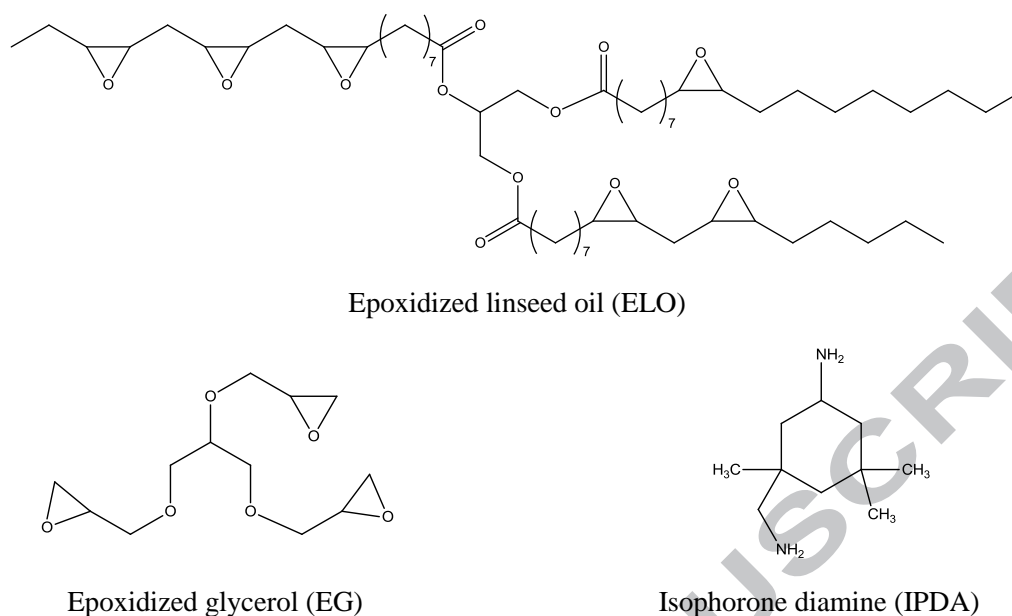


Figure 1. Chemical structures of the chemical compounds used in the bio-based epoxy resins used in this study.

Preparation of the bio-based epoxy resins

Epoxy reactive formulations were prepared in stoichiometric proportions, *i.e.* by considering that an amine function can react with one epoxy group. For instance, binary mixtures based on ELO and IPDA by taking 1.45 mol of hardener for 1 mol of ELO as described in Figure 2. Ternary formulations were named under the reference xELO – (100-x)EG – IPDA samples with x the percentage of epoxy groups brought by the epoxidized vegetable oil. Please note that these reactive mixtures are still characterized by a ratio (N-H/epoxy) equal to 1. All components were mixed at room temperature under mechanical stirring until apparent homogeneity. Then, both time and temperature conditions associated to their curing were determined for each formulation by DSC and rheological analyses.

Preparation of the foams

The epoxy compounds and the blowing agent were first mixed together. Then, the curing agent was added and the mechanical stirring of this epoxy formulation was pursued at

room temperature for about 3 min. Please note that no surfactant was used. First experiments were useful to evaluate that the quantity of blowing agent was necessarily of 40 parts for 100 parts of epoxy formulation. In other words, the weight percentage of the blowing agent in the final mixture was about 28.6% w/w. Finally, the final blend was poured in an aluminium open mould previously heated at a constant curing temperature T_c (160 or 180 °C). The curing/foaming time was set at 3 minutes.

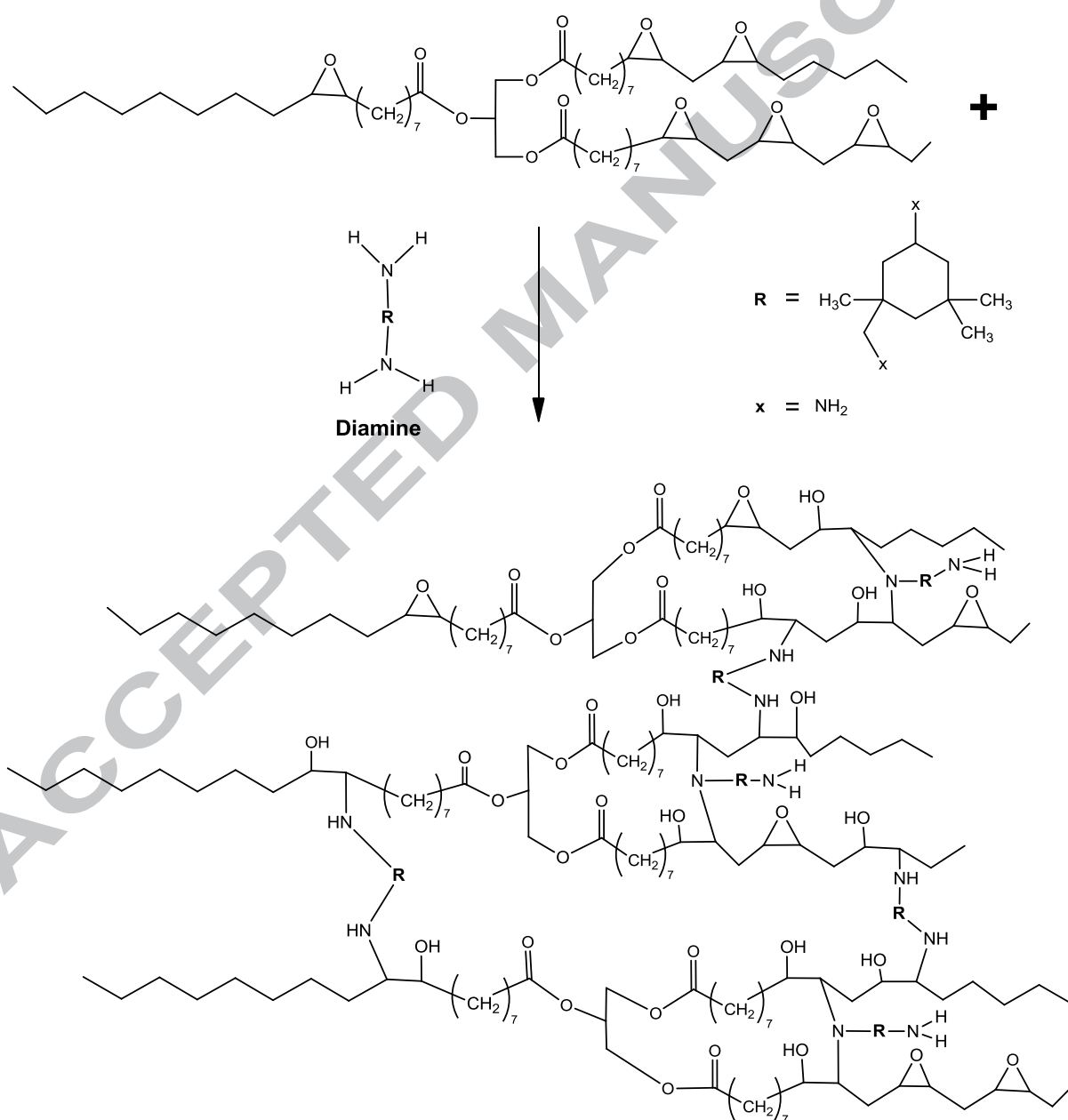


Figure 2. Schematic curing mechanism of epoxidized linseed oil with diamines.

Scientific characterization

The temperature domains and heat enthalpies attached to the different reactions (crosslinking of the thermoset formulation, decomposition of the blowing agent...) were evaluated by differential scanning calorimetry (DSC StarOne from Mettler Toledo®). The experiments were performed in dynamic mode between 10 and 400 °C at a heating rate of 5 °C min⁻¹ under inert atmosphere (N₂) using 40 µl aluminium capsules and an empty crucible as reference. The reactive formulations were prepared according to the experimental procedure described before and immediately poured in the measuring cell for analysis.

The temperature range characteristic of the decomposition of the blowing agent was determined using a Q50 thermogravimetric analyser (TGA) from TA Instruments®. The experiment consisted in registering the weight loss of the sample as a function of temperature from the ambient up to 600 °C. The temperature ramp was set at 5 °C min⁻¹ and the analysis conducted under air flow (25 mL min⁻¹).

First rheological experiments consisted in operating kinetic studies of each thermoset formulation without blowing agent in particular to determine the gel time of the system or the minimum time necessary for the complete consumption of the reactive components. These analyses were performed using a dynamic rheometer (MCR 102 from Anton Paar®) equipped with a cup-plate geometry that is well suited for the characterization of an evolutive polymer from the liquid to the solid state. In our research, the upper plate was $\phi_{plate} = 25$ mm whilst the inner diameter of the cup was chosen significantly higher ($\phi_{cup} = 40$ mm) to prevent undesirable side effects. An environmental testing chamber allowed the conduction of the rheological measurement under precise control of the temperature. The following procedure was strictly respected before the step of the data collection. First, the testing geometry was

heated at the temperature desired for the future kinetic analysis. Once the thermal equilibrium reached, the epoxy mixture initially liquid was poured into the measurement cup. Then, the upper plate was lowered until contact with the sample with an average gap about 3 mm. The dynamic experiment was conducted under constant strain (5%) and fixed angular frequency ($\omega = 1 \text{ rad s}^{-1}$). It consisted in registering the evolution of the complex shear modulus $G^* = G' + j G''$ as a function of curing time to observe and quantify the progressive transformation of the reactive mixture from liquid to solid state. The real component G' called “storage modulus” is specific of the elastic contribution of the sample. In other words, it is proportional to the mechanical rigidity of the polymer. The imaginary part G'' is classically named “loss modulus” and relates to the dissipated mechanical energy. When the polymer formulation is in the liquid state, the value of the loss modulus is higher than G' value. The reverse situation is observed in the gel and glassy states where the elastic character is predominant ($G' > G''$). The gel time could be evaluated by taking down the time where the divergence of both moduli was observed. The minimal period to observe the complete curing was defined at the time associated with the stabilization of the viscoelastic behaviour after the description of the gelation. Some experiments performed at low curing times required a registering of the viscoelastic data during different days.

The thermomechanical properties of the cured polymer were characterized using a stress-controlled dynamic rheometer (AR2000Ex from TA[®]) equipped with rectangular torsion geometry. Typical dimensions of the specimens were 45 mm x 10 mm x 1 mm. The thermomechanical tests were carried out at a heating rate of $3 \text{ }^\circ\text{C min}^{-1}$ from $-150 \text{ }^\circ\text{C}$ up to $150 \text{ }^\circ\text{C}$ with a strain value fixed at 0.1% and at a constant oscillating angular frequency ($\omega = 1 \text{ rad s}^{-1}$). At this precise angular frequency value, the glass transition temperature (T_g) of the polymer can be evaluated at the maximum of G'' peak.

Dynamic mechanical analyses (DMA) of the foams were registered using a 50N model from ACOEM-Metravib[®] using a parallel plate geometry in compressive mode and at a constant frequency (1 Hz). The temperature range was between -50 °C and 100 °C and the heating rate 2 °C min⁻¹.

The compressive properties of the foam at room temperature were measured using an Instron 5533 Universal Testing Machine equipped with a load cell of 10 kN. The crosshead speed was set at 5 mm min⁻¹. Typical dimensions of the specimens were 20 mm x 20 mm x 20 mm. For each kind of foam, eight specimens were tested and results were averaged. Young's modulus was estimated from the slope of stress-strain curves in the linear elastic domain. The compressive strength was taken as the stress value corresponding to a strain of 10%.

The apparent density of the foams (ρ expressed in g cm⁻³) was obtained as the ratio between the weight (m) and the volume (V) of parallelepiped samples.

Results and Discussion

Investigation of the reactivity of the ternary formulations

First dynamic DSC experiments were registered with the binary formulations ELO-IPDA and EG-IPDA to evaluate the temperature domains related to their respective curing reaction by the presence of specific exothermic peaks (Figure 3). In the case of the binary reactive mixture based on ELO, the minimal temperature T_{min} required for the crosslinking process is about 100 °C whereas the reaction is achieved for $T > 280$ °C. The use of EG in place of ELO induces a significant shift of the reaction domain to lower temperatures. Indeed, the reaction between EG and IPDA ranges now from 20 °C up to 150 °C. This latter evolution is likely due to the higher accessibility of the epoxy groups for the amine reactive functions.

At the same time, the crosslinking enthalpy value strongly increases (540 J g^{-1} for EG-IPDA against 239 J g^{-1} for ELO-IPDA mixture). The conversion of these values by reference to the epoxy equivalent weight shows that this difference is not a direct consequence of the smaller size of EG compared to ELO. It reveals that in the case of the EG-IPDA system, the hardener units are fully consumed by the epoxy groups whereas in the case of the formulation based on vegetable oil, a parasitic mechanism involving an amidation reaction between the ester groups (ELO) and the amine functions (IPDA) is possible. Further details as regards the molecular mechanisms and the techniques used to study this reaction can be found in literature [54-58].

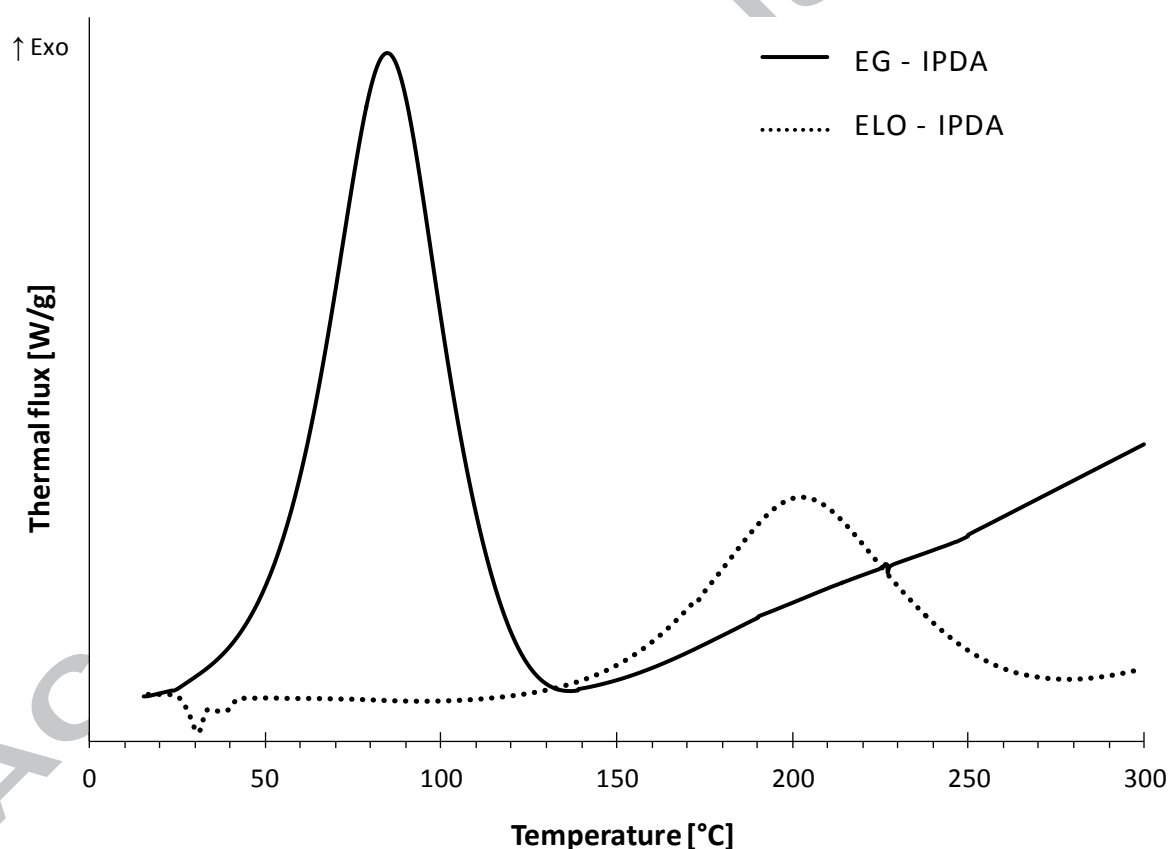


Figure 3. Dynamic DSC scans of binary epoxy reactive mixtures performed under nitrogen with a heating rate of 5 °C min^{-1} .

Ultimately, one can note that in the high temperature region ($T > 160 \text{ °C}$), the DSC signal increases with temperature. This phenomenon is characteristic of the thermal

degradation of the EG-IPDA material and is likely provoked by the excessive exothermicity of the crosslinking reaction.

In the case of ternary formulations, the reaction domain is clearly made by two separate peaks characteristic of the respective crosslinking of EG and ELO with the amine hardener (Figure 4). This means that the crosslinking of these ternary formulations requires a high curing temperature to obtain a fully consumption of all reactive components. In other words, a minimum value of 120 °C is necessary to proceed to the curing of ELO with IPDA while that characteristic of EG with IPDA started for $T > 25$ °C.

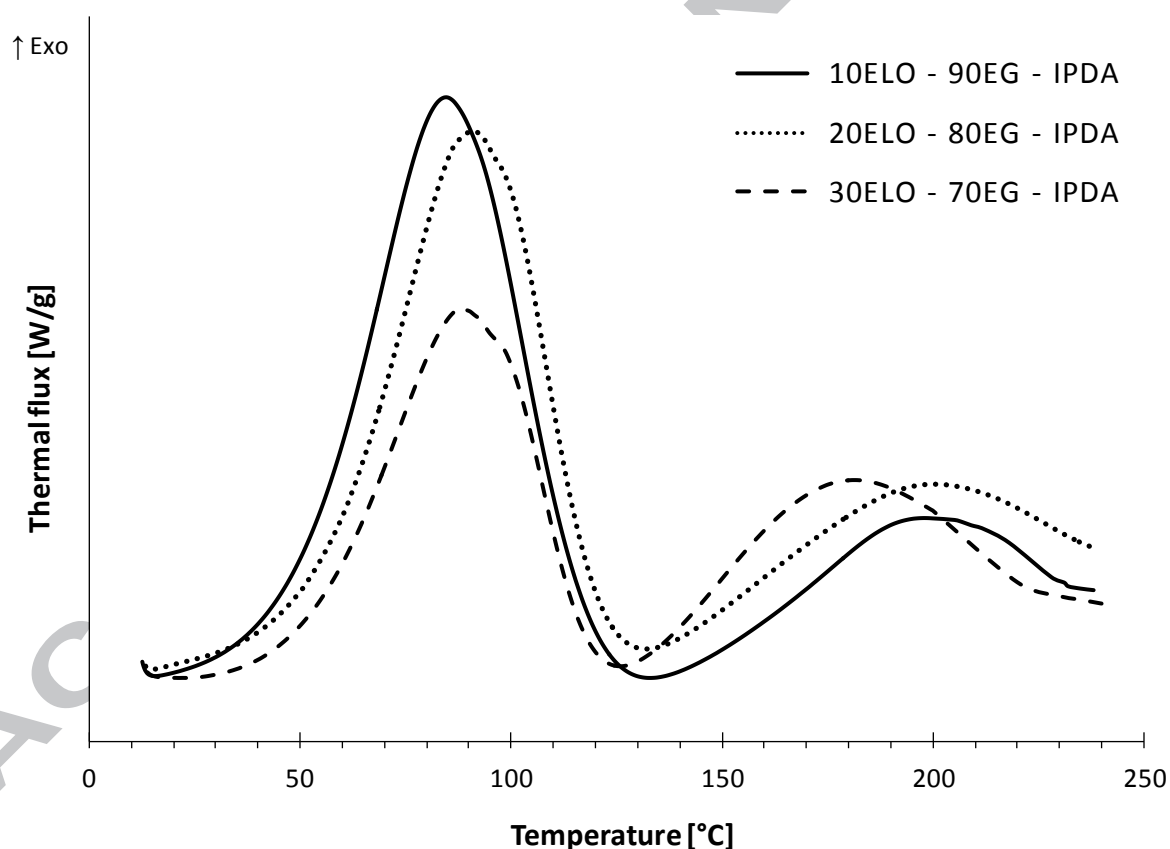


Figure 4. Dynamic DSC scans of several ternary epoxy reactive mixtures performed under nitrogen with a heating rate of 5 °C min⁻¹.

The total enthalpy can be evaluated by integration of the complete signal. Its value increases with the progressive substitution of ELO by EG units in the reactive mixture (Figure

5). This is logical considering that the binary formulation EG-IPDA showed previously a higher exothermicity compared to ELO-IPDA. It is to note that due to the reduction of exothermic character of the crosslinking reaction, no degradation is observed in the DSC signals characteristic of the ternary formulations contrarily to EG-IPDA.

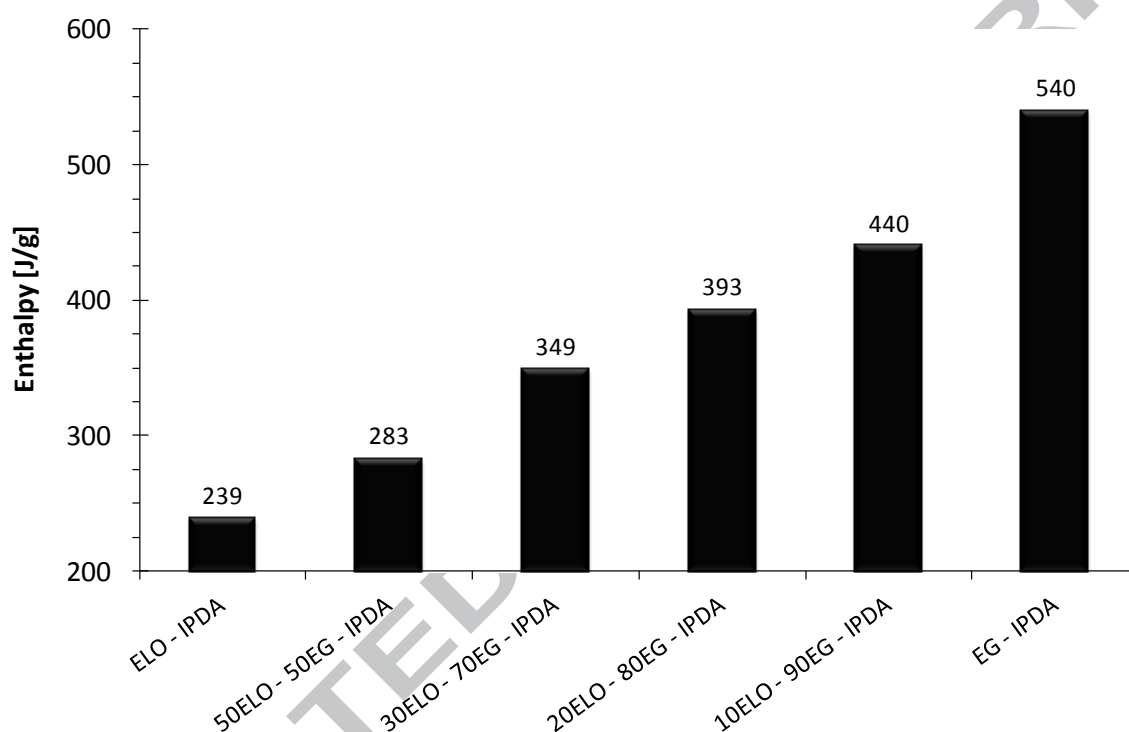


Figure 5. Influence of respective proportions of EG and ELO on the crosslinking enthalpy value of reactive ternary formulations using IPDA as hardener.

Kinetic rheological experiments were performed to complete the study of the reactivity of epoxy formulations. Figure 6 displays the evolution of the storage modulus (G') and loss modulus (G'') as a function of time and at the constant temperature of 140 °C. In the first period of the analysis, the reactive mixture is in the liquid state whatever its composition: the values of G' and G'' moduli remain weak but with $G'' > G'$. Then, for a critical value for time, the values of both moduli continuously increase and the elastic character becomes predominant ($G' > G''$). Finally, both curves tend to limit values. All this evolution is due to the crosslinking reaction. The gel time of each reactive formulation can be estimated by

taking the time related to the divergence of the viscoelastic curves. The progressive substitution of ELO by EG induces an important reduction in the gel time. For instance, it is close to 1 hour for 80ELO – 20EG – IPDA formulation whereas it is lower than 1 minute for 30ELO – 70EG – IPDA mixture. Above gelation step, the continuous increase of both moduli after gel point reveals that the crosslinking process continues. The time related to the limit consumption of the reactive units is clearly dependent on the initial proportion of each epoxy compound in the mixture. More precisely, it decreases when the EG content is increased due to its higher reactivity with IPDA compared to ELO. These data were useful to determine the optimal conditions of time and temperature for the formulations curing.

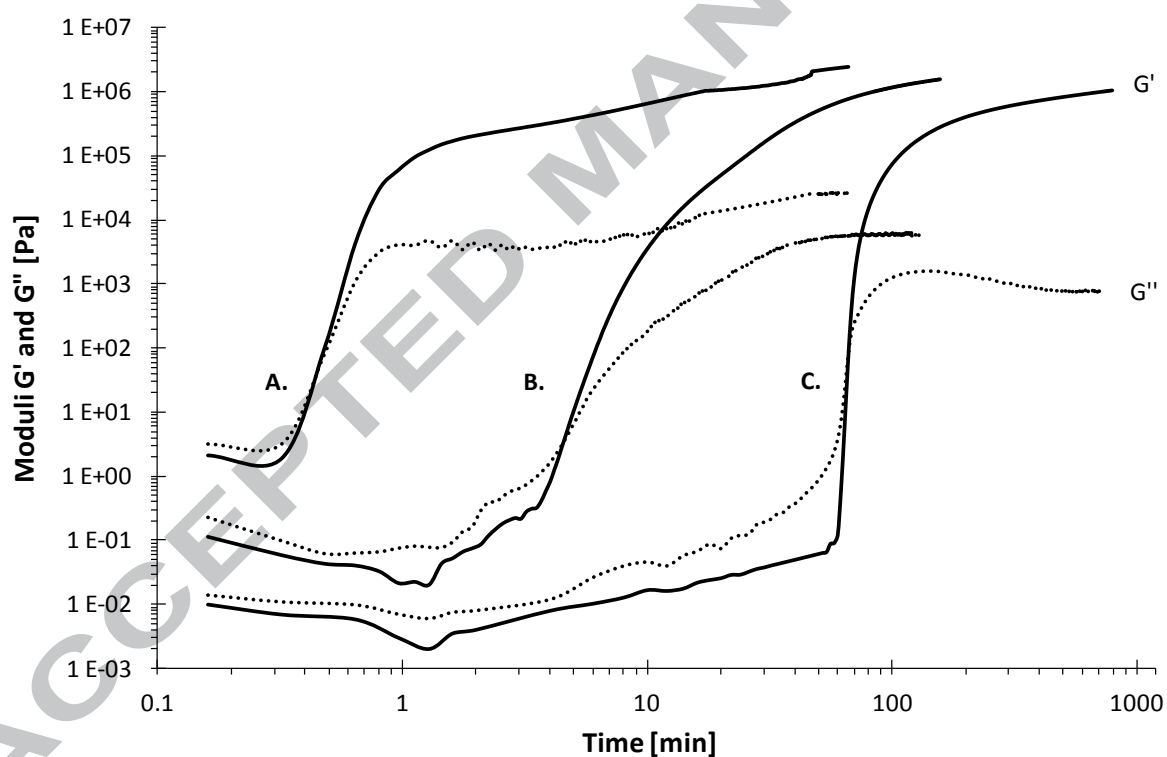


Figure 6. Kinetic rheological analyses of different epoxy reactive mixtures at $T=140\text{ }^{\circ}\text{C}$ with G' (solid line) and G'' (dashed line). A: 30ELO-70EG-IPDA, B: 50ELO-50EG-IPDA, C: 80ELO-20EG-IPDA.

Thermomechanical properties of cured resin samples

Dynamic rheology was also retained to evaluate the thermomechanical properties of cured materials. The results characteristic of 80ELO-20EG-IPDA and 30ELO-70EG-IPDA formulations are presented in Figure 7. Due to the low value of the angular frequency used for the rheological test ($\omega = 1 \text{ rad s}^{-1}$), the temperature taken at the maximum of G'' peak gives a reliable evaluation of the glass transition temperature of each crosslinked resin.

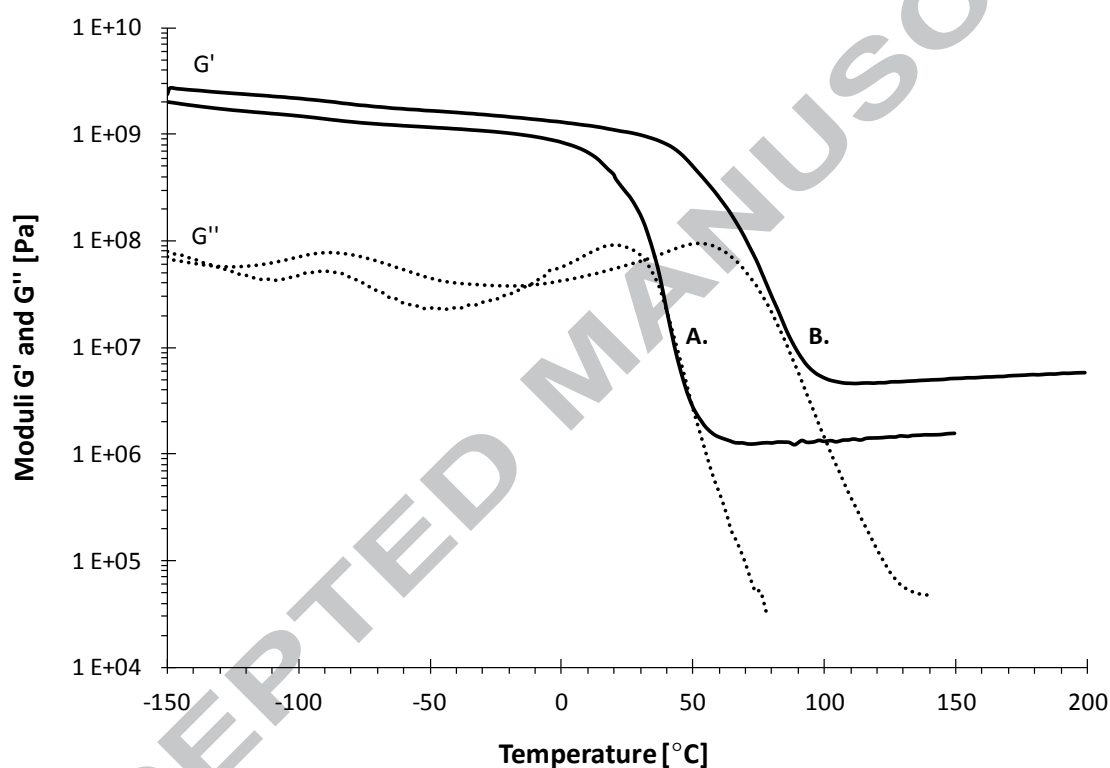


Figure 7. Rheological analyses of two cured materials produced from the curing of 80ELO-20EG-IPDA (series A) and 30ELO-70EG-IPDA (series B), respectively with G' (solid line) and G'' (dashed line).

In addition of the main relaxation peak, a “secondary” peak centred at -85 °C and with a reduced intensity can also be observed in the G'' curve. This phenomenon was reported in several papers dealing with epoxy systems cured with very different hardeners from polyamine [48, 59, 60] or anhydride categories [42, 61]. Often named “ β relaxation peak”, its existence is not influenced by the nature of the epoxy prepolymer since it is present in the

thermomechanical profile of material derived from DGEBA [48, 59-61] or from ELO [42]. Then, among the different interpretations proposed in literature, the most plausible one is the motion of the hydroxy-propyl ether units $[-O-CH_2-CH(OH)-CH_2-]$ that are present in all structures investigated.

Similar experiments were carried out with different materials obtained from the curing of formulations for which the epoxy groups are brought in variables proportions of EG and ELO. Figure 8 gives the results characteristic of the glass transition temperature of these cured materials.

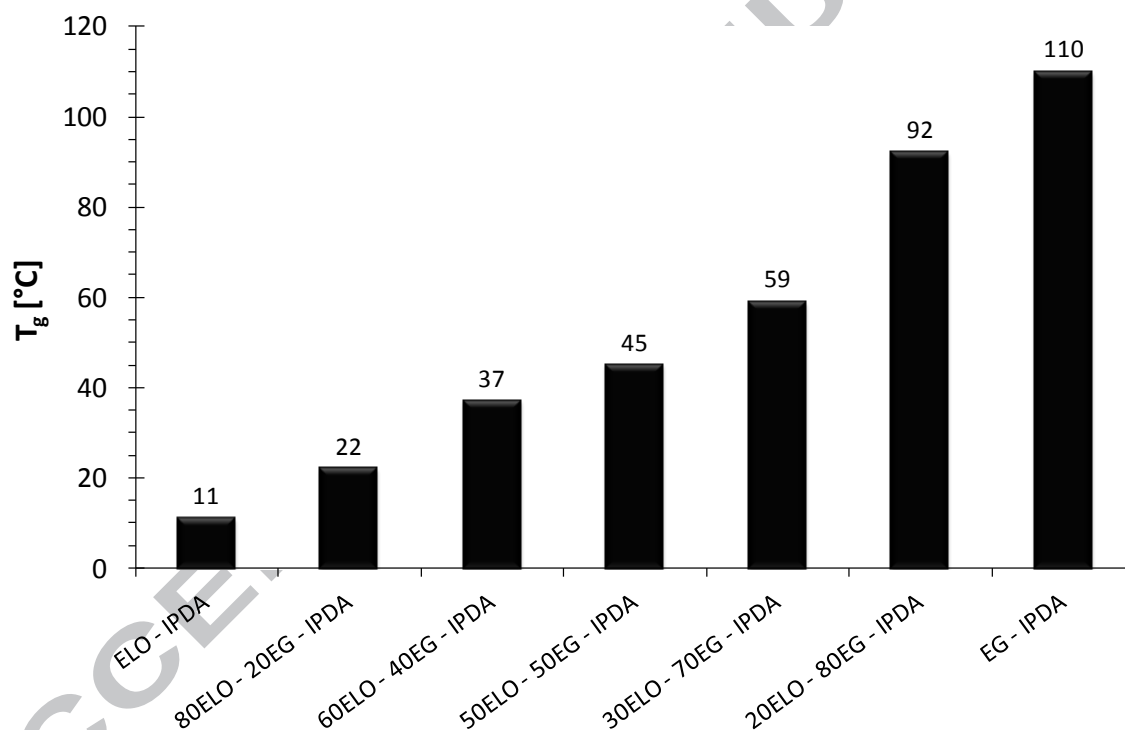


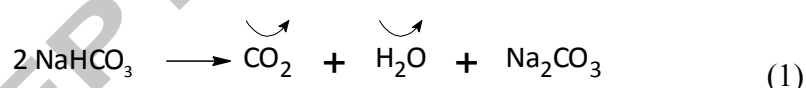
Figure 8. Influence of the chemical composition of x ELO-(100- x)EG-IPDA reactive mixture on the T_g related to the cured resin.

The gradual replacement of ELO by EG leads to an important increase of the T_g value. Indeed, the progression between the extremes cases represented by binary formulations is about 100 °C. Different formulations characterized by high ratio EG/ELO, *i.e.* high T_g value, will be preferred for the future production of structural foams. Indeed, the materials

containing a percentage of epoxy groups brought by the epoxidized vegetable oil higher than 80% are flexible at room temperature.

Foaming agent characterization

To investigate the possible production of polymeric foams from xELO-(100-x)EG-IPDA formulations, a foaming agent is required. Sodium bicarbonate (NaHCO_3) was pre-selected due to its safety and low-price suitable with automotive requirements. It is well known that this compound can react with weak acids in presence of water to produce carbon dioxide gas. But, this chemical process does not seem to be the most adequate with our formulations because it requires the addition of a surfactant to create a homogenous mixture between water and hydrophobic epoxy formulations [39, 40, 62]. In our study, this solution was not retained. Moreover, it is important to remind that acids can also react with epoxy groups [63-66] but in the present case, it will alter the network formation. However, NaHCO_3 can also decompose by an increase in temperature, producing carbon dioxide, water and sodium carbonate according to an endothermic reaction scheme defined by:



A simple thermogravimetric analysis performed in dynamic mode is valuable to determine the temperature range related to the self-decomposition of sodium bicarbonate since it is accompanied by a weight loss. Figure 9 shows that this temperature domain is comprised between 100 °C and 180 °C. For a temperature higher than 180 °C the residual weight is equal to 63%. This value corresponds to the ratio of the respective molar masses of formed sodium carbonate Na_2CO_3 (106 g mol⁻¹) upon initial NaHCO_3 (168 g mol⁻¹). This residue presents a double advantage: it is harmless and is likely to act as filler in the (future) polymeric foams.

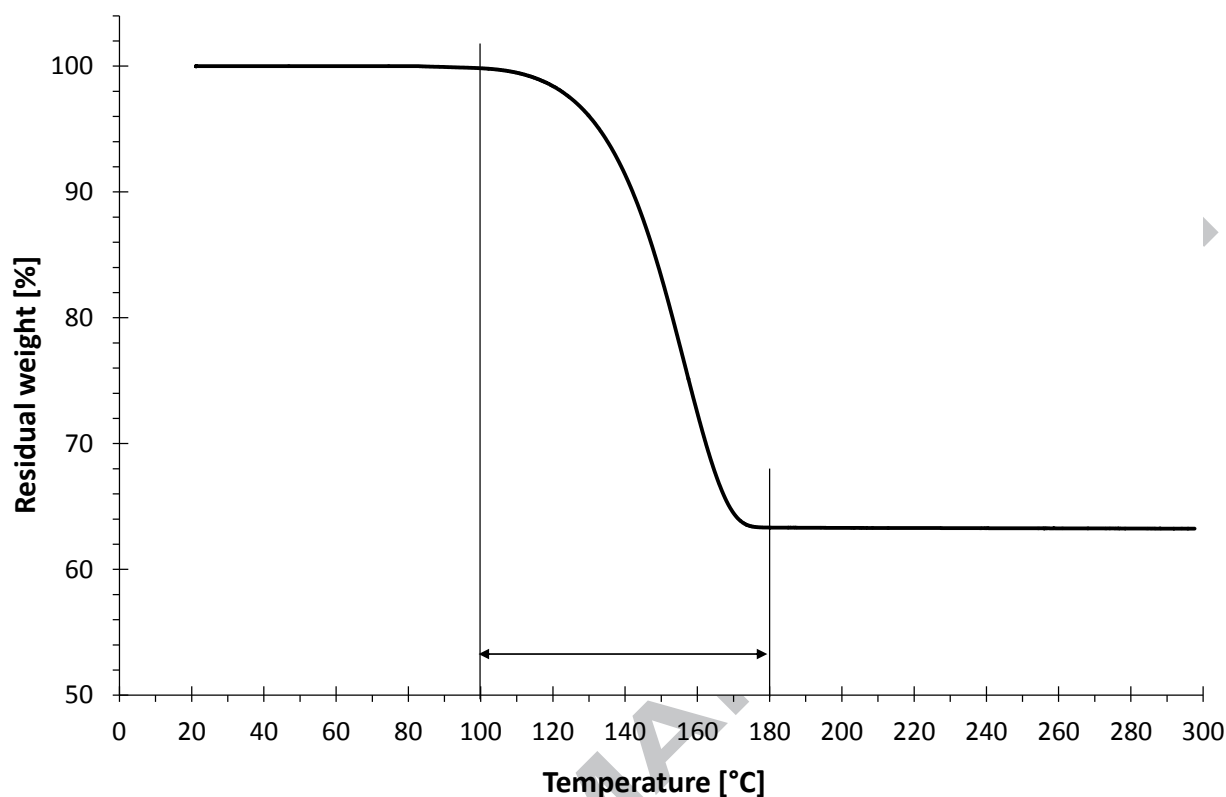


Figure 9. TGA analysis of the foaming agent (SB) under air at heating rate of 5 °C min⁻¹.

Choice of process parameters

In our concept, the production of thermoset polymeric foam will be possible if the resin gelation induced by the crosslinking reaction and the gas production due to the blowing agent decomposition are able to produce in the same temperature range. Moreover, the definition of the temperature that leads to equilibrium between the kinetics of both phenomena is of first importance for producing rigid and lightweight foams. Indeed, if the crosslinking of the reactive mixture prevails (formulations characterized by a very short gel time), the formation and growth of the cells is can be hindered by a sudden viscosity increase of the resin. Inversely, if the kinetics of decomposition of the blowing agent predominates, formed cells do not remain trapped in the resin because of the low viscosity of the reactive formulation and its excessive gel time. At the same time, the endothermic decomposition of NaHCO₃ must not prevent curing reaction that is thermally activated. The experimental data

reported in Figure 10 are useful to guide the choice of the process parameters. The dashed curve represents the first derivative versus temperature of the residual weight of the blowing agent (DTG curve). The same figure also shows the influence of both curing temperature and chemical composition of the resin on its gel time.

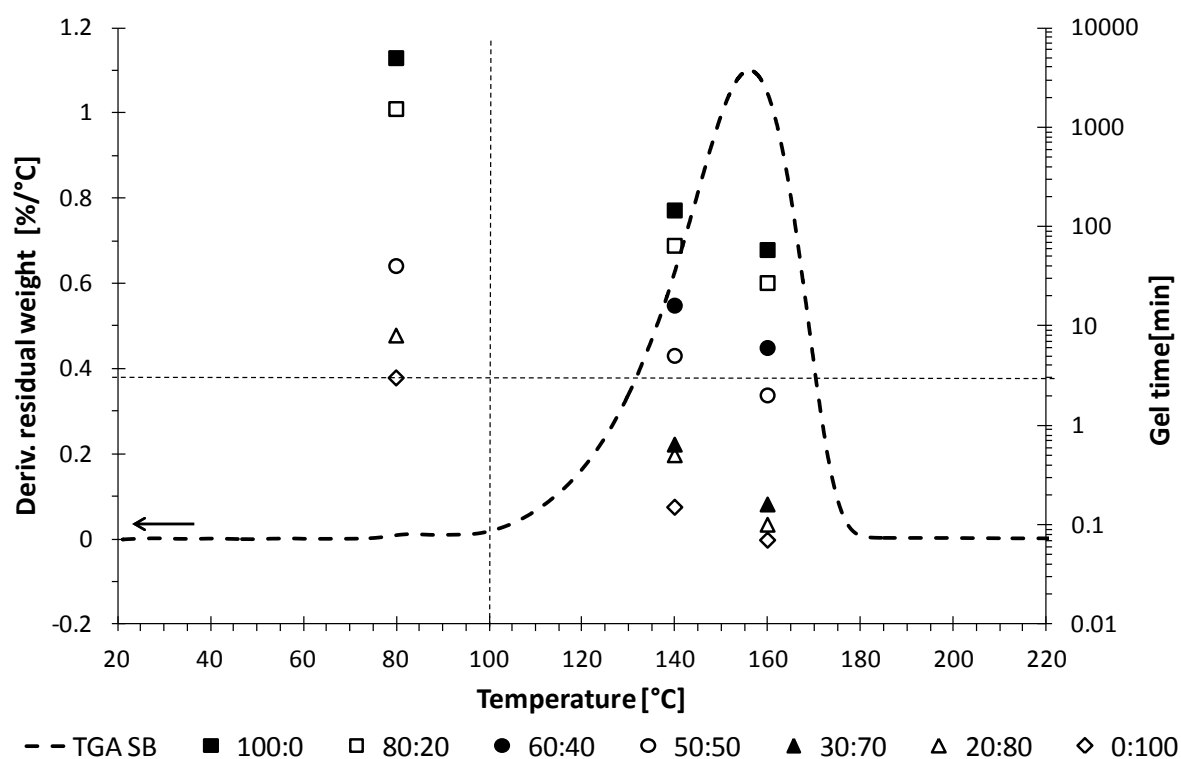


Figure 10. DTG curve of foaming agent (on the left) and gel time values at different temperatures for several reactive mixtures (on the right). The codes correspond to percentage of epoxy groups brought by ELO and EG, respectively.

Whatever the formulation considered, the gel time decreases when crosslinking temperature increases. Only the mixtures rich in EG are able to present low values of gel times in the temperature range where the SB decomposition is important. Then, considering that the industrial processing time is wished lower than 3 minutes to fulfil productivity requirements, a “working window” with suitable formulations and curing temperatures can be defined. 140 °C is identified as a minimum temperature for curing whereas formulations

comprising at least 70 % of the epoxy groups brought by EG units seem to be more appropriate for the fast production of epoxy foams.

Notably, foams were produced in 3 min at 160 °C using highly reactive epoxy formulations such as 20ELO – 80EG – IPDA or 10ELO – 90EG – IPDA with 40 parts of SB. The 10ELO – 90EG – IPDA composition leads to the highest T_g but is also characterized by an excessive exothermicity and the thermal degradation of the cellular material is finally observed as shown in Figure 11.

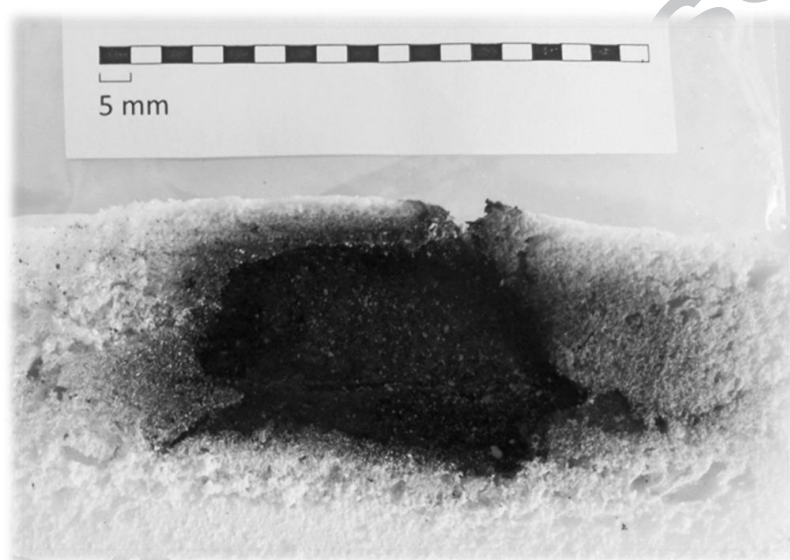


Figure 11. Overview of a foam produced from the mixing of 10ELO-90EG-IPDA with 40 parts of SB and after curing at $T = 160$ °C during 3 minutes: evidence for the thermal degradation.

To evaluate in a more precise way the inception of the degradation process, the thermal stability of the reactive 10ELO – 90EG – IPDA formulation was investigated by the conduction of a thermogravimetric test in dynamic mode. The corresponding data are presented in Figure 12. This analysis shows that the thermal degradation produces itself for $T \geq 200$ °C. This value can appear surprising since it is much higher than the curing temperature used previously (160 or 140 °C). In fact, it is likely that the exothermicity of the crosslinking

reaction is so high that the temperature in the polymeric mixture is much higher than the value initially set for the curing process and even exceeds 200 °C.

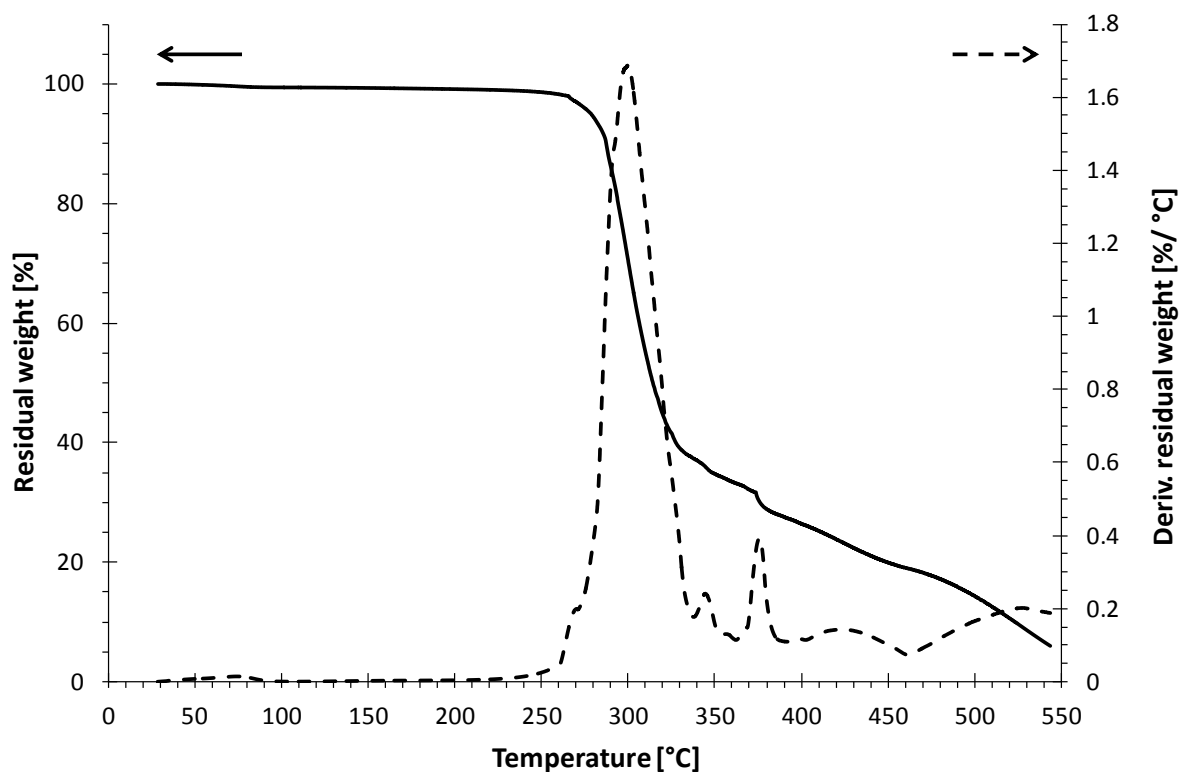


Figure 12. TGA (solid line) and DTG (dashed line) curves of 10ELO - 90EG - IPDA epoxy reactive mixture under air at heating rate 5 °C min⁻¹.

Several corrective actions were considered to limit the problem of thermal degradation of the foams. The first one consisted in reducing the curing temperature but this option slowed down at the same time the crosslinking and foaming reactions. Then, the material presented a higher compacity with a density close to 0.35 g cm⁻³. As the curing exothermicity was found to increase with EG proportion in the reactive mixture (Figure 5), the ratio EG/ELO was decreased in the reactive formulation. But, the final foam was characterised by T_g lower than 50 °C and could not fulfil the wished structural function in the temperature range required by the industrial application. Another possibility involved an increase of the amount of the foaming agent that decomposes itself *via* an endothermic reaction. However, this alternative produced limited effects due to the discrepancy in the temperature domains

characteristic of NaHCO_3 decomposition and reactive mixture degradation, respectively. Then, keeping in mind this latter concept, a new range of chemical compounds able to produce endothermic transformations were investigated to consume a part of heat released during the crosslinking of the reactive mixture so as to prevent the temperature from exceeding $200\text{ }^\circ\text{C}$. They are named as “exothermicity regulators” (ER) in this paper. They belong to mineral compounds family but their exact composition and their relative proportion cannot be specified due to industrial confidentiality attached to our research.

Physicochemical characterization of exothermicity regulators

The temperature domains and heat enthalpies attached to the endothermic transformation of each ER were quantified by differential scanning calorimetry. As shown in Figure 13, they are characterized by specific thermal zone of activity. A dashed line was drawn on the same figure to remind the temperature above which the thermal degradation of the 10ELO-90EG-IPDA reactive mixture was previously observed.

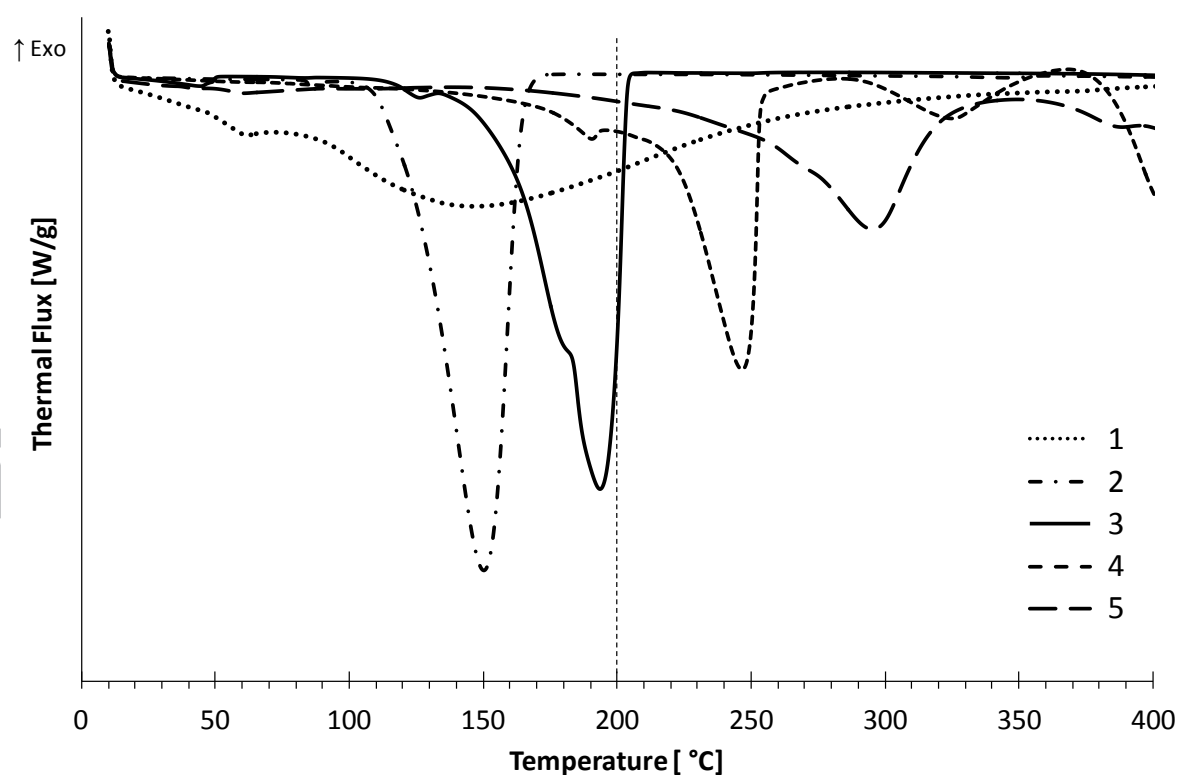


Figure 13. DSC analyses of “exothermicity regulators” registered at heating rate $5\text{ }^\circ\text{C min}^{-1}$.

Among different ER studied, the most interesting candidates are referenced under the codes “4” and “5”. If they are characterized by respective endothermic enthalpy ΔH_{endo} close to 565 J g^{-1} and 447 J g^{-1} , their efficiency is also due to the position of the attached temperature range. ER4 operates in a thermal zone corresponding to the beginning of the degradation while ER5 focuses its action in high-temperature field.

The amount of exothermicity absorbers in the final formulation was adjusted to reach a compromise between heat consumption and excess of released exothermicity. Indeed, if the exothermicity regulator is present in excess in the reactive mixture, the heat consumption is too important what alters both foaming process and crosslinking reaction. Once more, to produce lightweight rigid foam it is necessary to balance all these phenomena by the precise dosing of each component in the total mixture.

Characterization of final materials

By combining in precise quantities, 10ELO – 90EG – IPDA epoxy formulation, NaHCO_3 foaming agent and ER4 exothermicity regulator, foam was produced in 3 minutes at $180 \text{ }^\circ\text{C}$ without any apparent thermal degradation as shown in Figure 14. This material presents an apparent density of about 0.17 g cm^{-3} and is rigid at room temperature.

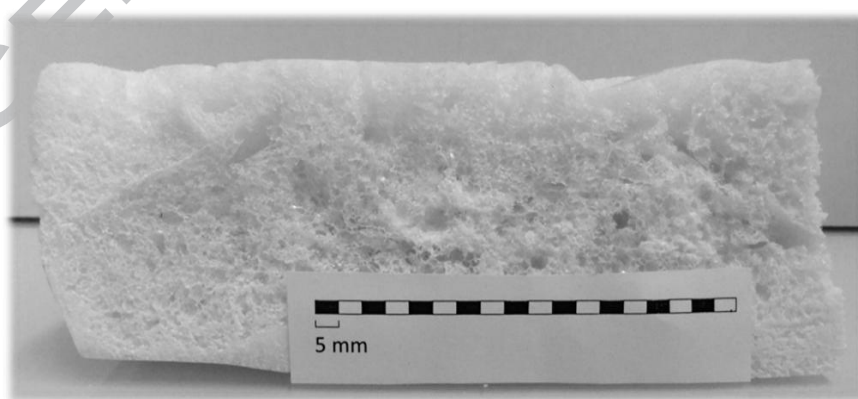


Figure 14. Overview of a foam obtained from the mixing and the reaction during 3 minutes at $180 \text{ }^\circ\text{C}$ of 10ELO-90EG-IPDA with SB and ER4.

Dynamic mechanical analyses of foams were performed using parallel plates geometry and working in compressive mode. Figure 15 shows as an example the results obtained with a formulation based on the mixing and reaction during 3 minutes at 180 °C of 10ELO-90EG-IPDA with SB and ER4.

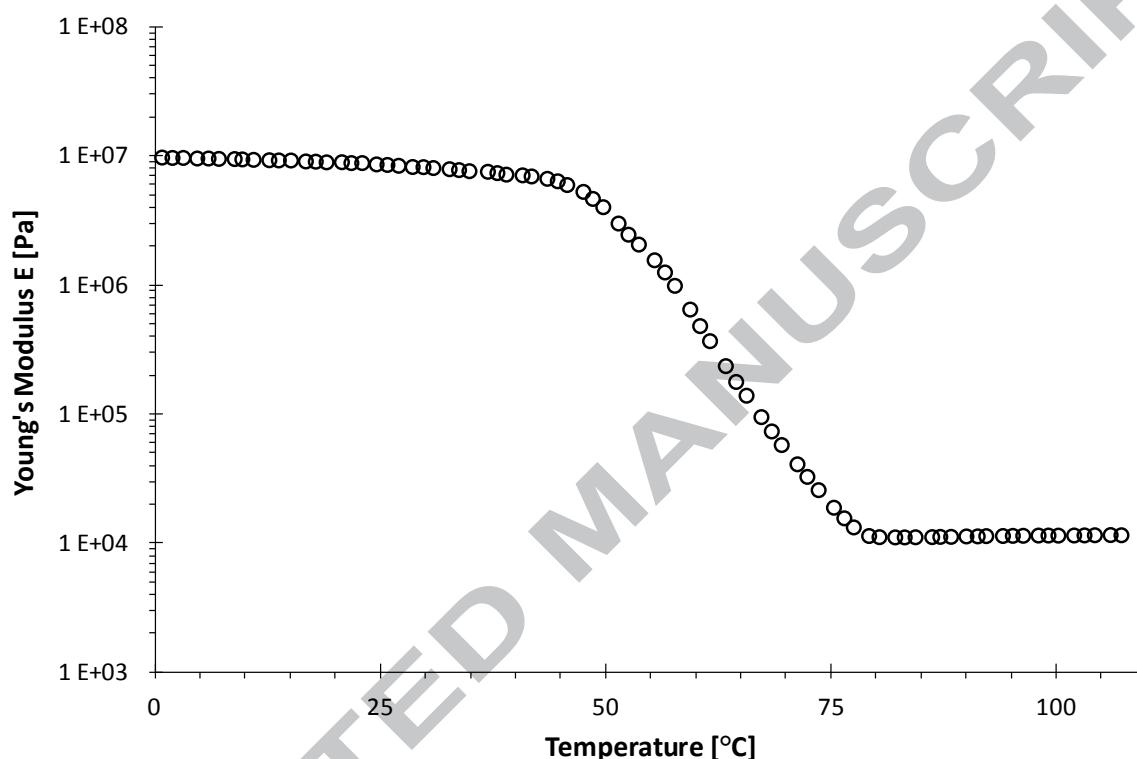


Figure 15. Thermomechanical profile of foam produced from the mixing and the reaction during 3 minutes at 180 °C of 10ELO-90EG-IPDA with SB and ER4.

The drop of the Young's modulus curve as a function of temperature is due to the glass transition of the material. The foam T_g is evaluated of about 48 °C close to the minimum value wished by the automotive partner.

The compressive mechanical properties of foams were also evaluated. A typical full stress-strain curve of one of our foams is presented in figure 16. It corresponds to the data registered with the material produced from the mixing and the reaction of the formulation 10ELO-90EG-IPDA with SB and ER4 (3 minutes at 180 °C). Three characteristic zones can be described.

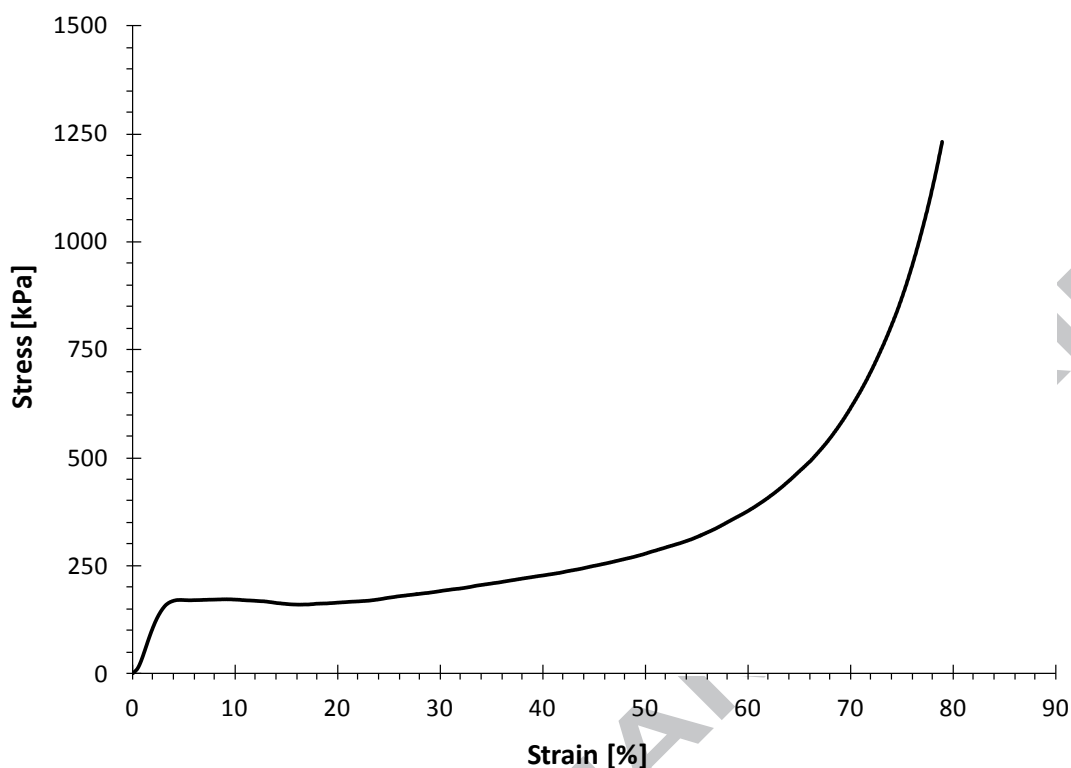


Figure 16. Compressive stress-strain curve of foam produced from the mixing and the reaction during 3 minutes at 180 °C of 10ELO-90EG-IPDA with SB and ER4.

First, the linear elastic domain is observed for strain values lower than 5%. This region makes it possible the evaluation of the “apparent” Young modulus of the foam that is mainly related to the bending stiffness of the cell walls [67]. The corresponding value is 8.0 ± 1.5 MPa. Then, increasing the strain, the cell walls collapse inducing the formation of a plateau-like region in the mechanical curve. The compressive strength measured at 10% strain is close to 200 ± 36 kPa. Finally, at higher strains, associated to the densification regime, opposite cell walls touch themselves what induces a strong stress increase with strain. This last step is currently called densification [67, 68]. The performance level of this foam generation is in agreement with the data reported in other studies dealing with partially bio-based rigid foams [12, 25, 29, 32].

All these results show that it is entirely possible to produce epoxy formulations of low toxicity using derivatives from vegetable oils and that are adequate for the manufacture of

lightweight and rigid foams in agreement with automotive industry requirements. In particular, this generation of foams is likely applicable as a core material in sandwich composite structures.

CONCLUSIONS

This paper aims to show that it is possible to produce in a few minutes lightweight and rigid foams using molecular platforms derived from vegetable oils. The concept proposed involves first two epoxy compounds with differentiated reactivity versus a cycloaliphatic diamine (IPDA). Then, by the progressive substitution of ELO by EG units, highly reactive ternary formulations can be obtained with possible low gel time values and high thermomechanical properties whereas binary mixtures seem of lesser interest for industrial applications. By adding to these ternary formulations, some sodium bicarbonate acting as temperature activated blowing agent and a mineral compound playing the role of exothermicity regulator, it is possible to produce lightweight, rigid and non-carcinogenic foams in a few minutes. Thanks to their characteristics, these materials are already identified as potential candidates for future application in automotive manufacturing. Actually, the concept developed in this paper presents an interesting versatility. Indeed, by changing the nature and/or quantity of each compound present in the initial chemical formulation, the development of a comprehensive range of biomass-derived epoxy foams could be foreseen with wished specific characteristics (T_g , stiffness, density, morphology...). However, it is important to keep in mind that many reactions have to obey to equilibrium rules but it is possible to optimise them with a rigorous scientific approach.

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CAPTIONS

Figure 1. Chemical structures of the chemical compounds used in the bio-based epoxy resins used in this study.

Figure 2. Schematic curing mechanism of epoxidized linseed oil with diamines.

Figure 3. Dynamic DSC scans of binary epoxy reactive mixtures performed under nitrogen with a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$.

Figure 4. Dynamic DSC scans of several ternary epoxy reactive mixtures performed under nitrogen with a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$.

Figure 5. Influence of respective proportions of EG and ELO on the crosslinking enthalpy value of reactive ternary formulations using IPDA as hardener.

Figure 6. Kinetic rheological analyses of different epoxy reactive mixtures at $T=140\text{ }^{\circ}\text{C}$ with G' (solid line) and G'' (dashed line). A: 30ELO-70EG-IPDA, B: 50ELO-50EG-IPDA, C: 80ELO-20EG-IPDA.

Figure 7. Rheological analyses of two cured materials produced from the curing of 80ELO-20EG-IPDA (series A) and 30ELO-70EG-IPDA (series B), respectively with G' (solid line) and G'' (dashed line).

Figure 8. Influence of the chemical composition of $x\text{ELO}-(100-x)\text{EG-IPDA}$ reactive mixture on the T_g related to the cured resin.

Figure 9. TGA analysis of the foaming agent (SB) under air at heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$.

Figure 10. DTG curve of foaming agent (on the left) and gel time values at different temperatures for several reactive mixtures (on the right). The codes correspond to percentage of epoxy groups brought by ELO and EG, respectively.

Figure 11. Overview of a foam produced from the mixing of 10ELO-90EG-IPDA with 40 parts of SB and after curing at $T = 160$ °C during 3 minutes: evidence for the thermal degradation.

Figure 12. TGA (solid line) and DTG (dashed line) curves of 10ELO - 90EG - IPDA epoxy reactive mixture under air at heating rate 5 °C min^{-1} .

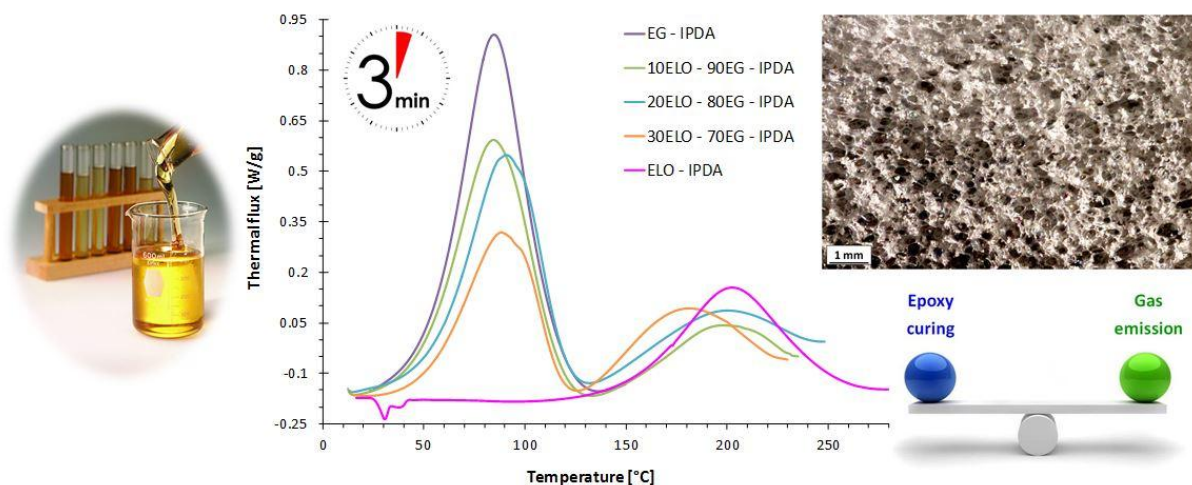
Figure 13. DSC analyses of “exothermicity regulators” registered at heating rate 5 °C min^{-1} .

Figure 14. Overview of a foam obtained from the mixing and the reaction during 3 minutes at 180 °C of 10ELO-90EG-IPDA with SB and ER4.

Figure 15. Thermomechanical profile of foam produced from the mixing and the reaction during 3 minutes at 180 °C of 10ELO-90EG-IPDA with SB and ER4.

Figure 16. Compressive stress-strain curve of foam produced from the mixing and the reaction during 3 minutes at 180 °C of 10ELO-90EG-IPDA with SB and ER4.

Graphical abstract



Highlights

- Ternary epoxy formulations derived from vegetable oils can present high reactivity.
- They can be used for the fast production of lightweight and rigid polymeric foams.
- Sodium bicarbonate can be used as blowing agent.
- An exothermicity reducer is also necessary in the reactive formulation.
- A T_g value higher than 48 °C and a density close 0.17 g cm⁻³ can be achieved.