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1 Biobased Structural Epoxy Foams Derived from 2 Plant-Oil: Formulation, Manufacturing and 3 Characterization

4 *Elena Mazzon¹, Pascal Guigues², Jean-Pierre Habas^{1*}*

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6 1 : Institut Charles Gerhardt Montpellier UMR 5253 CNRS-UM-ENSCM, Université de
7 Montpellier, Place Eugène Bataillon, CC 1702, 34095 Montpellier Cedex 5, France

8 2 : RENFORTECH, 33 Rue de Pierre Marie Fache, 52410 Chamouilley, France

9
10 *: Corresponding author

11 Pr. Jean-Pierre Habas, ICGM, Université de Montpellier, Place Eugène Bataillon, CC 1702,
12 34095 Montpellier Cedex 5, France.

13 Tel.: +33 4 67 14 37 80

14 E-mail address: jean-pierre.habas@umontpellier.fr

15 16 17 **ABSTRACT**

18 This paper is devoted to the description of the scientific method used for developing biobased
19 structural foams derived from highly reactive epoxy resins. The chemical formulations were
20 obtained from the mixing of two epoxidized plant oil-derivates (**epoxidized linseed oil ELO**
21 **and glycerol triglycidyl ether commonly named** epoxidized glycerol EG) with an anhydride
22 hardener and a **non-toxic** foaming agent. The optimization of the composition was achieved by
23 studying the influence of many parameters **such as the proportion of each epoxy molecule in**

1 the reactive formulation, the exact nature of the hardener or foaming agent retained by the use
2 of different complementary experimental techniques. For instance, the reactivity of four cyclic
3 anhydride compounds with ELO was investigated by differential scanning calorimetry and
4 rheometry in dynamic or kinetic mode. Two different blowing agents were initially retained for
5 the preparation of foams and their respective density and mechanical properties were evaluated
6 and compared. The proportion of each epoxy molecule (ELO and EG) was also tuned to achieve
7 a good equilibrium between the gelation and foaming mechanisms within a few minutes. The
8 definition of an optimized composition made it possible the production of rigid foams using a
9 short production time (i.e. lower than 3 min). These foams were characterized by a glass
10 transition temperature close higher than 80 °C and an apparent density comprised between 0.05
11 and 0.08 g/cm³. Their specific mechanical properties were judged convenient for a possible
12 valorisation as lightweight structural material.

13

14 **KEY WORDS.**

15 Plant-oil derivates; biobased epoxy foam; rheology; anhydride hardener; foaming agent;
16 thermal techniques.

17

18 **1. INTRODUCTION**

19 Polymer foams define a large range of lightweight materials with very different chemical and
20 physical characteristics that are influenced by the matrix properties, the proportion of the inner
21 cells but also the possible presence of filler in the initial formulation. Polymer foams can be
22 classified into several categories. For instance, they can be separated into either thermoset or
23 thermoplastic materials depending on the nature of the matrix. Each family can be further
24 divided into rigid or flexible substrates. If one considers the spatial repartition of the cells,

1 isolated gas bubbles are specific of closed-cell foams whereas open-cell structures are based on
2 gas tunnels (Bjork and Enochsson, 2009). Due to all these characteristics, polymer foams can
3 behave as shape memory materials or inversely are able to fulfil structural functions (Lavoie,
4 1976). Their atypical morphologies provide them outstanding aptitudes for thermal or acoustic
5 insulation. Not surprisingly, given all these properties, these lightweight materials are used in
6 a large range of applications such as building construction (Bogdan et al., 2005; Kallaos et al.,
7 2014; Richardson, 1980), transportation (Farkas et al., 2002; Sakly et al., 2016; Schmitt et al.,
8 2003; Zheng et al., 2011), food packaging (Ingrao et al., 2015; Paraskevopoulou et al., 2012)
9 furniture (Barker et al., 1992; Smardzewski et al., 2008) or sports (Chiu and Shiang, 2007;
10 Duncan et al., 2016).

11 A general survey shows that most of commercial polymeric foams are derived from
12 petrochemistry. However, for some decades, different elements support the development of
13 biobased foams. First, such materials are really interesting in the framework of a sustainability
14 policy. Indeed, by definition, biomass is renewable whereas crude oil is a fossil resource and
15 so with limited reserves. Secondly, the fluctuating prices of chemicals issued from petroleum
16 is another tangible reason because this makes difficult the choice of long-term technical or
17 scientific solutions (Dvir and Rogoff, 2014). The toxicity of many chemical compounds derived
18 from petroleum chemistry also provides motivation for the identification and use of harmless
19 products. **Such situation** is found with many conventional types of foams such as polyurethane
20 formulations that are based on isocyanate-functionalised molecules (Avashia et al., 1996;
21 Ganguly et al., 2018; Lee et al., 2003; Pauluhn, 2002). It is also encountered with epoxy foams
22 derived from DiGlycidyl Ether of Bisphenol A (DGEBA). Indeed, Bisphenol A (BPA) was
23 recently suspected to present endocrine disruptor properties **but this topic is still subject to**
24 **controversy** (Chen et al., 2002; Resnik and Elliott, 2015; Ruan et al., 2015). The use of other

1 aromatic prepolymers derived from crude-oil is a possible approach to avoid BPA toxicity but
2 it cannot be considered as a sustainable solution (El Gazzani et al., 2016).

3 In response to this situation, various studies were undertaken by several teams of researchers to
4 develop epoxy foams from less toxic precursor compounds, in particular through the use of
5 molecules derived from biomass. For instance, Brown et al. explored the interest of a
6 commercial formulation (under trade name Super Sap 100 from Entropy Resins) comprised by
7 epoxidized pine oil and DGEBA and (Brown et al., 2017). Using polymethylhydrosiloxane
8 (PMHS) as a foaming agent in combination with a polyamine hardener, they obtained foams
9 with bulk densities between 0.263 and 0.600 g/cm³ after curing for 24 hours at ambient
10 temperature. To develop resins with a higher biobased content, Agnihotri used this chemical
11 formulation with variable proportions of epoxidized soya oil ESO (Agnihotri et al., 2019). But,
12 an increase of the ESO content had detrimental impact on both mechanical properties and glass
13 transition temperature of the polymeric foam. Altuna et al. observed similar trend with foams
14 derived from the mixture of DGEBA and ESO (Altuna et al., 2010). This evolution is likely a
15 consequence of the higher molecular flexibility of aliphatic fatty chains compared to rigid
16 aromatic structures present in DGEBA. Generally speaking, epoxidized vegetable oils are
17 known as being characterized by low reactivity due to the poor steric position of oxirane rings
18 in the fatty chains with respect to the hardener (Alam et al., 2014; Biermann et al., 2000; Khot
19 et al., 2001). The time required to produce polymer foams derived from this class of compounds
20 is often several hours and can even be made worse by the choice of the hardener. For instance,
21 Dogan et al. proposed to use malonic acid to cure ESO and act as a blowing agent at the same
22 time. But, they described a slow process and the derived foams were characterized by low
23 performances (Dogan and Kusefoglul, 2008). Nevertheless, in a recent work, we showed that it
24 was possible to produce biobased epoxy foams (i.e. without BPA) within short processing times
25 by using plant-oil derivates and a cycloaliphatic diamine as hardener (Mazzon et al., 2015).

1 However, due to the excessive exothermicity of the curing reaction, this curing agent also
2 required the addition of other chemicals in the reactive mixture to act as "heat reducer" that is
3 say for preventing thermal runaway. The use of heat reducer made it possible the production of
4 foams. However, the physical characteristics of these foams such low thermomechanical
5 properties (T_g close to 50°C) and excessive density ($\approx 0.17 \text{ g/cm}^3$) were judged perfectible
6 considering their possible application in transportation. Then, in this paper, we decided to
7 explore another scientific pathway by the use of cyclic anhydrides that are known to release
8 less heat during their reaction with epoxy molecules (Kumar et al., 2017b). The choice of this
9 kind of hardener was also motivated by the intent to produce foams with higher mechanical
10 properties to fulfil structural applications, in particular for transportation field (Altuna et al.,
11 2015). More precisely, the minimal wished T_g value is about 70 °C whereas the density must
12 be lower than 0.1 g/cm^3 . It is important to keep in mind that in this latter sector, the final choice
13 is also oriented towards the formulation able to combine high reactivity during curing and good
14 performances after transformation.

15

16 2. EXPERIMENTAL SECTION

17 2.1 Materials

18 All raw materials are commercially available and they were used as received, i.e. without
19 further purification. Epoxidized linseed oil (ELO) with 5.8 epoxy groups per triglyceride and
20 molecular weight of 974 g mol^{-1} was kindly offered by ARD (France). Glycerol triglycidyl
21 ether named also epoxidized glycerol (EG) with 3 epoxy groups per molecule and a molecular
22 weight of 260 g mol^{-1} was purchased from Nagase ChemteX (Japan). The chemical structures
23 of these epoxy molecules are drawn in Figure 1.

24

25

Insert Figure 1

1

2 Different cyclic anhydrides were preselected keeping in mind the wish to get cured materials
3 with good mechanical properties. The different curing agents used in this study are reported in
4 **Table 1**. All were purchased from Acros Organics and used as received. It is well established
5 by now that the epoxy-anhydride reaction must be catalysed to achieve a full consumption of
6 the reagents and consequently get a material with higher performances. Then, 2-methyl
7 imidazole (2MI) was used as catalyst and was supplied by Sigma Aldrich. NaHCO₃ (sodium
8 bicarbonate, “SB”) and KHCO₃ (potassium bicarbonate, “PB”), purchased from Sigma Aldrich,
9 were used as foaming agent.

10

11

Insert Table 1

12

13 *2.2 Preparation of biobased epoxy resins*

14 All epoxy reactive formulations were prepared with an anhydride groups/epoxy groups ratio R
15 of 0.8 (Boquillon and Fringant, 2000; Gupta et al., 2010). A quantity of 1% wt 2-MI catalyst
16 based on anhydride weight was added to the reactive mixture. For instance, binary mixtures
17 ELO – MTHPA (MTHPA for **methyl tetrahydrophthalic anhydride**) were characterized by 4.64
18 mol of hardener for 1 mol of ELO. Ternary formulations are identified under the code
19 “xELO – (100-x)EG – hardener”, where x is the percentage of epoxy groups brought by
20 epoxidized linseed oil. Since ELO and EG have a different reactivity with a hardener, these
21 ternary formulations provide the ability to tune the properties of the reactive mixture and the
22 derived material (Habas et al., 2013). Reactive mixtures were prepared in a one-stage process
23 by mixing all chemicals at room temperature under mechanical stirring during 3 minutes until
24 apparent homogeneity. Optimal curing conditions (i.e. time and temperature) were determined
25 by differential scanning calorimetry and rheological analysis.

1

2 *2.3 Preparation of foams*

3 The epoxy prepolymers were first mixed together in varying proportions **but by keeping**
4 **constant the total number of epoxy groups in order to ensure a complete reaction with the**
5 **hardener units whatever the formulation studied.** Then, the foaming agent was added. Its
6 quantity was fixed between 10 and 50 parts for 100 parts of epoxy formulation corresponding
7 to a weight percentage between 9.1 and 33.3% wt. Finally, the curing agent and the catalyst
8 were also added. All components were mixed at room temperature for about 2-3 minutes. The
9 final blend was poured in an aluminium open mould previously heated at $T = 180\text{ }^{\circ}\text{C}$. The
10 curing/foaming time was set at 3 minutes in order to identify and retain the only formulations
11 compliant with an industrial productivity found in automotive sector.

12

13 *2.4 Methods*

14 The temperature domains and heat enthalpies attached to the different reactions (i.e. curing of
15 epoxy formulations and decomposition of foaming agents...) were evaluated by differential
16 scanning calorimetry (DSC StarOne from Mettler Toledo[®]). The dynamic scans were
17 performed with a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ under inert atmosphere (N_2) using a 40 μl perforated
18 aluminium capsules and an empty crucible as reference. Kinetic rheological experiments were
19 performed on crude reactive mixtures (i.e. without foaming agent) to determine from the
20 evolution of the complex shear modulus $G^* = G' + j G''$ their respective gel and vitrification
21 times. The real component G' , called storage modulus, is related to the elastic contribution of
22 the sample. The imaginary part G'' , named loss modulus, is specific of the dissipated
23 mechanical energy. These analyses were registered at constant temperature using a dynamic
24 rheometer (MCR 102 from Anton Paar[®]) equipped with cup-plate geometry. The diameter of
25 the upper plate was 25 mm and the inner diameter of the cup was 40 mm in order to prevent

1 parasitic side effects. After geometry preheating in the testing chamber up to the desired
2 temperature, the freshly prepared reactive mixture was poured in the measurement cup. Then,
3 the upper plate was lowered until contact with the sample surface. Storage modulus (G') and
4 loss modulus (G'') were recorded at constant strain (5 %) and fixed angular frequency
5 ($\omega = 1 \text{ rad s}^{-1}$). The gel time was evaluated by taking the time where the divergence of both
6 moduli was observed. The thermomechanical properties of the cured polymer were
7 characterized using a stress-controlled dynamic rheometer (AR2000Ex from TA Instruments®)
8 equipped with rectangular torsion geometry. Analyses were performed from $-50 \text{ }^\circ\text{C}$ to $150 \text{ }^\circ\text{C}$
9 with a heating rate of $3 \text{ }^\circ\text{C min}^{-1}$ and at a constant shearing angular frequency ($\omega = 1 \text{ rad s}^{-1}$).
10 Glass transition temperature (T_g) was evaluated by taking the temperature T_α at the maximum
11 of G'' peak that is characteristic of the main mechanical relaxation. Due to the value of the
12 shearing angular frequency used, $T_g \approx T_\alpha$. Dynamic thermogravimetric analyses were
13 performed from room temperature to $300 \text{ }^\circ\text{C}$ under air flow with the heating rate of $5 \text{ }^\circ\text{C min}^{-1}$
14 using a Q50 thermogravimetric analyser (TGA) from TA Instruments®. In isothermal
15 experiments, the weight loss of sample was registered during 60 minutes at a fixed temperature
16 comprised between $100 \text{ }^\circ\text{C}$ and $180 \text{ }^\circ\text{C}$. The density of the foams (ρ) was obtained as the ratio
17 between the weight and the volume of cubes of 25 mm of side. Reported results were the
18 average of measurements taken on three different samples issued from the same chemical
19 formulation. Dynamic mechanical analyses (DMA) of the foams were performed with a 50N
20 model from ACOEM-Metravib® using parallel plate geometry in compressive mode at a
21 constant frequency (1 Hz). The temperature ranged from $-50 \text{ }^\circ\text{C}$ and $130 \text{ }^\circ\text{C}$ with a heating rate
22 of $2 \text{ }^\circ\text{C min}^{-1}$. Glass transition temperature (T_g) of the foam was evaluated by taking the
23 temperature at the maximum of peak on E'' curve. This temperature also corresponds to the
24 beginning of the drop of the Young's modulus plot that is characteristic of the mechanical
25 rigidity. The compressive performances of the foam were also evaluated at room temperature

1 on cubic samples (20 mm x 20 mm x 20 mm) using a 5533 Universal Testing Machine from
2 Instron® with a crosshead speed of 5 mm min⁻¹. The compressive modulus was determined from
3 the slope of stress – strain curve in linear region associated with the elastic behaviour. The
4 compressive strength was taken at a strain of 10 %. Reported results were the average of at least
5 eight measurements on specific samples.

6

7 **3. RESULTS AND DISCUSSION**

8 *3.1 Choice of anhydride hardener*

9 The reactivity of ELO with each kind of anhydride hardener was first investigated with dynamic
10 DSC. The crosslinking thermal domain was detected by the presence of an exothermic peak
11 (Figure 2). Its position and respective area were observed to be slightly different from one
12 anhydride to other. The peak characteristic of the reaction between ELO and MHHPA (methyl
13 hexahydrophthalic anhydride) units presented a maximum centred at the lowest temperature
14 (i.e. T = 150 °C) and was judged as specific of the most reactive mixture. The reverse situation
15 (i.e. lowest reactivity) was observed with the use of METH (nadic methyl anhydride) hardener.
16 Such hierarchy was found consistent with literature data (Boquillon and Fringant, 2000).

17

18

Insert Figure 2

19

20 Then, kinetic rheological analyses could be recorded for each reaction mixture at different
21 constant curing temperatures taken in the thermal crosslinking range defined above. In
22 particular, the divergence of both viscoelastic moduli was used to evaluate the gel time. Figure
23 3 shows the gel times characteristic of the four couples "ELO-anhydride" registered at
24 T = 80 °C and 140 °C, respectively. At the lowest curing temperature, the mixtures based on
25 THPA (tetrahydrophthalic anhydride), MTHPA and MHHPA have similar reactivity with gel

1 times close to 200 minutes. In contrast, epoxy formulation based on METH is considerably less
2 reactive since its gel time close to 350 minutes. The same hierarchy is observed at high
3 temperature ($T = 140\text{ }^{\circ}\text{C}$). The lower reactivity of METH is likely a consequence of its bulky
4 nadic structure synonym of reduced molecular mobility (Table 1).

5

6

Insert Figure 3

7

8 The thermomechanical properties of “ELO – anhydride” cured materials were evaluated by
9 dynamic rheology. Figure 4 resumes glass transition temperature values after curing at
10 $T = 80\text{ }^{\circ}\text{C}$ during 24 hours or at $T = 140\text{ }^{\circ}\text{C}$ during 10 hours. After curing at $T = 80\text{ }^{\circ}\text{C}$, the
11 formulations with the highest T_g are ELO – MHHPA and ELO – MTHPA ($75\text{ }^{\circ}\text{C}$ and $73\text{ }^{\circ}\text{C}$
12 respectively). This result is not surprising since MTHPA and MHHPA show very similar
13 chemical structures and reactivity. In contrast, the lowest value ($30\text{ }^{\circ}\text{C}$) is obtained with the
14 ELO – METH formulation. Such result can be once more related to the lower reactivity of this
15 system. In this latter case, a curing time of 24 hours seems insufficient for the total consumption
16 of reactive compounds. A temperature increase to $T = 140\text{ }^{\circ}\text{C}$ provides a higher crosslinking
17 rate. Then, the T_g of ELO – METH formulation is close to that registered with ELO – MHHPA
18 and ELO – MTHPA cured materials. It is to note that the cured material based on ELO – THPA
19 displays the lowest T_g values for both curing temperatures used. Considering that THPA
20 anhydride is under solid state up to $102\text{ }^{\circ}\text{C}$, its use is less practical than liquid anhydrides such
21 as MHHPA and MTHPA. As the latter offer the best combination between reactivity and
22 ultimate performances, they will be the only anhydrides retained in the pursuing of our work.
23 In fact, only results related to formulations derived from anhydride MTHPA are presented
24 because those registered with MHHPA are very little different.

25

1 *Insert Figure 4*

2

3 *3.2 Study of ternary formulations*

4 Dynamic DSC analyses were performed on several “xELO – (100-x)EG – MTHPA” ternary
5 formulations in order to evaluate the temperature domains attached to the curing reaction. The
6 corresponding thermograms are presented in **Figure 5**. The binary ELO – MTHPA and
7 EG – MTHPA formulations exhibit specific exothermic reactions peaks attributed to the
8 epoxy – anhydride curing reaction. In case of reactive mixture based on ELO, the crosslinking
9 reaction starts at high temperature ($T \approx 80$ °C) and ends at 250 °C. The use of EG in place of
10 ELO shifts the reaction domain to lower temperature. Indeed, the reaction between EG and
11 MTHPA produces itself from 25 °C to 160 °C. This evolution is ascribed to higher accessibility
12 of oxirane groups to anhydride functions (Alam et al., 2014; Biermann et al., 2000; Habas et
13 al., 2013; Khot et al., 2001). The calorimetric response of ternary mixtures is characterized by
14 the presence of two partially overlapped exothermic peaks, the intensities of which are more or
15 less pronounced according to the initial composition of the formulation. They are easily
16 attributable to EG – MTHPA reactions for the lowest temperatures and to ELO – MTHPA for
17 the highest. A similar behaviour was already observed in the literature for systems based on
18 “DGEBA – epoxidized soybean oil – MTHPA” with increasing amounts of DGEBA (Altuna et
19 al., 2011).

20

21 *Insert Figure 5*

22

23 The total specific enthalpy of reaction (ΔH , in $J g^{-1}$) can be evaluated by direct integration of
24 the exothermic peaks. Then, it clearly appears that the progressive substitution of ELO by EG
25 in the reaction mixture provokes a slight increase of the released heat (**Figure 6**). Indeed, the

1 discrepancy between the extreme values corresponding respectively to ELO – MTHPA and
2 EG – MTHPA formulations remains limited (about 30 J g⁻¹) while the maximal value of
3 enthalpy does not exceed 350 J g⁻¹. In that sense, this behaviour is quite different from that
4 observed in the case of epoxy ternary formations based on ELO, EG and an amine hardener
5 (Mazzon et al., 2015). **Indeed, in this latter case, the crosslinking enthalpy was observed to**
6 **strongly increase with the EG content in the formulation. This evolution has been explained**
7 **and related to the parasitic consumption of amine functions by ester functions only present in**
8 **ELO. Such unwished reaction named "amidation" and described in other papers is not possible**
9 **here due to the nature of the hardener (Del Rio et al., 2011; Lee et al., 2008; Liu et al., 2005).**
10 **It is important to keep in mind that in the present study, the highest enthalpy value is well below**
11 **the minimal value above which the self-combustion of the sample cured with the diamine was**
12 **observed. In other words, anhydride-based formulations offer more comfortable and safe**
13 **manufacturing conditions.**

14

15 *Insert Figure 6*

16

17 Kinetic rheological experiments were performed at different constant temperatures to evaluate
18 the gel time of each formulation but also the minimum time required for the complete
19 consumption of all reactive components. **Figure 7a** shows the evolution of complex shear
20 modulus $G^* = G' + j G''$ of 80ELO – 20EG – MTHPA formulation as a function of time and
21 at two constant temperatures $T = 80\text{ }^\circ\text{C}$ and $140\text{ }^\circ\text{C}$. At the beginning of both analyses, moduli
22 G' and G'' have low values with $G'' > G'$. This means that the reactive mixture is still in the
23 liquid state and the reaction advancement remains limited. Then, the formation of a percolating
24 network induces the gelation of the system revealed by a sudden increase of both moduli. The
25 time related to this strong evolution is used to evaluate the gel time of the medium. As showed

1 before with calorimetry, a temperature increase boosts reactivity and a reduction of gel time.
2 After the gel point, the densification of the polymeric network provokes the pursuing of both
3 moduli increase. Then, the viscoelastic curves tend to a limit allowing the definition of the
4 minimal period required to achieve the curing reaction at the temperature used during the
5 experiment. **Figure 7b** presents the **different** gel times registered at $T = 80\text{ }^{\circ}\text{C}$ and $140\text{ }^{\circ}\text{C}$ **for**
6 several ternary formulations. Whatever the curing temperature is, the progressive replacement
7 of ELO by EG induces a reduction in gel time. Similar tendency is observed with the
8 vitrification time. These evolutions agree with the conclusions proposed after examination of
9 the DSC experiments. Compared to ELO molecules, EG units are more reactive with MTHPA
10 because they combine more accessible epoxy groups with higher molecular mobility. As
11 mentioned in introduction of this research, epoxy resins with high reactivity are often good
12 candidates for possible application in industry. Seen from this perspective, the most interesting
13 formulations are undeniably those with high amounts of EG **because they present a gel time**
14 **significantly lower than 3 minutes as required for the wished industrial application.**

15

16

Insert Figure 7

17

18 The thermomechanical properties of cured materials were investigated by dynamic rheology.
19 The analysis characteristic of the 10ELO – 90EG – MTHPA formulation after complete curing
20 is presented as example in **Figure 8a**. At low temperatures, the cured material is in the glassy
21 state. It is rigid and the storage modulus G' displays high values ($G' > 1\text{ GPa}$). Then, in the
22 “transition zone” the value of G' sharply decreases in a limited temperature range.
23 Simultaneously in the same area, the loss modulus G'' describes a peak commonly called
24 “ α peak” that is characteristic of the mechanical relaxation of polymeric network during the
25 glass transition. Taken at its maximum, the T_{α} temperature is evaluated close to $70\text{ }^{\circ}\text{C}$. Above

1 the glassy transition, the sample is in rubbery state. The storage modulus G' is still predominant
2 but its values are two decades lower than in the glassy state. **Figure 8b** resumes the T_g values
3 for several cured materials based on “xELO – (100-x)EG – MTHPA” reactive mixtures. **These**
4 **data reveal that the glass transition temperature of the cured material is poorly dependent on the**
5 **respective proportions of ELO and EG in the initial reactive mixture.**

6

7

Insert Figure 8

8

9 A possible explanation for this behavior can be found by examining the structure of the network
10 formed during curing. The smaller size of EG compared to ELO would suggest higher
11 crosslinking density, so higher final properties for cured materials with high amount of EG. But
12 in ELO, oxirane functions derived from epoxidation of native double bonds are much close to
13 each other. Each epoxy cycle is able to establish two covalent bonds with anhydride units. So
14 the distance between crosslinking points in cured network based on ELO is potentially lower
15 than in those based on EG. **Figure 9a** shows a schematic representation of an “ELO – anhydride
16 (A)” crosslinked structure, with different mesh sizes: 1) based on close epoxy groups and 2)
17 including "glycerol" core.

18

19

Insert Figure 9

20

21 The introduction of an increasing proportion of EG in the reactive formulation should increase
22 the density of the network due to the smaller size of the epoxy prepolymer. But mesh size could
23 be larger (**Figure 9b**). In conclusion mesh average sizes in “ELO – anhydride” and
24 “EG – anhydride” are likely to be equivalent what could justify that the initial composition has
25 slight influence on glass transition temperatures. **Such hypothesis seems to be supported by the**

1 direct comparison of the thermomechanical profiles of two cured materials (Figure 8a), the
2 former being rich in ELO, the latter in EG. In the rubbery plateau, both cured formulations
3 present almost the same value of the storage modulus. According to the law of rubber elasticity,
4 this means that the crosslink densities of these materials are quite close (Everaers and Kremer,
5 1995; Treloar, 1975).

6

7 *3.4 Characterization of foaming agents*

8 In order to produce polymeric thermosetting foams within short period, a polymeric formulation
9 rich in EG must be retained. Then, the formulation 10ELO – 90EG – MTHPA characterized by
10 very short gel times (i.e. close to 1 minute at $T = 140\text{ }^{\circ}\text{C}$) and good thermomechanical
11 properties after curing ($T_g > 70\text{ }^{\circ}\text{C}$), was selected. According to the method proposed by Pan
12 (Pan et al., 2011) the biobased content of this reactive mixture is about 38.6 %. A foam
13 production from a polymer matrix requires the addition of a blowing agent but its choice is not
14 trivial since a good equilibrium between the gas emission and the crosslinking reaction is
15 indispensable (M. O. Okoroafor, 1995; Mazzon et al., 2015; McElhanon et al., 2002; Takiguchi
16 et al., 2008). Among the different possible chemical agents, we decided to investigate the
17 interest of sodium bicarbonate (NaHCO_3 , SB) and potassium bicarbonate (KHCO_3 , PB).
18 Indeed, upon heating, these non-toxic compounds decompose producing carbon dioxide and
19 water in gaseous state (Scheme 1).

20

21

Insert Scheme 1

22

23 The range associated with the thermal decomposition of both bicarbonates was investigated by
24 thermogravimetric analysis in dynamic mode. Sodium bicarbonate decomposes between $80\text{ }^{\circ}\text{C}$

1 and 190 °C while the thermal decomposition of potassium bicarbonate is observed at higher
2 temperature between 100 °C and 195 °C (Figure 10).

3

4

Insert Figure 10

5

6 In both cases, a significant residual weight is observed, the value of which (63 % for SB and
7 69% for PB) agrees with the reaction scheme (i.e. production of Na_2CO_3 and K_2CO_3). To
8 evaluate which blowing agent is the most adequate with the reactive polymeric formulation, we
9 reported in Figure 11 the calorimetric behaviours of the reactive formulation 10ELO – 90EG –
10 MTHPA and those of SB and PB. All these experiments were recorded in the same conditions.
11 The crosslinking reaction is detected through the presence of an exothermic peak while the
12 respective decompositions of the blowing agents appear as endothermic phenomena. At first
13 sight, the use of SB seems to be preferable instead of PB because its decomposition thermal
14 range overlaps in a better way with that specific of the resin curing.

15

16

Insert Figure 11

17

18 But, other aspects must be considered such as the evolution of the resin viscosity with
19 temperature confronted with the gas generation. Figure 12 shows the viscosimetric profile of
20 the pure reactive mixture superimposed with the derivative of weight loss curve of each foaming
21 agent registered with the same heating ramp. The gelation of the only resin detected by the
22 divergence of the viscosity occurs in a temperature range for which SB start to decompose. At
23 first sight, this situation may appear ideal for the foaming process since the bubbles are likely
24 to be trapped (Hwang et al., 1994; McElhanon et al., 2002; Tungare et al., 1988). Nevertheless,
25 practical trials revealed that the crosslinking process is delayed when SB is added to the initial

1 resin. An apparent lack of curing is even observed since the resin is still sticky. These unwished
2 characteristics are likely provoked by the heat consumption during SB decomposition and so,
3 a reduction of the real curing temperature. Further possible factor is the production of water
4 molecules that consume anhydride molecules what affects the wished epoxy-hardener reaction.
5 Then, it appears that the blowing agent decomposition should take place in the last part of the
6 thermal domain characteristic of the resin curing so as to limit the parasitic influence of the
7 endothermic gas production on the temperature-activated crosslinking reaction.

8
9 *Insert Figure 12*

10

11 Both **Figures 11** and **12** show that such situation is encountered with the use of potassium
12 bicarbonate. Then, this latter compound was finally retained as foaming agent in order to
13 produce lightweight rigid foams.

14 In order to evaluate the kinetics of PB decomposition, different isothermal thermogravimetric
15 analyses of this compound were registered for temperatures comprised between 80 °C and
16 180 °C. The corresponding data presented in **Figure 13** demonstrate that the decomposition rate
17 increase with temperature. A process temperature of 180 °C seems adequate for the complete
18 gas production in very short delays.

19

20 *Insert Figure 13*

21

22 *3.5 Characterization of final materials*

23 Trials for production of macroscopic epoxy foams were undertaken at $T = 180\text{ °C}$ with a fixed
24 time of 3 minutes. The amount of foaming agent ranged from 10 to 70 parts for 100 parts of
25 epoxy formulation, corresponding to a weight percentage comprised between 9.1 and 41.1%

1 wt. **Figure 14a** clearly shows that the introduction of 10 parts of BP produces compact samples
2 due to a quite reduced foaming process. Then, it is observed that that the final volume of the
3 foam increases with the initial quantity of PB. But, please note that for PB amounts higher than
4 50 parts, the foam is made with big inner bubbles and is even quite brittle. Our trials lead to the
5 conclusion that the **highest** value of PB amount is 50 parts. In this case, the gas production self-
6 stops after 3 minutes at $T = 180\text{ }^{\circ}\text{C}$ and the expansion is quite acceptable.

7

8

Insert Figure 14

9

10 **Figure 14b** resumes apparent density of prism-shaped samples cut in the core of each foam for
11 an initial PB comprised 20 and 50 parts. **All registered values are lower than 0.10 g/cm^3 .**
12 **However, a big dispersion of density values is observed with the materials containing 20 parts**
13 **of PB and is probably a consequence of the samples heterogeneity before cutting process. The**
14 **apparent density decreases with an increasing amount of foaming agent and a better**
15 **reproducibility is obtained for the foams produced with the higher PB amounts.**

16 The same foams were also characterized by dynamic mechanical analysis in compressive mode
17 and as a function of temperature. **Above a critical temperature,** the E' curve **decreases faster** due
18 the material transition from the glassy state to the rubbery state. **This critical temperature**
19 provides a good evaluation of the T_g of the polymer matrix due to the value of the compressive
20 frequency used for this thermomechanical analysis ($f = 1\text{ Hz}$) (Chen et al., 2014; McElhanon et
21 al., 2002; Sankaran et al., 2006). The exploitation of DMA results is resumed in **Figure 15. The**
22 **T_g of the different foams is comprised between 80 and $87\text{ }^{\circ}\text{C}$. Then, it seems not to be dependent**
23 **on the amount of PB present in the initial mixture as found by Stefani with another kind of**
24 **epoxy foam (Stefani et al., 2003). Please note that this T_g value is higher than the minimal value**
25 **required for the wished application for all formulations studied.**

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Insert Figure 15

This point is particularly important because the first tests conducted with sodium bicarbonate revealed that this blowing agent significantly affected the foam thermomechanical properties by consuming heat at the expense of the resin crosslinking degree. In other words, by decomposing at higher temperature PB seems once more a better choice with our epoxy formulation.

To complete the mechanical characterisation section, compressive tests were also performed with the different foams produced with a PB content comprised between 20 and 50 parts Figure 16a depicts as example a typically stress–strain curve registered on a sample obtained with 30 parts of PB. This curve can be roughly divided into three different zones. The first one is characterized by a linear evolution of stress with strain. It corresponds to the linear elastic domain. It allows the evaluation of the “apparent” Young’s modulus of the foam, mainly related to the mechanical rigidity of cells walls. In the second zone, the collapse of cells walls induces the formation of a plateau-like region in the stress–strain curve. The compressive strength (σ_c) is measured at 10 % strain for further comparison between all samples. Finally, at higher strain, opposed cell walls touch each other what induces a strong increase of the curve. This last step is usually named “densification” (Avalle et al., 2001; Deschanel et al., 2009; Gibson and Ashby, 1982; Greco and Lionetto, 2009; Pampolini, 2010). Figure 16b summarizes the results of all compressive tests. These data reveal that the compression modulus value decreases with the amount of foaming agent. The same trend is also observed for the compressive strength. However, the foams produced with 20 parts of PB are characterized by a big dispersion of their mechanical compressive properties, probably due to their poor homogeneity. These results perfectly agree with density data presented above. Indeed, the gradual transition from a solid

1 material to a cellular structure induces a classical reduction in compressive mechanical
2 properties. The same evolution was observed by Altuna (Altuna et al., 2015) in case of
3 polymeric foams based on epoxidized soybean oil and MTHPA hardener. According to the
4 classification proposed in literature (Basso et al., 2011; Guo et al., 2000) foams with 20 and 30
5 parts of PB are defined as “rigid” while those obtained with 40 and 50 parts of foaming agent
6 are “semi-rigid”.

7
8 *Insert Figure 16*

9
10 Compared to the previous materials derived from the same epoxy compounds but using
11 isophorone diamine as hardener and SB as blowing agent (Mazzon et al., 2015), this new family
12 of foams offers real added value. In particular, due to the reduced exothermicity of the
13 crosslinking reaction, it does not require the use of any additive acting as heat absorber on the
14 opposite of the first generation. Moreover, the ultimate properties of the foams described here
15 are significantly superior to those previously described. For instance, the final Tg is 30°C higher
16 while the mechanical rigidity is increased by nearly 60%. It is important to note that these
17 improvements were not obtained at the expense of the density since in this research, it was
18 comprised between 0.05 and 0.08 g/cm³ against 0.17 g/cm³ for the best candidate developed in
19 our previous study. **Considering biobased epoxy foams produced from other resources, it is**
20 **worthy to note that the Tg of our materials are significantly higher than that obtained by**
21 **Khundamri and al. (close to -6 °C) with foams synthesized from various mixtures of epoxidized**
22 **soybean oil (ESO) and epoxidized mangosteen tannin cured with the same hardener (MTHPA)**
23 **used in our research (Khundamri et al., 2019). In this latter case, the absence of catalyst in the**
24 **reactive formulation but also the lower functionality of ESO (Kumar et al., 2017a) are likely at**
25 **the origin of this discrepancy. The macroscopic properties of our optimal foam are also**

1 significantly higher than those recently described by Agnihotri et al. with a foam produced from
2 the mixture of ESO, epoxidized pine oil and DGEBA with polyamines as hardener. Indeed, in
3 this study the maximal Tg is close to 56 °C while the minimal density is 0.53 g/cm³ (Agnihotri
4 et al., 2019). The elimination of ESO in the formulation to the benefit of DGEBA is a good way
5 for increasing the thermomechanical properties since the Tg rises up to 97 °C. But, the time
6 required for the curing (24 h) remains much higher than that described here. In our study, the
7 controlled addition of EG to ELO made it possible the reduction of the process time to 3
8 minutes. This approach offers a real implementation of the solution explored by Altuna et al.
9 from the mixture of ESO, MTHPA and SB since in this last case, gel times higher than 20
10 minutes are reported (Altuna et al., 2015).

11

12 **4. CONCLUSIONS**

13 This work shows that it is possible to produce epoxy foams for a structural purpose in a few
14 minutes using different chemical compounds derived from plant-oil and an inert blowing agent.
15 The proposed methodology emphasizes that several factors must be considered such as the
16 thermal domains associated with the crosslinking of the polymer formulation and the
17 decomposition of the blowing agent respectively. Based on our results, it is preferable to choose
18 a blowing agent the action of which occurs when the crosslinking has already reached an
19 advanced stage. Indeed, it is possible to trap the gas produced in the gelled polymer matrix
20 without affecting its cross-linking degree. In addition, the kinetics associated with each of these
21 phenomena must be carefully determined. In our study, the low reactivity of an epoxidized
22 vegetable oil is compensated by the use of epoxidized glycerol that presents oxirane groups
23 more accessible to the hardener units. This study also underlines that the use of several
24 experimental techniques is of first importance to identify the most performing formulation. The
25 **best one** is based upon the 10ELO – 90EG – MTHPA reactive mixture and ideally contains 30

1 parts of PB for 100 parts of resin (\Leftrightarrow 23.1% w/w). After 3 min of curing at $T = 180\text{ }^{\circ}\text{C}$, the
2 foam derived from this formulation combines good mechanical performances ($T_g > 80\text{ }^{\circ}\text{C}$, high
3 mechanical rigidity) with a quite low density (0.065 g/cm^3). Such mixture allows the description
4 of short processing times thus meeting the requirements of an industrial production line. All
5 these scientific elements but also the raw materials prices and their factual availability make it
6 realistic a possible valorisation of this plant-oil based formulation for producing foams at larger
7 scale.

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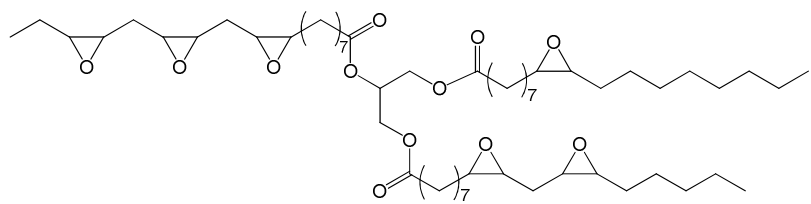
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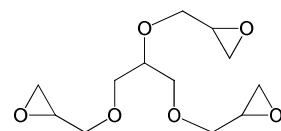
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Epoxidized Linseed Oil (ELO)



Epoxidized Glycerol (EG)

Figure 1. Epoxy prepolymers used in this study.

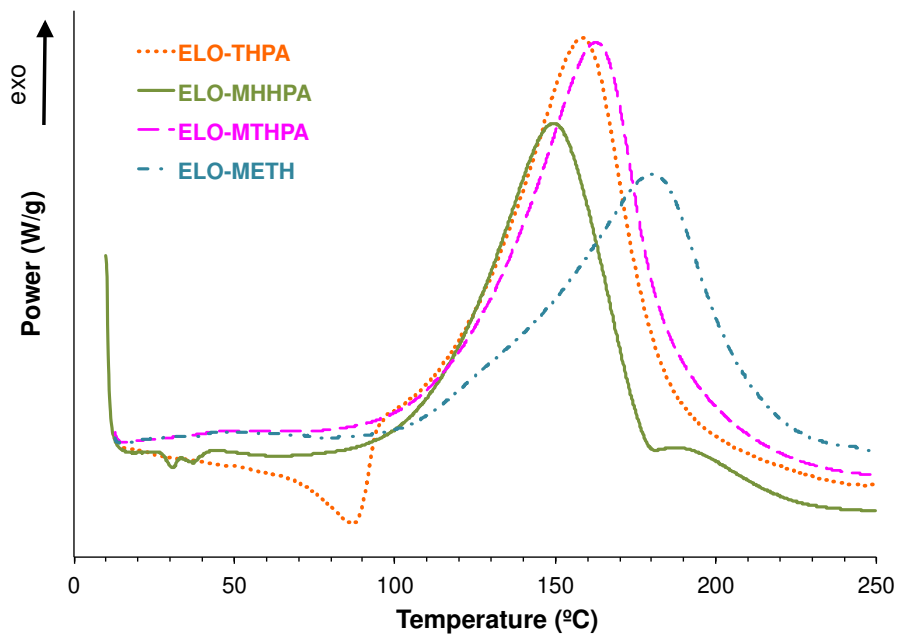


Figure 2. Dynamic DSC scans of several “ELO – anhydride” reactive mixtures performed under nitrogen with a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$.

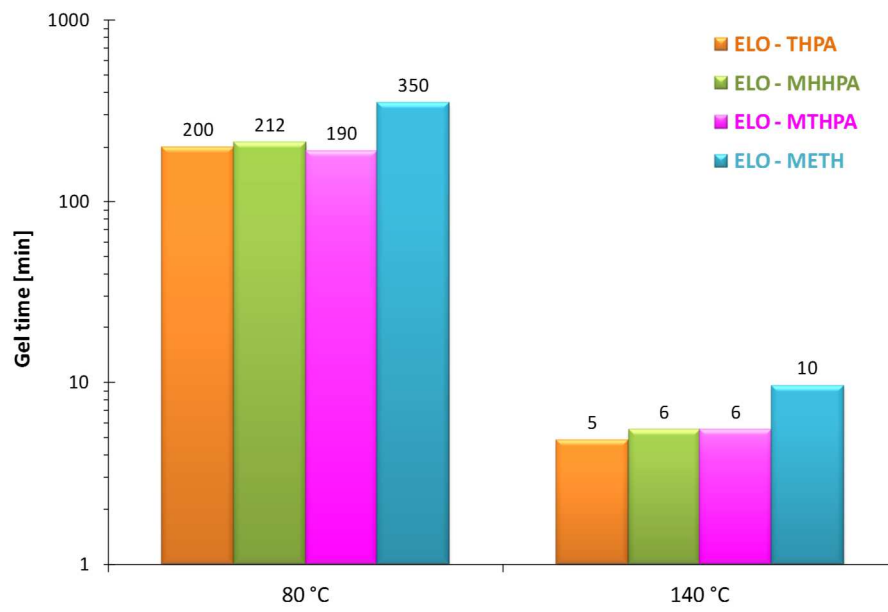


Figure 3. Gel times of several reactive mixtures “ELO – anhydride” at T = 80 °C and 140 °C.

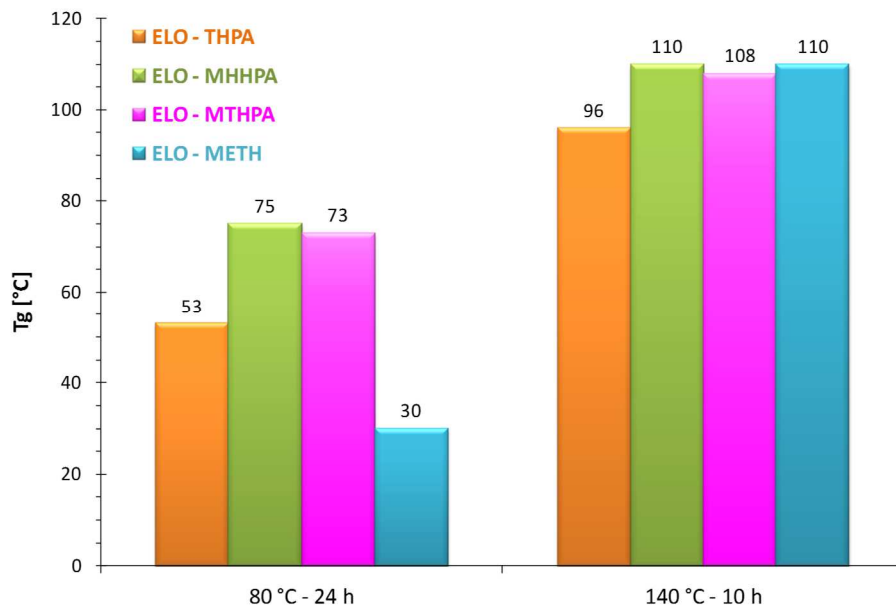


Figure 4. Glass transition temperatures of cured materials based on “ELO – anhydride” mixtures after curing at $T = 80\text{ }^{\circ}\text{C}$ during 24 hours or at $T = 140\text{ }^{\circ}\text{C}$ during 10 hours.

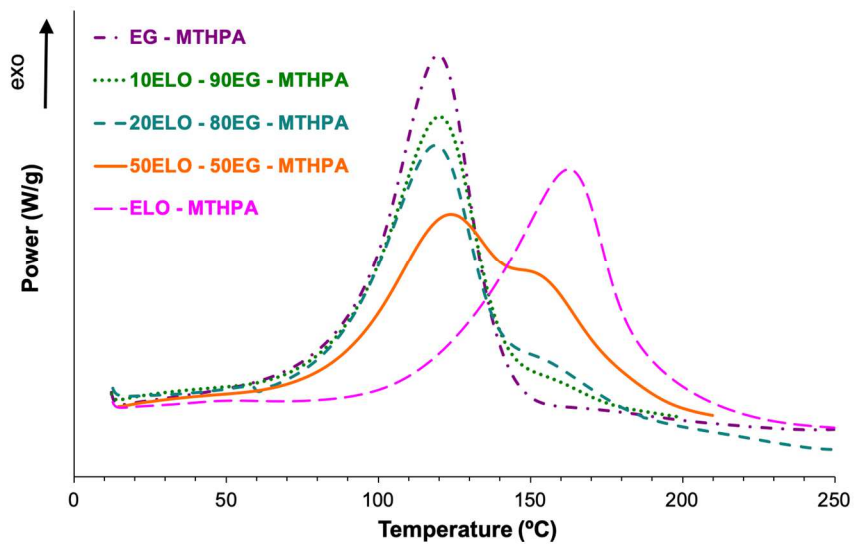


Figure 5. Dynamic DSC scans of several binary and ternary epoxy reactive mixtures performed under nitrogen with a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$.

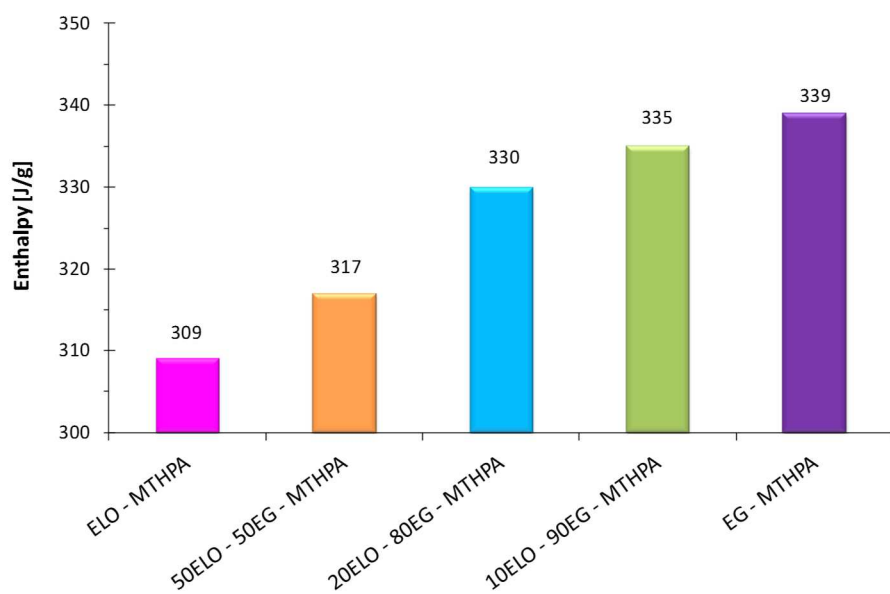


Figure 6. Influence of initial respective proportion of EG and ELO on enthalpy of crosslinking reaction released during curing.

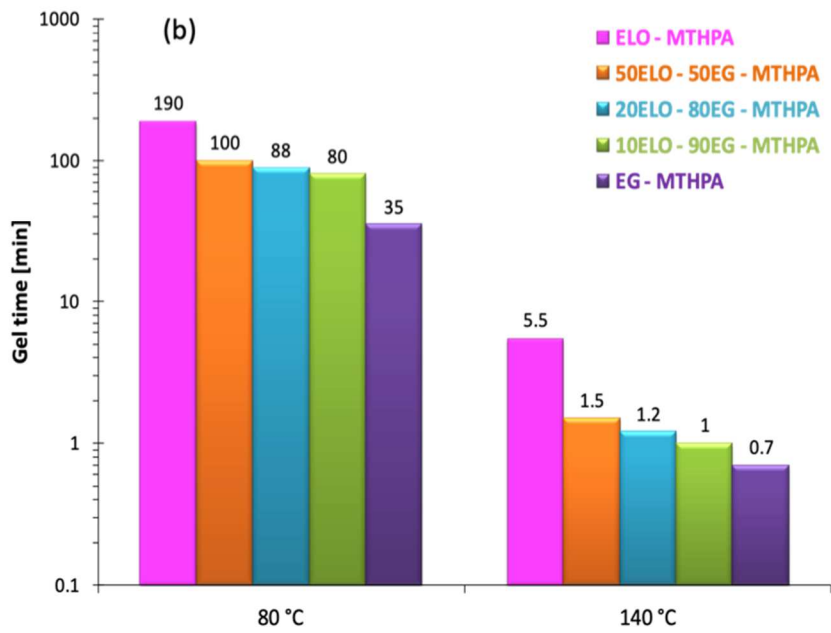
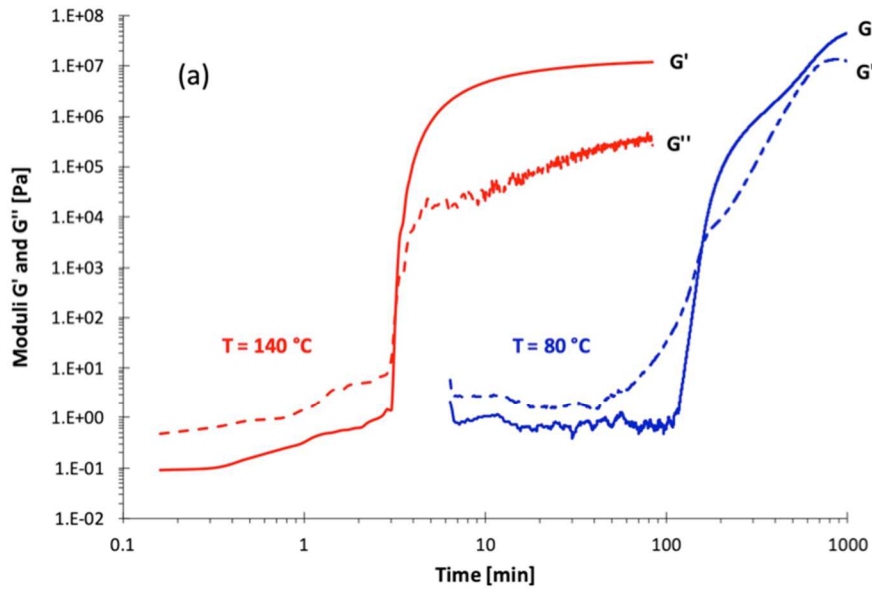


Figure 7. (a): Kinetic rheological analyses of 80ELO – 20EG – MTHPA reactive mixture and **(b):** gel times of other ternary mixtures registered at T = 80 °C and 140 °C .

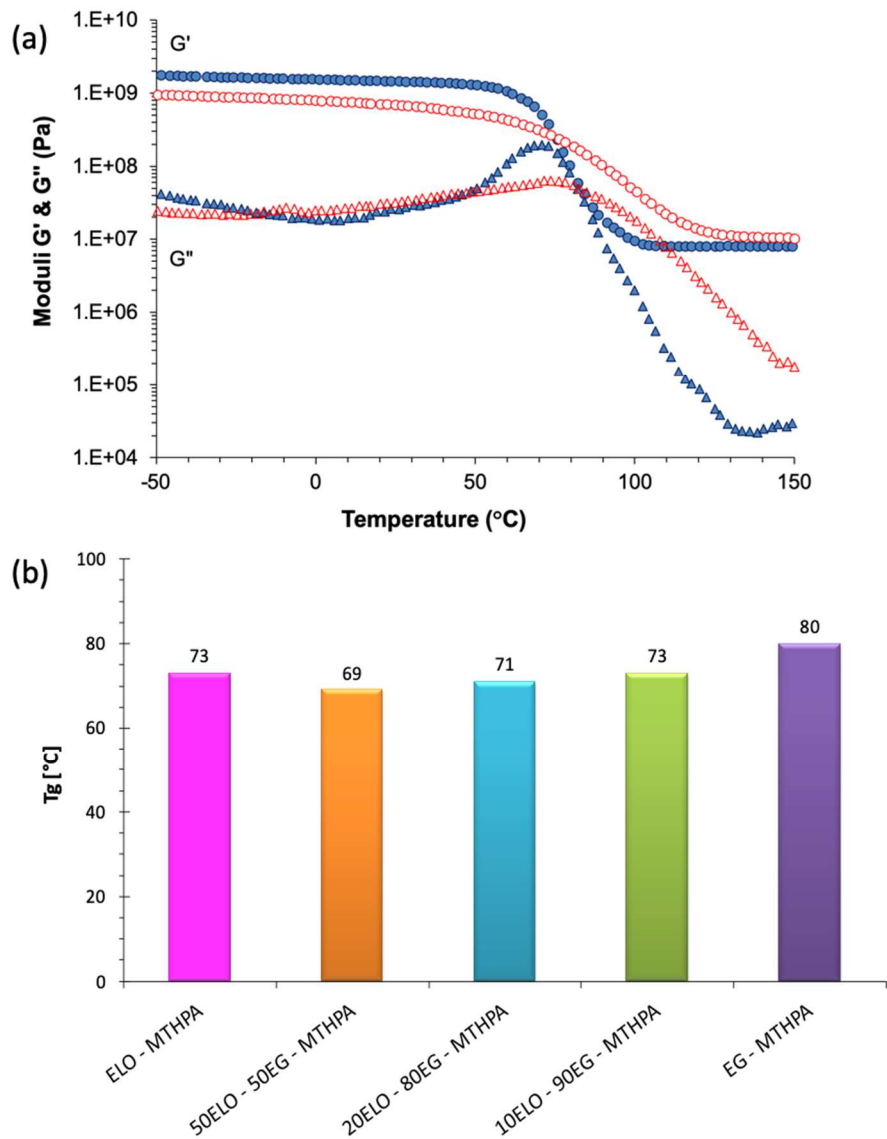


Figure 8. (a): Thermomechanical analyses of cured materials based on ELO-MTHPA (open symbols) and 10ELO – 90EG – MTHPA (full symbols) formulations.

(b): evolution of the Tg with the initial chemical composition of “xELO – (100-x)EG – MTHPA” reactive mixtures after curing.

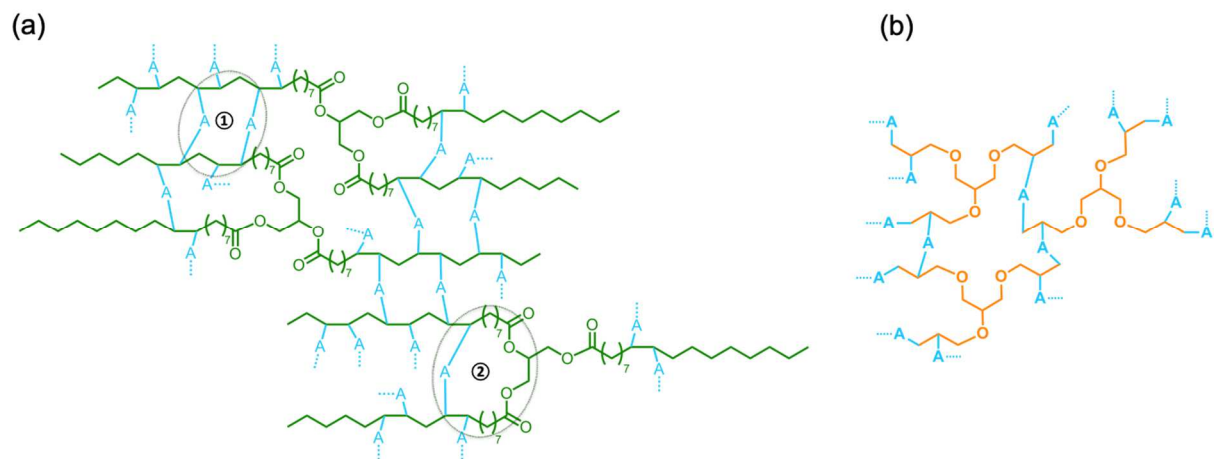


Figure 9. (a) : Representation of ELO – anhydride (A) and (b) : EG – anhydride networks after curing.

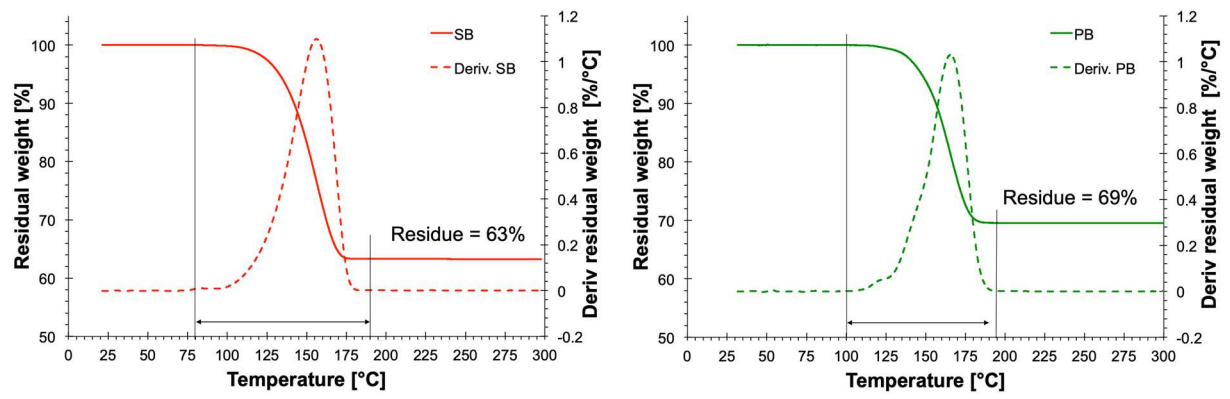


Figure 10. TGA (solid line) and DTG (dashed line) of sodium bicarbonate (left) and potassium bicarbonate (right) under air at the heating rate of 5 °C min⁻¹.

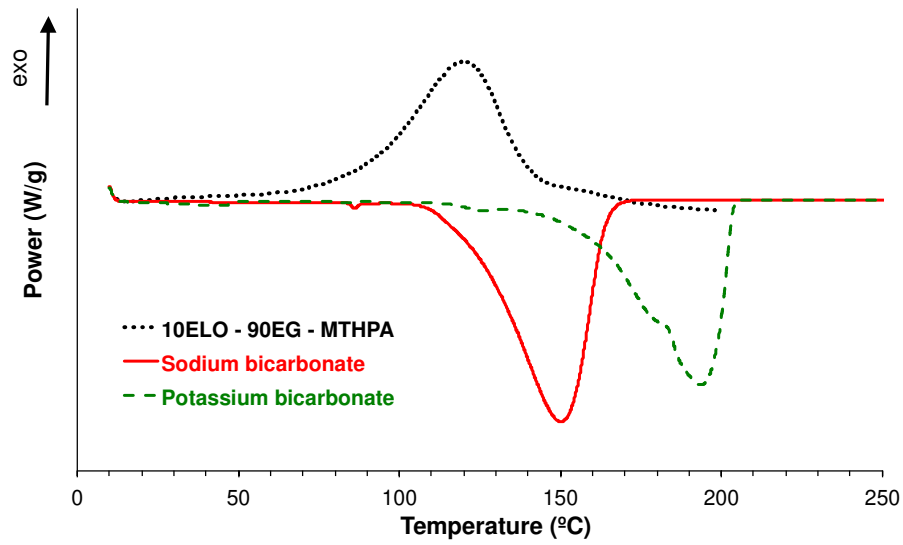


Figure 11. Dynamic DSC scans of epoxy reactive mixture and foaming agents (SB and PB) performed under nitrogen with a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$.

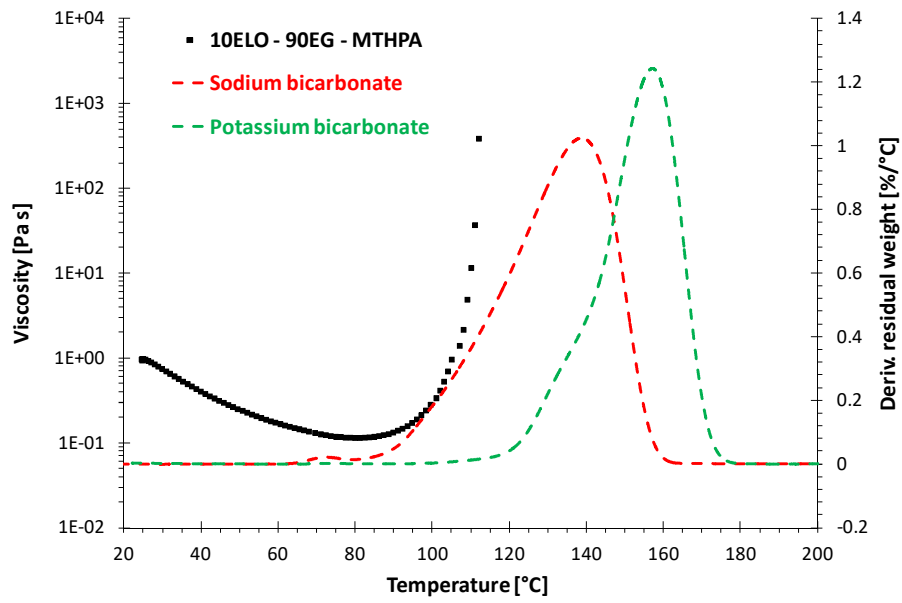


Figure 12. Epoxy reactive mixture viscosity evolution with temperature (on the left) and DTG curve of foaming agents SB and PB (on the right).

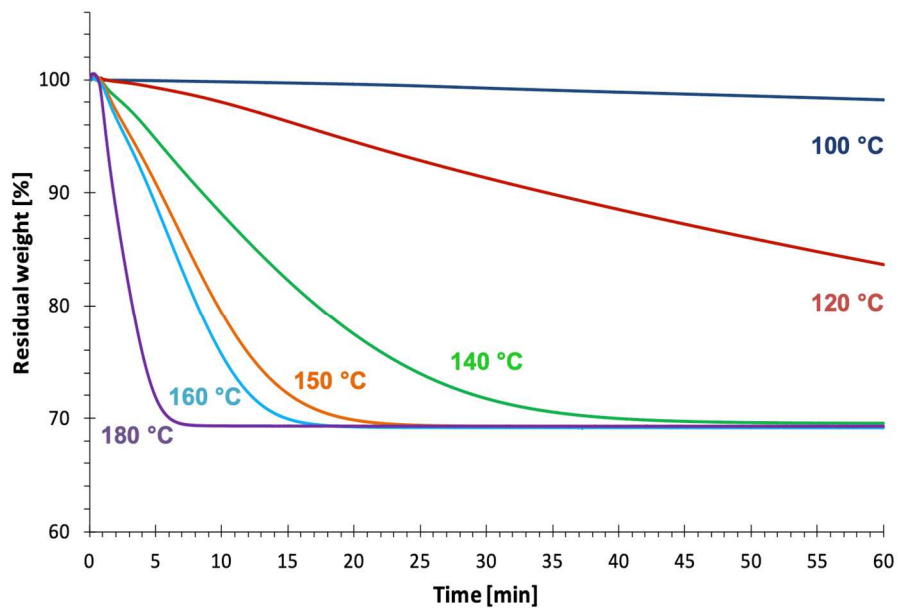


Figure 13. Isothermal TGA analyses of potassium bicarbonate under air at several temperatures between $T = 100\text{ °C}$ and 180 °C .

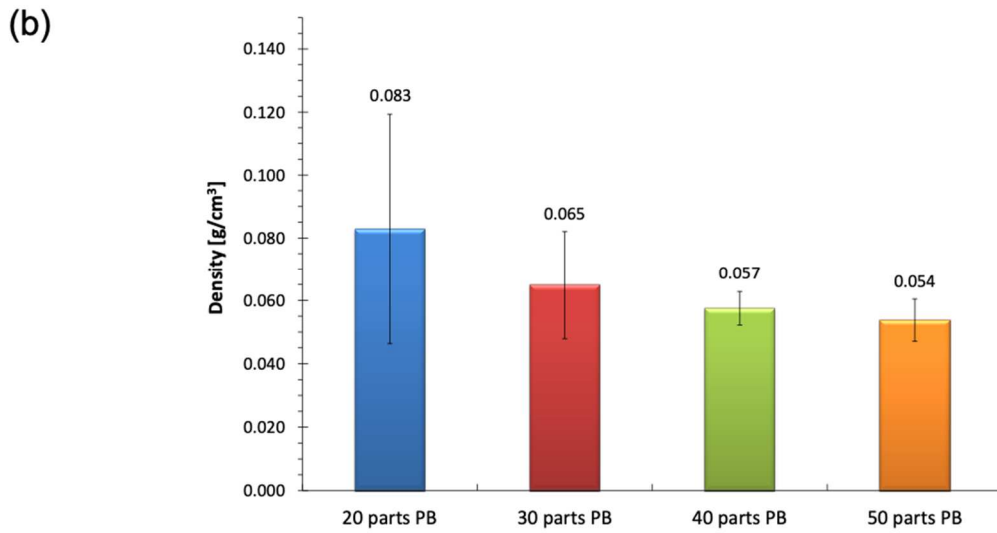
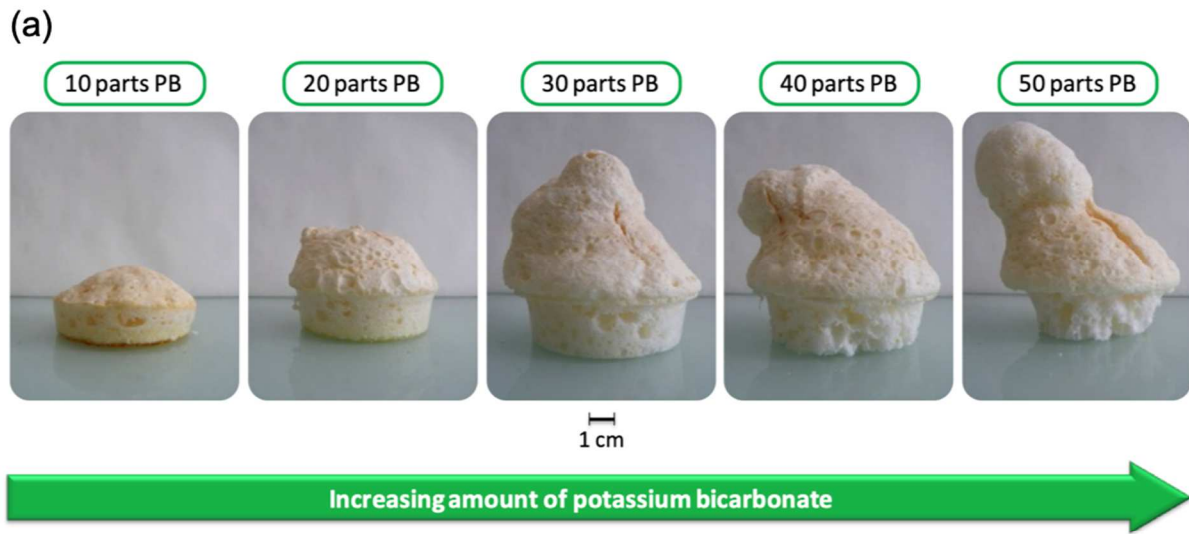


Figure 14. Overview of foams produced (during 3 minutes at $T = 180\text{ }^{\circ}\text{C}$) with an increasing amount of foaming agent and corresponding density values.

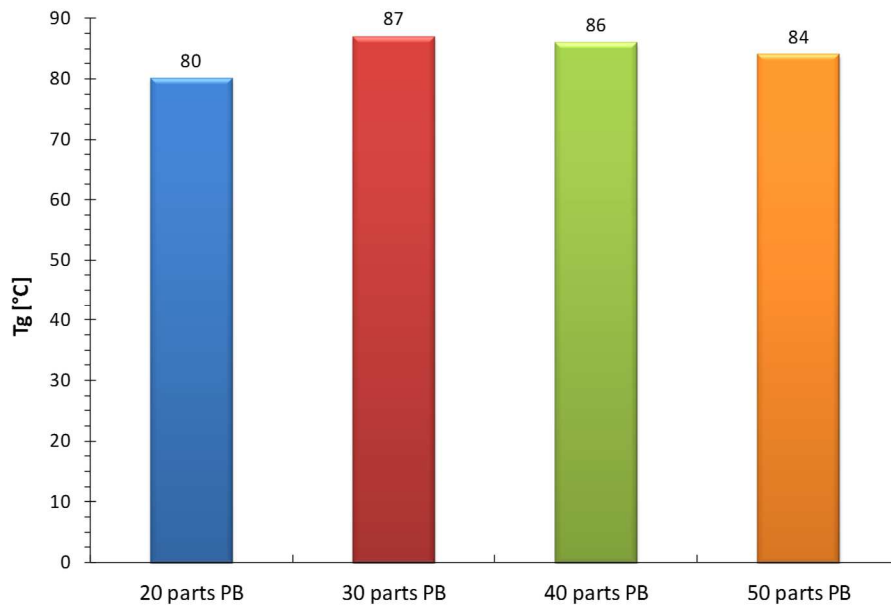


Figure 15. T_g values of foams produced during 3 minutes at T = 180 °C with an increasing amount of foaming agent.

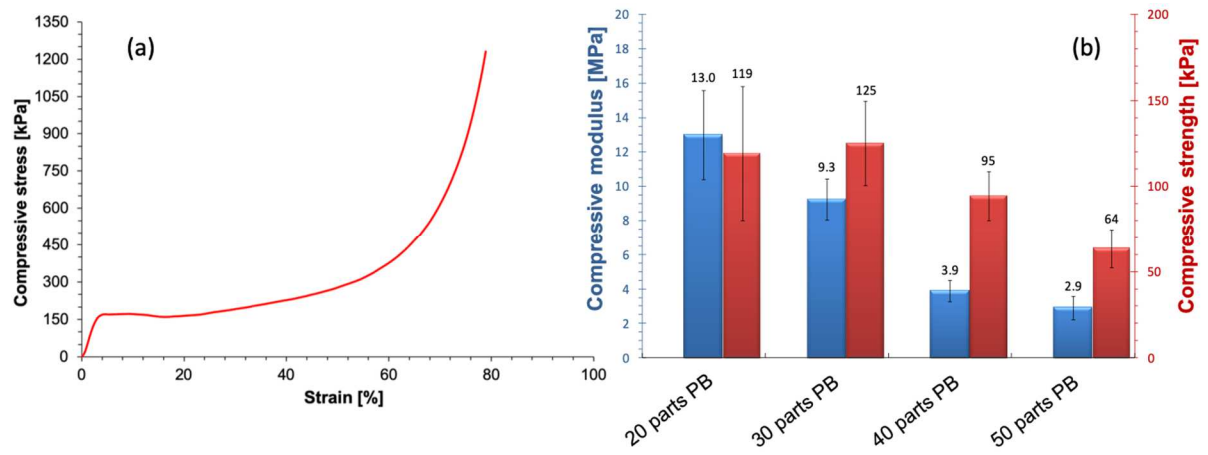


Figure 16. (a) : Compressive stress – strain curve of foam obtained in 3 minutes at $T = 180\text{ }^{\circ}\text{C}$ with 30 parts of foaming agent - (b) : Influence of foaming agent amount on compressive modulus and strength of foams produced in the same conditions.

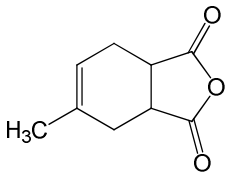
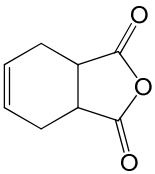
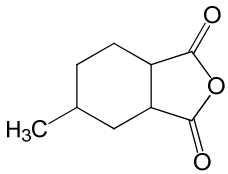
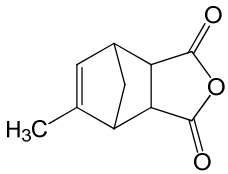
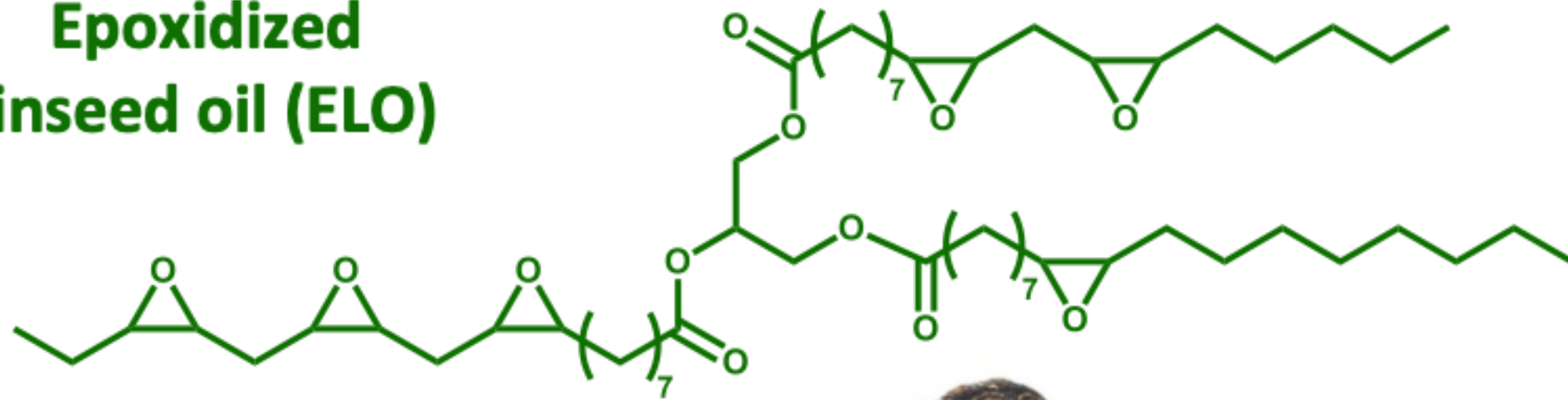
Name	Formula	CAS number	Molecular weight (g/mol)	Melting temperature (T _m , °C)
Methyl tetrahydrophthalic anhydride (MTHPA)		3425-89-6	166.2	-15
Tetrahydrophthalic anhydride (THPA)		935-79-5	152.2	102
Methyl hexahydrophthalic anhydride (MHHPA)		19438-60-9	168.2	-15
Nadic methyl anhydride (METH)		25134-21-8	178.2	-50

Table 1. Anhydride hardeners retained in this work.

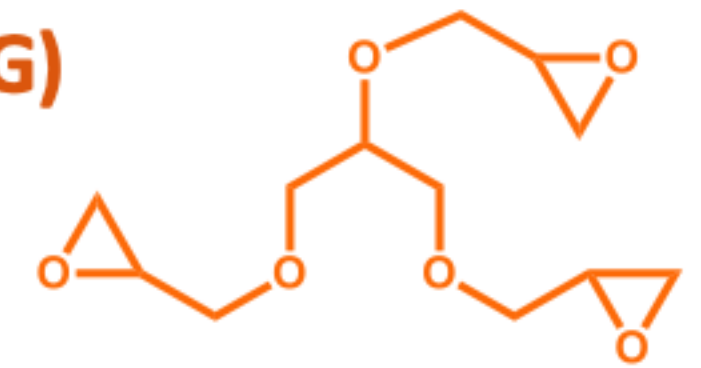
Epoxidized linseed oil (ELO)



Low reactivity



Epoxidized glycerol (EG)



High reactivity



Ternary formulations



$x \text{ ELO} - (100-x) \text{ EG} - \text{hardener}$



Increasing amount of foaming agent