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Guilhem Coste, Claire Negrell, Luc Averous, Sylvain Caillol. Green synthesis of biobased soft foams by Aza-Michael reaction. *ACS Sustainable Chemistry & Engineering*, 2022, 10 (26), pp.8549-8558. 10.1021/acssuschemeng.2c01885 . hal-03712818

HAL Id: hal-03712818

<https://hal.science/hal-03712818>

Submitted on 4 Jul 2022

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Green synthesis of biobased soft foams by Aza-Michael reaction

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Keywords: Foams; Biobased polymers; Aza-Michael; acrylate; amine; blowing agent

Abstract

The world has been facing a major resources crisis for few decades. In order to tackle with such environmental issues, new solutions have to be found in order to replace fossil resources by more sustainable, biobased resources. One of the most promising biobased resources are vegetable oils which are used as building blocks for renewable polymers synthesis. Industrial productions and the corresponding chemical structures make oleo-chemistry very attractive. Nevertheless, such building blocks have to compete with usual petrol-based monomers. Hence, this work focuses on the development of new foams in order to replace toxic isocyanate-based polyurethanes foams. Different efficient soft foams were obtained for the first time by Aza Michael reactions, using acrylated soybean oils and biobased amines, with an original chemical blowing system. Properties of the foams have been studied in order to determine the influence of the different structures in terms of morphologies, glass transition, hardness or deformation.... Homogeneous open cells foams with a pore size from 0.1 to 0.5 mm were obtained. Flexible foams were obtained with glass transition from -20 °C to -7 °C. These soft foams demonstrated a time recovery about few seconds and exhibited similar properties to equivalent commercial fossil-polyurethane foams, without the use of highly toxic chemicals.

I. Introduction

Nowadays, the development of polymer materials has been facing multiple challenges such as the depletion of some fossil fractions and globally, an increasing impact on the environment associated to an increasing lack of acceptance from the society and a « plastic-bashing ». In this current context, the development of new and greener polymeric materials which perform better with a lower environmental impact from cradle to grave than their traditional fossil-based equivalents, is now a strong priority.

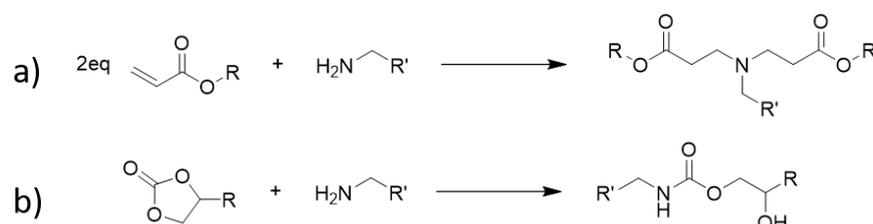
Biobased polymers are defined as polymers obtained more or less directly from biomass, *i.e.* from all living organisms, with a positive ¹⁴C content.¹ Interest in biobased polymers has grown exponentially in recent decades due to the drive to reduce greenhouse gas emissions and to improve the life-cycle analysis (LCA) of the materials. Since several decades, the production of biobased monomers for sustainable plastics or building blocks has been widely developed to design new macromolecular architectures such as polyurethanes, polyesters or polyolefins combining different disciplines such as biotechnology, chemistry and materials science.²⁻⁵

Among the different available renewable resources, vegetable oils and the corresponding fatty acids from the oleo-chemistry have emerged as attractive candidates to replace some fossil-based building blocks due to their different chemical structures, and their large availability.⁶⁻⁹ Taking into account the variety of glycerides and fatty acids, a large panel of chemical structures with different active

chemical groups are now available.¹⁰ Their structures could also be more or less easily modified since they are based on *e.g.*, unsaturated bonds. Hydroxylated,^{11,12} epoxidized,^{13,14} cyclocarbonated,^{15,16} siloxane modified¹⁷ or acrylated glycerides^{18–22} were synthesized from these double bonds even at an industrial level. For instance, the synthesis of these acrylated derivatives are easily obtained by the ring opening of the epoxidized glycerides using acrylic acid.²³

Glycerides derivatives have been largely used to produce polyurethanes (PUs). PUs are indeed, a major polymer family mainly obtained by reaction between polyisocyanates and polyols, with around 22 million tons produced in 2016.²⁴ Around 66% of PUs are foams with open cells foams obtained by reaction between isocyanate and water to produce carbon dioxide as a chemical blowing agent.^{25,26} The main drawback in the PUs fabrication is the used of highly toxic isocyanates^{27,28} As the regulation is changing and the isocyanate could be banned in the future, different pathways have been studied and developed to produce *e.g.*, the so-called non-isocyanate polyurethane (NIPU). The most explored route is the aminolysis of cyclic carbonate to obtain polyhydroxyurethanes (PHUs, scheme 1 b).^{29–33} Despite interesting final properties, the reactivity of amine/cyclocarbonate is much lower than the conventional isocyanate/hydroxyl reaction. The reactivity is the main parameter during foam synthesis. The gas need to be trapped in the polymer matrix before migrating out from the polymer. Hence, the reactivities of blowing and polymerization have to be concomitant. Hence, different strategies have been proposed to improve this reactivity, with the use of dithiocarbonates, different catalysts or by increasing the carbonate ring size.^{34–41} NIPU foams have already been synthesized. Nevertheless, these foams needed high temperature, a long curing time or the presence of catalyst. For example Blattman *et al.* synthesized a foam at 80°C in 14 hours. Cornille *et al.* obtained a foam at room temperature using 5-membered cyclic carbonate with highly reactive amine and a catalyst in two days.⁴² Finally, all these results highlighted the need of a more reactive system.

Recently, Aza-Michael reaction has been presented as another great alternative to replace the formation of conventional PUs. Michael reaction was named after Arthur Michael who discovered the reaction between a nucleophile (Michael donor) and an unsaturated bond (Michael acceptor).⁴³ The Aza-Michael reaction is derived from the Michael reaction and involves an amine as Michael donor and a double bond as Michael acceptor (scheme 1 a). In this context we can notice, for instance that the reactivity of the couple acrylate/amine is higher than the amine/cyclocarbonate reaction, which used for PHUs synthesis.^{37,44–46} Recently, Aza-Michael reaction has gained interest since this reaction fits with several green chemistry principles. Indeed, the Aza-Michael reaction has 100% atom economy and can be employed at room temperature.⁴⁷ Thus the reaction has been widely used to synthesize various polymers for multiple applications.^{48–52}



Scheme 1: a) Aza-Michael reaction, b) Aminolysis of a cyclic carbonate

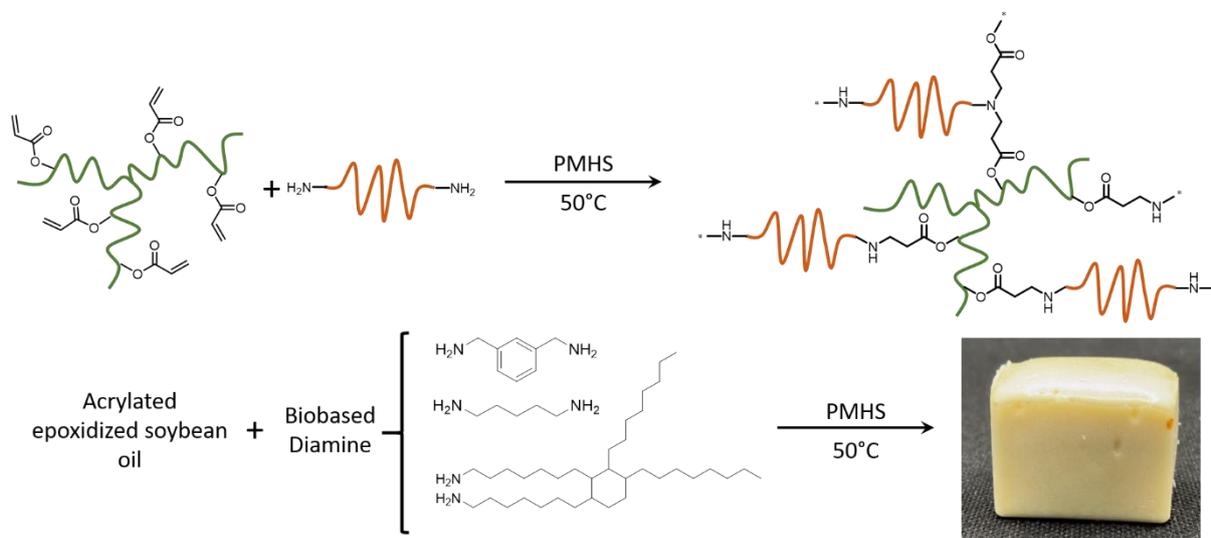
Nevertheless, the Aza-Michael reaction does not produce blowing agent to generate cells into the foam as *e.g.*, the reaction of isocyanate with water. In the literature, different pathways were developed to replace PU. Thus external blowing agent were required to produce non-isocyanates PU foams.^{42,53–55} Indeed, Cornille *et al.* used the polymethylhydroxysiloxane (PMHS) reaction with amine to produce dihydrogen.⁴² Blattman *et al.* used a physical blowing agent to produce a foam for NIPU

matrix.⁵³ In this frame, our groups recently published different reviews with several ways to blow different polymeric foams⁵¹. More recently, Moni *et al.* published an interesting review about self-blowing foams mostly at high temperature.⁵⁶ PMHS has been chosen for this study since it has been already described as a blowing agent under mild conditions and it is not a fossil carbon-based compound.



Scheme 2: Blowing reaction between the PMHS and the amine

The present paper reports the first synthesis of soft Aza-Michael foams using biobased Michael donors and acceptors and their characterizations in the goal to obtain foams with equivalent properties to PU ones. Acrylated epoxidized soybean oil has been selected as Michael acceptor. Then, the impact of three different biobased diamines structure was analyzed. The three selected diamines were the cadaverine, a fatty acid dimer diamine (DDA) (called Priamine[®] 1071 from Croda) and the *m*-xylylenediamine (MXDA).⁵⁷ The cadaverine was chosen for its simple structure and short carbon chain between the amine functionality. The DDA was selected because of the long aliphatic chain which should improve the flexibility of the foam. The longer carbon chain between the amine compared to the cadaverine was another interesting parameter studied. Finally, the MXDA was chosen for the aromatic ring which improves the hardness and the glass transition. To our knowledge no study has reported foam synthesis using the biobased Michael acceptor and Michael donor to cure foams with a non-petroleum based chemical blowing agent. PMHS has been selected for this study for the production of chemical blowing agent according to scheme 2. Acrylated epoxidized soybean oil (AESO) has been reacted with different biobased amines and the blowing agent in order to obtain different foams (scheme 3). Different amounts of blowing agent were used to determine the effect on the foam expansion and their associated properties. Then, a poly(ether-siloxane) block polymer was used as cells stabilizer to prevent cell coalescence and Ostwald ripening. The biobased foams were analyzed by scanning electronic microscopy (SEM), dynamic mechanical analyses (DMA), differential scanning calorimetry (DSC), thermogravimetric analyses (TGA) to determine their morphologies, physical and thermal properties.



Scheme 3: Main chemical reaction to synthesize Aza-Michael-based foams

II. Experimental part

Chemicals

Acrylated epoxidized soybean oil (AESO), *m*-xylylenediamine (MXDA, purity 99%), polymethylhydroxysiloxane (PMHS, $M_n=2300\text{g}\cdot\text{mol}^{-1}$) were purchased from Sigma-Aldrich (Darmstadt Germany). 1,5-diaminopentane or cadaverine were purchased from TCI EUROPE N.V (Zwijndrecht, Belgium). A poly(ether-siloxane) block copolymer called TEGOSTAB E 8930 used as structural additive was provided by Evonik (Amsterdam, Netherlands). Priamine 1071, a dimer diamine obtained from the dimerization of fatty acid and called DDA, was kindly provided by Croda (Gouda, Netherlands). The NMR solvents used are CDCl_3 and DMSO d_6 from Eurisotop (Saint Aubin, France).

Foams synthesis

Biobased materials were synthesized with an acrylate/amine ratio of 2/1 since the amine can react two times with an acrylate.

The Amine Equivalent Weight (AHEW) is the amount of product needed for one equivalent of reactive amine function. It was determined by ^1H NMR using an internal standard (benzophenone). Known masses of product and benzophenone were poured into an NMR tube and 550 μL of CDCl_3 or DMSO d_6 were added. The AHEW was determined using Equation (2) by comparing the integration value of the signals assigned to the benzophenone protons (7.5-7.8 ppm) with the integration of the signals arising from amine moiety protons (2.68 ppm for DDA, 3.82 ppm for MXDA, 2.68 ppm for cadaverine).

The Acrylate Equivalent Weight (AEW) is the amount of product needed for one equivalent of reactive acrylate function. It was determined by ^1H NMR using an internal standard (benzophenone). Known masses of product and benzophenone were poured into an NMR tube and 550 μL of DMSO d_6 were added. The AEW was determined using Equation (1) by comparing the integration value of the signals assigned to the benzophenone protons (7.5-7.8 ppm) with the integration of the signals arising from the acrylate (6.16 ppm).

$$AEW = \frac{\int_{\text{PhOCPH}} \times H_{\text{acrylate}}}{\int_{\text{acrylate}} \times H_{\text{PhOCPH}}} \times \frac{m_{\text{acrylate}}}{m_{\text{PhOCPH}}} \times M_{\text{PhOCPH}} \quad (1)$$

$$AHEW = \frac{\int_{\text{PhOCPH}} \times H_{\text{amine}}}{\int_{\text{amine}} \times H_{\text{PhOCPH}}} \times \frac{m_{\text{amine}}}{m_{\text{PhOCPH}}} \times M_{\text{PhOCPH}} \quad (2)$$

Where \int_{PhOCPH} is the integration of the signal from benzophenone protons; \int_{amine} is integration of the signals from protons in α the amine function; H_{amine} is number of protons in α of the amine function; H_{PhOCPH} is the number of benzophenone protons; m_{amine} is the amine mass; m_{PhOCPH} is the benzophenone mass; and M_{PhOCPH} is the benzophenone molar mass.

The formulations of Aza-Michael foams were calculated from two equivalents of acrylate, 1.1 or 1.5 equivalent of amine with 0.1 or 0.5 equivalent of PMHS. The same amount of additive (TEGOSTAB E 8930, 0.5 wt%) was used for all the foams. The final mass targeted for each formulation is approximatively 10g.

First, the acrylate, PMHS and additive (0.5 wt% of the total weight of the formulation) were poured in a vial and then mixed with a SpeedMixer[®] (Germany) for 1 minute at 2500 rpm. Then the amine was added to the mixture and vigorously stirred 1 minute manually. Finally, the mixture was poured in a silicon mold and cured four hours at 50°C and two additional hours at 120°C.

Materials characterization

Nuclear Magnetic Resonance

Proton Nuclear Magnetic Resonance (^1H NMR) analyses were carried out in deuterated chloroform (CDCl_3 and DMSO d_6 99.50% isotopic purity) using Bruker Avance III 400 MHz NMR spectrometer at a temperature of 25 °C. The monomers structure were determined by hydrogen nuclear magnetic resonance. The external reference used was trimethylsilane. Shifts were given in ppm.

Fourier Transform Infrared Spectroscopy

Infrared (IR) spectra were recorded on a *Nicolet 210 Fourier* (Germany) transform infrared spectroscopy (FTIR) spectrometer. For each spectrum, 32 scans were collected at a resolution of 0.421 cm^{-1} at room temperature. Only the main IR absorptions are mentioned in the text, in cm^{-1} .

Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) were carried out using TG 209F1 apparatus (Netzsch, Germany). Approximately 10 mg of sample were placed in an alumina crucible and heated from 30 °C to 800 °C at a heating rate of 20 °C/min under nitrogen atmosphere (40 mL/min).

Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) analyses were carried out using a NETZSCH DSC200F3 calorimeter (Germany), which was calibrated using indium, n-octadecane n-octane, adamantane, biphenyl, tin, bismuth and zinc standards. Nitrogen was used as purge gas. Approximately 10 mg of sample were placed in a perforated aluminum pan. The thermal properties were recorded between -150 °C and 120 °C at 20 °C/min to determine the glass transition temperature (T_g). T_g values were measured on the second heating ramp to erase the thermal history of the polymer. All the reported temperatures are average values from three different tries.

Dynamic Mechanical Analyses

Dynamic Mechanical Analyses (DMA) were carried out on Metravib DMA 25 (France) with Dynatest 6.8 Software. Uniaxial stretching of foam samples ($10 \times 12 \times 12\text{ mm}^3$) was performed while heating at a rate of $3\text{ °C}\cdot\text{min}^{-1}$ from -120 °C to 120 °C, keeping frequency at 1 Hz. A dynamic stretching of $1.10 \cdot 10^{-5}\text{ m}$ was applied to the sample after the determination of the linear region. The alpha transition temperature was determined at the maximum of the tangent delta curve.

Compression test

The compression behavior of the samples was measured at room temperature using a specific cells of $20 \times 15 \times 15\text{ mm}^3$ on the rheometer Thermo Fisher HAAKE MARS (Germany) The deformation applied to the samples were 30 % for the 0.1 eq. of blowing agent based samples and 70 % for the sample with 0.5 eq. of blowing agent. The deformation of 30 or 70 % was applied in 60 seconds. The measure of the force at 30 or 70 % was determined by dividing the normal force observed by the surface of the sample. Then, time recovery tests were carried out. In order to do this analysis three cycles of compression were carried out at 50 % of deformation. The samples ($5 \times 5 \times 6\text{ mm}^3$) were compressed 30 seconds. The recovery time was 60 seconds. It has been considerate that the samples recover their shapes at 2 % strain. The measure of the recovery time was determined after the 3 cycles thus after 90 sec of compression.

Renewable carbon content

The renewable carbon content (%rC) has been calculated using the equation 4, where N_{rAESO} corresponds to the number of renewable carbon in the oil (around 57). N_{rAMINE} corresponds to the number of renewable carbons for each amine (5 for the cadaverine, 8 for the MXDA and 36 for DDA).

The N_{amine} corresponds to the total carbon number in each molecule (5 for the cadaverine, 8 for the MXDA and 36 for the DDA). The N_{AESO} corresponds to the number of carbons in the AESO (66). To conclude, N_{PMHS} corresponds to the non-renewable carbons of the PMHS (6). However it has to be noted that the surfactant was not taken into account since the structure is not known by the authors.

$$\%rC = \frac{N_{rAESO} + n_{amine} \times N_{rAMINE}}{N_{AESO} + n_{amine} \times N_{amine} + n_{PMHS} \times N_{PMHS}} \quad (4)$$

Hardness

Shore 0 hardness for foams was measured on a durometer Shore Hardness Tester HD0 100-1 from Sauter (Germany). Samples with 1 cm thickness were prepared for the measurement. An average of five measurements was performed.

Gel content

Three samples from the same material, of around 20 mg each, were separately immersed in THF for 24 h. The three samples were then dried in a ventilated oven at 70 °C for 24 h. The gel content (GC) was determined from Equation (3) where m_2 is the mass of the dried material and m_1 is the initial mass. Reported gel content are the average values of the three samples.

$$GC = \frac{m_2}{m_1} \times 100 \quad (5)$$

Scanning electron microscopy

The morphology and the internal structure of the foams were analyzed by scanning electron microscopy (SEM) from the cut surface in the rise direction of the foam. A FEI Quanta 200 FEG (United States of America) was used to obtain foam images, at room temperature.

Densities:

The foams density (ρ_a) was calculated by the average of three measurements of cubic samples (size about 2x2x2 mm). The mass was divided by the samples volume.

Rheological experiments

The gelation times were measured using a Thermo Fisher HAAKE MARS rheometer (Germany) with a plate– plate geometry and a diameter of 25 mm. The gelation times were determined at the crossover of the storage modulus (G') and loss modulus (G'') from an oscillatory experiment at 1 Hz, 50 °C and 2 % of deformation, according to the previously determined linear domain.

III. Results and discussions

Raw chemicals characterizations

Before synthesis, all of the raw chemicals have been analyzed. First, the acrylate equivalent weight (AEW) was determined by 1H NMR titration using Equation (1) (Figure S1). AEW of AESO is 864 g.eq $^{-1}$. Then amine hydrogen equivalent weight (AHEW) was also determined by 1H NMR titration using Equation (2) (Figure S2, S3 and S4). All the results are summarized in Table 1. In order to obtain a complete characterization of the raw materials, IR analysis were carried out. The IR analysis confirmed the presence of NH_2 stretching at around 3300 cm^{-1} and the acrylate stretching around 800 cm^{-1} for the amines and the AESO, respectively (Figure S5)

Table 1: AHEW and AEW of the different raw chemicals η

	DDA	Cadaverine	MXDA	AESO
AHEW (g. eq $^{-1}$)	309	51.09	68.1	-
AEW (g. eq $^{-1}$)	-	-	-	864

Foam synthesis

In this study, six different foams formulations have been investigated (Table 2). The foams were prepared as described previously by reacting biobased amines with AESO and PMHS. The AESO have been chosen as biobased Michael acceptor since AESO is derived from epoxidized soybean oil. Then, the Michael donors selected in this study were the DDA obtained by dimerization of two fatty acids, the cadaverine and the MXDA. The MXDA is generally fossil-based. Nevertheless, a biobased synthesis route has been described and can be used.⁵⁸ The molar ratio 1:2 amine/acrylate is used in the formulations. The protocol described in the experimental part was used to obtain the biobased foams. The morphology of the different foams were visually analyzed and then, more precisely, with scanning electron microscopy (SEM). The polymer matrix formation was determined by the measurement of the gel content. Then, thermo-mechanical properties of the different foams were determined by DSC, rheometry and DMA. High renewable carbon content was obtained with these foams following the equation 4. The foams have rC% up to 80 % depending on the results presented in table 2. The effect of blowing agent amount is only slightly observed.

Table 2: Foams formulations

Foam	Amine	PMHS (molar eq.)	rC%
Cadav 0.1	cadaverine	0.1	86
Cadav 0.5	cadaverine	0.5	84
MXDA 0.1	MXDA	0.1	87
MXDA 0.5	MXDA	0.5	85
DDA 0.1	DDA	0.1	91
DDA 0.5	DDA	0.5	90

Structural analysis

After 6 h of curing, the different soft foams were analyzed, first, by FTIR in order to determine the conversion of the monomers. Figure 1 represents the foam obtained with the cadaverine. We observe the disappearance of both acrylate C=C at 810 cm^{-1} and NH_2 stretching at 3300 cm^{-1} which demonstrated the complete advancement of reaction. The FTIR of other foams demonstrated also full conversion (SI Figure S6 and S7).

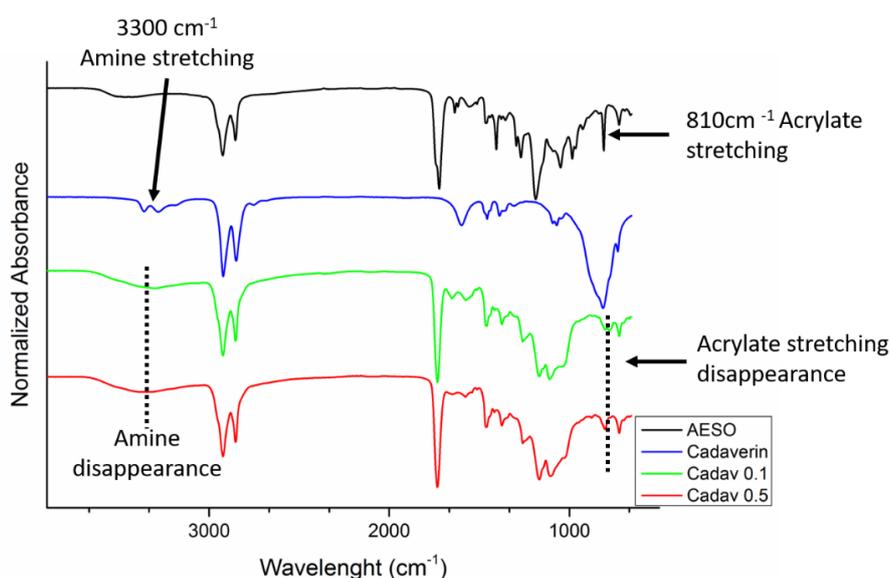


Figure 1: FTIR analysis of the monomers (AESO and cadaverine) and cadaverine-based foams. From top to bottom.

Additionally rheological experiments were carried out in order to determine the gel time at 50°C of the different bio-based formulations. A short gel time was observed as shown in Figure 2. This behavior is crucial in order to obtain foams. If the gel time is too long, the blowing agent can be released out of the foam before curing. The MXDA yielded the slower reaction with a gel time of 20 min (1200 s). The gel times of the two other formulations were shorter with around 12 min (706s) and 10 min (566s) with DDA and cadaverine, respectively. These results are consistent with the chemical structures of the amines. Indeed, the aromatic ring of the MXDA induces a lower availability of the doublet, hence a lower basicity which leads to a lower reactivity. Peyrton *et al.* described the phenomenon in a previous study.⁴⁶ In the same study the authors also described the possibility to reduce the gel time when primary amine NH₂ is considered as monofunctional. Thus the gel time could be optimized using different stoichiometry in the system to reach different properties. Then, the long aliphatic chain of the DDA brings steric hindrance and reduces the reactivity. The cadaverine with a five carbons chain length had logically the higher reactivity since there is neither steric hindrance nor interaction which reduces the reactivity.

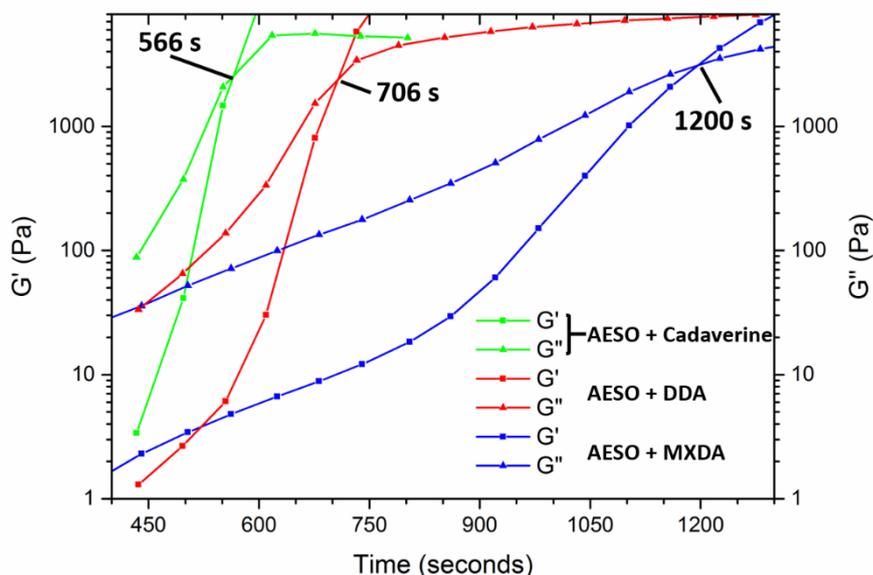
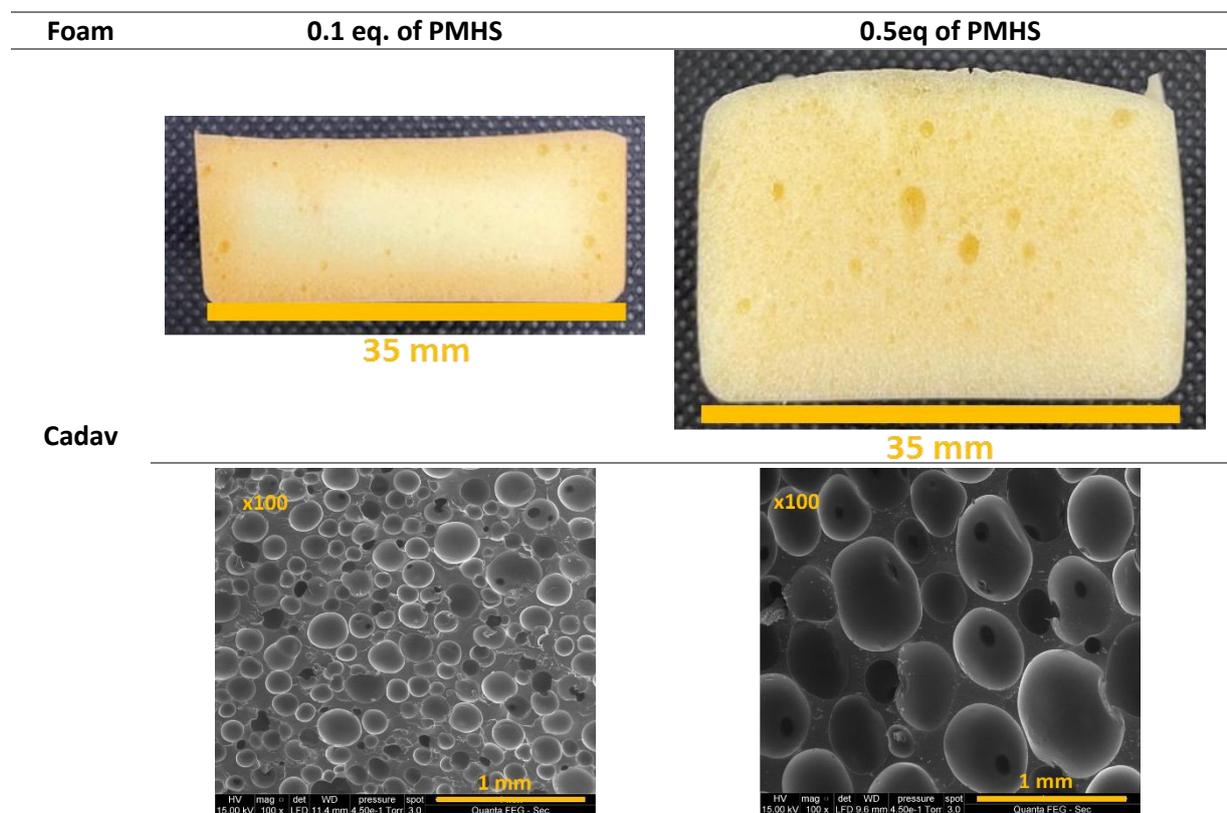


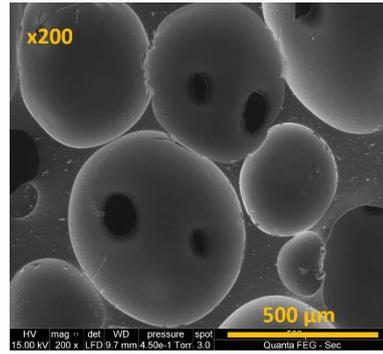
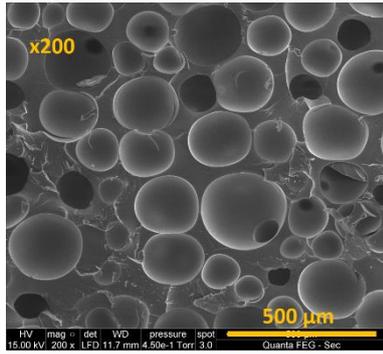
Figure 2: Gel times for the different formulations at 50°C.

The crosslinked polymer matrix formation was confirmed with the insoluble content measurement (Table 3). All the foams obtained a result higher than 90 % of insoluble content which confirmed the presence of a full crosslinked network. The morphologies of the foams have been analyzed (Figure 3). First, the foam morphologies were visually evaluated. As expected, smaller cells are obtained in the case of 0.1 eq. of PMHS. The cells with 0.5 eq. of PMHS are larger than the latter ones. The higher expansion of this foam can be easily observed in Figure 3. The different foams had a structure with little interconnection between pores, hence these foams could be defined as “closed-cells foams”. SEM was carried out (Figure 3) in order to deeply characterize these foams. The SEM analysis showed a high homogeneity of all foams. The average cells size increased with the PMHS content. Thus, the cells size is about 0.14 ± 0.06 mm for cadav 0.1 when the average size is about 0.5 ± 0.15 with cadav 0.5. Similar results were obtained with the foam with MXDA and DDA (Table 3). The cells size between MXDA, cadaverine and DDA based foams can also be compared. With 0.5 eq. of PMHS the foams with cadaverine and DDA had important cell increase compared to 0.1 eq. of PMHS. Nevertheless, MXDA based cells with 0.5 eq. of PMHS had lower increased compared to the other

foams due to the rigid aromatic structure. Ncell, the cells number in a given volume, was coherent with the cells size. In fact, as shown in Table 3, the Ncell with 0.1 eq. of PMHS was higher than with 0.5 eq. because the cells are smaller. According to these results, the density of the different foams is also reduced when 0.5 eq. is used. The density of the foams are approximately divided by two with 0.5 eq. The homogeneity observed by SEM analysis is linked to the use of a surfactant which avoids coalescence phenomenon and Ostwald ripening.⁵⁹ Then, the ratio holes area on cell area (A_h/A_c) was determined. This ratio gives information on the open cell structure of the foams. A ratio near one means fully interconnected cell whereas it is near zero it means the foam has few cell interconnected. A low A_h/A_c ratio was obtained with 0.1 eq. of PMHS. However, the ratio was higher with 0.5 eq. of PMHS (Table 3). The average cells size seems to increase with the PMHS content. Thus, cells coalescence phenomenon occurs a little more. Thus an open-cell structure was obtained for these non-isocyanate foams. Nevertheless, the ratio A_h/A_c showed a lower interconnection when 0.1 eq. of PMHS is used compared to 0.5 eq. Compared to PU flexible foams, the obtained foams with 0.5 equivalent of blowing agent showed similar characteristics in term of pore size and distribution.⁶⁰⁻⁶² Moreover the density was also similar to PU foams.⁶³ However the foam using 0.1 eq. of PMHS showed lower cells size. For all the foams, the density was highly reduced with the use of blowing agent (table 3). For example, the density of the MXDA foams was reduced by about 40 % with 0.1 eq. of amine and by about 60 % with 0.5 eq. of PMHS. Similar result is observed with the DDA. The cadaverin 0.1 eq has a density close to the non-foamed samples whereas 0.5 eq. is about 50 % reduction. It could be linked to the small cell size of the sample.

To conclude, these biobased foams showed similarities with PU flexible foams, which means similar open cells structures can be obtained using the Aza-Michael reaction with biobased monomers.⁶⁴⁻⁶⁶

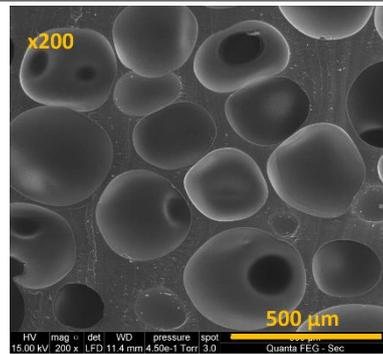
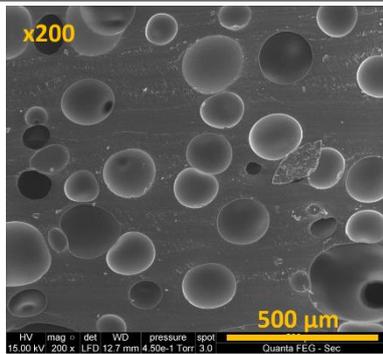
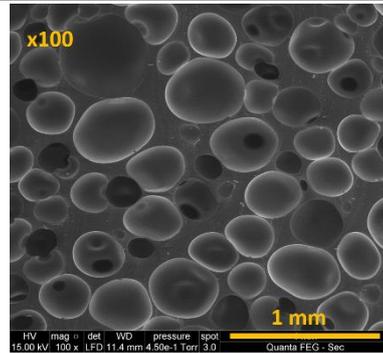
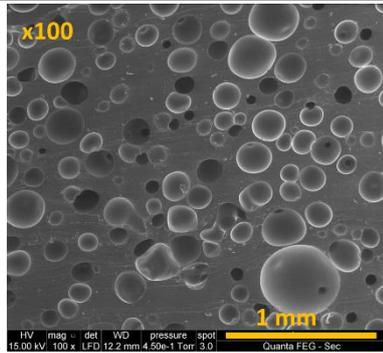




35 mm

35 mm

MXDA



DDA



35 mm

35 mm

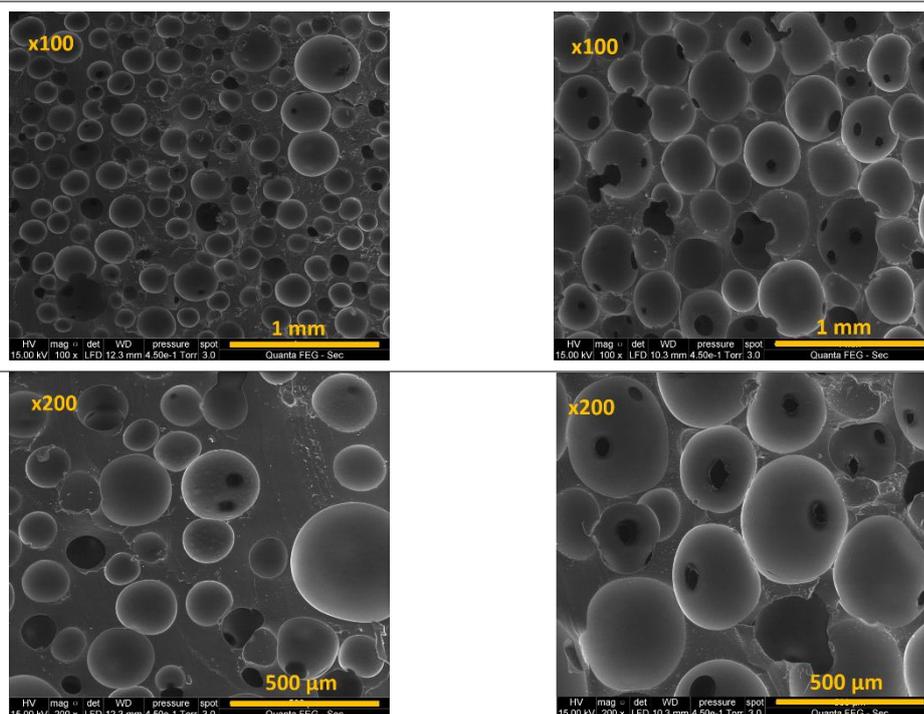


Figure 3: Foams photography and SEM pictures.

Thermal analyses

TGA analysis is used to determine the temperature which corresponds to 5 % weight loss ($T_{d,5\%}$) and the temperature at the maximum weight loss ($T_{d,max}$). The different results (Table 4 and Figure SI 8, 9 and 10) showed a small difference between 0.1 eq. and 0.5 eq. of blowing agent. The $T_{d,max}$ was measured and a relative difference between the foams has been observed. The cadaverine foams had the lower $T_{d,max}$ than MXDA foams. Contrariwise, the DDA foams had the higher temperature at the maximum weight loss, which means it had a better thermal resistance. The influence of the amine is observed also with the residual mass of the sample at 700°C (Residue, Table 4). A low residue at 700 °C is observed for the DDA based foams (only 3 and 5 % of char for 0.1 eq. and 0.5 eq., respectively) since the vegetable oils do not produce char. The cadaverine foams had 7 % of char and MXDA foams about 10 %. Aromatic rings are known to increase the char formation, which explains the last result.

Differential scanning calorimetry (DSC) was also carried out. The analyses were performed between -100 and +100 °C at 20 °C.min⁻¹ under nitrogen flow. The DSC thermograms can be found in SI Figure 11, 12 and 13 and T_g values in Table 4. The DDA foam exhibited the lowest T_g value (about -20 °C) due to the plasticizing effect of the carbon chain. Then, the T_g of the cadaverine and MXDA-based foams were about -11 and -7 °C, respectively. This difference is due to the amine structure. Aromatic rings improve rigidity and therefore T_g . Nevertheless MXDA impact is “diluted” among the long alkyl chain of the AESO which explained the low gap compared to the cadaverine.

Table 3: Structural analysis of the Aza-Michael foams

Foam	Cell size (mm)	ρ_a (g.cm ⁻³)	Cell density (NCell) (cells.cm ⁻³) ^a	A_h/A_c	Gel content (%)
Cadav 0.1	0.14 ± 0.06	0.54	14000	0.06	94
Cadav 0.5	0.5 ± 0.15	0.28	2500	0.20	93
MXDA 0.1	0.15 ± 0.07	0.65	4500	0.03	94

MXDA 0.5	0.29 ± 0.12	0.45	2300	0.13	95
DDA 0.1	0.13 ± 0.6	0.61	7000	0.03	91
DDA 0.5	0.43 ± 0.08	0.32	4500	0.15	95

^a: $N_{cell} = (nM/A)3/2\rho_s/\rho_p$; with the number in SEM image (n , average on 3 images), magnification (M), surface area of the image (A , mm^2), sample density of solid (ρ_s) and foam density (ρ_p). The solid density of non-foamed samples was estimated at $1.04 \pm 0.07 \text{ g.cm}^{-3}$ for the MXDA-based foams with, $0.57 \pm 0.04 \text{ g.cm}^{-3}$ for cadaverine-based foams, and $0.95 \pm 0.02 \text{ g.cm}^{-3}$ for DDA-based foams.

Finally, values obtained by DSC were confirmed by DMA in order to determine the alpha relaxation temperature (T_α) of the foams (Table 4, Figure SI 14, 15 and 16). T_α can be associated to the T_g from DSC with a transition from vitreous to elastic domain. The obtained T_α confirmed the results obtained by DSC. Hence, T_α values are shifted by about 20-30°C compared to the T_g . The MXDA has the highest T_α followed by the cadaverine and then by the DDA.

Table 4: Thermal, thermomechanical and mechanical analyses of the foams

Foam	$T_{d,5\%}$ (°C)	$T_{d,max}$ (°C)	Residue (%)	T_g (°C)	T_α (°C)	Shore test	Stress (kPa) ^a	Recovery time (s) ^b
Cadav 0.1	254	403	7	-12	17	34	-	-
Cadav 0.5	246	420	7	-13	15	4	80	5.7
MXDA 0.1	296	414	12	-7	20	42	-	-
MXDA 0.5	285	425	10	-9	19	25	374	7.8
DDA 0.1	329	450	3	-20	2	34	-	-
DDA 0.5	321	460	5	-25	4	8	76	3.2

^a: Stress measured at 70% deformation for the foam at 0.5 eq. of PMHS and 30% deformation for 0.1 eq. of PMHS, ^b: time measured on the third compression to reach 2% strain

Finally, the mechanical properties of the biobased foams were carried out. First, the hardness of the foams were determined using Shore test 0 designed for foams. The reference was a glass with a value about 100 of hardness. It resulted similar hardness for foams synthesized with DDA and cadaverine (Table 4). Such hardness range is suitable for seat mattress for example. The higher T_g of the MXDA foams induces higher hardness as shown in Table 4. The effect of the blowing agent content is clearly observed, since higher PMHS concentration reduced significantly the hardness of the foams. The low hardness is linked to the higher expansion and so, wider cells size which brings higher flexibility.

Mechanical analysis

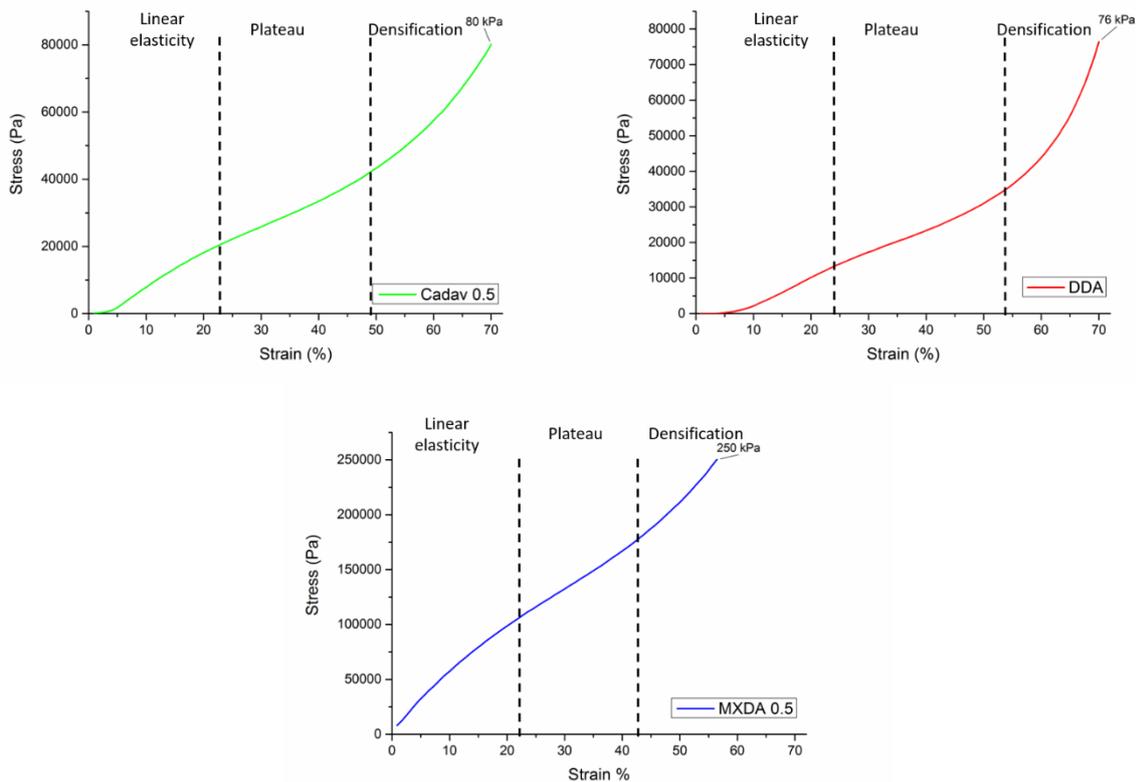


Figure 4: DMA analysis in monotonic tension at room temperature.

Compression tests were carried out. This analysis allowed the observation of three different regions: the linear elasticity, the plateau and the densification. The first region corresponds to the strain edge bending of the foam. The second region corresponds to the collapse due to the cells compression. Finally, all the cells have been compressed and densification of the foam is observed in the third region. In fact it corresponds to a high stress increased for a lower strain. The foams were compressed to 30 % of their heights with 0.1eq. of PMHS and 70 % with 0.5 eq. The compression has been increased for the foams with 0.5 eq. of PMHS since the cells size is bigger. Thus, in order to observe the three different regions, the foams have to be more compressed. Hence, after preliminary experiments, the 70 % of strain has been defined as the optimal compression for the more expanded foams. From this analysis several phenomena have been observed. First, the 0.1 eq. PMHS foams had small cells and the different regions were not clearly observed (Figure SI 17). The linear elasticity was slightly observed at the beginning of the analysis. Then foam densification was quickly observed until the maximum strength of the apparatus (60 N). The maximum strength was reached at different strains depending on the samples. That is why the stress values are not displayed in table 4. With the foam with 0.1 eq. of PMHS, the plateau was not observed. It might be due to the small size of the cells. For the three foams with 0.5 eq. of PMHS, the regions were well defined (Figure 4). The Figure 4 showed the quick increase of the stress compare to the two other foams with MXDA 0.5. For all the foams the linear elasticity was similar *e.g.* from 0 % to 22 %. However, as shown in Figure 4, the MXDA foams had a smaller plateau due to the lower cells size and density. Indeed, the plateau with MXDA foams was from 22 to 44 % of strain, when the plateau is from 22 to about 50 % of strain with cadaverine and 55 % of strain with DDA-based foams. From this analysis, MXDA foam exhibited a higher hardness but it still presents a three regions behavior. The two other foams were soft and their highly porous structures led to an important plateau (about 50

% strain). Moreover these foams had lower stress values (76 and 80 kPa at 70 % strain) due to the chemical structure of their building blocks compared to the MXDA (250 kPa at 55 % strain). An important difference toward compression could be observed between 0.1 and 0.5 eq of blowing agent. In fact the foam with 0.1 eq. did not exhibit the usual behavior of a foam toward compression. In another hand the foam with 0.5 eq. demonstrated a good behavior toward compression. The foams properties were tuned depending on the amount of blowing agent. For the recovery test only the foams with 0.5 eq. of blowing agent were studied.

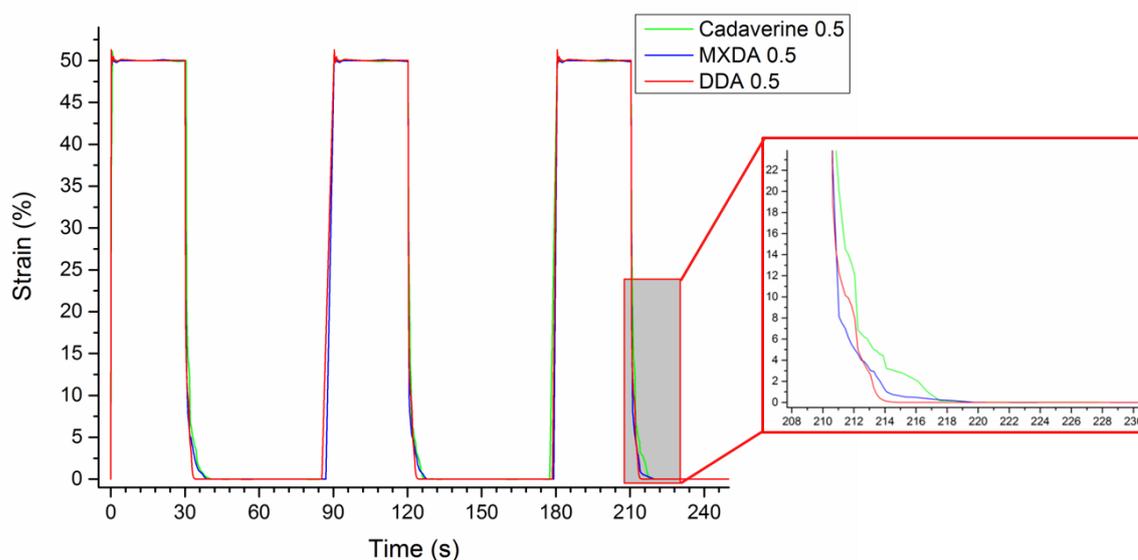


Figure 5: DMA analysis of the recovery time of the different biobased foams at 50% strain.

Recovery tests were finally carried out using DMA with compressing plate. The results from the foam synthesized with 0.5 eq. of PMHS are presented in Figure 5. Three cycles of 30 s compression at 50 % strain were applied to the foams to obtain the recovery time. The recovery time was measured when it reached 2% strain. From this analysis, MXDA 0.5 showed longest time recovery despite a structure with small cells and important density. Indeed, the time recovery was about 8 s after three cycles. Cadav 0.5 and DDA 0.5 had a recovery time of about 6 and 3 s, respectively. Depending on the literature about PU foams these foams could be defined as long time recovery foams as their time of recovery is about few seconds.⁶⁷ These results were coherent with the different results previously presented since the biobased foams were soft. The MXDA based foam was the hardest foam due to the aromatic structure with a higher recovery time.

IV. Conclusion

To conclude, the strategy to obtain biobased foams using a chemical blowing agent under mild conditions has been successful. Different promising foams have been obtained for the first time using acrylated epoxidized soybean oil and biobased amines. Different polyamines have also been tested. The Aza-Michael reaction quickly allowed to cure the foams at moderate temperature (50 °C) to trap the released gas. SEM analyses have demonstrated the homogeneous structure of these foams with open cells morphology. The morphologies and properties of the foams can be tailored using different amounts of blowing agent as well as different amine structures. These parameters modified the properties of the resulting foams. These soft foams showed interesting properties with low T_g leading

to long recovery times. The thermal degradations are also interesting with $T_{d,5\%}$ of about 280 °C. Finally, biobased flexible foams were synthesized at mild temperature which correspond to most of PU foam applications. Hence, the use of such foams could be envisaged for mattress or automobile seats. These foams showed properties close to the usual flexible PU foams. Thus we showed the possibility to use biobased acrylate to obtain renewable foams with attractive properties, comparable to commercial PU foams. Moreover, depending on the last researches carried out on materials synthesized using the Aza-Michael reaction, it results a great interest for the reshaping of such materials.⁶⁸

As perspectives and to improve the end of life and the LCA of these materials, covalent adaptable network (CAN) could be developed in order to easily recycle these thermoset-based foams. A second life could be imagined for these foams after reshaping, which could improve the sustainability of this materials. The end of life of the thermosets can also be studied to avoid the production of long lasting waste. Thus, the use of enzymes could be imagined to obtain foam degradation and improve the circularity of these materials.^{69,70}

Supporting information

The Supporting Information is available free of charge at

¹H NMR raw material, Infrared of the foams, DSC of the materials, DMA to determine the T_α , compression test.

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Acknowledgments:

The authors would like to acknowledge Frédéric Fernandez from the MEA platform, Université de Montpellier, for the SEM experiments and sample preparation.

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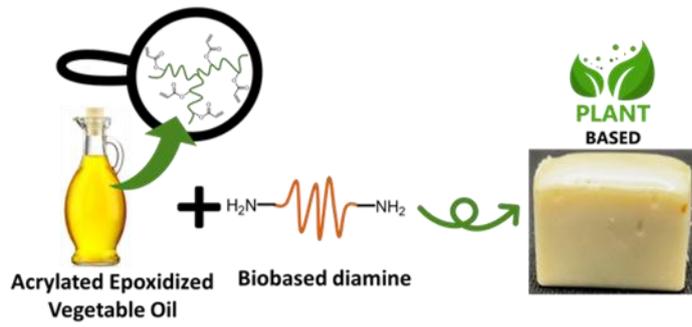
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Synopsis:

To provide a durable answer to toxic isocyanates, biobased foams were synthesized under mild condition using the Aza-Michael reaction.