Biobased Polyurethane foams based on new polyols architectures from microalgae oil

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ABSTRACT: Environmental concerns continuously drive research to find alternatives to fossil-based constituents in a greener way. Industrial polyurethane foams are usually obtained from the polyaddition reaction between fossil-based polyols and polymeric 4,4'-methylene bis(phenyl isocyanate). The very recent development at the industrial scale of microalgae production provides accessibility to original building blocks and new macromolecular architectures. In this study, the green chemistry principles were highly prioritized to synthesize different polyols from microalgae oil. The resulting microalgae derived polyols were structurally, chemically and physically characterized, and then compared. Polyurethane foams were synthesized using a conventional fossil-based polyol substituted incrementally by microalgae derived polyols. The corresponding cellular materials were extensively

characterized in terms of reactivity, morphology and performances, and then compared to conventional foams. A new biobased foam formulation containing 25 wt% biobased polyols matched the compliance levels of a fossil-based reference foam. For the first time, a catalyst-free foam with a similar density as the reference was achieved with a biobased triglyceride catalytic polyol.

INTRODUCTION

Nowadays, our society is facing severe and urgent challenges. Among them, there is climate change, the depletion of some fossil resources and environmental degradation. To address these challenges, industries and academics of the material science community focus their research on the use of renewable sources. This recent trend is also driven by the development of new molecular architectures that can be extracted from various types of biomass. Nevertheless, these developments must be done without competition with food resources. In this way, the growth of engineered microalgae technology seems to fulfill this requirement.

Microalgae are unicellular photosynthetic organisms cultivated without the mobilization of arable land. The cultivation can be conducted in fresh, sea and waste-water using CO₂ as raw materials.¹ Microalgae are a diverse family with an estimated 20-800 000 different species,² which can be engineered to biosynthesize particular unsaturated lipids and fatty acids compared to the conventional ones obtained from plants.³ Lipids are mainly composed of triglycerides with fatty acid chemical structures that vary in terms of length (number of carbons), number of double bonds and with or without the presence of reactive groups such as epoxides or hydroxyl groups. The tremendous potential of lipids accumulation⁴ of this resource captivates the interest of the biodiesel industry⁵⁻⁷ to supplant the 2nd generation biodiesel, based on residues and non-edible crops. The advantages of the microalgae are the low production cost, sustainability,^{8,9} no competition with food and high productivity.¹⁰ The microalgae market is not limited to the production of lipids for biodiesel production; all biomass components can be valorized.¹¹ Lipids, carbohydrates, proteins and minerals are transformed into monomers (e.g. lactic acid, diols),¹² basic chemicals (e.g. ethanol, butanol, acetic acid),¹³ added-value products (e.g. iodine, omega fatty acid)¹⁴ or pigments (e.g. beta-carotene).¹⁵

As is the case of conventional vegetable oils, the fatty acid composition of microalgae is species and growing conditions dependent.¹⁶⁻¹⁸ In comparison to vegetable oils derived from

agricultural resources, microalgae oil (MAO) fatty acids can contain longer unsaturated chains, up to 24 carbons long. The triglyceride structure offers high functionality, which is often required in thermoset polymer synthesis.¹⁹ Then, a large variety of macromolecular architectures can be obtained.

The Oleochemistry produces biobased polyols mainly from vegetable oil, e.g., for polyurethanes (PU). This production based on several steps is now worldwide developed.²⁰⁻²² For such a synthesis, epoxidation of the double bond is efficient and industrially accessible. The epoxide group can undergo a ring-opening reaction by several nucleophiles, leading to a myriad of biobased polyols.²³⁻²⁵ Different PU morphologies can be tailored according to the used polyols. For example, PU foams (PUF) are mainly obtained from a blowing agent expansion during the polyaddition between a polyisocyanate and a polyol. The non-isocyanate polyurethane is shown the interest by the scientific community for the elaboration of sustainable foams despite a slow process and low mechanical properties.²⁶⁻²⁸ However, the substitution of fossil-based polyols in PUF has received a significant attention due to environmental and economic concerns.²⁹⁻³² The synthesis of polyols for PUF derived from MAO has been only scarcely explored via two main pathways: i) epoxidation and ring-opening by methanol,^{33,34} ethylene glycol³⁵ and lactic acid,³⁵ and ii) hydroformylation.³⁴ The high potential of this bioresource for PUF has mainly been demonstrated through these preliminary studies. Complete and transversal studies from the elaboration to the full evaluation of the morphology and behavior of PUF were marginal in the literature.

The objective of this work is to present a complete and transversal study from the synthesis to an extensive characterization of biobased PUF with closed-cells using MAO derivatives in connection with potential applications. MAO chemical transformations were realized following, to the best extent, the main principles of green chemistry. In this approach, the numerous carbon-carbon double bonds in this oil were converted into epoxides to yield

epoxidized microalgae oil (EMAO). This step was followed by the ring-opening reaction by the respective use of acetic acid (AA), diethylamine (DEA), ethanol (EtOH) or hydrochloric acid (HCl) to yield the corresponding biobased polyols. The biobased polyols synthesized were extensively characterized, most notably in terms of viscosity, molar mass, functionality, hydroxyl, epoxide and acid content. The biobased polyols were used in combination with a fossil-based polyether polyol for the elaboration of PUF. In the first set of experiments, 25 wt% of the fossil-based polyol was replaced by the respective newly synthesized biobased polyols for foam elaboration. In a second set 25, 35, 50 and 75 wt% of fossil-based polyol were exclusively substituted by one biobased derived polyol. A catalyst-free foam was achieved by the replacement of the conventional catalyst by a catalytic polyol synthesized by the ring-opening reaction of epoxidized soybean oil (ESO) by diethylamine. The PUF results were compared to an industrial fossil-based PUF reference in terms of foaming reactivity, cell size and density. In order also to evaluate this global and transversal process based on several green principles, the best performing biobased foams from microalgae were also characterized mainly in terms of performance by mechanical, thermal conductivity and flammability tests and indicated several perspectives for several potential applications.

EXPERIMENTAL SECTION

Materials and chemicals

MAO was kindly supplied by Fermentalg (France) and was extracted from microalgae (*Schizochytrium sp.*). The microalgae were cultivated in a 180 m³ reactor in the dark with an external carbon source for energy (heterotrophic system). After cultivation, the unicellular biomass was lysed to liberate the lipids, which were then isolated by centrifugation. The process was carried out under a nitrogen (N₂) atmosphere to prevent the oxidation of the oil. The double bond content of MAO was 336 g I₂/100 g (13.2 mmol double bond/g). The fatty acid composition

of the unsaturated MAO was presented in Table S1 in SI. Glacial acetic acid, toluene (99 %), ethyl acetate (99 %), methyl ethyl ketone (MEK), diethyl ether, cyclohexane, sodium thiosulfate, potassium iodide and Wijs solution were obtained from Fisher Scientific (France). Amberlyst® 15H (strongly acidic cation exchanger dry), CDCl_3 , hydrochloric acid (37 % in water), diethylamine (99 %) and 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane were provided by Sigma-Aldrich (France). Absolute ethanol was purchased from VWR (France). Commercially available ESO Weepox01 was provided by Brenntag (Germany).

The polyisocyanate used is the polymeric 4,4'-methylene bis(phenyl isocyanate) identified as pMDI (NCO index = 31 %), Desmodur 44V70L from Covestro (Germany). N,N-dimethylcyclohexylamine (DMCHA) provided by Sigma-Aldrich (France) was used as a balanced catalyst between blowing and gelling reactions. Tegostab B84501 from Evonik (Germany), a polyether polysiloxane copolymer, was used as a surfactant. Tris(1-chloro-2propyl) phosphate (TCPP) (Shekoy-China) was used as a flame retardant. Isopentane (boiling point 28 °C) (Inventec-Dehon-France) and demineralized water were used as a physical and chemical blowing agent, respectively. Daltolac R570 (Huntsman-Germany) was used as the reference fossil-based polyether polyol. It is mainly composed of alkoxylated glycerol.

All chemicals were used without any purification.

Triglyceride modifications to obtain polyols

The epoxidation of MAO (1 eq.) was performed by ITERG (France) via an in-situ peracid formation using formic acid (0.33 eq.), toluene (0.5 L/kg of MAO) and H_2O_2 (2.5 eq.) according to a previously described protocol.^{33,34} The resulting EMAO was obtained with a 74 wt% yield. Polyols were obtained by ring-opening of EMAO by AA, HCl, DEA or EtOH to yield the corresponding respective polyols: EMAO-AA, EMAO-HCl, EMAO-DEA or EMAO-EtOH. The detailed synthesis and characterization procedures of the polyols are given in Supporting information (SI).

Foam synthesis

The isocyanate/hydroxyl molar ratio (NCO/OH) was set at 1.15 in all formulations. Every reactive hydroxyl in the formulation was accounted for, i.e., water and polyols, to determine the isocyanate quantity. The isocyanate group is very reactive with water present in the air. The polyisocyanate was introduced in excess to counter the side reaction with air humidity and maximize the conversion of hydroxyl into urethane. The fossil-based polyol was progressively replaced in weight by biobased polyols. Foams were prepared via an A-B composition. In a plastic cup, the A-part consists of the polyol mixture, the catalyst (DMCHA), the surfactant (Tegostab B84501), the flame retardant (TCPP), the physical (isopentane) and chemical (water) blowing agents. They were weighed and mixed using a mechanical stirrer. The water, TCPP and surfactant were kept constant at 1.6, 10 and 2.5 parts by weight (pbw), respectively. The isopentane content was determined to obtain foams with similar densities. The B-part containing the polyisocyanate is quickly added. The final mixture is vigorously stirred with a mechanical stirrer for 5 seconds, and the foam is let to rise freely in a plastic cup for the reactivity study or poured into a mold for other characterizations. The foams were kept for one week at room temperature and 50 % RH to allow the system to cure before analysis and to be stabilized. The detailed characterization procedures of the foams are given in SI.

RESULTS AND DISCUSSION

The oil extract from microalgae is an orange liquid with a marine smell. The highly unsaturated triglycerides structure explains the color. The MAO fatty acid composition was determined by gas chromatography and presented in Table S1 in SI. The predominant fatty acids in MAO were docosahexaenoic (C22:6) (60 %), palmitic (C16:0) (22 %) and docosapentaenoic (C22:5) (10 %) acids. At first, MAO obtained from microalgae was epoxidized via the in-situ formation of performic acid to obtain an odorless, yellowish waxy product (EMAO). The stacked ^1H NMR of MAO and EMAO are shown in Figure 1, with characteristic signals of the double bonds and epoxide highlighted.

Figure 1. ^1H stacked NMR spectra of MAO and EMAO

The NMR analysis of MAO and EMAO structure is detailed in Figures S1 and S2 in SI. The successful epoxidation of the double bonds is indicative of the substantial decrease of vinyl protons at $\delta=5.4$ ppm and the appearance of the epoxide signal at $\delta=2.8-3.2$ ppm. According to NMR calculations, 80 % of double bonds were transformed into epoxide groups, 6 % were epoxidized and underwent ring-opening by the water in the medium and 14 % were unconverted (Table S2 in SI). The transformation of the double bonds into epoxides is performed at the oil-water interphase. The incomplete reaction can be explained by the difficulty for the performic acid to access all the double bonds linked to the polyunsaturated MAO structure. The reaction can be further hindered by the increasing viscosity of the oil phase during the reaction. The reaction temperature was set at 70 °C to favor the epoxide formation, all the while minimizing further ring-opening with water.²⁷

EMAO was used as a starting material to build a chemical platform of several polyols via ring-opening reactions using of different nucleophiles including: ethanol (EMAO-EtOH), acetic acid (EMAO-AA), hydrochloric acid (EMAO-HCl) or diethylamine (EMAO-DEA). The detailed synthesis procedures of the polyols are given in SI. The ring-opening reactions were carried out to adhere to the best possible extent to the principles of green chemistry. In addition to the MAO, several ring-opening reagents can be biobased (ethanol and acetic acid). The principle of atom economy was applied in all syntheses to achieve polyols. Reactions were carried in reactive solvents, except for EMAO-HCl, where the minimum amount of acetone (1.2 mL/g) was used. For the synthesis of EMAO-EtOH and EMAO-DEA, heterogeneous catalysts were used and can be recovered and re-used. The resulting polyols were then used without further purification from any side-products in order to minimize the generation of additional waste, in agreement with some principles of green chemistry. Green chemistry is an essential tool for the design of sustainable molecular architectures.³⁶ The application to the best

possible extent of the green chemistry principles was achieved, most notably by atom economy, catalysis, use of renewable feedstock and minimized use of solvents.

The synthesized polyols were characterized by the following characterizations: hydroxyl (I_{OH}), epoxide (EI) and acidity index (I_A), functionality, viscosity, melting temperature and thermogravimetric analysis (TGA), and these results are summarized in Table 1. The I_{OH} was determined by ^{31}P NMR titration using 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane as phospholane reagent. Detailed ^{31}P NMR spectra of the polyols are available in Figure S3 in SI. The phospholane reagent is also reacting with epoxides, and the suggested mechanism is described in Scheme S1 in SI. The ^{31}P NMR titration quantifies the sum of the epoxide and hydroxyl groups.

Table 1. Characteristics of the different polyols: fossil-based, MAO and their derivatives.

Polyol	I_{OH} exp	I_{OH} th	OH molar yield	EI	Functionality	I_A	Viscosity at 25 °C	Melting temperature	DTG peak ^[a]
	(mg KOH/g)	(mg KOH/g)	(%)	%		(mg KOH/g)	(Pa.s)	(°C)	(°C)
Daltolac R570	570 ± 10				3.0		0.70 ± 0.07		
(fossil-based)									
MAO					12 ^[b]		0.10 ± 0.01	0 ± 10	412 ± 10
EMAO				10 ± 0.2	10 ^[b]		900 ± 90	10 ± 10	298 ± 10
EMAO-EtOH	260 ± 10	410	63 %	0.03 ± 0.002	7.6 ± 0.6	1.8 ± 0.1	3400 ± 300	30 ± 20	315 ± 10
EMAO-AA	70 ± 10	370	19 %	0.30 ± 0.02	2.4 ± 0.1	21.8 ± 0.1	300 ± 30	24 ± 10	332 ± 10
EMAO-HCl	180 ± 10	440	41 %	0.60 ± 0.03	5.0 ± 0.5	9.4 ± 0.1	(5.3 ± 0.5)*10 ⁴	40 ± 10	365 ± 10
EMAO-DEA	130 ± 10	340	38 %	0.30 ± 0.02	4.7 ± 0.3	NA ^[c]	(3.8 ± 0.4)*10 ⁶	45 ± 15	311 ± 10

^[a] Determined by the higher value of weight loss derivative (DTG) of thermogravimetric analysis (TGA) ^[b] Determined by NMR ^[c] The basicity of the amine is superior to the acidity index

The EMAO has an EI of 10 %. The polyol synthesis was monitored by epoxide titration. The reactions were stopped when more than 90 % of epoxide groups were consumed. The nearly complete reaction of the epoxide groups was confirmed by the low final EI values depicted in Table 1. The ^{31}P NMR measured I_{OH} is then predominantly accounting only for hydroxyl groups for the synthesized polyols. The disappearance of the epoxide stretching band located at $\tilde{\nu}=826\text{ cm}^{-1}$ on the FTIR spectra of polyols, depicted in Figure S4, is indicative of the total epoxide consumption. Furthermore, the appearance of the OH stretching band at $\tilde{\nu}=3400\text{ cm}^{-1}$ is indicative of the formation of hydroxyl groups. The low hydroxyl index is explained by the numerous side reactions decreasing the selectivity of the ring-opening reaction. The main side reactions are detailed in Scheme S2 in SI and confirmed by the NMR presented in Figures S5 and S6 in SI.

The occurrence of side reactions during polyol synthesis can be further observed by size-exclusion chromatography (SEC) characterization. The calibration method for the SEC is defined using the molar mass of a polystyrene standard. The interactions between the columns and the studied samples do not coincide with polystyrene, therefore the exact molar mass was not determined. However, the samples can be studied and compared in terms of retention time. As a reminder, the smaller the molecules are, the higher their retention time will be. As shown in Figure 2, MAO and EMAO present a narrow distribution, which corresponds to the unsaturated and epoxidized triglycerides, respectively. Polyols present a broader distribution in molar mass. During epoxide ring-opening, chains with lower molar mass were formed, and this can be due to the ester scission side reactions, as presented in Scheme S2 in SI. Transesterification³⁷ and transamination³⁸ represented in Scheme S2 divide the triglycerides into diglycerides and fatty acids. This side reactions are confirmed by the acidity index as described in SI. Only EMAO-EtOH presents a significant portion of high molar masses with

retention time close to the one of the EMAO distribution. For a portion of the EMAO-EtOH polyol, the triglyceride structure is conserved. As depicted in Table 1, this is confirmed by the average functionality of EMAO-EtOH, which is the highest. Significant portions of low molar masses were formed for EMAO-HCl, EMAO-DEA and EMAO-AA.

Figure 2. Size exclusion chromatogram of EMAO-HCl, EMAO-DEA, EMAO-AA, EMAO-EtOH, EMAO and MAO.

For the PUF synthesis, the viscosity of the polyol plays a crucial role. The quantity of air bubbles trapped in the liquid foam mixture and the diffusion of isocyanate molecules toward polyol is controlled by the viscosity. In the PUF industry, the polyol used are required to have a viscosity preferentially under 50 Pa.s.³⁹ As stated in Table 1, the measured viscosity of the fossil-based polyol is 0.7 Pa.s, and the biobased polyols range from 10^2 to 10^6 Pa.s. The viscosity of all bio-based polyols is high compared to fossil-based polyol. One reason for this

high viscosity can be related to the crystalline structure of oils. The crystallization of triglycerides is a complex phenomenon⁴⁰ depending on numerous factors such as the symmetry of the chain, the number of carbon atoms, the interactions between the chains (H-bonding)⁴¹ and the fatty acid/diglyceride content.⁴² DSC experiments realized on MAO, EMAO and the polyols, presented in Table 1 and Figures S7-S12 in SI, show the primary crystallization and melting temperature. Among the EMAO derived polyols, EMAO-AA has the lowest viscosity. According to DSC, it also has the lowest melting temperature, lower than 20 °C. This melting temperature can be explained by the low I_{OH} content in the polyol. On the contrary, the EMAO-DEA has an extremely high viscosity, exhibiting an almost solid behavior at room temperature. This high melting point can be explained by the presence of H-bonding atom, such as nitrogen in the polyol enhancing the crystal stability. The DSC results show a high melting point, superior to 40 °C, which explains the soaring viscosity. The significant thinning effect with the temperature is presented in Figure S13 in SI.

The thermal stability of the polyols was evaluated with thermogravimetric analysis. The main degradation temperature, determined at the maximum of the weight loss derivative (DTG) curve of MAO, EMAO and the polyols are presented in Table 1. The detailed TGA and DTG results are presented in Figure S14-S19 in SI. The epoxidation reaction shifted the main degradation from 412 °C for MAO to 298 °C for EMAO. The introduction of a three-membered ring with oxygen increased chain scission and thus induces degradation. EMAO-AA, EMAO-EtOH and EMAO-DEA exhibit similar main degradation temperatures around 320 °C. The main degradation in EMAO-HCl polyols is around 365 °C. This 45 °C difference can be explained by the chlorine introduced in the polyols structure, which could trap radicals in the gas phase, thus limiting initial thermal degradation.⁴³

Reactivity of foams synthesis

The foams were prepared via an A-B composition procedure. The detailed formulations of the studied PUF were presented in Table 2. The foams are denoted according to the ring-opening nucleophile used for the polyol synthesis and the weight percentage of fossil-based substituted by the biobased polyol. For example, the foam made with 25 wt% of the fossil-based polyol substituted by EMAO-AA is denoted AA25. The A-part was composed of polyols, a catalyst, a surfactant, a flame retardant and two blowing agents. The catalyst was miscible in the polyol phase, and the surfactant reduced the surface tension between the polyol and the blowing agent phase. The low viscosity of this complex blend was driven by the primary component: the polyol mixture. As previously discussed, the biobased polyols were more viscous than the fossil-based polyol. Furthermore, the biobased polyols were not miscible into the fossil-based polyols at room temperature. To address this issue, each biobased polyol was mixed with a fossil-based polyol in the proportion described in Table 2, at 60 °C. The polyol mixture was cooled down to room temperature and then introduced into the A-part as a sole polyol. The B-part composed of the polymeric 4,4'-methylene bis(phenyl isocyanate) (pMDI) was then added to the A-part under vigorous stirring for 5 seconds. The foams were let to rise freely in a plastic cup.

Table 2. Formulation in parts of the total polyol content of the different PUF studied systems.

Foam formulation		Ref	AA 25	DEA 25	EtOH 25	HCl 25	EtOH 35	EtOH 50	EtOH 75
<i>A-Part</i>									
Polyols	Daltolac R570 (fossil-based)	100	75	75	75	75	65	50	25
	EMAO-AA		25						
	EMAO-DEA			25					
	EMAO-EtOH				25		35	50	75
	EMAO-HCl					25			
Catalyst ^[a]	DMCHA	2.0	1.76	1.79	1.85	1.81	1.79	1.7	1.55
Surfactant	Tegostab B84501	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
	TCPP	10	10	10	10	10	10	10	10
Flame retardant									
Blowing agent	Water	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
	Isopentane	15.0	12.4	12.7	13.4	13.0	12.7	11.8	10.1
<i>B-Part</i>									
Isocyanate	pMDI	168	155	158	168	162	159	145	122

^[a] Catalyst was set at 0.63 % of the total weight of all compounds in all formulations

The expansion behavior of PUF was first evaluated by two methods. The first method is the determination of characteristic times during PUF formation such as the cream, gel and tack-free times. The second method is based on temperature and expansion rates recorded with a Foammat device. As a reminder, the results of PUF foams containing biobased polyols were compared to a reference containing solely a fossil-based polyol formulation, identified as Ref. Figure 3 and Table S3 in SI present the PUF formation characteristic times. Characteristic times of Ref were 12, 47 and 62 seconds for cream, gel and tack-free time, respectively. The cream, gel and tack-free times were higher with the biobased polyols except in the case of EMAO-DEA polyol. The slow reactivities of HCl25 and AA25 were further confirmed by the corresponding increased expansion rates (Figure 4 and Figure S20 in SI). The lower reactivity of the biobased polyols can be explained by the hydroxyl group position, which was in the middle of a hindered chain. Moreover, the hydroxyl groups of the biobased polyols are

secondary hydroxyls, whereas the fossil-based polyol contains primary hydroxyls and have an increased reactivity to isocyanate groups. Furthermore, the acidity index of HCL25 and AA25 were the highest of all biobased polyols. As explained in SI, the catalyst can be deactivated by the residual acidity explaining the slow reactivity of these two polyols. The gel time of EMAO-DEA was 12 seconds faster than the Ref. The epoxide ring-opening with secondary amine forms tertiary amine in beta position of the hydroxyl. This tertiary amine included on the polyol catalyzes the reaction between isocyanate and hydroxyl groups.⁴⁴ The expansion rate of DEA25 detailed in Figure 4, confirms the acceleration of the blowing reaction.

Figure 3. Characteristic times of the different foams. The y-axis was broken since the gel time and tack-free time of ESO-DEAcat surpass 600 s and 1200 s, respectively.

The substitution of 25 wt% of fossil-based polyol by EMAO-EtOH in a PUF formulation has little influence on the foam reactivity. The corresponding lower I_{OH} value seems to be balanced out by the higher functionality of this biobased polyol. The transition between 25 to 75 wt% of EMAO-EtOH in PUF results in an increased gel time from 53 to 91 seconds. PUF made with increasing amounts of EMAO-EtOH were less reactive than the reference. This is confirmed by the expansion profiles of these PUF (Figure S20 in SI), where the peak of the expansion rate was delayed in time. Moreover, the maximum rate and acceleration were lower than the Ref PUF. With increase weight substitution of EMAO-EtOH, the lower I_{OH} became critical for the reactivity of the PUF.

Figure 4. Expansion rates (mm/s) determined with Foamat device for DEA25 (—), Ref (—), EtOH25 (—), HCl25 (—) and AA25 (—).

Analysis of the foam cell morphology

The cell morphology of PUF foams impacts their mechanical and thermal properties directly. The anisotropic coefficient (R) presented in Figures 5A and 5B is a parameter of the cells shape of the foams observed by microscopy. The R coefficients range between 1 (spherical cell) and 2 (ellipsoidal cell).⁴⁵ The cells were elongated in the longitudinal (parallel to the foam rise direction, Figure 5A) direction, as shown by a higher anisotropy coefficient of 1.6. Cells stretched in the longitudinal direction were characteristic of a partially free foaming process performed in an open cylindrical mold.⁴⁶ For the reference PUF, in the transverse direction (perpendicular to the foam rise direction, Figure 5B), R was between 1.2 and 1.3, relatively close to a spherical cell. The emission scanning electron microscope (SEM) images of Figure 6 and Figure S21 in SI exemplify the spherical and ellipsoidal cell shapes in the transverse and longitudinal direction, respectively. The substitution of the fossil-based polyol by synthesized polyols in the formulation did not influence R in the transverse direction. However, in the longitudinal direction, the introduction of 25 wt% of EMAO-HCl, EMAO-DEA and EMAO-EtOH decreases significantly R . The polyols structure was composed of long non-polar carbon chains and chains with polar groups such as hydroxyls and esters. This combination of polar and non-polar groups is generally specific to surfactants.⁴⁷ The lower R coefficient could be explained by reduced surface tension between the polymers mixture and the blowing agent. Furthermore, the substitution of the fossil-based polyol by biobased polyols increased the viscosity of the premix. In the case of AA25 and EtOH35, the anisotropy coefficient was 1.8 and 1.9, respectively. Higher R compared to Ref can be an indication of low compatibility between these polyols and the reference polyols. The introduction of 35 wt% of EMAO-EtOH could be a critical value for the polyols' compatibility. The decrease of R with the increasing portion of EMAO-EtOH after 35 wt% of substitution supports this theory.

Figure 5. Feret diameters and aspect ratio in the longitudinal (A) and transversal (B) direction.

The cell sizes of PUF foams were measured on SEM images in the transverse and longitudinal direction, represented in Figure 6 and Figure S21 in SI, respectively. The wide distribution of cell sizes observed on SEM photos results in a high standard deviation for the cell size measurement. A portion of DEA25 cells in the transverse direction seem damaged (Figure 6). This unusual cell morphology was due to the fast expansion of the DEA 25 foam (Figure 4). In this case, the cream and gel times were 25 % shorter than the Ref, which generates

a more sudden foaming behavior of the reaction mixture. This faster reactivity allows less time for the organization of the cells in the medium before gelation. The corresponding distribution, modeled by a central binomial distribution, was represented in Figure S22 in SI. The EtOH75 cell sizes were larger than the reference ones. The EtOH75 formulation was the slowest to cross-link, with a gel time two-fold longer than the reference. The cell size was controlled by the polymerization of the solid PU struts and walls around air bubbles. The classical theory of nucleation is based on the generation of cells from the isopentane droplet.⁴⁸ This theory is partially discussed and contested for the benefit of the pockets of air entrapped during the mixing stage.⁴⁹ The blowing agent droplets migrate into the air bubbles. In the case of a slow network formation, air bubbles and thus cells grow bigger through a coalescence phenomenon combined with Ostwald ripening.⁵⁰ Furthermore, the EtOH75 formulation has the lowest temperature throughout the foaming process, as depicted in Figure S23 and S24 in SI. Thus, a long gel time combined with low exothermic behavior results in coarser cell morphology.

Figure 6. SEM images of all formulations in the transverse direction (Scale = 500 microns).

Despite the various reaction times, expansion rates and cell sizes, the final synthesized PUF densities ranged between 28 and 32 kg/m³, and are detailed in Table S4 in SI. The foams were produced at 20 °C, and isopentane has a boiling point of 28 °C. Thus, a small increase in the core temperature of the material is sufficient enough to vaporize the physical blowing agent. The volume change from liquid to gas (expansion ratio) is around five times for the isopentane.⁵¹ According to the perfect gas law, in order for its volume to double, a mole of gas needs to increase its temperature of 300 °C. The principal volume change is done by the state change between liquid and gas. The reaction between isocyanate and water occurs first and liberates enough energy to vaporize the isopentane. Moreover, the reaction generates gaseous

CO₂, accounting for a third of the total gas amount in the foam, thus contributing to the expansion.

Biobased catalyst

As previously described, the substitution of 25 wt% of fossil-based polyol by EMAO-DEA in a PUF increases the reactivity of the foam. The EMAO-DEA was described as a catalytic polyol because the structure contained tertiary amines that increased the isocyanate and hydroxyl groups reactivity. As previously discussed, EMAO-DEA exhibits an almost solid behavior at room temperature. This high viscosity caused mixing issues that made it difficult to be used solely as a catalyst. Thus, to achieve a biobased PUF catalytic polyol with lower viscosity, epoxidized soybean oil (ESO) underwent a ring-opening reaction by DEA to yield ESO-DEA. The detailed synthesis procedure of ESO-DEA is detailed in SI. The viscosity of ESO-DEA was 33 Pa.s at ambient temperature and six orders of magnitude lower than EMAO-DEA (Figure S13 in SI). The epoxide signal located at $\delta=2.8-3.2$ ppm in ¹H NMR of ESO-DEA presented in Figure S25 in SI demonstrated an incomplete epoxide conversion. As previously discussed, the ³¹P NMR I_{OH} measurement is not selective toward hydroxyl groups. The detailed estimation of the epoxide and hydroxyl groups content in ESO-DEA is depicted in Equations S7-10 in SI. The epoxide conversion was estimated at 59 % by ¹H NMR analysis, 66 % by OH titration and 68 % by epoxide titration (Table S5 in SI). ESO-DEA was a polyol with two different catalytic sites: tertiary amine for the urethane, urea and isocyanurate formation and epoxide for the isocyanurate formation.⁵² The retention time of ESO and ESO-DEA, determined by SEC analysis (Figure S26 in SI), were similar. In contrast to EMAO-DEA, the structure of the triglycerides of ESO-DEA is mainly conserved after the ring-opening reaction.

Table 3. Formulation in parts of the total polyol content of the fossil-based reference (Ref) and the catalyst-free foam (ESO-DEAcat).

Foam formulation		Ref	ESO-DEAcat
<i>A-Part</i>			
Polyols	Daltolac R570 (fossil-based)	100	100
Catalyst ^a	DMCHA	2.0	
	ESO-DEA		4.57 ^[a]
Surfactant	B84501	2.5	2.5
Flame retardant	TCPP	10	10
Blowing agent	Water	1.6	1.6
	Isopentane	15.0	15.4
<i>B-Part</i>			
Isocyanate	pMDI	168	193

^[a] the OH groups were taken into account for the index calculation.

A trial foam was carried out by a complete substitution of the fossil-based catalyst, as depicted in formulation ESO-DEAcat in Table 3. The other parameters were kept constant with respect to Ref formulation. The hydroxyl content of the ESO-DEA was taken into account to calculate the index and the isocyanate quantity. The ESO-DEAcat PUF rise time was 15 times longer than the Ref with fossil-based catalyst. The reactivity was sluggish (Figure S20 in SI), and the core temperature was close to room temperature (Figure S23 in SI). The slow reactivity can be possibly explained by the presence of hydroxyl groups near the tertiary amine. The electron-withdrawing effect of the hydroxyl groups decreased the catalytic activity of the tertiary amine.⁵³ The slow rise of the foam led to cells almost twice as large as Ref cells (Figure 6 and Figure S21 in SI). ESO-DEAcat has a density of 36 kg/m³. The density is almost not impacted by the slow reactivity of the foam. As previously explained, the main volume change was due to the transition between liquid to gas state.⁵⁸ The physical blowing agent, isopentane, vaporizes at 28 °C to form the foam. The foam produced with a biobased catalyst has an acceptable density but rather low reactivity and large cells.

Fire behavior, mechanical and thermal analysis of foams

The characteristic times and cell size investigation empowers the selection of foams with comparable reactivity and cell morphology compared to Ref for further characterization. EMAO-EtOH was the most suitable polyol and EtOH25 formulation was the closest to Ref in terms of reactivity. PUF EtOH25, EtOH50, AA25 and HCl25 were further thoroughly investigated by compression tests, flammability tests and thermal conductivity measurements. These properties are specifically linked to requirements for applications, such as, thermal insulations (foams for buildings, transportation and housing).

The conductivity was measured according to the EN 12667 standard procedure which requires the measurement to be performed at an average temperature of 10 °C. Nevertheless, at this temperature, water condensation could happen at the surface of the sample and thus distort the results. Thus, PUF were also measured at an average temperature of 20 °C to confirm the observed trend. The theory of the thermal conductivity is described with Equation S11 and S12 in SI. As depicted in Table 4, the thermal conductivity of the reference foam was 23.9 mW/(K.m). The foams with biobased polyols have a similar thermal conductivity. The q_{gas} represents 65 % of q_t .⁵⁴ Isopentane was used as a physical blowing agent for all foams; thus, the thermal conductivity was similar. The variation of thermal conductivity can be explained by the conduction through the matrix and the radiation. It was demonstrated that smaller cell size decreases lambda values via the expression of q_{rad} by the Rossland equation.^{45,55} The larger cells of EtOH50 and AA25 and the smaller closed-cell content could explain the higher thermal conductivity. The substitution of 25 wt% of the fossil-based polyol by EMAO-HCl or EMAO-EtOH did not influence λ .

Table 4. Thermal conductivity, closed-cell content and compression strength for Ref, AA25, HCl25, EtOH25 and EtOH50 foam.

		Ref	AA25	HCl25	EtOH25	EtOH50
Thermal conductivity 10 °C initial value	$mW/(K.m)$	23.9 ± 0.5	24.6 ± 0.5	24.3 ± 0.5	24.0 ± 0.5	24.5 ± 0.5
Thermal conductivity 20 °C initial value	$mW/(K.m)$	25.4 ± 0.5	26.1 ± 0.5	25.7 ± 0.5	25.2 ± 0.5	26.1 ± 0.5
Closed-cell content	%	93 ± 1	91 ± 1	93 ± 1	93 ± 1	92 ± 1
Compression strength	kPa	330 ± 20	260 ± 20	300 ± 20	290 ± 20	270 ± 20

The foam mechanical properties depend on numerous factors such as the macromolecular architecture of polyol and polyisocyanate, density, cell sizes and morphology. As previously discussed, the foam densities were comparable. As depicted by the values in Table 4, compression strength measured in the longitudinal direction ranges from 261 to 334 kPa. The identification of the primary moieties present in the foams was performed by FTIR, presented in Figure S27 in SI. All foams present similar FTIR spectra and characteristic PUF peaks,⁵⁶ such as the N-H stretching band between $\tilde{\nu}=3400\text{-}3200\text{ cm}^{-1}$ for the urethane group. The signal at $\tilde{\nu}=1715\text{ cm}^{-1}$ was due to the different C=O stretching of ester and urethane groups. The Ph-H stretching in the phenyl group from the polymeric isocyanate was located at $\tilde{\nu}=1595\text{ cm}^{-1}$. Surprisingly, band at $\tilde{\nu}=1410\text{ cm}^{-1}$ attributed to the isocyanurate ring appears. Isocyanurates were isocyanate trimers formed by the isocyanate excess in the presence of an amine catalyst at high temperature during the foaming process.^{52,57} The I_{OH} value is a representation of the density of hydroxyl groups in the polyol. The microalgae derived polyols present a lower I_{OH} than the fossil-based polyol. As the ratio NCO/OH was kept constant, a slightly higher cross-linking density was obtained with the reference foam. The mechanical properties of HCl25 and EtOH25 were similar to the reference. Compared to EMAO-AA, the

value of I_{OH} of EMAO-EtOH and EMAO-HCl is higher. The lower cross-link density could explain the lower mechanical properties of AA25.

The dimensional stability was performed by dimension measurement of foam specimen before and after being placed for 48 hours in a cold (-20 °C) or warm and humid (70 °C and 90 % relative humidity (RH) environment. The dimensional stability at 70 °C under 90 % RH demonstrates the soaking properties of the foam. As presented in Table 5, the dimension of all foams increased by a maximum of 1.4 % in the warm environment. The humidity present in the chamber soaks the foam. Foams obtained with MAO derived polyols tend to absorb less water. The hydrophobic character of the polyol must be reducing the water absorption. This point was confirmed by the EtOH50 dimension evolutions, which were the lowest.

The cold environment reduces the pressure applied by the gaseous blowing agents on the closed-cell walls. The glass transition temperature of the PUF system is around 50 °C,⁵⁸ so the decrease in temperature reduces the chain mobility. In PU, the glass transition temperature is closely related to the chain mobility of the soft segments. The shrinkage of the foam in a cold environment was minimal (inferior to 0.5 %). Nevertheless, EtOH50 and AA25 have a slight tendency to contract more than the reference foam. The cells sizes impact the dimensional variation. A higher gas volume causes a more significant pressure drop. As a confirmation, AA25 and EtOH50 both have coarser cells and higher shrinkage than the reference.

Table 5. Dimensional variation of Ref, AA25, HCl25, EtOH25 and EtOH50 foams in both environments (cold or warm & humid).

		Ref	AA25	HCl25	EtOH25	EtOH50
48h at 70 °C, 90 % RH						
<i>Length</i>	%	1.4	1.3	1.2	1.3	0.9
<i>Width</i>	%	1.4	1.3	1.2	1.2	0.9
<i>Thickness</i>	%	0.2	0.1	0.3	0.1	0.1
48h at -20 °C						
<i>Length</i>	%	-0.2	-0.3	-0.2	-0.2	-0.3
<i>Width</i>	%	-0.1	-0.3	-0.2	-0.2	-0.3
<i>Thickness</i>	%	0.1	0.1	0.1	0.1	0.1

The substitution of a fossil-based by biobased polyols was performed, and the impact on the main foam properties was minimal. The introduction of MAO derived polyols slightly improves the dimensional foam stability in a warm and moist environment. Furthermore, fire behavior tests, detailed in Figure S28 and S29 and Table S6 in SI were realized. No significant negative or positive impact of the biobased polyols was noticed.

CONCLUSION

This study shows the great interest in developing closed-cell PUF from microalgae resources, more particularly polyunsaturated triglycerides from extracted oil, without competition with food applications. Several biobased PUF systems have been successfully elaborated using different green chemistry approaches. Compared to fossil-based systems, they present high performances in connection with, e.g., insulation applications.

The modification of unsaturated MAO into efficient polyols through epoxidation and ring-opening was successfully accomplished. The biobased polyols reported lower overall hydroxyl functionality than expected due to the inherent side reactions of the ring-opening of epoxides via ethanol, diethylamine, acetic acid and hydrochloric acid. Nevertheless, the I_{OH} of

the newly synthesized biobased polyols were controlled and suitable for PUF synthesis. The substitution of a conventional fossil-based polyol by microalgae derived polyol was examined up to 75 wt% and well-performing rigid PUF were obtained. The substitution of 25 wt% of the fossil-based polyol by EMAO-EtOH produces foams with low thermal conductivity of 24.0 mW/(K.m), which is comparable to commercial systems. The cells are slightly smaller than the fully fossil-based foam and the corresponding compression strength is 290 kPa. The other properties were similar in every aspect to the reference. In this study, for the first time, a catalyst-free rigid PUF was synthesized with a triglyceride-based catalytic polyol. Despite a slow expansion rate, ESO-DEAcac PUF has a density of 36 kg/m³. The regulation on volatile compounds in the building industry makes the catalytic polyol a viable solution. Nevertheless, the actual slow reactivity is a problem for the adaptation to an industrial process.

The perspectives of this work are vast. The optimization of the ring-opening reaction of epoxidized microalgae oil with ethanol could lead to biobased polyols which present high performance in connection with the targeted materials. The reduction of side reactions could be achieved by decreasing the temperature or the use of a solvent. This optimization should increase the I_{OH} and functionality of the polyol and lead to higher reactivity, cross-link density and, thus, mechanical properties of the foam. The ring-opening of biobased oils with secondary amine paves the way to a new generation of biobased catalytic polyol. Future works should focus on the development of more efficient catalysts by the introduction of more sterically hindered secondary amine on oils. To further assess the intumescent properties of chlorine-containing polyols such as EMAO-HCl, limiting oxygen index or calorimetric cone experiments could be further investigated.

The ring-opening reaction on MAO could be used to produce surfactants by the introduction of a long alkyl chain or, similarly, a flame retardant component by the introduction of phosphorous moieties. With some additional studies, polyols, catalysts, surfactants and fire

retardants could be synthesized by ring-opening of the platform molecule MAO. And finally, the utilization of biobased dimeryl diisocyanate could lead to a fully biobased PUF.

SUPPORTING INFORMATION contains the detailed polyols and foams analysis procedures, the ^{31}P NMR spectra, FTIR spectra, side reactions during epoxide ring opening, DSC and TGA thermograms, viscosity measurements, cells size distribution, biobased catalyst analysis and the fire behavior of the foams.

AUTHOR CONTRIBUTIONS

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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The microalgae oil was epoxidized and ring-opened to be introduced into rigid polyurethane foams which were fully characterized.