

## Research Article

# Synthesis of new polyester polyols from epoxidized vegetable oils and biobased acids

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Biobased polyols were synthesized from reaction between epoxidized soybean oil and lactic, glycolic, or acetic acids. Polyols were characterized by NMR, alcohol and acid titration, and SEC. These analyses allowed to determine an average hydroxyl functionality between 4 and 5, with an oligomer content close to 50 wt%. Synthesized polyols were formulated with isocyanate to yield polyurethanes (PUs). Thermal and mechanical properties of obtained materials showed that synthesized polyols lead to rigid and brittle material with Young moduli higher than 900 N/mm<sup>2</sup> at RT and with  $T_g$  values around 50°C.

**Practical application:** The products of the chemistry described in this contribution, i.e.: polyol from vegetable oils and lactic, glycolic, or acetic acids, provide biobased building blocks for further PUs syntheses by reaction with diisocyanates. The obtained PUs are partially biobased and may be applied as binders and coatings.

**Keywords:** Biobased polyols / Epoxidized oils / Glycolic acid / Lactic acid / Polyurethane

Received: May 28, 2012 / Revised: July 17, 2012 / Accepted: August 15, 2012

DOI: 10.1002/ejlt.201200199



Supporting information available online

## 1 Introduction

The epoxide ring-opening reaction is a widespread method for the functionalization of vegetable oils. Indeed, epoxidation of vegetable oils is an industrial process, mature, well controlled, and little expensive. For example, JEFFADD<sup>TM</sup> B650 product is a vegetable oil based polyol which has been commercialized since March 2010 by HUNTSMAN, aimed at polyurethane (PU) spray foams, rigid foams, coatings, adhesives, and sealants markets, as well as at hybrid polyureas. This biobased polyol is synthesized from the reaction between an alcoholamine with an epoxidized oil, yielding a mixture of compounds with primary and secondary hydroxyl groups [1]. Epoxide function allows to access different derivatives owing to the variety of nucleophiles used for

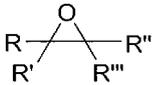
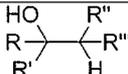
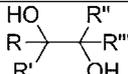
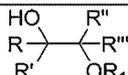
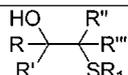
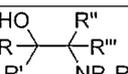
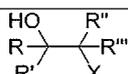
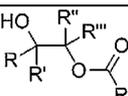
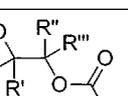
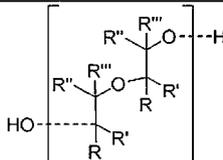
epoxide ring opening. One or more alcohol functions are added on each aliphatic chain, based on the nucleophile used (Fig. 1).

Epoxides groups could be directly hydrogenated by dihydrogen, Raney nickel acting as catalyst [2], leading hydrogenated triglycerides with one secondary hydroxyl function by epoxide group. It is interesting to note the similarity between the hydroxyl structure obtained by this method and natural castor oil. Another interest of hydrogenation lies in removing the unsaturations present in triglycerides, and thus improving their resistance to oxidation. Epoxidized oils can undergo an accelerated alcoholysis with acid catalysts to yield hydroxylated oils. With monoalcohols, this process leads to the formation of polyols with secondary hydroxyl functions [3]. Thus, a very simple method consists in using water with acid catalyst to obtain a hydroxylated oil [4–9]. Moreover, alcohols such as methanol [10, 11], ethylene glycol [12–14], butanol [15], or triethanolamine [16] could be used as nucleophiles to open epoxide ring. The use of a polyol as nucleophile allows to graft at least one primary hydroxyl function and one secondary hydroxyl function on each unsaturated chain of triglyceride. Concerning catalysts, the most

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Substrate	Reactant	Product	Reference
	H <sub>2</sub>		29
	H <sub>2</sub> O		2-7
	HOR <sub>1</sub>		8-18
	HSR <sub>1</sub>		19
	HNR <sub>1</sub> R <sub>2</sub>		1, 20, 21
	HX, X=Cl, Br		22, 23
	HOC(O)R <sub>1</sub>		24-28, 30
	Carbonatation + HNR <sub>1</sub> R <sub>2</sub>		31
	Polymerization		32

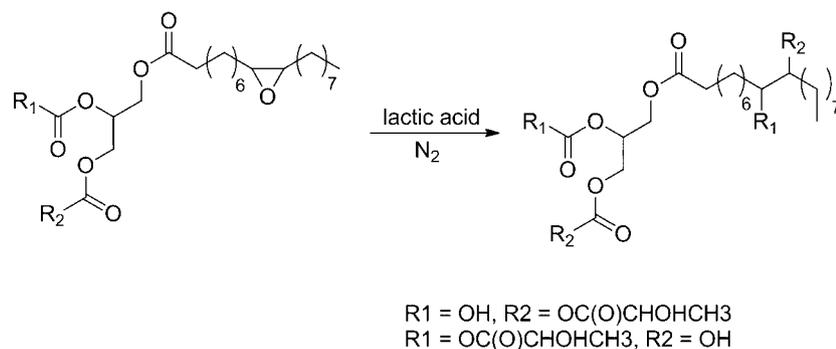
**Figure 1.** Summary of the possible reactions leading to alcohol from epoxidized vegetable oils.

used are sulfuric acid, *p*-toluenesulfonic acid or tetrafluoroboric acid [17]. Heterogeneous catalysts such as activated clays [18] or ion exchange resins [19] were also reported.

During the hydroxylation of epoxidized oils with alcohols, side reactions have been evidenced [20]. Firstly, oligomerization occurs, due to the opening of epoxide ring by alcohol function of hydroxylated oil. And this oligomerization side-reaction depends on reaction parameters. Indeed, degree of oligomerization increases with high concentration of catalyst or low concentration of alcohol reactant. Moreover, transesterification reaction on ester group of vegetable oil is competitive with epoxide ring opening by alcohol. The modification of experimental conditions may favor epoxide ring opening rather than transesterification on ester group. The obtained polyether polyols could react with diisocyanates to yield PUs, particularly in cationic aqueous dispersion, in order to promote the

formation of PU films with interesting stretching properties [21]. Other methods are reported for the epoxide ring-opening reaction, such as the use of a thiol as nucleophile [22]. Amines, such as diethylamine [23] or diethanolamine [24], could also be used as nucleophiles for hydroxylation of epoxidized oils. In that case, reaction parameters, such as catalyst, reaction duration, and temperature should be optimized in order to favor epoxide opening rather than amide synthesis. Indeed, the reaction of amine with ester of triglyceride may be competitive with epoxide ring opening.

Reactions with halogenated reactants, such as HCl or HBr, were also studied [25, 26]. Chlorinated or brominated polyols obtained exhibit densities and viscosities higher than those of methoxylated or hydrogenated polyols. Moreover, ring opening by carboxylic acids such as fatty acids [27], acetic acid [28], acrylic acid [29], hexanoic, or octanoic acids



**Figure 2.** Triglyceride epoxide ring opening with lactic acid.

[30, 31] leads to polyester polyols with interesting properties, particularly as anti-wear lubricants. Carbonation of epoxidized oils followed by addition of alcohol amine led also to polyols [33]. A study reports the ring opening polymerization of epoxidized methyl oleate in presence of  $HSbF_6$  [34]. This reaction was followed by a partial reduction of ester functions, yielding a polyether polyol. This route enables to synthesize polyols with functionality comprised between 2 and 5, allowing interesting formulations for PUs synthesis. A recent study reported epoxide ring opening of epoxidized oils with lactic acid (Fig. 2). Reaction takes place under nitrogen atmosphere during 6 h at  $90^\circ C$ , with a final conversion around 70% [32]. Pan and Webster [35] reported recently the synthesis of polyols with low viscosity synthesized from epoxidized vegetable oil and acetic acid.

This route appears very interesting to us, particularly since it uses only biobased products. The aim of our work was to synthesize biobased polyols by epoxide ring-opening reaction of epoxidized vegetable oils with other biobased acids, with different hydroxyl functionality, in order to compare synthesized polyols toward isocyanates and PU materials properties. Therefore three different acids were selected: lactic and glycolic acids since they are both biobased and present, respectively, a secondary and a primary hydroxyl group. Acetic acid, without hydroxyl group, was selected due to its low cost and widespread use in chemical industry. Epoxide ring opening reaction was studied. Products and by-products were identified. Finally we investigated the effect of different alcohol class on the properties of PU materials obtained from these biobased synthesized polyols.

## 2 Materials and methods

### 2.1 Materials

Epoxidized soybean oil ( $f = 4.1$ ) was supplied by Univar. Voramer 2093, obtained from Dow, is a liquid prepolymer of 4,4'-diphenylmethane diisocyanate (MDI). Acetic acid (>99%), lactic acid (>98%), and glycolic acid (>97%) were purchased from Sigma–Aldrich and used without any purification.

### 2.2 Analytical techniques

SEC was performed on a Varian ProStar Model 210 equipped with an RI refractive index detector. Two PL gel 5  $\mu m$  MIXED-C 600 mm were used at  $70^\circ C$  with a 0.8 mL/min flow rate of THF, calibrated using PMMA standards.

All NMR ( $^1H$ ,  $^{13}C$  NMR) measurements were recorded on a Bruker AC-400 MHz spectrometer at RT in deuterated chloroform ( $CDCl_3$ ). The chemical shifts were reported in ppm relative to tetramethylsilane.

Acid value, IA, represents potassium hydroxide quantity needed to neutralize acid functions present in 1 g sample. A mass of sample of around 0.2 g is exactly weighed and solubilized in 5 mL ethanol. Titration is performed with potassium hydroxide solution (0.01 M), with phenolphthalein as indicator. Each sample is titrated three times. Acid value is calculated with following equation:

$$IA = \frac{V_{eq} \times [KOH] \times 56.1}{ms} \quad (1)$$

where  $[KOH]$  is the molar concentration of potassium hydroxide solution,  $V_{eq}$  is equivalent volume of introduced KOH, and ms is the mass of the sample.

The hydroxyl values of the polyols were determined using the reaction with phenylisocyanate at  $70^\circ C$  for 8 h. The derivated products were then analyzed by  $^1H$  NMR in  $CDCl_3$ .

Isocyanate content in V2093 is measured by indirect titration of dibutylamine in excess by HCl solution, owing to ISO NF EN 1242 standard. In a 100 mL beaker are introduced around 0.4 g of isocyanate exactly weighed, 10 mL of toluene and 10 mL dibutylamine with a 1 M concentration. Solution is completed to 50 mL with acetone. The beaker is closed then stirred during 15 min. Two drops of bromophenol (1% in ethanol) are then added with 100 mL ethanol under vigorous stirring. Solution is then titrated with a 1 M HCl solution. Each sample is titrated three times. Reference sample without isocyanate is also titrated in same conditions in order to determine total quantity of introduced dibutylamine. Isocyanate content, %NCO, is calculated with

following equation:

$$\%NCO = \frac{4.2 \times [HCl] \times (V_0 - V_{eq})}{ms} \quad (2)$$

where [HCl] is the molar concentration of HCl solution,  $V_0$  is the equivalent volume of HCl introduced to titrate total quantity of dibutylamine,  $V_{eq}$  is the equivalent volume of HCl introduced to titrate quantity of unreacted dibutylamine, and  $ms$  is the mass of introduced sample.

Gel time measurements were performed with a AR1000 TA instrument rheometer, equipped with a steel cone 2° of 60 mm diameter with a truncation of 58  $\mu\text{m}$  (angle 2:00:35). Measurements were performed in oscillation mode for a deformation of 1%, with a sampling time of 10 s. Reaction middle is mixed 1 min at 20°C before being casted on Peltier plane at 20°C. Multifrequency procedure is then run rapidly (0.5/1.077/2.321/5 and 10 Hz). Gel time was determined according to the Winter–Chambon criterion that implies the independence of the loss factor,  $\tan \delta = G''/G'$ , as a function of frequency.

Swelling measurements of the networks were carried out using toluene as the diffusing agent. The swelling percentage was calculated from the differences in weight between dried and swollen networks. Bars samples (3 mm<sup>3</sup>) of the cured epoxy resins were cut, weighed, and immersed in toluene for 24 h. The samples were then swollen with solvent quickly blotted between sheets of paper and finally weighted. The swelling percentage was calculated as follows:

$$\text{Swelling} = \frac{(W_s - W_d)}{W_d} \times 100 \quad (3)$$

where  $W_s$  and  $W_d$  are the weights of the swollen bar and the dried bar, respectively.

The swollen bars were put in an oven at 110°C for 24 h to dry them. Then, the bars were weighed  $W_{do}$ :

$$\text{Soluble part} = 100 - \left( \frac{W_{do}}{W_d} \right) \times 100 \quad (4)$$

Thermogravimetry analyses (TGA) were performed on a Q50 from TA Instrument. Ten milligram of sample in an aluminum pan was heated from RT to 500°C under a nitrogen or air flow (60 mL/min). The experiments were carried out at a heating rate of 10°C/min.

DSC analyses were carried out on a NETZSCH DSC200 calorimeter. Cell constant calibration was performed using indium, *n*-octadecane and *n*-octane standards. Nitrogen was used as the purge gas. Ten to 15 mg samples were sealed in hermetic aluminum pans. The thermal properties were analyzed at 20°C/min between –100 and 250°C to observe the glass transition as well as crystallization/fusion processes. All the reported temperatures are onset values. For each sample, the thermal history was erased with a first heating ramp up to 100°C.

Mechanical tensile tests were performed on a Zwick metrology Z010 apparatus owing to NF EN ISO 527-1 standard

in order to determine mechanical properties of materials. The apparatus is equipped with pneumatic grips, with 100 mm spacing, a sensor of 500 N, or 5 kN depending on the tested materials and a thermostatically controlled chamber for testing at –10/23/50°C. Traction speed is 10 mm/min, controlled by position regulation, with a preload of 2 N before measurement. Rupture is measure at a force variation of 5% and an elongation variation of  $\pm 1\%$ . Tests need plane specimen samples, of 100 mm length, 10 mm width, and a thickness of around 2 mm. Thickness is measured at three points on each sample and the lowest value is uploaded in the measurement software. After the test, this value is corrected owing to the rupture zone on the sample. Results are an average of measurements performed on three samples.

Dynamic mechanical analysis (DMA) analyses were performed over a temperature range from –150 to 150°C with a heating rate of 3°C/min, using an angular frequency of 1 rad/s. The instrument used was a DMTA Metravib VA815-RDS. DMA specimens were in the form of rectangular bars of nominal size 2 × 10 × 30 mm<sup>3</sup>. Each sample was tested twice.

## 2.3 Syntheses

Syntheses were performed in a unique step in a 2 L round bottom flask equipped with a cooler and a mechanical stirrer. In case of lactic and glycolic acids, epoxidized soybean oil (500 g) was mixed with acid with epoxide/acid ratio of 4:2. Reaction middle was heated at 80°C during 4 h. In case of acetic acid, epoxide/acid ratio was 5:1 and reaction middle was heated at 100°C during 40 h. Products were purified by chloroform/water extraction to eliminate residual acids. Organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated and concentrated under vacuum to obtain viscous yellow oils.

Studied materials are only formulated from synthesized polyols and MDI V2093 prepolymer, with a NCO/OH ratio of 1:1. MDI prepolymer is a viscous liquid constituted of MDI isomers and oligomers. Before casting formulation, reaction mixes are stirred 2 min with spatula.

Tensile tests, TGA and DSC analysis were performed on 170 g formulation samples, casted on plates of 0.2 cm thickness, coated with Teflon.

## 2.4 NMR chemical shifts of epoxidized soybean oil

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 0.85 (9H, a, CH<sub>3</sub>), 1.15–1.6 (71, b, CH<sub>2</sub>), 1.6 (6, c, CH<sub>2</sub>), 2.25 (6, d, CH<sub>2</sub>COO), 2.8–3.2 (8, g, CH), 4.1–4.45 (4, e, CH<sub>2</sub>O), 5.2–5.3 (1, f, CHO).

## 2.5 NMR chemical shifts of AAP polyol

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 0.85 (9H, a, CH<sub>3</sub>), 1.15–1.6 (71, b, CH<sub>2</sub>), 1.6 (6, c, CH<sub>2</sub>), 2.05 (12, j, CH<sub>3</sub>CO), 2.25 (6, d, CH<sub>2</sub>COO), 2.8–3.2 (8, g, CH), 3.3–4.0 (4, h, h', h'', CHOH), 4.1–4.45 (4, e, CH<sub>2</sub>O), 4.75–4.85 (4 – x, i, CHOC), 5.2–5.3 (1, f, CHO), 5.4 (x, i', CHOC).

## 2.6 NMR chemical shifts of GAP polyol

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 0.85 (9H, a,  $\text{CH}_3$ ), 1.15–1.6 (71, b,  $\text{CH}_2$ ), 1.6 (6, c,  $\text{CH}_2$ ), 2.25 (6, d,  $\text{CH}_2\text{COO}$ ), 2.8–3.2 (8, g, CH), 3.3–4.0 (4, h, h', h''), 4.1–4.45 (4, e,  $\text{CH}_2\text{O}$ ), 4.75–4.85 (4 – x, i, CHOC), 5.2–5.3 (1, f, CHO), 5.4 (x, i', CHOC), 4.45 (8, m,  $\text{OCCH}_2\text{OH}$ ).

## 2.7 NMR chemical shifts of LAP polyol

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 0.85 (9H, a,  $\text{CH}_3$ ), 1.15–1.6 (71, b,  $\text{CH}_2$ ), 1.30 (12, k,  $\text{CH}_3\text{C}$ ), 1.6 (6, c,  $\text{CH}_2$ ), 2.25 (6, d,  $\text{CH}_2\text{COO}$ ), 2.8–3.2 (8, g, CH), 3.3–4.0 (4, h, h', h''), 4.1–4.45 (4, e,  $\text{CH}_2\text{O}$ ), 4.30 (4, l, CHOH), 4.75–4.85 (4 – x, i, CHOC), 5.2–5.3 (1, f, CHO), 5.4 (x, i', CHOC).

## 3 Results and discussion

### 3.1 Polyols syntheses

Polyols studied are synthesized by epoxide ring opening reaction on soybean epoxidized oil (HSE) with different carboxylic acids: lactic acid (polyol noted LAP), glycolic acid (polyol noted GAP), and acetic acid (polyol noted AAP; Fig. 3). A mix of different regio-isomers could be synthesized owing to the attack of nucleophile. Disappearance of epoxide functions was monitored by  $^1\text{H}$  NMR. After reaction

completion, products were purified by liquid–liquid extraction with chloroform/water mix.

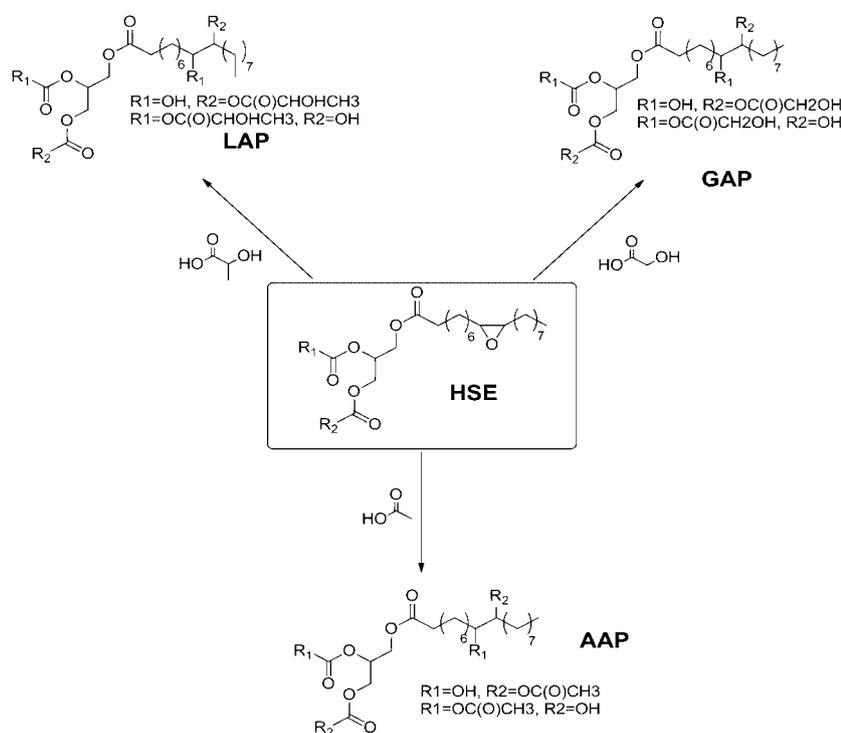
The aimed number of hydroxyl functions per polyol was four for each polyol. In case of reaction of soybean epoxidized oil with lactic or glycolic acids, the initial ratio epoxide/acid was 4:2. In case of acetic acid, the ratio epoxide/acid was 4:5.

With lactic and glycolic acids, ring opening reaction was carried out at  $80^\circ\text{C}$ . In the case of acetic acid, heating was increased up to  $100^\circ\text{C}$  to allow a good yield. Generally, epoxide ring-opening reactions with carboxylic acids are performed above  $120^\circ\text{C}$ . It is interesting to note that presence of hydroxyl function in alpha position seems to activate this reaction, allowing lower reaction temperatures, which is particularly advantageous with vegetable oils to prevent any side-reaction. Acetic acid, with no activating hydroxyl function, needs a higher temperature reaction with reaction duration 10 times longer.

Polyols obtained after purification are soluble in chloroform, acetone, ethyl acetate, tetrahydrofuran, or toluene and are non-soluble in water, hexane, or cyclohexane. Polyols were characterized by  $^1\text{H}$  NMR, SEC in THF. Density was determined with a pycnometer, and acid value was determined by potassium hydroxide titration. Characteristic of polyols are summarized in Table 1.

Acid titration (IA) shows the effectiveness of liquid–liquid extraction performed to purify products since very few carboxylic acid functions are detectable.

Polyols obtained by epoxide ring-opening reaction exhibit a high density and also various viscosities. We observed



**Figure 3.** Syntheses of biobased polyols from reaction between epoxidized soybean oil (HSE) and lactic acid (LAP), glycolic acid (GAP), and acetic acid (AAP).

**Table 1.** Characteristics of synthesized polyols from epoxidized soybean oil

Polyol	Description	Density $\mu$ (g/cm <sup>2</sup> )	$F^{a)}$	Viscosity $\eta_{\text{polyol}}$ (Pa s)	Eq. wt. <sup>b)</sup> (g/eq)	Oligomers <sup>c)</sup> (wt%)	$I_A$ (mg KOH/g)
LAP	HSE + lactic acid	1.04	5.3	47	328	44	3.6
GAP	HSE + glycolic acid	1.05	4.9	221	276	63	2.6
AAP	HSE + acetic acid	1.03	4.3	55	298	57	1.8

<sup>a)</sup> Average functionality determined by <sup>1</sup>H NMR after reaction with phenylisocyanate,

<sup>b)</sup> Equivalent weight of hydroxyl functions,

<sup>c)</sup> Oligomer content in synthesized polyols determined by SEC.

increasing viscosities as following: LAP < AAP << GAP. But viscosity seems resulting from the presence of oligomers in polyols. Indeed SEC measurements showed oligomer contents of 44, 57, and 63 wt% for LAP, AAP, and GAP, respectively (Fig. 4). Thus, the viscosity of polyols seems directly linked to the oligomer content.

Synthesized AAP polyol should be similar to the polyol synthesized by Campanella et al. [28] who reported the synthesis of lubricants from epoxidized vegetable oils reacted with acetic acid. However, this article does not report the presence of oligomers.

In order to determine the precise functionality of synthesized polyols and to identify the oligomerization mechanism, synthesized polyols were characterized by <sup>1</sup>H NMR. Quantities of acid reactants were chosen in order to reach a final functionality of four functions per molecule for each polyols. Indeed, polyols could be compared with identical functionalities. Moreover, a higher functionality would entail higher quantities of isocyanate for synthesis of materials, which would dramatically increase prices of PU. The maximum functionality for LAP and GAP polyols is 4, which will let two unreacted epoxide rings per molecule. However,

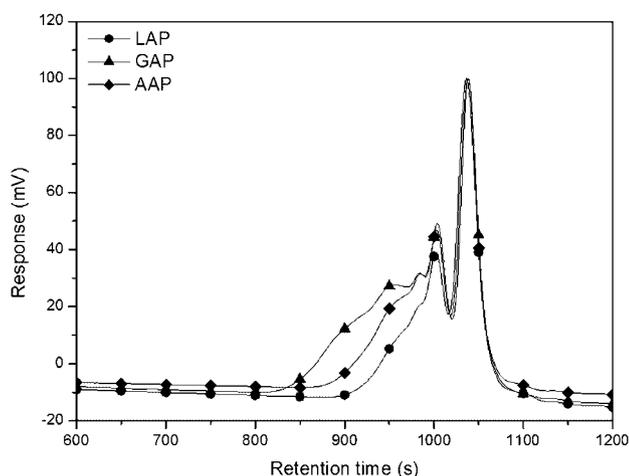
integration of characteristic signals of epoxide ring at 3 ppm (s) on <sup>1</sup>H NMR spectra of LAP and GAP in Supporting Information, Fig. SI1 and SI2, indicates the presence of less than one epoxide per triglyceride. This result indicates that side-reactions of epoxide ring opening occurred during polyol synthesis. And we could conclude that oligomers identified by SEC in polyol were synthesized from these side-reactions.

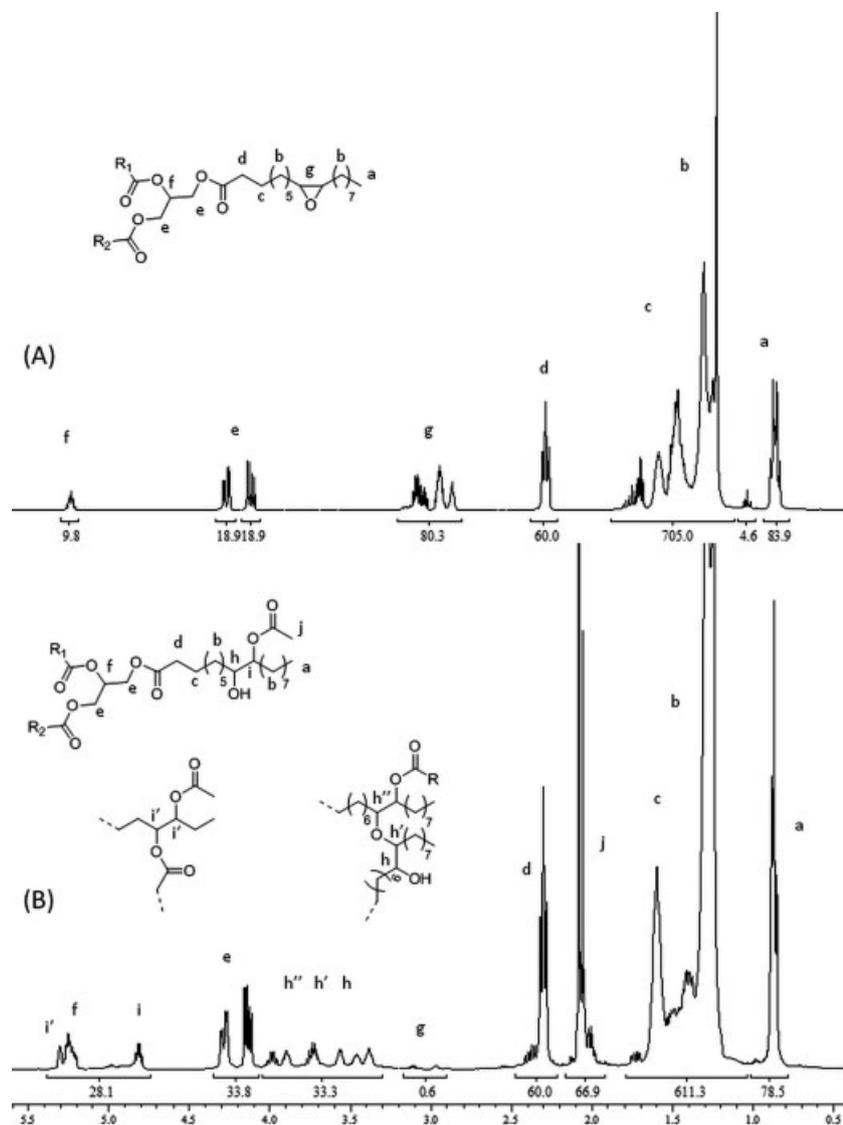
Concerning AAP polyol, we observe on <sup>1</sup>H NMR spectrum < 1% of unreacted epoxide ring (spectrum B, Fig. 5); it seems that the maximum functionality of 4 was reached.

Since that polyols are a complex blend of products, identification was performed by zone on the NMR spectra. Each zone gives indications on average structure of polyols (Table 2). Zone between 2.8 and 3.2 ppm shows evidences on the number of unreacted epoxide rings. Protons in alpha position of secondary hydroxyl functions yielded by epoxide ring opening (CH–OH, h) and protons in alpha position of ethers hinges in case of oligomerization (CH–O–CH, h') are evidenced by the signals between 3.3 and 4.1 ppm, respectively. The zone 4.1–4.6 ppm comprises not only signals of glycerin protons (CH<sub>2</sub>–OCO, e), but also signals of protons in alpha position of hydroxyl functions of glycolic and lactic acids (O–CO–CH/O–CO–CH<sub>2</sub>). Finally, protons in alpha position of ester functions (CH–OCO, f, i, and i') are evidenced by signals between 4.8 and 5.3 ppm. And the signal at 2 ppm is characteristic of protons of methyl group of acetic acid (OCO–CH<sub>3</sub>, j).

Titration by phenylisocyanate (isocyanatobenzene) monitored by <sup>1</sup>H NMR allowed to evidence the presence of primary or secondary hydroxyl functions in the three synthesized polyols (Fig. 6). Indeed, we observed the shift of protons in alpha position of hydroxyl functions in the zone between 4.5 and 5.5 ppm, which is characteristic of presence of carbamate bonds. It is important to note that ether functions close to hydroxyl functions that reacted with phenylisocyanate shifted also by 0.3 ppm. Interpretation of NMR analysis leads to the average hydroxyl functionality of triglycerides (Table 2).

Also, formation of oligomers during triglyceride functionalization could be due to a side-reaction of transesterification (reaction 1, Fig. 7) or ring opening polymerization of epoxide group (reactions 2 and 3, Fig. 7).

**Figure 4.** SEC chromatograms of different polyols LAP, AAP, and GAP.



**Figure 5.**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ) of epoxidized soybean oil (A) and of AAP (B) polyol.

Hypothesis of oligomerization by reaction of epoxide functions is also possible. Thus, a study reported oligomerization of epoxidized fatty esters with  $\text{HSbF}_6$  acid catalyst [36] (reaction 3, Fig. 7). This homopolymerization hypothesis is also supported by Miao et al. [37] for the polymerization of epoxidized oleic acid. This phenomenon could occur in our case, but used acids have not a weak pKa. Moreover, if we

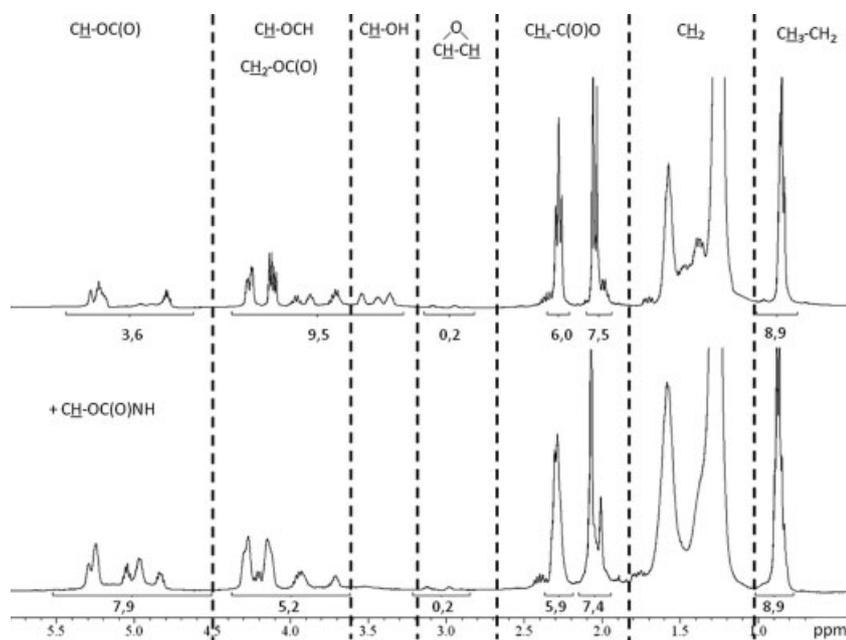
suppose that quantity of oligomers depends on strength of acid, therefore acid ability to catalyze oligomerization reaction, then glycolic and lactic acids, with very close pKa (3.83 and 3.86) should lead to similar contents of oligomers – but it is not the case.

Finally, epoxide ring opening by alcohols is also possible, since it could be catalyzed by acids (reaction 2, Fig. 7). Petrovic

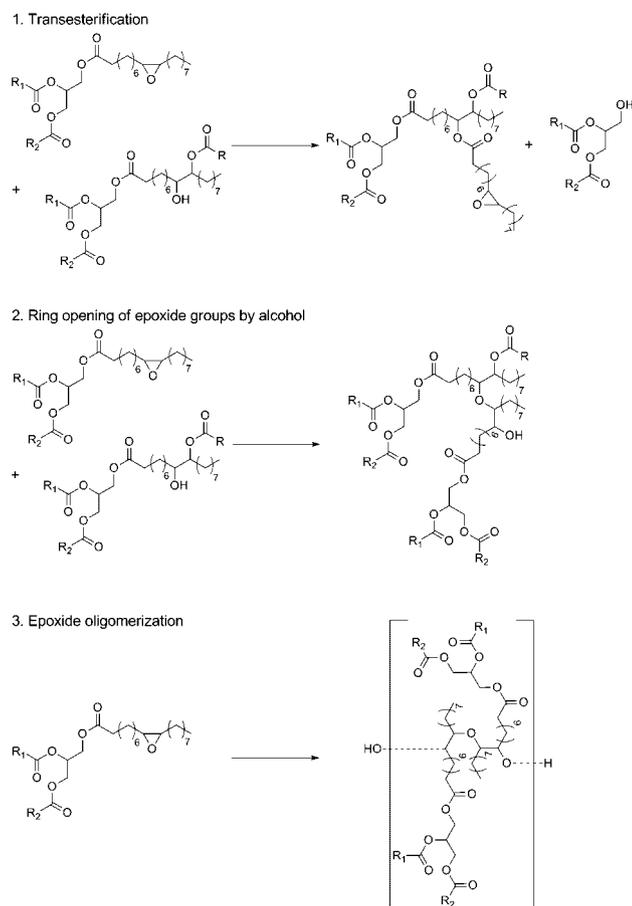
**Table 2.**  $^1\text{H}$  NMR determination of average structure of synthesized polyols

Determined value	Unreacted epoxide rings	Grafted acid functions	Ether hinges	Hydroxyl functions created <sup>a)</sup>
Studied zone in ppm	2.8–3.2	4.6–5.8	4.1–4.6/2	3.2–4.1
LAP	0.8	2.1	1.6	1.2
GAP	0.7	1.6	1.6	1.5
AAP	0.1	2.6	2.5	1.1

<sup>a)</sup> Identified by par  $^1\text{H}$  NMR after reaction with phenylisocyanate.



**Figure 6.**  $^1\text{H}$  NMR spectra of AAP polyol before and after titration with phenylisocyanate.



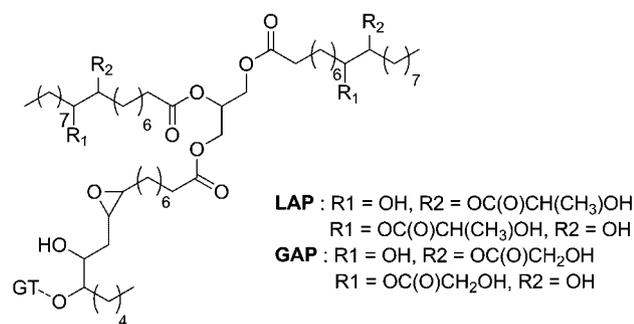
**Figure 7.** Possible side-reactions yielding oligomers during triglyceride epoxide ring-opening reaction with acids.

and coworkers [25] proposed reaction of new hydroxyl functions grafted onto epoxidized vegetable oils to explain the presence of oligomers in case of epoxide ring opening reaction by methanol. This mechanism could well explain formation of the higher quantity of oligomers in case of GAP polyol which presents primary hydroxyl functions which are more reactive. However, this mechanism should yield to the less quantity of oligomers in case of AAP polyol since it presents only secondary hydroxyl functions, less available due to steric hindrance. But it is not the case. Indeed, in the case of AAP, this mechanism is also balanced with a longer reaction duration and a higher temperature which could also favor side-reactions. This side-reaction was also observed by Pan and Webster [35] and they proposed “starved epoxide” conditions to suppress oligomerization between newly formed secondary hydroxyl groups and epoxides. Thus, to determine the mechanism of oligomer formation requires a real modelization work which is not the objective of our study. Our work is focused on the formulation and characterization of materials from synthesized polyols.

Finally, epoxidized vegetable oils ring opening reaction is an interesting method to synthesize biobased polyols. However, side-reactions were evidenced, whose explanation is complex. Anyway, these side reactions lead always to polyols. Thus, epoxidized vegetable oils ring opening reaction leads easily to biobased polyols, odorless, with high viscosity, usable for PUs synthesis.

### 3.2 Polyurethane synthesis

Before considering the PUs, it is noted that unreacted epoxy functions in LAP and GAP polyols (Fig. 8) are able to react with isocyanates introduced for the formulation of the PU



**Figure 8.** Idealized structures of polyols LAP and GAP.

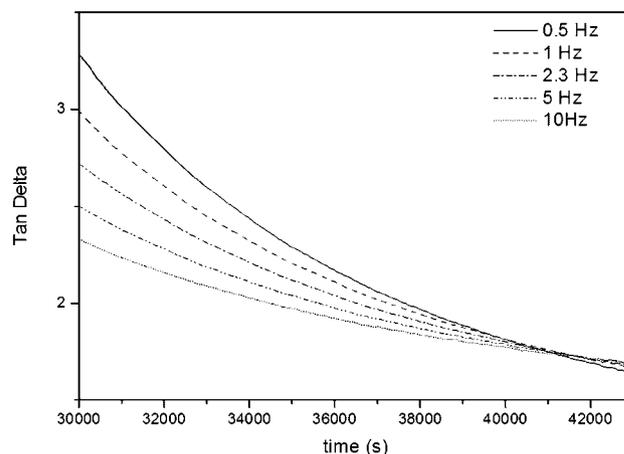
yielding oxazolidone rings. But this reaction is not favored compared to alcohol/isocyanate reaction, since it requires a higher temperature. Indeed, examples of epoxy/isocyanate reaction were reported at 200 °C without catalyst [38], or at temperatures slightly higher than 110 °C but in the presence of imidazole [39] or tertiary amine [40] catalysts. In addition, the V2093 was introduced in stoichiometric quantities with the four alcohol functions present in polyols. The idealized structure of polyol is presented in Fig. 8.

The materials were crosslinked in mass, without catalyst and at RT. The three synthesized polyols (LAP, GAP, and AAP) were reacted with a MDI prepolymer named V2093, to yield, respectively, PU-LAP, PU-GAP, and PU-AAP. The same lot of V2093 was used for the syntheses of all PU materials in order to enable the comparisons. V2093 specifications were a content of isocyanate NCO = 30.46% and an equivalent weight Eq. wt = 137.9 g/eq.

### 3.3 Mixtures analyses

Gel time was determined according to the Winter–Chambon criterion that implies the independence of the loss factor,  $\tan \delta = G''/G'$ , as a function of frequency (Fig. 9).

For polyols resulting from the opening of the epoxide rings, gel time of mixtures ranges as AAP > LAP > GAP (Table 3). It is possible that the observed order is in connection with the type of hydroxyl functions in polyols. Indeed, whereas GAP has primary alcohol functions with



**Figure 9.** Rheology assisted determination of gel time of mixtures polyol AAP/voramer 2093 at 20 °C.

**Table 3.** Results of rheology analyses of reaction mixtures from synthesized polyols

Polyol	LAP	GAP	AAP
$t_{gel}$ (min)	486	371	686

high reactivity, LAP and AAP polyols have only less reactive, secondary alcohol functions. In addition, in the case of AAP, steric hindrance of alcohol functions may explain their low reactivity, and therefore a very high gel time.

### 3.4 Thermal analyses of materials

DSC allows to determine the glass transition temperature of synthesized PUs. The PUs are in the glassy state at RT. And synthesized polyols present all a functionality of 4, yielding polymers of close  $T_g$  values. Transitions of materials are also wide, mainly due to the heterogeneity of composition of polyols. It is noted that the PUs are totally amorphous, since no temperature of melting/crystallization is detected (Table 4).

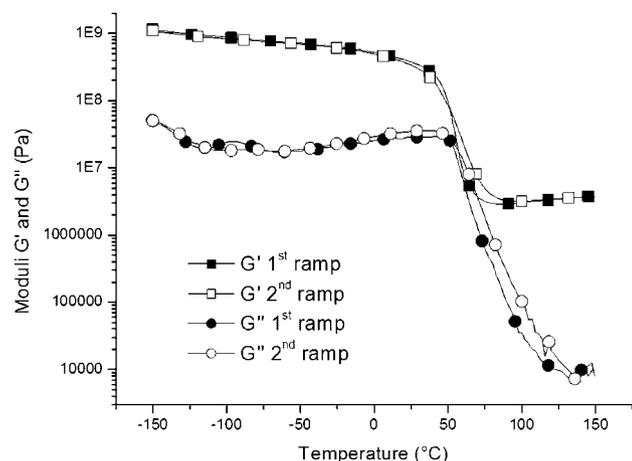
**Table 4.** Summary of thermal characteristics of synthesized polyurethanes

Polyurethane	$T_g^a$ (°C)	$T_g^b$ (°C)	$T_{max}^c$ (°C)	$T_{5\%}^c$ (°C)		Char 500 °C <sup>c</sup> (%)	
				Air	N <sub>2</sub>	Air	N <sub>2</sub>
PU-LAP	52	55	379	295	298	24	10
PU-GAP	47	60	383	300	301	27	12
PU-AAP	43	55	383	293	294	24	10

<sup>a)</sup> Determined by DSC,

<sup>b)</sup> Determined by DMA,

<sup>c)</sup> Determined by TGA.



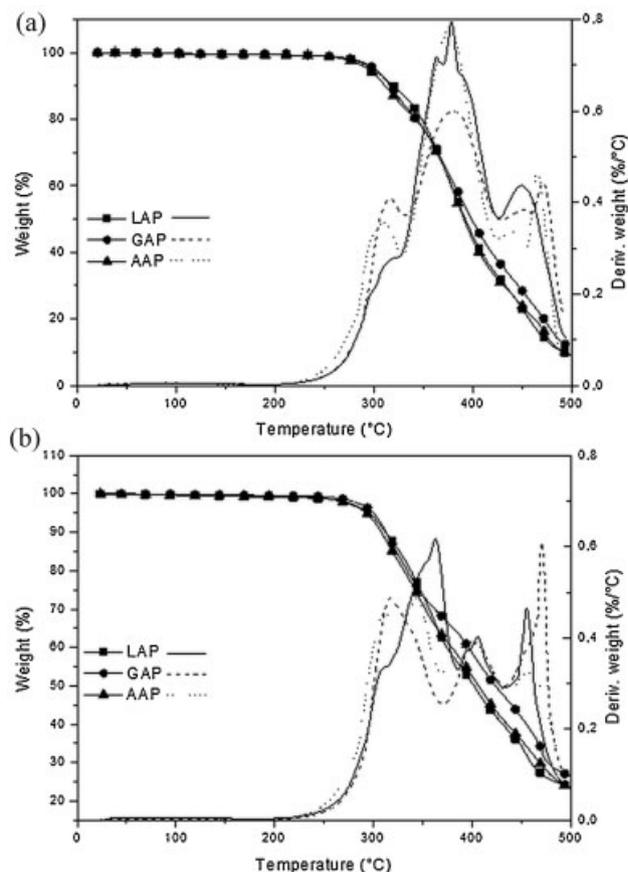
**Figure 10.** DMA analysis of PU-LAP during two heating ramps between  $-150$  and  $150^{\circ}\text{C}$ .

Synthesized LAP polyol is similar to the polyol obtained in the works of Miao et al. [32]. Indeed, both polyols have respective hydroxyl functionality of 4 and 4.2. The NCO/OH ratio varied from 0.63 to 1.05 in the study of Miao et al., and the  $T_g$  values obtained were measured between  $31$  and  $96^{\circ}\text{C}$ . Whereas in our case, we introduced a lack of isocyanate by comparison of hydroxyl functions of LAP and GAP polyols in order to reduce cost and be comparable with AAP. This explains the slightly lower  $T_g$  value measured with LAP polyol in our case, still close to  $T_g$  measured by Miao et al. [32].

The three materials were also analyzed by DMA (Fig. 10 and Supporting Information, Fig. SI3 and SI4). Two measurements were recorded and enabled to determine  $T_g$  values around  $50^{\circ}\text{C}$ , with relatively large transition zones, close to the values obtained by DSC. During the first measurement, we observed a cross-linking reaction with the increase of  $G'$  modulus for all polymers. This result was expected since all materials were cross-linked at a temperature lower than their  $T_g$ . No cross-linking reaction was detected at the end of the second measurement, confirming that cross-linking is complete.

The average  $T_g$  values obtained during the second measurements remain very close to the first values. Indeed, despite an incomplete cross-linking, the properties of the three synthesized PU are close to the “maximum” properties. The reaction of cross linking is favored. The glass transition zone widens between the first and the second heating, indicating a dispersity of the macromolecular chains between nodes of cross-linking. The diversity of the hydroxyl functions present in polyols may help to explain this phenomenon. Indeed, these different hydroxyl groups have different reactivity and steric hindrance. Some hydroxyl functions do not react at RT and their cross-linking is initiated at higher temperatures.

Thermogravimetry analysis provides information on the thermal behavior of materials. The analyses were done at



**Figure 11.** Thermogravimetric results under nitrogen and air of mixtures Voramer 2093/synthesized biobased polyols.

$10^{\circ}\text{C}/\text{min}$  between  $20$  and  $500^{\circ}\text{C}$  under nitrogen and air (Fig. 10). The three PU materials present quite similar degradation mechanism. Under nitrogen, all PU materials present a thermal decomposition in three steps from around  $275^{\circ}\text{C}$ . Decomposition under air is more complex but begins also below  $300^{\circ}\text{C}$ , showing that the first step of the degradation concerns non-oxidative mechanisms (Fig. 11). This behavior is common to polyester polyols, whereas polyether polyols present a better thermal stability under inert atmosphere [41]. The degradation mechanism of carbamate bond, the weakest bond in PUs ( $\text{EC-NH} = 98 \text{ kJ/mol}$ ), is assumed to be identical under air and nitrogen. The differences observed on thermogravimetric results are due to the oxidation mechanism of degradation products. The initial decomposition temperature of C–NH bond in PU depends both on the structure of isocyanate and alcohol, and can follow different routes.

Indeed, Javni et al. have shown that the first step of degradation of PUs obtained from functionalized vegetable oils only leads to the emission of carbon dioxide. This  $\text{CO}_2$  could be due to the formation of carbodiimides groups,

and more probably comes from the cleavage of carbamate bond [42].

While the first degradation step concerns the decomposition of the hard segments, under nitrogen the second and third steps concern the decomposition of the soft segments. Isocyanates formed in the first step could dimerize in the second step to yield carbodiimides which could react with isocyanates, leading to a crosslinked network, or with alcohols, thus yielding substituted ureas. These various relatively stable structures break down in the third degradation step [43]. Under air, the MDI unit could yield benzophenone [44]. Concerning the polyester segment, it leads to the formation of alkyl chains, alcohols, CO, alkenes but also polyenes which form a cross-linked polyaromatic residue [43] (Fig. 12).

Between 300 and 500°C weight loss is less important under air than under nitrogen. For example, the weight loss of the PU-AAFC between 300 and 500°C reaches 84% under nitrogen, whereas it is only 69% under air. This difference can be explained by the cross-linking mechanism which compensates the chain cleavages [41]. Concerning the residue at 500°C, under nitrogen the residue is close to 10% whereas under air, the residue is always higher than 20% (Fig. 11). It is therefore impossible to correlate this residue with isocyanate ratio introduced in formulations as it was suggested by Javni et al. [42] Indeed, this ratio is comprised between 27 and 29% in weight for all samples.

### 3.5 Mechanical tests

The materials were characterized with traction tests at  $-10$ ,  $23$ , and  $50^\circ\text{C}$ . Maximum elongation ( $\epsilon_R$ ), tensile strength at break ( $\sigma_R$ ), and the Young modulus ( $E$ ) were measured (Fig. 13).

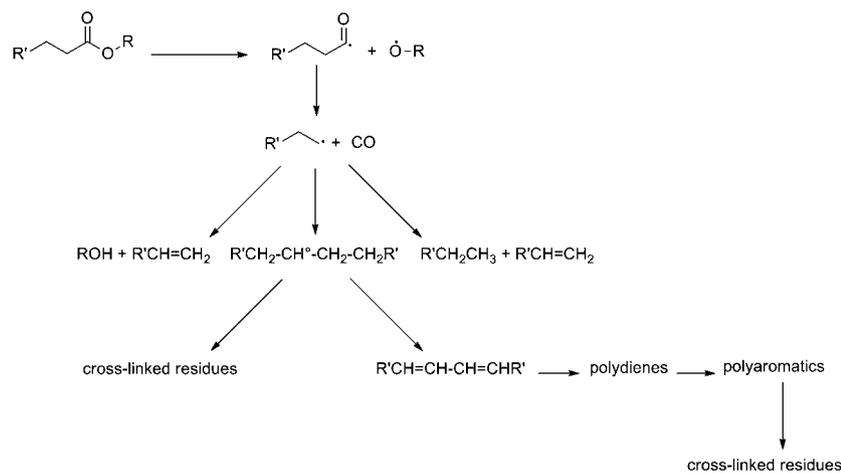
The three polyols lead to rigid materials. At RT as well as  $-10^\circ\text{C}$ , they present low elongations, with high tensile strengths at break ( $>20$  MPa at  $23^\circ\text{C}$ ) and high Young moduli ( $>900$  N/mm<sup>2</sup>). At  $50^\circ\text{C}$ , the  $T_g$  of the materials are reached and they present the behavior of a flexible

material, with higher maximum elongations, lower tensile strengths at break ( $<10$  MPa) and Young moduli around  $80$  N/mm<sup>2</sup> for PU-AAP and PU-LAP, and around  $400$  N/mm<sup>2</sup> for PU-GAP (Table 5).

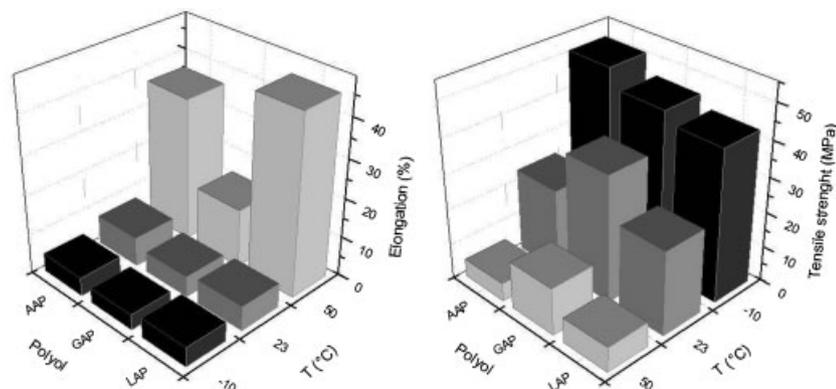
Swelling tests were performed on the synthesized materials. The soluble fraction was also determined in these tests. Materials obtained from synthesized polyols present a soluble fraction lower than 3%, which indicates a quantitative cross-linking (Table 5). Concerning the swelling index, they are low, around 40–60% and the following classification can be established: PU-LAP > PU-AAP > PU-GAP. Petrovic et al. reported also soluble fractions lower than 3% and swelling indexes between 80 and 95% in toluene for PU obtained from different oils functionalized by ring opening of epoxides groups by methanol. They demonstrated that swelling index increases when the functionality of oils decreases [17]. Moreover they obtained swelling index higher than 80% and soluble fractions higher than 2% in the case of hydroformylated vegetable oils [45]. PUs obtained in our study present lower swelling index, probably due to a higher crosslinking density. This low swelling index could also be due to the presence of additional ester functions resulting of epoxide ring-opening reaction by acids. Indeed, these groups are responsible for a higher cohesion in the material (Ecohesive = 2.9 kcal/mol) than ether hinges, e.g. (Ecohesive = 1.0 kcal/mol), limiting penetration of toluene in the PU matrix.

### 4 Conclusions

The epoxide ring-opening reaction of epoxidized soybean oil by glycolic, lactic, and acetic acids allowed the synthesis of biobased polyols used for the formulation of PU materials. This reaction is really easy with lactic and glycolic acid whereas with acetic acid it is necessary to heat at higher temperature during a longer time. The three synthesized polyols led to materials with similar thermal and mechanical properties, except the gel time which strongly depends on the type of hydroxyl function of polyol. Polyol obtained from



**Figure 12.** Degradation mechanisms of esters under oxidizing atmosphere.



**Figure 13.** Maximum elongation and tensile strength at break of PUs obtained from synthesized biobased polyols at  $-10$ ,  $23$ , and  $50$  °C.

**Table 5.** Summary of mechanical tests performed at  $23$  °C on materials obtained from the three synthesized polyols

PU	$T_g$ (°C)	$\epsilon_R$ 23°C (%)	$\sigma_R$ 23°C (MPa)	$E$ 23°C (N/mm <sup>2</sup> )	Soluble part (%)	Swelling (%)
PU-LAP	52	6.1	23.9	954	2.8	60
PU-GAP	47	5.2	35.9	1284	0.1	36
PU-AAP	43	7.4	23.7	977	2.5	53

acetic acid is less expensive, and its longer gel time could be interesting for the application. The polyol obtained from lactic acid is the more interesting in terms of renewable carbon content. However, the three PUs obtained from these polyols all present a high content of renewable carbon. It is noted that reactions occurred in mass, at relatively low temperatures, without initiator or purification, which meets the principles of green chemistry.

The authors have declared no conflict of interest.

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