Research article

# Design of biobased non-isocyanate polyurethane (NIPU) foams blown with water and/or ethanol

Vincent Valette, Nasreddine Kébir<sup>\*®,</sup> Fabrice Burel, Laurence Lecamp<sup>®</sup>

Univ Rouen Normandie, INSA Rouen Normandie, CNRS, PBS UMR 6270, F-76000 Rouen, France

Received 26 April 2023; accepted in revised form 13 June 2023

**Abstract.** A promising process to design non-isocyanate polyurethane (NIPU) foams has been developed. The transurethane polycondensation reaction between fatty biscarbamates, fatty diols, and diamines was used to synthesize a biobased amino-telechelic NIPU oligomer. The prepared oligomer (hard phase) was mixed with an amino-telechelic polydimethylsiloxane (PDMS, soft phase) and then reacted with a biosourced tri-epoxide molecule as crosslinking agent, in the presence of water/ethanol mixtures as physical blowing agents. The crosslinking reaction was followed by Fourier transform infrared spectroscopy (FTIR) and rheometry. The foams can be obtained in less than 2 hours at 95 °C. The prepared foams exhibited cell diameters ranging from 130 to 3090  $\mu$ m, as well as densities ranging from 55 to 950 kg/m<sup>3</sup>. Their thermal stability thresholds were above 300 °C. They displayed glass transition temperature values ranging from -20 to -18 °C, and low values of the Young modulus ranging from 2.0 ·10<sup>3</sup> to 5.7 ·10<sup>3</sup> Pa. The hysteresis loss, the recovery time, and the firmness of these foams were dependent on the PDMS content and/or the morphological parameters.

Keywords: processing technologies, polymer synthesis, thermosetting resins, NIPU, foam

## **1. Introduction**

Polyurethanes (PUs) are a family of versatile and essential polymers that can be found in many application fields such as construction, furniture, bedding, transportation, footwear, and everyday appliances. Polyurethane foams have a significant share of the polyurethane market that is projected to attain 13 million tons in 2024 [1–4].

Commercial PUs foams are usually prepared by reaction of poly-ols with poly-isocyanates. Often, CO<sub>2</sub> is used as a blowing agent and is produced *in-situ* by the reaction between water and isocyanate [5–7]. A wide range of versatile PU foams can be designed using this straightforward pathway. Nevertheless, isocyanates are toxic chemicals triggering social and health concerns, which have led to a strengthening of the law against them. For instance, PU formulations containing more than 0.1% w/w of residual isocyanate are forbidden since 2009. To face this worldwide issue, the development of new isocyanate-free processes is of great interest. Today, the literature mentions very few processes for the synthesis of nonisocyanate polyurethane foams (NIPU). These processes are mainly based on the synthesis of a poly(hydroxyurethane) (PHU) matrix from diamine and cyclic carbonates [8–18]. Nevertheless, with one exception, the final foam can only be obtained using high temperatures and/or reaction times, due to the low reactivity of the cyclocarbonate groups.

One technique to design PHU foams is to use physical blowing agents that evaporate during the polymerization process. Solkane, which is a fluorocarbon, was used to prepare PHU foams. The process was performed during 14 h at 80 °C [8]. Supercritical  $CO_2$  was also used as a blowing agent to prepare PHU foams [9, 10]. Grignard *et al.* [9] conducted the

<sup>\*</sup>Corresponding author, e-mail: <u>nasreddine.kebir@insa-rouen.fr</u> © BME-PT

foaming process at 40 °C under 100 or 300 bars for 3 to 24 h, then at 80 °C for 1 min. Mao *et al.* [10] performed the foaming process at 80 °C under pressurization by  $CO_2$  at 150 bar for 6 h.

The second and major technique involves the use of chemical blowing agents. Cornille et al. [11] have prepared PHU foams using a self-blowing process. Poly(hydrogenomethylsiloxane) (PHMS) was used as a foaming agent that releases H<sub>2</sub> in-situ by the reaction of its SiH groups with a (di-)polyamine during the polymer network formation. The foams were obtained upon heating at 80 °C for 12 h, then at 120 °C for 4 h, respectively. They also succeeded in preparing these foams at room temperature for three days, using a thiourea catalyst [12]. Using the same process, Sternberg and Pilla [13] have prepared carbonated Kraft Lignin, using glycerol carbonate or dimethyl carbonate, and have reacted them with hexamethylenediamine (HMDA) in the presence of PHMS as a blowing agent, and dimethyl sulfoxide (DMSO) to dissolve the lignin part. The foams were obtained at 150 °C after 12 hours.

Clark *et al.* [14] have developed an exotic self-blowing PHU foam through the reaction of polyamine with cyclocarbonated sorbitol. A concomitant side reaction led to release of  $CO_2$  at 100 °C, forming the foam after 20 h of reaction.

Monie *et al.* [15] prepared a self-blowing poly(hydroxyurethane-co-hydroxythioether) foam by reacting a cyclocarbonate, a diamine, and a thiol for 4 h at 100 °C. CO<sub>2</sub> was generated *in-situ* as a result of the reaction of the thiol groups with the cyclocarbonates. In another work, they reacted a thiolactone with amine groups to generate the thiols. The prepared foams had several bonds (hydroxyurethanes, thioethers, and amides) [16]. Coste et al. [17] used aminolysis of a thiocyclic carbonate to initiate the reaction between the released thiols and cyclic carbonates, resulting in the release of CO<sub>2</sub> and blowing out the PHU matrix. Recently, Bourguignon et al. [18] reported a promising process to prepare water-induced self-blown PHU foams. They added water and a catalyst, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or KOH, to hydrolyze 5 membered cyclic carbonates in the temperature range of 80–100 °C, for 3-5 hours. This hydrolysis reaction released insitu CO<sub>2</sub> that acted as a blowing agent in PHU formulations composed of a tris(cyclic carbonate) and a diamine. In addition, they showed that by preheating all the components of the formulation separately for 5 minutes at  $100 \,^{\circ}$ C, mixing them and injecting them into a preheated mold ( $100 \,^{\circ}$ C), they reduced the foaming time from 3 h to 30 min. The resulting foams exhibited properties quite similar to those of their analogues prepared without preheating (3 h), except for a lower density.

The transurethane polycondensation reaction between dialkyl dicarbamates [19-24] and diols, or between dialkyl carbonates and diamines [25-31], is one of the most attractive route to NIPUs. Indeed, compared to PHUs, NIPUs exhibit conventional polyurethane structures. In addition, NIPUs can be made from a large selection of dialkyl dicarbamates or dialkyl dicarbonate molecules, ccomparedto the few commercially available diisocyanate analogues that are precursors of PUs. However, unlike the polyaddition reaction between polyamine and poly(cycliccarbonates), the transurethane polycondensation cannot be used directly to prepare crosslinked NIPU because it is achieved at high temperatures and vacuum to remove the released methanol and to displace the equilibrium. This problem can be circumvented by preparing telechelic NIPU oligomers allowing post-crosslinking via polyaddition reactions under mild conditions [21–32].

Xi et al. [25] have prepared NIPU foams by reaction of glucose with dimethylcarbonate (DMC), followed by a reaction with hexamethylene diamine, in the presence of silane as a crosslinking agent. They used NaHCO3 as a chemical foaming agent that decomposes at high temperature releasing CO<sub>2</sub>. The foaming process took 30 min at 200 °C. These authors prepared similar NIPU foams using maleic acid as foaming initiator and glutaraldehyde as crosslinking agent. The final foams were obtained at room temperature for 5 h, followed by curing at 103 °C for 4 h [25–27]. In another work, they used this same process at room temperature to prepare NIPU foams based on mimosa tannin. The curing of the obtained foams was performed at 70-80 °C overnight [27, 28]. Recently, they prepared self-blowing NIPU foams from tannic acid and citric acid, using a similar procedure [29]. The curing process was performed overnight at 70 °C then at 25 °C for 2 days. Singh and Kaur [30] have prepared similar foams through a reaction between xylose, dimethyl carbonate and hexamethylene diamine, in the presence of citric acid. The foaming/curing process lasted 2 h at 90 °C then 24 h at room temperature. Smith et al. [31] have used this methodology to produce foams from tannic acid, chitosan and DMC, in the presence of glutaraldehyde and other carboxylic acids, *i.e.* malic acid, maleic acid, citric acid and aconitic acid. The final foams were obtained after 72 h at room temperature.

Recently, our team has prepared several biobased amino-terminated NIPU using the transurethane polycondensation between dimethylcarbamates, diols and diamines [32]. Then, they reacted them with a polyepoxide molecule, in the presence of PHMS or its copolymer poly(methylhydroxysiloxane)-*co*-poly (dimethylsiloxane) (PHMS-*co*-PDMS) as blowing agents, to obtain NIPU foams displaying conventional PU structures. The foams were obtained after 30 min of heating at 100 °C (without any preheating) or after 14.5 h at room temperature, which was, as far as we know, the faster process to get NIPU foams [32]. However, this process releases hydrogen, which may limit its use in industry for safety reasons.

In this paper, we propose a solution to this problematic by implementing a green and straightforward process allowing the preparation of biobased NIPU foams from biobased diols and diamines (derived from vegetable oils), dimethyl carbonate (which can be produced from CO<sub>2</sub>), a biobased polyepoxide (derived from glycerol) as a crosslinking agent, an amino terminated PDMS as a soft segment template and surfactant, and water and/or ethanol as a blowing agent. The morphological, thermal and mechanical properties of these materials were investigated.

## 2. Materials

Dimethyl carbonate (DMC, 99%, Sigma Aldrich, France), poly(dimethylsiloxane) bis(3-aminopropyl) terminated (PMDS-A, Sigma Aldrich, France) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%, Sigma Aldrich, France). Polyglycerol polyglycidyl ether (DENACOL EX512, Nagase ChemteX, France). Dimer fatty diamide (Priamine<sup>®</sup> 1074, Cargill, France) and dimer fatty diol (Pripol<sup>®</sup> 2033, Cargill, France). All solvents and other reagents were used as received.

#### 3. Synthesis

# 3.1. Synthesis of bis-methyl dicarbamate based on Priamine<sup>®</sup> 1074 (BMC)

Priamine<sup>®</sup> 1074 (1 eq.), TBD (0.1 eq.) and DMC (10 eq.) were mixed and stirred for 6 h at 80 °C, in a single-neck round-bottom flask furnished with a magnetic stirrer. The mixture was then cooled down to

room temperature, and then washed with water in diethyl ether. The organic phase was dried over MgSO<sub>4</sub>, which was then removed by filtration. After solvent evaporation, the product was recovered as an orange viscous liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm]: 4.64 (broad, 2H; N*H*), 3.65 (s, 6H; OC*H*<sub>3</sub>), 3.15 (m, 4H; NHC*H*<sub>2</sub>), 2.52 to 1 (m, 56H; C*H* and C*H*<sub>2</sub>), 0.87 (m, 6H, C*H*<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm]: 157.1 (C=O), 52.0 (OCH<sub>3</sub>), 41.1 (NHCH<sub>2</sub>), 32.0 to 22.8 (CH<sub>2</sub>), 19.8 (CH), 14.2 (CH<sub>3</sub>).

# 3.2. Synthesis of methylcarbamate-terminated NIPU oligomer (NIPU-MC)

Pripol<sup>®</sup> 2033 (6 g, 11.2 mmol), BMC (16.74 g, 25.7 mmol), and TBD (0.16 g, 1.1 mmol) were mixed under a nitrogen stream and stirred for 16 h at 160 °C, in a neat three-neck round-bottom flask furnished with a mechanical stirrer. Then, the medium was placed under vacuum at 0.5 mbar, during 2 h at 160 °C. The product was recovered as an orange viscous oil. <sup>1</sup>H NMR (300 Hz, CDCl<sub>3</sub>)  $\delta$  [ppm]: 4.66 (broad, 3H; N*H*), 4.02 (t, 4H; OC*H*<sub>2</sub>), 3.65 (s, 6H; OC*H*<sub>3</sub>), 3.14 (m, 8H; NHC*H*<sub>2</sub>), 2.52 to 1 (m, broad, 173H; C*H* and C*H*<sub>2</sub>), 0.85 (m, 6H, C*H*<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  [ppm]: 157.1 (C=O), 156.8 (C=O), 64.83 (C=O), 51.9 (OCH<sub>3</sub>), 41.0 (NHCH<sub>2</sub>), 40.9 (NHCH<sub>2</sub>), 37.4 to 22.7 (CH<sub>2</sub>), 19.8 (CH), 14.2 (CH<sub>3</sub>).

# 3.3. Synthesis of amine-terminated NIPU oligomers (NIPU-A)

Priamine<sup>®</sup> 1074 (32.72 g, 60.6 mmol), NIPU-MC (35.79 g, 20.2 mmol.), and TBD (0.28 g, 2.0 mmol) were mixed under a nitrogen stream and stirred for 16 h at 160 °C, in a neat three-neck round-bottom flask furnished with a mechanical stirrer. The medium was then placed under vacuum at 0.5 mbar, during 2 h at 160 °C. The final product was recovered as an orange viscous oil. NIPU-A: <sup>1</sup>H NMR (300 Hz, CDCl<sub>3</sub>) δ [ppm]: 4.68 (broad, 8H; N*H*), 4.02 (t, 3H; NH(CO)OCH<sub>2</sub>), 3.65 (s, residual; OCH<sub>3</sub>), 3.62 (t, 2H; HOCH<sub>2</sub>), 3.14 (m, 12H; NHCH<sub>2</sub>), 2.6–2 (m, 392H; CH and CH<sub>2</sub>), 0.88 (m, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ [ppm]: 163.7 (C=O), 158.9 (C=O), 157.1 (C=O), 156.8 (C=O), 64.8 (C-O), 53.4 (OCH<sub>3</sub>), 42.2 (NHCH<sub>2</sub>), 40.4 (NHCH<sub>2</sub>), 37.4 to 22.8 (CH<sub>2</sub>), 19.8 (CH), 14.2 (CH<sub>3</sub>).

## 3.4. Preparation of NIPU foams

In a polypropylene mould, NIPU-A, DENACOL EX512, PDMS-A and a mixture of water/ethanol

were mechanically blended together at variable molar ratio. Then, the formulation was stirred during 2 min at 2400 rpm using a Speedmixer DAC 150.FVZ.K. A homogenous blend was obtained. The formulation was then placed in an oven at 95 °C during 120 min to produce the final NIPU foam.

### 4. Analysis

# 4.1. Fourier transform infrared spectroscopy (FTIR)

FTIR analysis was achieved with PerkinElmer Spectrum 2000 FTIR (France). This instrument was furnished with a diamond attenuated total reflectance (ATR) device (ATR MK II Golden Gate, Specac, France). Spectra were acquired in the 600 to 4000 cm<sup>-1</sup> range, using 10 scans in a nominal resolution of 8 cm<sup>-1</sup>.

# 4.2. Nuclear magnetic resonance (NMR)

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were acquired with a Bruker 300 Fourier transform spectrometer (France) at 300 and 75 MHz, respectively. The prepared oligomers were analysed in CDCl<sub>3</sub>, in the presence of tetramethylsilane (TMS) as an internal standard.

#### 4.3. Size exclusion chromatography (SEC)

Average molecular weights ( $M_n$  and  $M_w$ ) and dispersity ( $\mathcal{D} = M_w/M_n$ ) of NIPU-MC, NIPU-A, and PDMS-A were evaluated by size exclusion chromatography (SEC). These compounds were dissolved in dichloromethane, filtered (0.45 µm) and analysed at 25 °C by a Varian PL-GPC50 instrument (France) furnished with two mixed packed columns (PL gel mixed type C). The mobile phase was dichloromethane. Calibration was performed using poly(methyl methacrylate) (PMMA) standards (from 875 to 62 000 g/mol).

# 4.4. Assessment of $M_n$ of NIPU-A and PDMS-A by titration of amine groups

NIPU-A or PDMS-A (1.5 g) was dissolved isopropanol/toluene mixture (25 ml, volume ratio 1/1) at 50 °C. The assay was then performed using a solution of HCl in isopropanol (0.1 mol/l). Bromocresol green was used as a colorimetric indicator. Assuming an average amine functionality of 2.0 for these oligomers, the average molecular weight was calculated using Equation (1):

$$M_{\rm n} = \frac{2 \cdot m_{\rm oligomer}}{[\rm HCl] \cdot V_{\rm eq}} \tag{1}$$

where  $m_{\text{oligomer}}$  is the weight of oligomer sample, [HCl] is the concentration of the HCl titrant solution,  $V_{\text{eq}}$  is the volume at the equivalence (or stoechiometric) point.

# 4.5. Determination of *phr:* stoichiometric parts by weight of curing agent per 100 parts of epoxy resin

The *phr* value was calculated as Equation (2):

$$phr = \frac{AHEW}{EEW} \cdot 100 \tag{2}$$

Amine hydrogen equivalent weight (*AHEW*) was determined as Equation (3):

$$AHEW = \frac{M(amine - terminated \ oligomer)}{number of \ active \ amine \ hydrogen}$$
(3)

Epoxy equivalent weight (*EEW*) was determined as Equation (4):

$$EEW = \frac{M(epoxy\ resin)}{number\ of\ epoxy\ function} \tag{4}$$

#### 4.6. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) analysis was achieved under a nitrogen flow, using a DSC Q2000 instrument (TA Instruments, France) with a heating rate of 10 °C/min, in the range of -50 to 200 °C. The glass transition temperature ( $T_g$ ) was calculated from the second heating cycle using the midpoint method. The area and width of the exothermic peak were used to determine the enthalpy of reaction and the curing range, respectively.

## 4.7. Thermogravimetric analysis (TGA)

Thermo-gravimetric analysis (TGA) was performed under a nitrogen flow, using a TGA Q500 device (TA Instruments, France), with a heating rate of 10 °C/min. The thermal stability of the prepared NIPU foams was estimated through the temperature at 10% of weight loss ( $T_{10\%}$ ).

#### 4.8. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis was achieved with the DMA Q800 (TA Instrument, France). Each sample

was cut into a  $10 \times 4$  mm cylinder. The mechanical behaviour of the foams was measured with compression clamps in strain ramp mode at room temperature. A preload force of 0.02 N and a strain rate of 2%/min were used, up to 75% of the total foam strain. The resilience was measured in the creep mode at room temperature. The foams were compressed to 50% of their initial thickness with a displacement time of 10 min and a recovery time of 20 min.

#### 4.9. Scanning electron microscopy (SEM)

The prepared NIPU foams were imaged with JEOL scanning electron microscope (JEOL Neoscope JCM-6000, France). Samples were sputter-coated with gold (JFC 1300 Autofine coater: JEOL, France) before imaging. Cross-section morphologies were recorded at 15 kV accelerating voltage, in high vacuum secondary electron mode.

#### 4.10. Rheological study

Rheological analysis was performed on a DHR-2 rheometer (TA Instruments, France) using a parallel plate geometry ( $\emptyset$ 25 mm), with a geometry gap of 500 µm and a shear rate of 10 s<sup>-1</sup>. Measurements were performed on a temperature range of 30 to 200 °C with a heating rate of 3 °C/min. Viscosity measurements were conducted in the flow temperature ramp mode. The gel point (GP) was assessed using isothermal and temperature ramp tests in oscillatory mode with a frequency of 1 Hz.

#### 4.11. Swelling index (SI)

Each NIPU foam was immersed in 20 ml of  $CH_2Cl_2$ and stirred for 24 h. Swelling index was calculated as Equation (5):

$$SI = \frac{m_{\rm f} - m_{\rm i}}{m_{\rm i}} \cdot 100 \tag{5}$$

where  $m_{\rm f}$  is the mass of the sample after 24 h of immersion in CH<sub>2</sub>Cl<sub>2</sub> and  $m_{\rm i}$  its initial mass.

## 4.12. Extractible content

Extractible content was calculated as Equatiom (6):

Extractible content = 
$$\frac{m_{\rm i} - m_{\rm r}}{m_{\rm i}} \cdot 100$$
 (6)

 $m_i$  is the initial mass of the sample,  $m_r$  is the residual mass after extraction in CH<sub>2</sub>Cl<sub>2</sub> for 24 h, followed by drying at 50 °C for 24 h.

#### 4.13. Apparent density

Cylindrical NIPU foams were prepared in a specific mould. The top of the foam which was out of the mould was carefully cut to afford a perfect cylindrical geometry. Apparent density ( $\rho_a$ ) was calculated as Equation (7):

$$\rho_{\rm a} = \frac{m_{\rm i}}{\pi \cdot r^2 \cdot h} \tag{7}$$

 $m_i r$ , and h are the initial mass, the radius and the height of the cylindric foam, respectively.

A digital caliper was used to measure the dimensions of the foams.

#### 5. Results and discussion

# 5.1. Preparation of an amino-telechelic NIPU (NIPU-A)

An amine terminated NIPU oligomer (NIPU-A), based on fatty branched diamines (Priamine<sup>®</sup> 1074) and dialcohols (Pripol<sup>®</sup> 2033), was prepared in three steps in bulk conditions without any purification (Figure 1). In order to limit the chain extension during the polymerization process, an excess higher than 2 in BMC (for preparation of NIPU-MC) and in Priamine<sup>®</sup> (for the preparation of NIPU-A) was used (Figure 1). Consequently, free Priamine<sup>®</sup>, playing the role of reactive diluent, was present in the final liquid product, which exhibited suitable viscosity for the preparation of initial foam mixtures.

The bis-methyl dicarbamate based on Priamine® 1074 (BMC) was prepared by the reaction of a large excess of DMC (10 eq) with Priamine<sup>®</sup> 1074, in the presence of TBD as catalyst. The reaction was conducted at 80 °C for 6 h, as previously described [19-24, 32]. The <sup>1</sup>H NMR analysis displayed a total disappearance of the signal of amine groups at 2.65 ppm. The signal of the methyl protons arose at 3.65 ppm. The signal of the methylene groups in the a position of the methyl carbamate groups was observed at 3.15 ppm. The signal at 4.64 ppm arose from the nitrogen proton of the carbamate groups. The band at 1715  $\text{cm}^{-1}$  in the FTIR spectrum (Figure 2) corresponds to the H bonded stretching vibration of C=O of the methyl carbamate groups. The bands at 1526 and 3300 cm<sup>-1</sup> correspond to the bending and stretching vibrations of N-H bonds, respectively. The DSC analysis did not show any thermal phenomenon above 80 °C. The TGA analysis showed good thermal stability with  $T_{10\%} > 200 \,^{\circ}\text{C}$ .



Figure 1. Synthesis pathway of the NIPU-A oligomer.



Figure 2. FTIR spectra of compounds BMC, NIPU-MC and NIPU-A.

The NIPU oligomer with methylcarbamate chainends (NIPU-MC) was prepared by reacting 2.3 eq of BMC with Pripol<sup>®</sup> 2033 at 160 °C, under a nitrogen flow overnight, and then under vacuum for 2 h, in the presence of TBD, as similarly performed in a previous work [32]. The FTIR spectrum (Figure 2) showed the persistence of the urethane bands. The <sup>1</sup>H NMR analysis revealed the decrease of the peak of the methyl carbamate groups at 3.65 ppm as well as the absence of a triplet at 3.62 ppm arising from protons in the alpha position to the primary alcohol function. One can also observe the presence of a peak at 4.03 ppm arising from protons in the alpha position to the oxygen of the median urethane function, suggesting that the oligomerization was successful (Figure 3). SEC analysis showed a mixture



Figure 3. <sup>1</sup>H NMR spectrum in CDCl of methylcarbamateterminated NIPU oligomers (NIPU-MC).

of oligomers and BMC (Figure 4). The obtained  $M_n$  value for NIPU-MC was 2520 g/mol with a dispersity of 2.8 (Table 1).

Finally, the NIPU-MC was reacted with 3 eq of Priamine<sup>®</sup> 1074 leading to a NIPU oligomer with amine end-groups (NIPU-A), as similarly performed in a previous work [32]. The FTIR spectra of this oligomer (Figure 2) displayed urea bands at 1630 cm<sup>-1</sup> (C=O stretching) and 1575 cm<sup>-1</sup> (N–H bending), suggesting that the excess of amine groups caused a side transurethane reaction along the chain of the NIPU-A, releasing mono- and/or di-alcohols. This supposition was confirmed by <sup>1</sup>H NMR analysis



**Figure 4.** SEC chromatograms in CH<sub>2</sub>Cl<sub>2</sub> of amine-terminated NIPU (NIPU-A) (Molecular weight values in PMMA equivalent).

(Figure 5), which showed a decrease in the signal of the median urethane function at 4.03 ppm, an increase of the peak at 3.13 ppm emanating from both urea and urethane groups, and an appearance of a triplet at 3.62 ppm coming from released alcohol groups. SEC analysis confirmed also this hypothesis by displaying a mixture of oligomers, Pripol<sup>®</sup> 2033 and Priamine<sup>®</sup> 1074 (Figure 4) with  $M_n$  value of 1240 g/mol, and dispersity of 1.6 (Table 1). The



Figure 5. <sup>1</sup>H NMR spectra of the prepared NIPU-A oligomer.

absolute  $M_n$  value (considering an ideal structure with an average functionality in amine groups of 2) of the prepared NIPU-A was determined by amine titration (amine index) and was 1385 g/mol (Table 1).

<sup>1</sup>H NMR analysis allowed the calculation of the urea/urethane ratio (x/y) in the NIPU-A oligomer, as Equation (8):

$$\frac{x}{y} = \frac{\% \text{Urea}}{\% \text{Urethane}}$$
(8)

where:

%Urethane =  $y/(x + y) \cdot 100$ ; %Urea =  $x/(x + y) \cdot 100$ ;  $y = I_{4.03 \text{ ppm}}/2$ ;  $x = (I_{3.13 \text{ ppm}} - I_{4.03 \text{ ppm}})/4$ ; *I*: the integration of peaks. This ratio was about 86/14 (Table 1).

NIPU-A displayed viscosity values of 39 Pa $\cdot$ s at 30 °C and 0.40 Pa $\cdot$ s at 100 °C. PDMS-A displayed relatively lower viscosity values, *i.e.* 0.04 and 0.01 Pa $\cdot$ s, respectively.

TGA analysis showed  $T_{10\%}$  of 289 °C for PDMS-A and of 316 °C for NIPU-A. The  $T_g$  values of these compounds are supposed to be lower than -50 °C because they were not detectable by DSC in the temperature range of -50 to 200 °C.

## 5.2. Preparation of the NIPU foams

The NIPU foams were prepared by the epoxy-amine reaction between NIPU-A, PDMS-A and DENACOL EX512, which is a bio-based tri-epoxy compound, prepared from glycerol. Foaming was then carried out by adding water/ethanol mixtures at different ratios as physical blowing agents, and heating between 73 to 120 °C for evaporation (Figure 6). PDMS A was chosen as a soft phase model to obtain foams with chemical structures close to those previously prepared using PHMS and its PDMS-PHMS copolymer as crosslinking and blowing agents, and to compare

 Table 1. Physico-chemical properties of the NIPU-MC, NIPU-A and PDMS-A.

Oligomer code	R	R′	M <sub>n</sub> <sup>a</sup> [g/mol]	Ð	Mn <sup>b</sup> [g/mol]	T <sub>10%</sub> [°C]	Viscosity η <sub>30 °C/100 °C</sub> [Pa·s]	Urea/urethane (x/y ratio) <sup>c</sup>	AHEW <sup>d</sup>	phr <sup>d</sup>
NIPU-MC	Priamine <sup>®</sup> 1074	Pripol <sup>®</sup> 2033	2520	2.8	-	-	-	0/100	-	-
NIPU-A	Priamine <sup>®</sup> 1074	Pripol <sup>®</sup> 2033	1580	1.9	1420	316	39/0.40	86/14	337	200
PDMS-A	-	-	1040	1.6	1020	289	0.04/0.01	-	255	152

<sup>a</sup>Determined by SEC;

<sup>b</sup>Determined by titration;

<sup>c</sup>Determined by <sup>1</sup>H NMR;

<sup>d</sup>phr: stoichiometric parts by weight of curing agent per 100 parts of epoxy resin;

AHEW: Amine hydrogen equivalent weight. The epoxy equivalent weight (EEW<sub>DENACOL EX512</sub>) was fixed at 168.



Figure 6. The chemical process implemented for the preparation of NIPU foams.

their properties as a function of the nature of the blowing agent and the crosslinking density [32]. Indeed, PDMS-A has no reactive groups along the chain that increase the crosslinking density, and it cannot release hydrogen gas.

The amine and epoxy groups were introduced in the stochiometric proportions, considering that one amine group can react with two epoxy groups. Therefore, the amine-index of NIPU-A and PDMS-A assessed by titration was used for calculation of *AHEW* (Equation (2)) and *phr* (Equation (1)) (Table 1).

The average functionality of the starting monomers mixture of 3.4 and the critical conversion at the gel point of 0.58 were calculated using Carothers' equations ( $\bar{f}$ , Equation (9) and  $P_c$ , Equation 10)):

$$\bar{f} = \frac{\sum n_{\rm i} f_{\rm i}}{\sum n_{\rm i}} \tag{9}$$

$$P_{\rm c} = \frac{2}{\bar{f}} \tag{10}$$

where  $n_i$  is the molar quantity of the monomer *i* and  $f_i$  is the functionality of the monomer *i* ( $f_i = 4$  for NIPU-A and PDMS-A (since one amine group can react twice) and  $f_i = 3$  for DENACOL EX512).

The crosslinking reaction was first monitored by dynamic rheology, in the absence of foaming agent. The approximative temperature of the gelling point (GP), at a low heating rate of 3 °C/min, was determined as the temperature where G' (storage modulus) was equal to G'' (loss modulus), *i.e.* at the cross-section



Figure 7. Rheological study of NIPU-A/PDMS-A/ DENACOL EX512 formulations as a function of temperature, at a heating rate of 3 °C/min.

of the two curves (Figure 7). One can observe that the gelling point temperature was about 116 °C regard-less the PDMS-A concentration. However, this temperature is very high and may cause all the foaming agent to evaporate before gelling begins.

Since the boiling temperature of water is 100 °C and the water/ethanol mixture boils at temperatures ranging from 78 °C (azeotropic) to about 95 °C (waterrich mixture), we have tested foaming at close temperatures, *i.e.* 73, 74, 76, 79, 85, 95, 100, 105 and 120 °C. Formulations based on NIPU-A, PDMS-A and a blowing agent (water/ethanol mixtures at several ratios) were heated at the set temperature for 2 h, which is more than enough time for the expansion and evolution of the foam (Table 2). Photos of some prepared NIPU foams are depicted in Figure 8. This preliminary study showed that 95 °C was the best temperature to get foams combining good expansion



Figure 8. Photos (on the left) of NIPU foams based on 2% of PDMS-A and water as foaming agent at different temperatures (F1, F9, F11 to F13) and their corresponding SEM images (on the right).

and apparent mechanical properties. Indeed, at a temperature below or equal to 85 °C, foams could not be obtained, whereas above 95 °C, the blowing agent evaporation was very fast leading to foams presenting macro-cellular morphologies and/or a thick layer of crust, as well as poor mechanical properties.

An isothermal study, in the absence of the blowing agent, was then conducted at 95 and  $100 \,^{\circ}$ C to have an idea about the minimal time required to get the gel point (Figures 9 and 10) and to define a universal time for the process. The GP was reached after 194 to 354 s at 95  $\,^{\circ}$ C (using formulations with 0 to 10% of PDMS) and after 133 s at 100  $\,^{\circ}$ C (using formulation with 2% of PDMS).

In complement to this study, we have performed an isothermal DSC study at the same temperatures (formulations with 2% of PDMS) to evaluate the time required to get the critical conversion of the epoxyamine system (Figures 11 and 12). The formulations having a high reactivity at 95 and 100 °C, the baseline of the DSC curve couldn't be observed at the beginning. However, the end of the epoxy-amine reaction, attested by the end of energy release, was observed



**Figure 9.** Isothermal rheological study at 95 °C of NIPU-A/ PDMS-A/DENACOL EX512 formulations as a function of time.



**Figure 10.** Isothermal rheological study at 100 °C of NIPU-A/PDMS-A (2%)/EX512 formulation as a function of time.

after about 45 min at  $95 \,^{\circ}$ C and after about 30 min at  $100 \,^{\circ}$ C, which is well after the gel point and well within the two-hour curing time.

# 5.3. Characterizations of the prepared NIPU foams

The composition and properties of the prepared NIPU foams at the optimal process conditions are depicted in Table 2.

It is noteworthy that the foams were elaborated following three main parameters:

- The molar content of PDMS-A (from 0 to 10%) for a fixed blowing agent composition (H<sub>2</sub>O 100%) and a fixed temperature (95 °C) (Foams: F1, F6, F7 and F8);
- 2 The blowing agent composition (water/ethanol ratios (mol/mol): 100/0, 90/10, 75/25, 50/50, 0/100) for a fixed value of concentration of PDMS-A (2%), a fixed temperature and a fixed total volume of the blowing agent at the liquid state (80 ml) (Foams: F1 to F5; F9 vs. F10);
- 3 The foaming temperature for a fixed formulation (Foams: F1, F9, F11 to F13; F2 *vs.* F14; F3 *vs.* F15; F4 *vs.* F16 and F5 *vs.* F17).



Figure 11. Isothermal DSC study at 95°C of NIPU-A/ PDMS-A (2%)/EX512 formulation as a function of time.



Figure 12. Isothermal DSC study at 100°C of NIPU-A/ PDMS-A (0 to 10%)/EX512 formulations as a function of time.

Foams	PDMS-A, p	Water/ethanol, z	T <sub>foaming</sub>	$\rho_a$	Average cell diameter	Extractible	Swelling index
[F <i>n-p-z</i> ] <sup>a</sup>	[%]	[mol/mol]	[°C]	[kg/m <sup>3</sup> ]	[µm]	[wt%]	[wt%]
[F1-2%-100/0]	2	100/0	95	190±40	590±270	15±2	1180±410
[F2-2%-90/10]	2	90/10	95	90±4	1540±400	21±2	1350±90
[F3-2%-75/25]	2	75/25	95	115±40	430±150	20±1	1480±210
[F4-2%-50/50]	2	50/50	95	125±20	465±215	19±3	730±130
[F5-2%-0/100]	2	0/100	95	280±25	280±120	13±2	1100±150
[F6-0%-100/0]	0	100/0	95	325±60	600±500	13±1	650±130
[F7-5%-100/0]	5	100/0	95	120±7	400±250	19±5	1500±170
[F8-10%-100/0]	10	100/0	95	160±60	830±300	13±3	1200±130
[F9-2%-100/0]	2	100/0	85	950±60	140±125	9±1	290±10
[F10-2%-75/25]	2	75/25	85	830±20	140±85	14±1	260±9
[F11-2%-100/0]	2	100/0	100	140±6	580±250	23±3	1150±70
[F12-2%-100/0]	2	100/0	105	55±7	3090±880	25±4	1820±160
[F13-2%-100/0]	2	100/0	120	80±17	1240±430	25±2	1400±410
[F14-2%-90/10]	2	90/10	79	670±30	n.a	25±3	260±10
[F15-2%-75/25]	2	75/25	76	880±40	n.a	13±1	280±10
[F16-2%-50/50]	2	50/50	74	790±10	n.a	11±2	290±10
[F17-2%-0/100]	2	0/100	73	910±50	n.a	16±1	300±5
F-commercial PU [12]	-	-	RT	100	600±250	8	980
F-NIPU reference [32]	-	-	100	170±40	360±220	18±2	840±110

**Table 2.** Composition, apparent density ( $\rho_a$ ), physical and thermal properties of the prepared NIPU foams.

<sup>a</sup>F: means foam, n: is the number of the prepared foam, p: is the percentage of PDMS-A, z: is the water/ethanol ratio.

The properties of the prepared NIPU were compared to those of a selected commercial conventional PU foam recently described in the literature [12]. They were also compared to a NIPU foam previously prepared from the same NIPU-A and DENACOL EX512 in the presence of PHMS as a crosslinking and *in-situ* hydrogen-releasing chemical blowing agent [32].

FTIR analysis of the prepared foams exhibited a small residual band of the epoxide group at  $830 \text{ cm}^{-1}$  (Figure 13). The urethane/urea ratio was similar to that of the NIPU-A precursor.

Scanning electron microscopy (SEM) was used to analyse the morphologies of the prepared foams.



Figure 13. FTIR spectra of some prepared foams.

Some images are depicted in Figure 14. All the prepared foams exhibited open cells. Foams prepared above 95 °C presented heterogeneous macro-cellular morphologies with cell size above 1 mm and standard deviation ranging from 430 to 880 µm (Table 2). Surprisingly, the foam F2-2%-90/10 prepared at 95 °C also exhibited a macro-cellular morphology (1540±400 µm). The non-expanded materials prepared at 85 °C exhibited little cells with low size of about 140 µm. All the other foams prepared at 95 °C displayed micro-cellular morphologies with cell sizes ranging from 280±120 to 830±300 µm. The foams prepared with 50 to 100% of ethanol exhibited the lowest cell sizes. Furthermore, it seems that the amount of PDMS-A in the formulation has not a significant impact on the cell size values, considering the standard deviations. Furthermore, one can observe that these values are in the range of the F-commercial PU (600±250 µm) [12] and the F-NIPU reference (360±220 µm) [32].

Foams prepared at temperatures above  $100 \,^{\circ}$ C as well as the foam F2-2%-90/10 prepared at 95 °C exhibited the lowest density values (55 to 90 kg/m<sup>3</sup>), which is in consistency with their macro-cellular morphologies and cell size values (Table 2). According to the literature [11] these foams can be considered as low-density flexible foams. As expected, the non-expanded



Figure 14. SEM images of the prepared foams, as a function of the  $H_2O/E$ thanol ratio (z) and the PDMS content (p).

material prepared at 73 to 85 °C displayed the highest apparent density (670±30 to 950±60 kg/m<sup>3</sup>). All the other foams exhibited apparent density values between 115±40 and 325±60 kg/m<sup>3</sup>, consistent with their corresponding average values of cell size. These foams can be considered as high-density flexible foams [11]. These values are also consistent with those of PHU foams (190 to 300 kg/m<sup>3</sup>), described recently in the literature [11, 12]. They were also in the range of the F-commercial PU (100 kg/m<sup>3</sup>) [12] and F-NIPU reference (170±40 kg/m<sup>3</sup>) [32].

The crosslinking densities of the prepared foams were estimated through their swelling and extractible percentages in dichloromethane (Table 2). Because of their affinity with dichloromethane and their porous structure, the prepared foams displayed high swelling percentages, ranging from 730 to 1820%. The foam prepared at 105 °C (F12) exhibited the highest value of swelling percentage (1820%) and extractible (25%), suggesting the lowest degree of crosslinking. The foam prepared at 120 °C (F13) also possessed a low crosslinked density since they exhibited 25% of extractible percentage and a relatively high swelling percentage (1400%). The foam prepared at 100°C (F11) displayed lower crosslinking density than its analogue prepared at 95 °C (F1), with extractible values of 23 vs. 15%, respectively, and close swelling percentages (about 1160%). The non-expanded materials prepared at 73 to 85 °C exhibited the lowest swelling percentages due to their non-alveolar structures (256 to 300%). On the other hand, they displayed similar extractible percentages ranging from 9 to 25%, compared to the other foams. All the foams prepared at 95 °C with 2% of PDMS exhibited good and intermediate crosslinking densities with swelling

percentages ranging from 730 to 1480% and extractible percentages of about 19%. The foam without PDMS-A showed the lowest swelling and extractible percentages (650 and 9%, respectively), whereas the foams based on PDMS-A (2 to 10% of PDMS-A) showed higher values of these two parameters. This can be explained by the higher solubility of the PDMS chains in dichloromethane compared to NIPU-A. Furthermore, the F-commercial PU and the F-NIPU reference exhibited close swelling percentages of 980 and 840%, respectively, compared to the prepared foams. Nevertheless, the commercial foam presented a higher crosslinking degree attested by a lower extractible content (8%). The higher extent of extractables in the case of the prepared foams can be explained by a lower theoretical critical conversion at their gel point (58%) as well as by the residual presence of non-reactive chemical functions in the NIPU-A.

Thus, on the base of the morphological characterizations, we could confirm that 95 °C was the optimal temperature to prepare the foams. The thermomechanical properties were then performed only on foams prepared at this temperature (Table 3).

Differential scanning calorimetry was used to assess the thermal properties of the prepared foams. Typical DSC curves are displayed in Figure 15. The foams exhibited close  $T_g$  values ranging from -17 to -20 °C regardless of their PDMS content (Table 3), which is close to the  $T_g$  value of the F-NIPU reference (-16 °C) [32]. The F commercial PU showed a higher  $T_g$  value of 0 °C [12].

Thermogravimetric analysis was used to evaluate the thermal stability of the prepared foams. Typical TGA curves are presented in Figure 16. The thermal

Foam [Fn-p-z] <sup>a</sup>	HL <sup>b</sup> [%]	R <sub>95%</sub> <sup>b</sup> [s]	ILD <sub>25%</sub> <sup>b</sup> [kPa]	Young modulus [10 <sup>3</sup> Pa]	<i>T</i> g [°C]	<i>T</i> <sub>10%</sub> [°C]
[F1-2%-100/0]	257±4	7	1.12±0.05	3.7±0.02	-19	314
[F2-2%-90/10]	24±5	9	0.77±0.05	2.0±0.01	-20	311
[F3-2%-75/25]	24±4	19	0.74±0.05	3.0±0.01	-19	305
[F4-2%-50/50]	22±4	9	1.21±0.10	3.0±0.01	-18	316
[F5-2%-0/100]	32±3	9	3.58±0.18	5.7±0.03	-20	322
[F6-0%-100/0]	48±2	7	3.79±0.50	4.0±0.02	-20	325
[F7-5%-100/0]	32±5	23	1.09±0.06	3.3±0.01	-18	308
[F8-10%-100/0]	25±4	7	0.93±0.08	2.1±0.01	-19	320
F-commercial PU [12]	-	35	-	230.00	0	328
NIPU reference [32]	21±1	13	-	20.0±0.20	-16	323

Table 3. Mechanical and thermal properties of the optimal NIPU foams prepared at 95 °C.

<sup>a</sup>F: means foam, *n*: is the number of the prepared foam, *p*: is the percentage of PDMS-A, *z*: is the water/ethanol ratio.

<sup>b</sup>*HL*: hysteresis loss; *R*<sub>95%</sub>: Recovery time to 95% of the initial height of the foam; *ILD*<sub>25%</sub>: indent load deflection at 25%.



Figure 15. DSC curves of a) F2 to F5 compared to F1 and b) F6 to F8 compared to F1.



Figure 16. TGA curves of a) F2 to F5 compared to F1 and b) F6 to F8 compared to F1.

temperature at 10% of weight loss ( $T_{10\%}$ ) varied from 305 to 325 °C (Table 3), which is close to the values of the two foams used as references (323 and 328 °C) [12, 32].

Flexible foams can be used in a wide range of applications and their specifications for PU foam can be very different. In this work, we have chosen to use DMA as ultimate tool to characterize the mechanical properties of our foams. Three main mechanical parameters are studied in industrial foam, especially for bedding and seating:

1 Firmness or Indent load deflection (*ILD*), which is evaluated by the force required to compress a foam to 25% of its original height. Commonly used in the mattress foam industry, this parameter is an indicator of the softness of the foam [32]. The lower the force applied, the softer the foam.

- 2 Hysteresis loss (HL), which is assessed by subtracting the total energy (area under the loading stress-strain DMA curve) and the return energy (area under the recovery curve) divided by the total energy [33]. This parameter indicates the material's ability to absorb energy. Usually, a strain of 75% is employed to assess the hysteresis loss (Figure 17).
- 3 The recovery time to 95% of the initial height of the foam ( $R_{95\%}$ ) is recorded after a starting 50% compression.

The values of these three parameters for foams prepared at the optimal temperature of 95°C are depicted in Table 3.



Figure 17. Mechanical properties by DMA of the optimal NIPU foams prepared at 95 °C. a) Stress-strain curves, b) creep mode: 10 min at 50% strain at 35 °C.

However, in the case of foams, there are too many morphological parameters (such as porosity, number of open cells, cell size, wall thickness, bulk density, and degree of crosslinking) that could have an impact on the mechanical properties. It is therefore often difficult to find structure/property relationships easily, except in the case where only one or two parameters are preponderant. In this case, we will note it in the discussion.

Three parts can be distinguished in the DMA stressstrain curves (Figure 17). The first one, between 0 to 10% of strain, is the region of linear elasticity; it is correlated to the deformation required to cause the bending of the foam edges. The plateau zone between 10 and 50–60% deformation is attributed to the collapse of the foam after cell compression. The last part, where the stress is significantly increased over a lower strain, is attributed to the complete compression of the cells (foam densification). Therefore, due to their smaller cell volume, denser foams tend to have a smaller plateau.

The NIPU foams F2, F3, F4 and F8 exhibited HL values varying between 22 and 25%, close to the F-NIPU reference (21%). The foam F6 exhibited an HL value close to 50%. Foams F5 and F7 displayed intermediate HL value of 32%. For probably morphological reasons, the foam F1 exhibited a very high value of HL (257%).

The prepared foams exhibited low  $R_{95\%}$  values ranging from 7 to 23 s (Table 3). The F NIPU reference was in this range (13 s). Foams F3 and F7 exhibited the highest values of  $R_{95\%}$  (19 and 23 s, respectively). This can be correlated to their lowest crosslinking density attested by their highest swelling and extractible percentages.

The prepared foams showed  $ILD_{25\%}$  values ranging from 0.74 to 3.79 kPa (Table 3). It can be observed that this parameter is influenced by the PDMS-A content in the foams. Indeed, the  $ILD_{25\%}$  value decreased from 3.8 kPa to about 1.1 kPa, then to about 0.9 kPa, when the percentage of PDMS-A increased from 0 to 2–5%, then to 10%, respectively. This is probably due to the soft character of the PDMS chain. We can also notice that when the percentage of ethanol in the blowing agent increases from 10–25% to 50%, then to 100%, the  $ILD_{25\%}$  increases from 0.7 to 1.2 kPa, then to 3.6 kPa.

Finally, due to their softness and alveolar microstructures, the prepared NIPU foams showed low values of Young's modulus, ranging from  $2.0 \cdot 10^3$  to

 $5.7 \cdot 10^3$  Pa (Table 3). For the same reason, this parameter changed in the same way as ILD<sub>25%</sub> with the percentage of PDMS-A in the foam, i.e., it decreased from  $4.0 \cdot 10^3$  Pa to about  $3.5 \cdot 10^3$  Pa and then to  $2.1 \cdot 10^3$  Pa when the percentage of PDMS-A increased from 0 to 2-5% and then to 10%, respectively. All the prepared foams exhibited lower Young's modulus values than the F-commercial PU  $(230 \cdot 10^3 \text{ Pa})$  and the reference F-NIPU  $(20 \cdot 10^3 \text{ Pa})$ , which could be explained by the fact that these reference materials lack PDMS-like soft phase. The Young's modulus also changed similarly as  $ILD_{25\%}$ with the ethanol/water ratio in the blowing agent, *i.e.*, it increased from  $2 \cdot 10^3$  to  $3 \cdot 10^3$  Pa and then to  $5.7 \cdot 10^3$  Pa when the percentage of ethanol in the blowing agent increased from 10 to 25-50% and then to 100%, respectively.

## 6. Conclusions

In this work, we have successfully prepared partially biobased flexible NIPU foams from a biobased synthesized amino-terminated NIPU (NIPU-A), a biobased polyepoxide molecule (DENACOL EX512) and an amino-terminated PDMS (PDMS-A), using water/ethanol mixtures as blowing agent. NIPU-A was obtained through the transurethane polycondensation approach from a fatty diamine, a fatty diol and DMC (a CO<sub>2</sub> derivative). DSC and dynamic rheology revealed that the operating conditions to get foams from the different starting formulations were at least 45 min at 95 °C. The obtained optimal foams displayed heterogeneous cell diameters ranging from 400 to 1540 µm and high apparent densities changing from 90 to 320 kg/m<sup>3</sup>. They showed thermal stabilities above 300 °C. They presented negative  $T_{\rm g}$ values (from -18 to -20 °C) as well as low Young modulus values (from  $2.0 \cdot 10^3$  to  $5.7 \cdot 10^3$  Pa), which is in consistent with their soft physical character. The prepared high-density flexible polyurethane foams exhibited disparate values of hysteresis loss. The recovery time was short and seemed to be mainly impacted by the crosslinking density of these foams. The indent load deflection at 25% as well as the Young modulus were mainly influenced by the PDMS-A content within the foams, which also would explain the differences observed with the F-commercial PU and the F-NIPU reference. Finally, this work highlights the interest of the transurethane polycondensation route to prepare telechelic oligomers, which can be used in the preparation of valuable NIPU materials. The new process developed in this work can be extended to a variety of chemical structures leading to a variety of foam properties.

#### Acknowledgements

The authors gratefully acknowledge the 'Région Haute-Normandie' (project PhotoNIPUfoam) for the financial support.

## References

 Dworakowska S., Cornille A., Bogdał D., Boutevin B., Caillol S.: Formulation of bio-based epoxy foams from epoxidized cardanol and vegetable oil amine. European Journal of Lipid Science and Technology, **117**, 1893– 1902 (2015).

https://doi.org/10.1002/ejlt.201500232

- [2] Kausar A.: Polyurethane composite foams in high-performance applications: A review. Polymer-Plastics Technology and Engineering, 57, 346–369 (2018). https://doi.org/10.1080/03602559.2017.1329433
- [3] Somarathna H. M. C. C., Raman S. N., Mohotti D., Mutalib A. A., Badri K. H.: The use of polyurethane for structural and infrastructural engineering applications: A state-of-the-art review. Construction and Building Materials, **190**, 995–1014 (2018). https://doi.org/10.1016/j.conbuildmat.2018.09.166
- [4] Ates M., Karadag S., Eker A. A., Eker B.: Polyurethane foam materials and their industrial applications. Polymer International, **71**, 1157–1163 (2022). https://doi.org/10.1002/pi.6441
- [5] Gama N., Ferreira A., Barros-Timmons A.: Polyurethane foams: Past, present, and future. Materials, 11, 1841 (2018).
   https://doi.org/10.3390/ma11101841
- [6] Akindoyo J. O., Beg M. D. H., Ghazali S., Islam M. R., Jeyaratnam N., Yuvaraj A. R.: Polyurethane types, synthesis and applications – A review. RSC Advances, 6, 114453–114482 (2016).

https://doi.org/10.1039/c6ra14525f

- [7] Cornille A., Auvergne R., Figovsky O., Boutevin B., Caillol S.: A perspective approach to sustainable routes for non-isocyanate polyurethanes. European Polymer Journal, 87, 535–552 (2017).
- https://doi.org/10.1016/j.eurpolymj.2016.11.027 [8] Blattmann H., Lauth M., Mülhaupt R.: Flexible and
- bio-based nonisocyanate polyurethane (NIPU) foams. Macromolecular Materials and Engineering, **301**, 944–952 (2016).

https://doi.org/10.1002/mame.201600141

[9] Grignard B., Thomassin J. M., Gennen S., Poussard L., Bonnaud L., Raquez J-M., Dubois P., Tran M-P., Park C. B., Jerome C., Detrembleur C.: CO<sub>2</sub>-blown microcellular non-isocyanate polyurethane (NIPU) foams: From bio- and CO<sub>2</sub>-sourced monomers to potentially thermal insulating materials. Green Chemestry, 18, 2206 (2016).

https://doi.org/10.1039/c5gc02723c

- [10] Mao H-I., Chen C-W., Yan H-C., Rwei S-P.: Synthesis and characteristics of nonisocyanate polyurethane composed of bio-based dimer diamine for supercritical CO<sub>2</sub> foaming applications. Journal of Applied Polymer Science, **139**, e52841 (2022). https://doi.org/10.1002/app.52841
- [11] Cornille A., Dworakowska S., Bogdal D., Boutevin B., Caillol S.: A new way of creating cellular polyurethane materials: NIPU foams. European Polymer Journal, 66, 129–138 (2015). https://doi.org/10.1016/j.eurpolymj.2015.01.034
- [12] Cornille A., Guillet C., Benyahya S., Negrell C., Boutevin B., Caillol S.: Room temperature flexible isocyanate-free polyurethane foams. European Polymer Journal, 84, 873–888 (2016).

https://doi.org/10.1016/j.eurpolymj.2016.05.032

- [13] Sternberg J., Pilla S.: Materials for the biorefinery: High bio-content, shape memory Kraft lignin-derived nonisocyanate polyurethane foams using a non-toxic protocol. Green Chemestry, 22, 6922–6935 (2020). https://doi.org/10.1039/D0GC01659D
- [14] Clark J. H., Farmer T. J., Ingram I. D. V., Lie Y., North M.: Renewable self-blowing non-isocyanate polyurethane foams from lysine and sorbitol. European Journal of Organic Chemestry, **2018**, 4265–4271 (2018). https://doi.org/10.1002/ejoc.201800665
- [15] Monie F., Grignard B., Thomassin J-M., Mereau R., Tassaing T., Jerome C., Detrembleur C.: Chemo- and regioselective additions of nucleophiles to cyclic carbonates for the preparation of self-blowing non-isocyanate polyurethane foams. Angewandte Chemie, 132, 17181– 17189 (2020).

https://doi.org/10.1002/ange.202006267

- [16] Monie F., Grignard B., Detrembleur C.: Divergent aminolysis approach for constructing recyclable selfblown nonisocyanate polyurethane foams. ACS Macro Letters, 11, 236–242 (2022). https://doi.org/10.1021/acsmacrolett.1c00793
- [17] Coste G., Negrell C., Caillol S.: Cascade (dithio)carbonate ring opening reactions for self-blowing polyhydroxythiourethane foams. Macromolecular Rapid Commuication, 43, 2100833 (2022). https://doi.org/10.1002/marc.202100833
- [18] Bourguignon M., Grignard B., Detrembleur C.: Waterinduced self-blown non-isocyanate polyurethane foams. Angewandte Chemie International Edition, 61, e202213422 (2022).

https://doi.org/10.1002/anie.202213422

[19] Duval C., Kébir N., Charvet A., Martin A., Burel F.: Synthesis and properties of renewable nonisocyanate polyurethanes (NIPUs) from dimethylcarbonate. Journal of Polymer Science Part A Polymer Chemistry, 53, 1351–1359 (2015).

https://doi.org/10.1002/pola.27568

- [20] Kébir N., Nouigues S., Moranne P., Burel F.: Nonisocyanate thermoplastic polyurethane elastomers based on poly(ethylene glycol) prepared through the transurethanization approach. Journal of Applied Polymer Science, **134**, 44991 (2017). https://doi.org/10.1002/app.44991
- [21] Boisaubert P., Kébir N., Schuller A. S., Burel F.: Photocrosslinked non-isocyanate polyurethane acrylate (NIPUa) coatings through a transurethane polycondensation approach. Polymer, 206, 122855 (2020). <u>https://doi.org/10.1016/j.polymer.2020.122855</u>
- [22] Boisaubert P., Kébir N., Schuller A. S., Burel F.: Photocrosslinked coatings from an acrylate terminated nonisocyanate polyurethane (NIPU) and reactive diluent. European Polymer Journal, **138**, 109961 (2020). https://doi.org/10.1016/j.eurpolymj.2020.109961
- [23] Martin A., Lecamp L., Labib H., Aloui F., Kébir N., Burel F.: Synthesis and properties of allyl terminated renewable non-isocyanate polyurethanes (NIPUs) and polyureas (NIPUreas) and study of their photo-crosslinking. European Polymer Journal, 84, 828–836 (2016). https://doi.org/10.1016/j.eurpolymj.2016.06.008
- [24] Boisaubert P., Kébir N., Schuller A-S., Burel F.: Polyurethane coatings from formulations with low isocyanate content using a transurethane polycondensation route. Polymer, 240, 124522 (2022). https://doi.org/10.1016/J.POLYMER.2022.124522
- [25] Xi X., Pizzi A., Gerardin C., Du G.: Glucose-biobased non-isocyanate polyurethane rigid foams. Journal of Renewable Materials, 7, 301–312 (2019). https://doi.org/10.32604/jrm.2019.04174
- [26] Xi X., Pizzi A., Gerardin C., Lei H., Chen X., Amirou S.: Preparation and evaluation of glucose based non-isocyanate polyurethane self-blowing rigid foams. Polymers, 11, 1802 (2019). https://doi.org/10.3390/polym11111802

- [27] Chen X., Xi X., Pizzi A., Fredon E., Zhou X., Li J., Gerardin C., Du G.: Preparation and characterization of condensed tannin non-isocyanate polyurethane (NIPU) rigid foams by ambient temperature blowing. Polymers, 12, 750 (2020). https://doi.org/10.3390/POLYM12040750
- [28] Chen X., Li J., Xi X., Pizzi A., Zhou X., Fredon E., Du G., Gerardin C.: Condensed tannin-glucose-based NIPU bio-foams of improved fire retardancy. Polymer Degradation and Stability, **175**, 109121 (2020). https://doi.org/10.1016/j.polymdegradstab.2020.109121
- [29] Azadeh E., Chen X., Pizzi A., Gérardin C., Gérardin P., Essawy H.: Self-blowing non-isocyanate polyurethane foams based on hydrolysable tannins. Journal of Renewable Materials, **10**, 3217–3227 (2022). https://doi.org/10.32604/jrm.2022.022740
- [30] Singh P., Kaur R.: Sustainable xylose-based non-isocyanate polyurethane foams with remarkable fire-retardant properties. Journal of Polymers and the Environment, **31**, 743–753 (2023). https://doi.org/10.1007/s10924-022-02638-4
- [31] Smith D. L., Rodriguez-Melendez D., Cotton S. M., Quan Y., Wang Q., Grunlan J. C.: Non-isocyanate polyurethane bio-foam with inherent heat and fire resistance. Polymers, 14, 5019 (2022). https://doi.org/10.3390/polym14225019
- [32] Valette V., Kébir N., Tiavarison F. B., Burel F., Lecamp L.: Preparation of flexible biobased non-isocyanate polyurethane (NIPU) foams using the transurethanization approach. Reactive and Functional Polymers, 181, 105416 (2022).

https://doi.org/10.1016/J.REACTFUNCTPOLYM.2022.105416

[33] Alzoubi M. F., Tanbour E. Y., Al-Waked R.: Compression and hysteresis curves of nonlinear polyurethane foams under different densities, strain rates and different environmental conditions. in 'Proceedings of the ASME 2011 International Mechanical Engineering Congress and Exposition. Denver, USA', Vol. 9, 101–109 (2011).

https://doi.org/10.1115/IMECE2011-62290