A new way of creating cellular polyurethane materials: NIPU foams

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Abstract
This article describes, for the first time, the synthesis of polyurethane foams from the reaction between cyclic carbonates and diamines to yield NonIsocyanate PolyUrethane (NIPU) foams. A poly(methylhydrogenosiloxane) was used as blowing agent to foam the NIPU by reaction with diamines. The raw materials were characterized in order to determine reaction stoichiometry. NIPU foams were characterized by scanning electron microscopy and by measurement of their swelling index and apparent density. The mechanical compression and the recovery of these NIPU foams were analyzed by dynamic mechanical analyses at room temperature. The foams exhibited glass transition temperature between −18°C and 19°C and a thermal stability above 300°C.

1. Introduction

The development of polyurethanes (PUs) began in 1937 at I.G. Farbenindustrie where Bayer with coworkers discovered the addition polymerization reaction between diisocyanates and diols. Since their discovery, the demand in PUs has continued to increase and it will attain in 2016 a production of 18 million tons [1,2] of which 75% are foams. With a market share of 7% of total demand, the PUs are ranked fifth in the world production of plastics. Among the wide range of PU applications, the PU foams represent the two-thirds of the global PU market [3]. Basically, PU foams are classified into two distinct groups, rigid and flexible foams, depending on their mechanical properties and cross-linking densities [4,5]. The flexible foams are used in many diverse applications such as automotive, bedding and furniture industry. This is explained by their exceptional characteristics such as sound insulation, energy and shock absorption, consumer comfort and protection from impact. These characteristics result from a specific open cell structure of flexible foams [4–7].

PUs are important versatile polymers varying from thermoplastics to thermosets [8], obtained by step growth polymerization between diisocyanate or polyisocyanate and hydroxyl terminated oligomer (polyl) having at least two reactive hydrogen atoms. However, polyl/isocyanate (gelling) and isocyanate/water (blowing) reactions are competing reactions [9] (Scheme 1). The reaction between polyl and isocyanate forms urethane linkages, while reaction between isocyanate and water yields amine and carbon dioxide allowing for foaming in the preparation of PU foams. Amines continue to react with isocyanate to yield urea linkages. However, some catalysts need to be used in order to control and balance properly gelling and blowing reactions. Even if water is the mostly used blowing agent for the formation of polyurethane foams, other foaming agents were also reported in the literature [4,5]. Since the first syntheses of PUs, many metal complexes

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were used for the gelling reaction. Among them, there were lead compounds before the 50s’, replaced later by mercury complex [10–14]. Tin compound derivatives quickly became among the most used catalysts in order to favor gelling reaction [15–18]. Nowadays, there is used mostly a mixture of organometallics with amine catalysts. The best known example in the world of PU foams is dibutyltin dilaurate (DBTDL)/1,4-diazabicyclo-[2.2.2]-octane (DABCO) association [19]. Catalysts used in the PU foams preparation cause environmental pollution when they are released to atmosphere. However, some companies introduce non-volatile catalysts, which do not create toxic vapors.

The main environmental issue of PU materials concerns the use of isocyanate raw materials. In fact, these compounds are harmful for human and environment. Methylenediphenyl 4,4’-diisocyanate (MDI) and toluene diisocyanate (TDI), the most widely used isocyanates in PU industry, are classified as CMR (Carcinogen, Mutagen and Reprotoxic) [20].

Some of us already reported on the synthesis of vegetable oil-based PU flexible foams using TDI [21,22]. In order to design isocyanate-free materials, an interesting alternative is the use of Nonisocyanate PolyUrethane (NIPU) by reaction between cyclic carbonate and polyfunctional amines [23]. Recently, Thebault et al. [24,25] prepared non-isocyanate polyurethanes by carbonation of hydrolysable tannin followed by reaction with a primary amine. The cyclic carbonate/amine reaction, already studied in the past by Whelan et al. and Mikheev et al. [26,27], avoids the use of isocyanates and diamines and permits the formation of poly(hydroxyurethane)s (PHUs) with hydroxyl groups. This method was tremendously studied and has recently attracted much attention, particularly by Endo et al. [23,28–31] and Figovsky et al. [32,33]. The main problem concerning NIPU synthesis relates to the low reactivity of carbonate/amine reaction. Many studies in the literature have been conducted to design NIPU materials from reactive cyclic-carbonates bearing electro-withdrawing substituent [23,30,34–43] or by using six-, seven-membered or thio-cyclic carbonate [31,41,44–46].

In order to improve the kinetics of the carbonate/amine reaction, much research has been devoted to develop novel catalysts. Blain et al. [47] and Lambeth et al. [48] showed that the 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and cyclohexylphenyl thiourea are the best catalysts for carbonate/amine reaction. However, the reaction between carbonate and amine does not yield any gas, therefore cannot lead to NIPU foam as easily as in the case of PUs. Moreover, to the best of our knowledge, no literature has been published on the preparation of NIPU foams, therefore, we aspired to synthesize the first NIPU foams as an original work.

We chose five-membered cyclic carbonates since their synthesis does not require any phosgene derivative as in the case of six- or seven-membered cyclic carbonates. NIPU foams were obtained by step growth polymerization of two types of five-membered cyclic carbonates, trimethyleneolpropane tris-carbonate (TMP-Tri-C5) and polypropylene oxide bis-carbonate (PPO-Bis-C5), in combination with aliphatic amines. The development of NIPU foams is a challenge which lies in the coordination of gelling reaction (carbonate/amine reaction) and foaming reaction. We used Momentive MH 15 as blowing agent which was already reported in epoxy foams preparation [49]. MH 15 is a poly(methylhydrogenosiloxane) which reacts with amines, releasing dihydrogen (Scheme 2) which allows to expand the NIPU materials. The synthesis of various NIPU foams from cyclic carbonate/amine reaction with MH 15 as blowing agent is summarized in general Scheme 2.

2. Experimental

2.1. Materials

Poly(propylene oxide) bis-carbonate (PPO-Bis-C5, SP-1P-0-004) and trimethyleneolpropane tris-carbonate (TMP-Tri-C5, SP-3-00-003) were purchased from Specific Polymers. Acetic anhydride, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and tetrahydrofuran (THF) were purchased from Sigma Aldrich. Jeffamine EDR-148 was obtained from Huntsman and Priamine 1073 was obtained from Croda.Poly(methylhydrogenosiloxane) Momentive MH 15 was obtained from Momentive.

2.2. Nuclear magnetic resonance

Chemical structures of the molecules were determined by 1H NMR spectroscopy using a Bruker Avance 400 MHz spectrometer equipped with a QNP z-gradient probe at room temperature. External reference was trimethylsilane (TMS). Shifts were given in ppm. NMR samples were

![Scheme 1. Isocyanate reactions with hydroxyl compounds, water and amine.](image1)

![Scheme 2. General scheme of formation of NIPU foams by reaction between cyclic carbonate, amine and MH 15.](image2)
prepared as follows: 10 mg of product for $^1$H experiment in 0.5 mL of CDCl$_3$.

2.3. Size exclusion chromatography

Size exclusion chromatography (SEC) analyses were carried out with a Varian PL-GPC-50 chromatography apparatus equipped with a RI detector. Two PL Gel Mixed-E columns and one PLgel 3 lm-100A thermostated at 35°C were used with an eluent flow of 1 mL/min. Columns were calibrated with polystyrene (PS) standards. SEC analyses were performed for Priamine 1073 deactivated in THF with a small amount of toluene as flow rate marker.

2.4. Dynamic mechanical analyses

2.4.1. Creep mode

Dynamic mechanical analyses (DMA) were carried out using a Metravib DMA 25 with Dynatest 6.8. The mechanical compressions of the samples were measured using $20 \times 20 \times 10$ mm$^3$ foam samples in the creep mode with tension holders at room temperature. The measurements were repeated three times. The static displacement was fixed to $-6$ mm with time of loading of $1$ s, a maximum strength of $-10$ N and an application time of $120$ s.

2.4.2. Relaxation mode

The resilience of foams was measured using above mentioned DMA (Metravib DMA 25) with Dynatest 6.8 for the same foam samples. Samples were first compressed to 50% of their original thickness during 600 s with maximum strength equal to $-10$ N and the time of loading was $1$ s. Then the time for the recovery of the shape was measured during $300$ s. Measurements were repeated three times for the same samples.

2.5. Thermogravimetric analyses

Thermogravimetric analyses (TGA) were performed using a TGA Q50 (TA instrument) at a heating rate of $10$ °C/min. Approximately 10 mg of sample was placed in an aluminum pan and heated from room temperature to $500$ °C under nitrogen atmosphere (60 mL min$^{-1}$).

2.6. Differential scanning calorimetry

Differential scanning calorimetry (DSC) analyses were carried out using a NETZSCH DSC200F3 calorimeter. Constant calibration was performed using indium, $n$-octadecane and $n$-octane standards. Nitrogen was used as the purge gas. 10–15 mg samples were sealed in aluminum pans. The thermal properties were analyzed at $20$ °C/min in the range between $-100$ and $100$ °C to observe the glass transition temperature at the second ramp. All the reported temperatures are on set values.

2.7. Titration of the cyclic-carbonate by $^1$H NMR

A specified amount of cyclic-carbonate (around 10 mg) and a standard (toluene, around 6 mg) were weighed into an NMR tube. Once the $^1$H NMR acquisition was completed, the characteristic peaks of carbonate $a$ (4.90 ppm) and $\text{CH}_3$ (2.49 ppm) of toluene were integrated (Fig. 1). The integration of $\text{CH}_3$ of toluene was fixed to 300. The carbonate contents (CC) of PPO-Bis-C$_5$ and TMP-Tri-C$_5$ were calculated according to Eq. (1), where $I_a$ - an integration of peak $a$, $m_{\text{standard}}$ - mass of toluene introduced into the NMR tube, $I_{\text{CH}_3}$ - integration of peak $\text{CH}_3$ of toluene, $M_{\text{standard}}$ - molar mass of toluene and $m_{\text{cyclocarbonate}}$ - mass of PPO-Bis-C$_5$ or TMP-Tri-C$_5$ introduced into NMR tube. The CC values for each carbonate were obtained in triplicate determinations.

![Fig. 1. $^1$H NMR spectra of (A) PPO-Bis-CS with toluene and (B) TMP-Tri-CS with toluene.](image-url)
2.8. Synthesis of NIPU foams

The formulations of NIPU foams were calculated from 1 equivalent of carbonate (PPO-Bis-C$_5$ or TMP-Tri-C$_5$), 1.05 equivalent of amine (Jeffamine EDR-148 or Priamine 1073), 0.05 equivalent of MH15 compared to the amine and 0.05 equivalent of TBD in relation to the carbonate.

First, the five-membered cyclocarbonate (PPO-Bis-C$_5$ or/and TMP-Tri-C$_5$) and the TBD were placed in the silicone mold and stirred mechanically for 3 min. Then, the amine (Jeffamine EDR-148 or Priamine 1073) was added and the mixture was, once again, stirred mechanically for around 3 min. Once the homogenous mixture was obtained, the blowing agent, MH 15, was added and the mixture was stirred for 2 min. The obtained foamed mixtures were heated at 80°C for 12 h and 120°C for 4 h.

2.9. Deactivation of Priamine 1073

Stoichiometric amounts of acetic anhydride and Priamine 1073 were placed together in a round bottom flask, assuming the molecular weight of the amine equal to 600 g mol$^{-1}$. The reaction was continuously stirred for 7 h at 60°C.

2.10. Swelling index

Three samples (30 mg each) were separately put into 30 mL THF for 24 h. The swelling index, SI, is given by Eq. (2), where $m_0$ is initial mass of tab and $m_1$ is mass of tab after swelling in solvent.

$$SI = \frac{m_1 - m_0}{m_0} \times 100$$

2.11. Apparent density

The NIPU foams were cut into samples in the cuboid shape. Their dimensions were measured using caliper and the apparent density, $\rho_a$, was calculated from Eq. (3), where $m$ express the mass of the foams samples in kg and $V$ is volume of the samples in m$^3$.

$$\rho_a = \frac{m}{V}$$

3. Results and discussion

3.1. Characterization of reactants

3.1.1. Carbonates: PPO-Bis-C$_5$ and TMP-Tri-C$_5$

Specific Polymers company synthesized two five-membered cyclic carbonates by carbonation of poly(propylene oxide) diglycidyl ether and trimethylolpropane triglycidyl ether to obtain respectively poly(propylene oxide) bis-carbonate (PPO-Bis-C$_5$) and trimethylolpropane tris-carbonate (TMP-Tri-C$_5$) (Scheme 3). The carbonate contents (CC) of these products were determined by $^1$H NMR titration. The real molar masses were obtained from Eq. (4) using calculated CC values and functionalities of carbonates, $f_{\text{carbonate}}$, i.e. 2 for PPO-Bis-C$_5$ and 3 for TMP-Tri-C$_5$. The determination of real molar masses of carbonates was necessary to calculate the quantities of amines, blowing agent and catalyst to introduce in the NIPU foam formulations.

$$M_{\text{carbonate}} = \frac{f_{\text{carbonate}}}{CC}$$

3.1.2. Amines: Jeffamine EDR-148 and Priamine 1073

In order to apply the alternative NIPU for design of new foams, two amines were used in combination with PPO-Bis-C$_5$ and TMP-Tri-C$_5$. The first amine was Jeffamine EDR-148 from Huntsman. The $^1$H NMR of Jeffamine EDR-148 (Fig. 2) confirms the di-functionality of this amine. Indeed, three signals for $a$, $b$ and $c$ protons present on the $^1$H NMR spectrum are integrated respectively for 4, 4.02 and 4.04 protons. In addition, protons corresponding to amine function ($\text{NH}_2$) integrate for 3.84 protons. Therefore, this amine contains two primary amine groups in gamma position of ethylene glycol. Thus, the oxygen atoms in gamma position relative to amine group give a high reactivity to the amine [50]. The molar mass of Jeffamine EDR-148 equal to 148 g mol$^{-1}$, was given owing to technical data sheet of Huntsman.

The second amine used in the foams formulation was Priamine 1073 from Croda company. This amine is a difunctional derivative of C$_{18}$ fatty acids resulting from dimerization or/and trimerization process. Consequently,
it contains 100% renewable carbon. This structure could bring flexibility to the NIPUs. In order to characterize the Priamine 1073 and to check its functionality, a SEC analysis was performed, after deactivation of amine by an acetalization reaction with acetic anhydride. The distribution of molar masses shown in the SEC chromatogram (Fig. 3) displays two distinctly separated peaks for the molar masses of the species present in the product. The two peaks correspond to two polyamines of different functionalities. The first peak (1) around 900 g mol⁻¹ corresponds to the difunctional amine derived from a dimerization process of C₁₈ fatty acid. The second peak (2) which is twice the molar mass of the first peak (1800 g mol⁻¹), corresponds to a trimerization of C₁₈ fatty acid and gives a tri-functional amine. However, the SEC trace gave noticeably wider peak for the molar mass related to the di-functional amine compared to tri-functional amine. This characterization proves that Priamine 1073 is mainly a di-functional amine.

In order to formulate NIPU foams from cyclocarbonate and Priamine 1073, the molar mass of amine was determined from AHEW (Amine Hydrogen Equivalent Weight) value given by Croda: 139 g eq⁻¹ [51]. This value is the ratio of molar mass (M) to the number of active hydrogens. Therefore, the molar mass is AHEW multiplied by the number of active hydrogens equal to 4 for this amine. As a result, the molar mass of Priamine 1073 is 556 g mol⁻¹.

\[
AHEW = \frac{M}{\text{Number of active hydrogens}}
\]  

where \( M \) - molar mass, \( AHEW \) - Amine Hydrogen Equivalent Weight.

### 3.1.3. Blowing agent: MH 15

The blowing agent, MH15 from Momentive company, is a polymethylhydrogensiloxane (Scheme 2). It contains SiH groups capable of reacting with compounds bearing amine. In this study, MH 15 reacts with equimolar amount of amine releasing the dihydrogen. In order to calculate the molar mass of this blowing agent, two procedures were established. The first procedure consisted of calculating the theoretical molar mass from data given by Momentive while in the second procedure the real molar mass was determined by \(^1\)H NMR.

The release of gas was responsible for the expansion of materials to get NIPU foams. According to the technical data sheet of Momentive MH15, 1 g of MH 15 which react with amine releases 340 mL of dihydrogen. This data allows for determining the number of repetition units of CH₄SiO denoted as \( n \) (Eq. (6)), and, therefore, the theoretical molar mass of MH15. Solution of this equation enabled to determine the number of repetition of SiH group, \( n \), being equal to 28 and the theoretical molar mass of 1843 g mol⁻¹.

\[
V_{\text{gas released}} = \frac{rn}{M \text{C}_6\text{H}_{18}\text{OSi}_2 + nM \text{CH}_4\text{SiO}}
\]  

where \( r = 22,400 \text{ mL mol}^{-1}, M \text{C}_6\text{H}_{18}\text{OSi}_2 = 162.38 \text{ g mol}^{-1}, M \text{CH}_4\text{SiO} = 60.02 \text{ g mol}^{-1} \) and \( V_{\text{gas released}} = 340 \text{ mL g}^{-1} \).

To compare this theoretical molar mass with real molar mass, \(^1\)H NMR of product was performed (Fig. 4). In the spectrum, integration of the characteristic peak of CH₃ end chain, 0.14 ppm, denoted as \( a \), was fixed at 18 protons. Therefore, the protons \( c \), 4.74 ppm, characteristic for SiH in unity of repetition CH₄SiO are integrated for 32.42 protons. Consequently, the number of repetition of CH₄SiO pattern determined by \(^1\)H NMR, \( n \), is 32. Accordingly, the real molar mass of MH 15 is 2083 g mol⁻¹. For the formulations of NIPU foams, only the real mass of MH 15 was used. The summary of the characterization of reactants is given in Table 1.

### 3.2. Preparation of NIPU foams

In this study, five NIPU foams were synthesized: one with TMP-Tri-C₅ and Jeffamine EDR-148, two with TMP-Tri-C₅ and two with TMP-Tri-C₅.
Tri-C₅ and PPO-Bis-C₅ in combination with Jeffamine EDR-148 and, finally, two with TMP-Tri-C₅ and PPO-Bis-C₅ in combination with Priamine 1073. The properties of NIPU foams were affected by the differences in the functionalities of the cyclic-carbonates as well as the structures of the carbonates and amines. These foams were prepared by using well-established formulations based on molar equivalent of reactants (Table 2, Fig. 5). In the first formulation (1), TMP-Tri-C₅ was used in combination with Jeffamine EDR-148. The functionality of this carbonate is equal to 3, therefore, this TMP-Tri-C₅ brings rigidity to system by crosslinking with diamine. On the contrary, the formulations 2 and 3, with respectively 0.5 and 0.3 equivalents of PPO-Bis-C₅ in combination with 0.5 and 0.7 equivalents of TMP-Tri-C₅ and Jeffamine EDR-148 could lead to a lower rigidity. The long carbon backbone of PPO-Bis-C₅ decreased the rigidity to system of carbonate/amine. The formulations 4 and 5 used the Priamine 1073. This

![Fig. 4. 1H NMR spectrum of blowing agent MH 15.](image)

**Table 1**
Characterization of substrates.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Carbonate content a (meq g⁻¹)</th>
<th>AHEW b (g eq⁻¹)</th>
<th>Functionality carbonate or amine</th>
<th>Number of active hydrogens</th>
<th>M (g mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPO–Bis-C₅</td>
<td>2.76</td>
<td>–</td>
<td>2</td>
<td>–</td>
<td>725 c</td>
</tr>
<tr>
<td>TMP–Tri-C₅</td>
<td>5.28</td>
<td>–</td>
<td>3</td>
<td>–</td>
<td>568 d</td>
</tr>
<tr>
<td>Jeffamine EDR-148</td>
<td>–</td>
<td>37</td>
<td>2</td>
<td>2</td>
<td>148 e</td>
</tr>
<tr>
<td>Priamine 1073</td>
<td>–</td>
<td>139</td>
<td>2</td>
<td>2</td>
<td>556 f</td>
</tr>
<tr>
<td>MH15</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1843 (g)</td>
</tr>
</tbody>
</table>

|              |                               |                 |                                  |                           | 2083 (b)    |

a Carbonate content determined by 1H NMR titration with standard: toluene.
b AHEW (Amine Hydrogen Equivalent Weight) determined by Huntsman for Jeffamine EDR-148 and Croda for Priamine 1073.
c Molar mass of PPO-Bis-C₅ and TMP-Tri-C₅ determined from Eq. (4).
d Molar mass of Jeffamine EDR-148 from data provided by Huntsman.
e Molar mass of Priamine 1073 determined from Eq. (5).
f Theoretical and real molar mass of MH 15 determined by (a) theoretical data of Momentive or (b) 1H NMR.

**Table 2**
NIPU foam formulations in equivalent.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPO–Bis-C₅</td>
<td>–</td>
<td>0.5</td>
<td>0.3</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>TMP–Tri-C₅</td>
<td>1</td>
<td>0.5</td>
<td>0.7</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>Jeffamine EDR-148</td>
<td>1.05</td>
<td>1.05</td>
<td>1.05</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Priamine 1073</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.05</td>
<td>1.05</td>
</tr>
<tr>
<td>MH15</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>TBD</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

a Quantities in equivalent of MH 15 introduced in the foams formulations compare to amine.
b Quantities in equivalent of TBD introduced in the foams formulations relative to carbonate.
amino has a long carbon backbone which, as PPO-Bis-C5, could increase the flexibility of NIPU foams.

The main disadvantage of the alternative NIPU foams is the low reactivity of carbonate/amine reaction. In order to increase this reactivity, a catalyst was used in the formulations. A lot of catalysts were reported in the literature, but the best were thiourea (1-(3,5-bis(trifluoromethyl) phenyl)-3-cyclohexylthiourea) and TBD [47,48]. However, only TBD is a commercial product, therefore we chose it. Moreover, the results of Blain et al. [47] showed that the optimal amount of TBD introduced into the formulation was 5% relative to carbonate to obtain the same catalytic activity of thiourea.

In the case of blowing reaction, MH 15 was used in the carbonate/amine/TBD formulation providing the foaming of the material by releasing di-hydrogen during the reaction between amine and blowing agent. Stefani et al. [49] showed that the blowing agent influences the apparent density of the foam. Therefore, in our study, the same quantities of MH 15 equal to 5% relative to amine, were used in the foam formulations. The amount of amine used is adjusted (1.05 equivalent) to compensate the amount of PEOxolane in the system to be in a stoichiometric amount of cyclic carbonate and amine. The differences between the structures of NIPU foams were characterized by the measurement of the apparent density, scanning electron microscopy (SEM) and dynamic mechanical analysis (DMA). Then, the degree of cross-linking was analyzed by measurement of swelling index. Finally, thermal properties of NIPU foams were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

3.3. Structural characterization of NIPU foams

3.3.1. Density of NIPU foams

Generally, at the macroscopic scale, the cellular materials are described by their relative density, $\rho_r$, defined as the ratio of apparent density of bulk cellular material, $\rho_s$, to the density of the solid material of which the foam is made, $\rho_s$ (Eq. (7)). In the case of polyurethane foams, the reference solid density $\rho_s$ is 1150 kg m$^{-3}$ [52]. Above $\rho_r = 0.3$, the material goes from a cell structure to a solid containing isolated pores [53]. In the case of polymeric materials, $\rho_r < 0.3$.

Flexible foams are used for insulation, packaging and shock absorption and possess relative density values between 0.05 and 0.2. Apparent density values of low density flexible foams vary in the range 10–80 kg m$^{-3}$, whereas, high density flexible PU foams exhibit apparent density of about 100–900 kg m$^{-3}$ [54]. In order to determine the apparent density values of NIPU foams, the foams

\[ \rho_s = \frac{\rho_s}{\rho_r} \quad (7) \]

Apparent density of NIPU foams varies in the range 194–295 kg m$^{-3}$ (Table 3), therefore they can be classified as high density foams. First of all, these results show that the use of only tri-functional cyclic carbonate increases the apparent density of foams. In fact, for the same amine (Jeffamine EDR-148), the density of 1 is 295 kg m$^{-3}$ whereas the densities of 2 and 3 are respectively 248 and 242 kg m$^{-3}$. The increase in apparent density is related to the degree of cross-linking of the foam. On the other hand, the comparison of the apparent densities between 2 and 4, or, 3 and 5 shows that the long carbon chain of Priamine 1073 decreases the apparent density of the foams. The NIPU foams can be considered for use as integral foams to make molded parts with cellular core and relative dense decorative skin. The potential applications are related to their cushion and shock adsorption abilities and include furniture, automobile and packaging.

3.3.2. Morphological characterization of NIPU foams

The NIPU foams were analyzed by scanning electron microscopy (SEM) in order to determine their morphology relative to used raw materials (Fig. 7). The first picture (1) shows a network with a higher apparent density than the other foams. Indeed, foam (1) was prepared from only TMP-Tri-C5 whereas the other four were prepared from mixture of PPO-Bis-C5 and TMP-Tri-C5 in various ratios (0.5 or 0.7 TMP-Tri-C5 and 0.5 or 0.3 PPO-Bis-C5). The TMP-Tri-C5 plays the role of cross-linking agent and increases the apparent density of foam. On the contrary, PPO-Bis-C5 provides flexibility to materials by its aliphatic chain and provides more uniform cellular structure with smaller cells ((1) respectively compared to (2) and (3)). Moreover, two different amines were used to prepare NIPU foams: Jeffamine EDR-148 and Priamine 1073. The second one, has in its chemical structure a long aliphatic chain, which, as the PPO-Bis-C5, provides flexibility to the materials and increases the sizes of cells of NIPU foams ((4) and (5) respectively compared to (2) and (3)). All these charac-

Fig. 5. Picture of the different NIPU foams.

Fig. 6. Picture of measuring of volume of NIPU foams.
characteristics are closely related and checked by determination of apparent density calculated previously. Finally, all the pictures show interconnected cells and thus open porosity of NIPU foams.

### 3.3.3. Dynamic mechanical analysis (DMA)

The mechanical properties of the NIPU foams were analyzed by dynamic mechanical analysis (DMA). Two tests were made for flexible foams: the first corresponded to the behavior of the foam subjected to a stress in monotone tension exceeding the region of linear elasticity and the second showed the time of recovery of the flexible foams. For this purpose, the foams were cut into cuboid shapes of $20 \times 20 \times 10$ mm and analyzed with tension holders at room temperature. Measurements were realized three times for the same samples.

The first experiment shows the same behavior of the NIPU foams in monotone tension. Indeed, the five curves presented by Fig. 8 can be divided into three regions corresponding to different mechanisms. The first region, of the lower strain (between 0% and 10–15% for 1, 2 and 3; and 5% for 4 and 5), is the linear elasticity. This domain

<table>
<thead>
<tr>
<th>Foams formulations</th>
<th>$\rho_s$ (kg m$^{-3}$)</th>
<th>$\rho_i$</th>
<th>Swelling index (%)</th>
<th>$T_{dsf}$ (°C)</th>
<th>Char at 500 °C (%)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>295</td>
<td>0.257</td>
<td>42</td>
<td>310</td>
<td>8</td>
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<tr>
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<td>0.216</td>
<td>153</td>
<td>320</td>
<td>14</td>
<td>-12</td>
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<tr>
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<td>242</td>
<td>0.210</td>
<td>147</td>
<td>314</td>
<td>6</td>
<td>-2</td>
</tr>
<tr>
<td>4</td>
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<tr>
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<td>194</td>
<td>0.169</td>
<td>211</td>
<td>352</td>
<td>14</td>
<td>-13</td>
</tr>
</tbody>
</table>

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Fig. 7. SEM micrographs of NIPU foams with different formulations. (1) TMP-Tri-C5/MH 15/EDR-148 (1/0.05/1.05); (2) TMP-Tri-C5/PPO-Bis-C5/MH 15/EDR-148 (0.5/0.5/0.05/1.05); (3) TMP-Tri-C5/PPO-Bis-C5/MH 15/EDR-148 (0.7/0.3/0.05/1.05); (4) TMP-Tri-C5/PPO-Bis-C5/MH 15/Priamine 1073 (0.5/0.5/0.05/1.05) and (5) TMP-Tri-C5/PPO-Bis-C5/MH 15/Priamine 1073 (0.7/0.3/0.05/1.05).
is due to the strain for bending of the edge of the foam. The second region of these curves is characterized by a plateau. Physically, this part corresponds to the collapse of foam caused by the compressibility of the cells. Finally, the last region is the densification of the foam: when the stress is important, the opposite cells walls are crushed and they have formed a compressed material itself. However, only the values of stress to the different threshold depend on the type of studied foam. In fact, the foam 1 presents a more important stress for to deform the foam compare to other foams. This foam was prepared with only tri-carbonate (TMP-Tri-C5) which provides rigidity to the foam through more crosslinking of NIPU foam. The foam 2 and 3 as 4 and 5 present a lower stress on the strain because PPO-Bis-C5 used in the formulations provided flexibility to foams. Finally, the structure of amine influences also the stress–strain curves. The long aliphatic chain of the Priamine 1073 which gives the flexibility for the foams thus reduces their stress to strain compare to foams 2 and 3.

The second experiment shows the recovery of the NIPU foams. For this reason, all the foams were compressed at 50% of strain during 10 min and the time of recovery of these foams was saved (Fig. 9). All the curves of recovery foams overlays indicating that time back to the initial state is the same regardless of the formulation used to form the NIPU foams.

3.4. Degree of cross-linking characterization of NIPU foams

In order to compare the degree of crosslinking of the different NIPU foams, the swelling indices were measured. Three samples of known mass \(m_0\) of NIPU foams were immersed in 30 mL of THF during 24 h, and then reweighed to get the wet mass \(m_1\). The swelling index was calculated from Eq. (2). The results are summarized in Table 3. The lowest swelling index and the highest index gel content correspond to the optimum crosslinking of polymer. 1 gives a lower swelling index compare to other formulations. This result is due to the use of only trifunctional cyclic carbonate (TMP-Tri-C5) which brings more cross-linking NIPU foam. All other NIPU foams have swelling indices higher than 1. This arises from the use of difunctional cyclic carbonate (PPO-Bis-C5) besides TMP-Tri-C5. This PPO-Bis-C5 gives flexibility to the foams through carbon backbone and, therefore, a higher swelling index because of the decrease of crosslinking of materials allowing the solvent to penetrate into the material more easily. This is confirmed by comparing the formulation 2 and 3, and, 4 and 5. In fact, the formulations 2 and 4 include 0.5 equivalent of PPO-Bis-C5 while the formulations 3 and 5 involve 0.3 equivalent of this cyclic carbonate. Furthermore, the swelling index of 4 and 5 are higher than 2 and 3. This is due to the long carbon backbone of the Priamine 1073 which brings, as PPO-Bis-C5 compare to TMP-Tri-C5, the flexibility to the materials.

All these characterizations of morphology of the foams allow relating following formulations used. Indeed, the use of crosslinking agent (TMP-Tri-C5) in the formulation imply the decrease the swelling index and the increase the apparent density and the stress at strain. The SEM pictures show a denser network and smaller porosity. On the contrary, the use of long aliphatic chain (PPO-Bis-C5 and Priamine 1073) gives foams with a higher swelling index but lower apparent density and stress at strain. The MEB pictures show a lower apparent density of the foams and larger pore size.

3.5. Thermal characterization of NIPU foams

First, thermal properties were measured by DSC. Two dynamic temperature ramps were performed between −100 and 100 °C at 20 °C min\(^{-1}\) under nitrogen flow. Results of DSC measurements are shown in Table 3. The glass transition temperature values \(T_g\) obtained for foams of 1, 2, 3, 4, 5 formulations are equal to 19, −12, −2, −18 and −13 °C, respectively. \(T_g\) of foam 1 is higher than others, because of the higher cross-linking resulting from containing only tri-functional carbonates which cross-linked the material. Moreover, the PPO-Bis-C5 and Priamine 1073 contain long carbon backbones which could bring flexibility to materials and, therefore, decrease the \(T_g\) of foams from 2, 3, 4, 5 formulations.
TGA analyses were performed for all NIPU foams in order to determine thermal stability of synthesized networks under nitrogen. Table 3 gives the temperature at 30% of degradation and the char contents at 500 °C. The thermal stability of the NIPU foams 1, 2 and 3 are similar with Td30% around 320 °C. The thermal stability values of NIPU foams 4 and 5 are higher, with a Td30% equal to 360 °C, due to the absence of ether hinges in the Priamine 1073, by comparison toJeffamine EDR148, which increases the thermal resistance.

4. Conclusions

Nowadays, the alternative NIPU (NonIsocyanate Poly-Urethane) constitutes a significant opportunity to replace isocyanate in the formulation of PU materials. This study reports, for the first time, the synthesis of PU foams without isocyanate. NIPU foams were prepared from carbonate i.e. poly(propylene oxide) bis carbonate and trimethylolpropane tri carbonate and two amines. To ensure the reaction expansion, the same quantities of blowing agent (MH 15) were used in the foams formulations. The blowing reaction proceeded between amine and SiH groups of MH 15 by releasing of dihydrogen. NIPUs foams were then studied by characterizing the structure (apparent density, SEM, DMA), the degree of crosslinking (swelling index, TGA and DSC). All these characterizations showed that the synthesized foams were high apparent density flexible foams and their structure and thermal properties depend on degree of crosslinking provided by the difference in functionality of cyclic carbonate and the structure of amine.

Acknowledgements

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References