

# Fully Renewable Thermoplastic Poly(ester urethane urea)s from Bio-based Diisocyanates

Donglin Tang<sup>1,2</sup>, Shanmugam Thiagarajan<sup>2,3</sup>, Bart A.J. Noordover<sup>1\*</sup>, Cor E. Koning<sup>1</sup>, Daan S. van Es<sup>3</sup> and Jacco van Haveren<sup>3</sup>

<sup>1</sup>Laboratory of Polymer Materials, Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, the Netherlands

<sup>2</sup>Dutch Polymer Institute, P.O. Box 902, 5600 AX Eindhoven, the Netherlands

<sup>3</sup>Food & Biobased Research, Wageningen University and Research Center, P.O. Box 17, 6700 AA, Wageningen, the Netherlands

Received March 26, 2013; Accepted April 29, 2013; Published online May 15, 2013

**ABSTRACT:** A series of fully renewable poly(ester urethane urea)s (PEUs) were synthesized from bio-based starting materials, e.g., the polyester diol, the diisocyanates including L-lysine diisocyanate (LDI) and isoidide diisocyanate (IIDI), the chain-extenders including 1,4-diaminobutane (bDA), diaminoisoidide (iDA) and di(aminobutyl) urea (b<sub>2</sub>DA). It is found that the PEU based on the novel diisocyanate, IIDI, exhibits satisfactory thermal and mechanical properties. The LDI-based PEUs show less favorable thermal and mechanical properties than the IIDI-based counterpart, since the chemical structure of LDI is less regular than that of IIDI. However, by introducing a urea-containing dimeric diamine (b<sub>2</sub>DA) instead of the monomeric diamines, the properties of the LDI-based PEU can be improved significantly. For instance, the flow temperature increases 100°C and the E-modulus also increases from 1 MPa to approximately 20 MPa. These fully renewable PEUs seem to be interesting materials and they can potentially be used in biomedical or packaging applications.

**KEYWORDS:** Isoidide diisocyanate, L-lysine diisocyanate, polyester, renewable resources, thermoplastic polyurethanes

## 1 INTRODUCTION

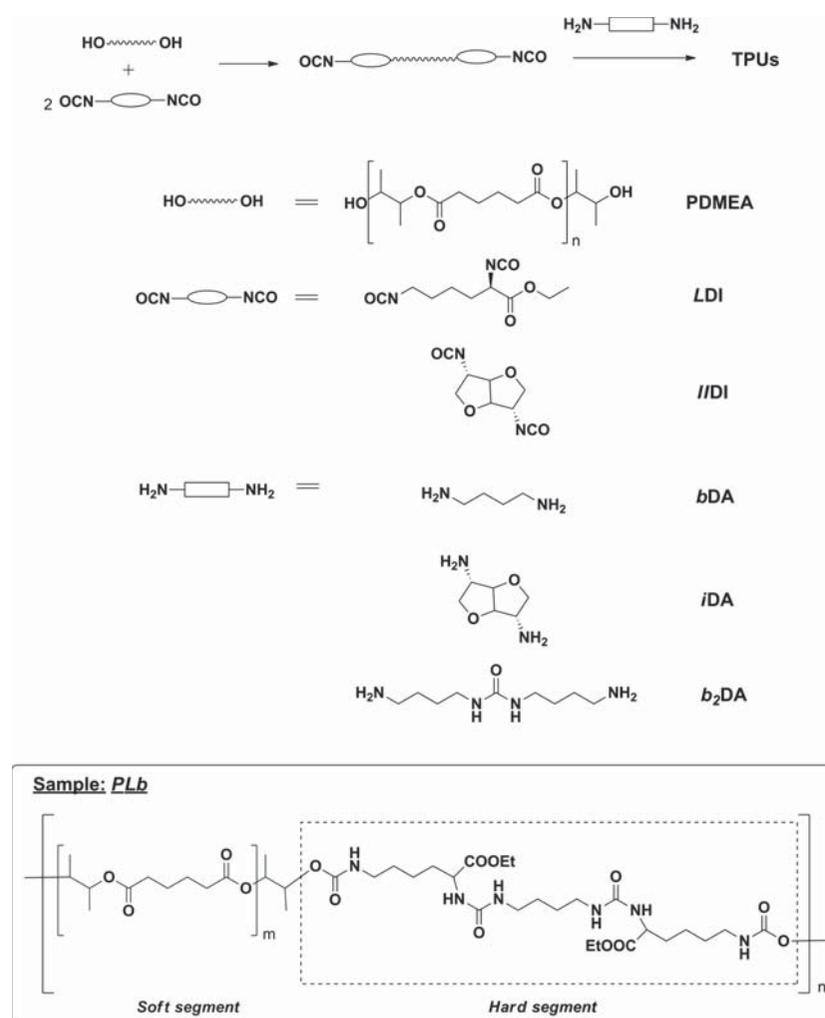
Bio-based, renewable resources are considered potential substitutes for crude oil as feedstocks for polymer materials. These bio-based compounds have chemical structures different from the conventional petrochemicals, offering polymers with differentiated properties. Thermoplastic polyurethane elastomers (TPU) are important polymer materials with interesting properties, such as tunable stiffness, excellent biocompatibility, good wear resistance and transparency. As a result, they are used in a plethora of applications, for instance, in furniture, the automotive industry, clothing and sports appliances. Therefore, it is of great interest to develop and study renewable TPUs.

As described in our previous work [1], the renewable polyester diol poly(1,2-dimethylethylene adipate)

(PDMEA, chemical structure see Scheme 1) is a good candidate precursor for TPU preparation, since it is fully amorphous and has a glass transition temperature ( $T_g$ ) as low as  $-38^\circ\text{C}$ . To synthesize fully renewable TPUs, not only the polyester diol but also the diisocyanate (DI) and the chain extender (CE) should be obtained from renewable sources. To date, many renewable short-chain diols or diamines, such as ethylene glycol (from cellulose [2]), 1,4-butanediol (from glucose [3]), 1,4-diaminobutane (also named putrescine, from glucose [4]), etc., have been applied as chain extenders. However, only a few diisocyanates are available from renewable resources. Ethylester-L-lysine diisocyanate (LDI) and 2,5-diisocyanato-2,5-dideoxy-1,4:3,6-dianhydro-L-iditol (which is also called isoidide diisocyanate, abbreviated as IIDI) are two of them (for their chemical structures, see Scheme 1). LDI can be obtained from L-lysine, which is based on arabinose [5]. IIDI is derived from 1,4:3,6-dianhydro-D-mannitol (isomannide) which can be obtained from cellulose or starch [6, 7]. In the first step the two *endo*-oriented hydroxyl groups are transferred into two *exo*-oriented

\*Corresponding author: b.a.j.noordover@tue.nl

DOI: 10.7569/JRM.2013.634116



**Scheme 1** The scheme of PEU preparation, as well as the chemical structures of starting materials and the idealized chemical structure of PLb.

primary amine groups, [8, 9] which are subsequently transferred into two *exo*-oriented isocyanate groups.

This study describes the preparation and the characterization of a series of fully renewable TPUs, based on a renewable polyester diol PDMEA, two bio-based DIs (LDI and IIDI), and several renewable diamine CEs, namely 1,4-diaminobutane (bDA, can be produced from glucose by a metabolically engineered strain of *Escherichia coli* [4]), 2,5-diamino-2,5-dideoxy-1,4:3,6-dianhydro-L-iditol which is also called diaminoisoidide (iDA, can be obtained from isomannide from polysaccharides [10, 11]) and di(4-aminobutyl) urea ( $b_2$ DA, from putrescine and urea). To be exact, the prepared TPUs are poly(ester urethane urea)s (PEUs), because of the coexistence of ester groups, urethane groups and urea groups along the backbone of these polymers. In addition, it is important to mention that the TPUs based on LDI may be suitable for biomedical

applications since its degradation product during metabolism is the nontoxic lysine which occurs naturally in human and animal bodies [12].

## 2 EXPERIMENTAL

### 2.1 Materials

The polyester diol (PED), *viz.* poly(1,2-dimethylethylene adipate) (PDMEA,  $M_n = 890$  g/mol), was prepared in our laboratory (for details concerning its preparation see our previous work [1]). Diaminoisoidide (iDA) were prepared [9] by Food & Biobased Research, part of Wageningen University & Research Center (FBR- WUR). 1,4-diaminobutane (bDA, and dibutyltin dilaurate (DBTDL) were purchased from Aldrich. Urea was bought from Merck. Ethylester-L-lysine diisocyanate (LDI) was purchased from Chemos GmbH (Germany).

All solvents were purchased from Biosolve. All chemicals were used as received without further purification.

## 2.2 Synthesis of Isoidide Diisocyanate (IIDI)

A nitrogen-degassed 3-necked 250 mL round-bottom flask was charged with iDA (6.9 mmol) and 100 ml of anhydrous ethyl acetate. The suspension was stirred at 83°C. At this temperature, triphosgene (13.8 mmol) in 50 mL of anhydrous ethyl acetate was added dropwise into the reaction mixture and further stirred for 48 h. After the reaction had cooled down to room temperature, the iDA-HCl salt formed was filtered through the G-3 glass filter funnel and washed intensively with anhydrous ethyl acetate (25 mL × 3). The combined filtrates were stirred with activated carbon at 50°C for 30 min. The resulting solution was then filtered over Celite contained in a G-3 filter funnel. The filtrate was evaporated under reduced pressure using a rotatory evaporator giving colorless semi-solid of 0.54 g (40%) of isoidide diisocyanate which is analytically pure. The crude product was further purified by short path distillation using a Kugel-rohr oven at 135–145°C for 30 min at 50 mbar yielding pure IIDI as colorless crystalline solid.

IIDI: <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 4.72 ppm (s, 2H), 4.09 (d, 2H); 3.96–3.93 (dd, 2H), 3.90–3.87 (dd, 2H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, δ): 124.1 ppm (NCO), 87.6 (CHO), 74.3 (CH<sub>2</sub>O), 59.5 (CHNCO)

## 2.3 Synthesis of Di(4-aminobutyl)urea (b<sub>2</sub>DA)

The bDA (88 g, 1.0 mol) was weighed into a 250 mL three-necked flask which was then placed in an oil-bath. A condenser was fitted on the flask. The reactant was stirred and heated up to 150°C. A solution of urea (6.0 g, 0.1 mol) in 12 mL of water was added to the flask at a rate of 5.0 mL/h. Then the reaction was carried out for 24 h. After cooling, the crude product was washed with ethanol in a Soxhlet extractor to remove the excess of bDA. The residue was collected and dried *in vacuo*. The yield of b<sub>2</sub>DA was 47%. The sample for NMR and ESI-MS measurements was a salt, which was obtained by neutralizing the crude solid in a 0.5 N hydrochloric acid (HCl) solution, followed by removal of water using a rotavap and then *in vacuo* at 70°C overnight.

b<sub>2</sub>DA salt: <sup>1</sup>H-NMR (400 MHz, D<sub>2</sub>O, δ): 2.95 ppm (t, 2H, CONHCH<sub>2</sub>), 2.48 (m, 2H; CH<sub>2</sub>NH<sub>3</sub><sup>+</sup>); 1.33 (m, 4H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub><sup>+</sup>); <sup>13</sup>C-NMR (400 MHz, D<sub>2</sub>O, δ): 161.35 ppm (C=O), 40.16 (CONHCH<sub>2</sub>); 39.65 (CH<sub>2</sub>NH<sub>3</sub><sup>+</sup>); 28.78 (CONHCH<sub>2</sub>CH<sub>2</sub>); 26.27 (CH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub><sup>+</sup>); ESI-MS m/z: [M + 2HCl] calcd. for C<sub>9</sub>H<sub>24</sub>N<sub>4</sub>OCl<sub>2</sub>, 274.13; found, 273.4.

## 2.4 Synthesis of PEUs

The preparation of PEUs follows the same procedures for all samples. The preparation of PLb is represented as an example (see Scheme 1). A 3-necked 250 mL round-bottom flask was equipped with a mechanical stirrer, and an argon inlet and outlet. The diisocyanate LDI (4.52 g, 20 mmol), catalyst DBTDL (0.05 g) and the solvent dimethyl acetamide (DMAc, 13.5 mL) were added into the flask. The system was then heated to 80°C under argon flow. A solution of PDMEA (8.90 g, 10 mmol) in DMAc (27 mL) was added dropwise into the reaction system. The solid content of the reaction mixture was kept at 25 wt%. The prepolymerization took place under argon flow at 80°C for four hours. Then the reaction solution was diluted to a solid content of 10 wt% and cooled to room temperature. Chain extension was carried out by the dropwise addition of a solution of diamine bDA (0.88 g, 10 mmol) in DMAc. After the chain extension, the product was precipitated by pouring the viscous product solution into water. The precipitate was collected and dried *in vacuo*. The PEU samples are yellow materials, either soft or elastic. The yields of the PEUs were all in the range of 60–80%.

## 2.5 Characterization

<sup>1</sup>H- and <sup>13</sup>C-nuclear magnetic resonance (NMR) spectra were recorded using a Varian Mercury V × (400 MHz) spectrometer at 25°C. Size exclusion chromatography (SEC) in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was performed on a system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector (35°C), a Waters 2707 autosampler, and a PSS PFG guard column followed by 2 PFG-linear-XL (7 μm, 8 × 300 mm) columns in series at 40°C. HFIP with lithium chloride (2 g/L) was used as eluent at a flow rate of 0.8 mL/min. The molecular weights were calculated against poly(methyl methacrylate) standards (Polymer Laboratories, M<sub>p</sub> = 580 Da up to M<sub>p</sub> = 7.1 × 10<sup>6</sup> Da). Dynamic mechanical thermal analysis (DMTA) was performed on the PEU films (with dimensions around 10 × 5.3 × 0.5 mm) with a TA Instruments Q800 analyzer in tension film mode at a maximum strain of 0.1% and a frequency of 1 Hz. The sample was heated from –100 to 250°C at a heating rate of 3°C/min. The glass transition temperature (T<sub>g</sub>) was selected as the temperature at the maximum value of the loss modulus while the flow temperature (T<sub>f</sub>) was determined as the temperature at which the storage modulus had decreased to 0.1 MPa. The PEU films for both DMTA and tensile testing (see below) were prepared by compression molding at 80°C (for PLb, PLi and Pli) or 150°C (for the sample PLb<sub>2</sub>) for 5 min. The tensile

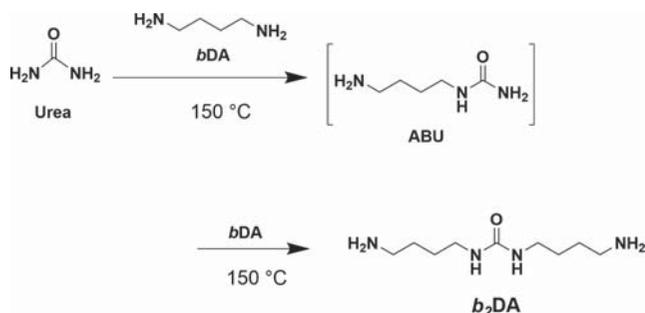
testing measurements were performed on a Zwick 100 universal tensile testing machine equipped with a 100 N load cell. The strain rate applied during the measurements was 60 mm/min (according to ISO 37). The sample bars for the tensile testing were cut into dumb-bell (ISO 37 type 3) shapes.

### 3 RESULTS AND DISCUSSION

#### 3.1 Preparation of PEUs

In our previous work [1], poly(1,2-dimethylethylene adipate) (PDMEA, chemical structure see Scheme 1) was found to be fully amorphous with a glass transition temperature ( $T_g$ ) as low as  $-38^\circ\text{C}$ . Therefore it is a good candidate precursor for TPU preparation. The poly(ester urethane urea)s (PEUs) were prepared by a conventional two-step polymerization procedure (see Scheme 1). In the first step, prepolymerization of diisocyanate (DI) with PDMEA was carried out by using a feed ratio of  $[\text{DI}]/[\text{PDMEA}] = 2.0/1.0$ . The PDMEA solution in the solvent dimethyl acetamide (DMAc) was added dropwise into the DI solution to make sure that all of the hydroxyl groups of the PDMEA are end-capped with DI and, at the same time, to limit the occurrence of chain extension. In the second step, chain extension took place by adding diamines. Three diamines, namely 1,4-diaminobutane (bDA), diaminoisoidide (iDA) and di(4-aminobutyl)urea ( $b_2\text{DA}$ ) were employed as the chain extenders (CE). Their chemical structures are shown in Scheme 1.

Among these CEs,  $b_2\text{DA}$  contains a urea group offering an additional hydrogen-bonding moiety, which might contribute to a better self-organization of the hard segments (HS) in the PEUs and, as a result, improve the phase separation of the HSs from the soft segments (SS). The flow temperature ( $T_f$ ) of the PEUs will probably be increased as well. The preparation of  $b_2\text{DA}$  is depicted in Scheme 2. During the reaction between urea and bDA, the mono-substituted urea



Scheme 2 Preparation of  $b_2\text{DA}$ .

4-aminobutylurea (ABU) is formed first, which is subsequently followed by the reaction of ABU with bDA to form the di-substituted product  $b_2\text{DA}$ . The urea is totally consumed within four hours, as determined by  $^1\text{H-NMR}$  (see Figure 1). In the meantime, part of the formed ABU was converted into  $b_2\text{DA}$ . The conversion of ABU into  $b_2\text{DA}$  reaches 100% in 24 hours.

Table 1 shows the starting materials including DIs and CEs for each polymerization. The polyester diol used for all polymerizations is the same: PDMEA with a number average molecular weight of 890 g/mol. The names given for the PEU samples are indicative of the diisocyanate and chain extender used: DI-CE (taking PLb as an example: L = LDI; b = bDA. The other symbols indicate: I = IIDI; i = iDA;  $b_2$  =  $b_2\text{DA}$ ). The theoretical hard segment contents ( $\text{HSC}_{\text{th}}$ ) were calculated assuming that the structures of the DIs are part of the HS (taking PLb as an example, see Scheme 1). The number average molecular weights ( $M_n$ ) of the PEUs obtained are around 30 kg/mol, which is usually sufficiently high to achieve good physical/mechanical properties [13]. The polydispersity indices ( $\mathcal{D}$ ) of most polymers are around 2.0, which is in agreement with the theoretical number for step-growth polymers according to Flory's theory [14].

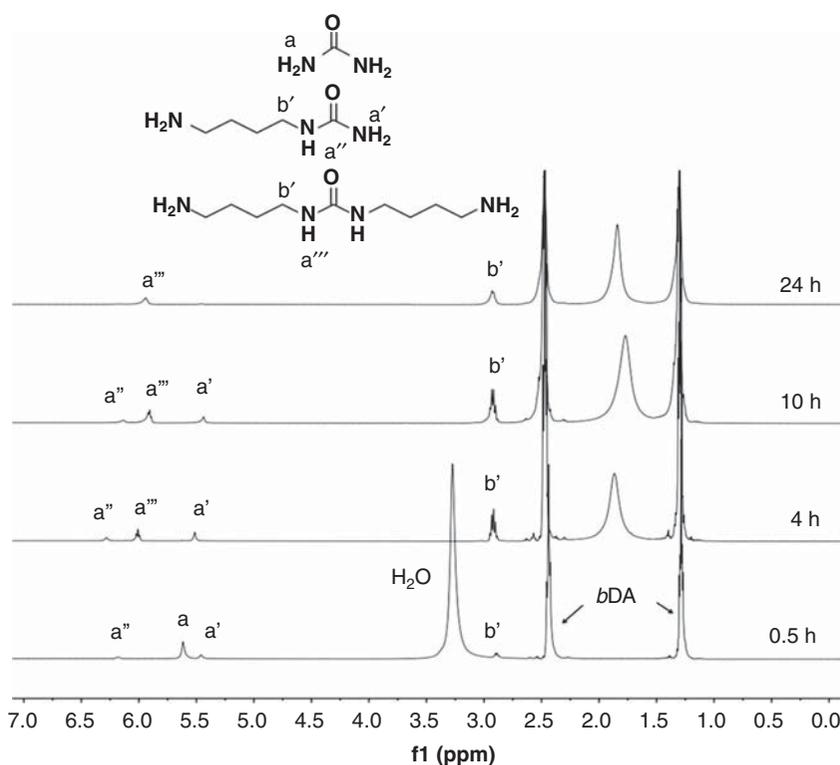
#### 3.2 Properties of PEUs

##### Thermal Stability

The thermal stability of the prepared PEUs was determined by thermogravimetric analysis (TGA). The TGA traces are shown in Figure 2 and the results are listed in Table 2, from which it is observed that these PEUs exhibit rather similar thermal stabilities. The temperature at which a maximum weight loss occurs is about  $340\text{--}360^\circ\text{C}$ . The thermal stability of these fully bio-based PEUs is similar to that of HDI-based polymers [15].

##### Thermo-mechanical Properties

The most useful technique for measuring the thermal transitions of thermoplastic polyurethanes is dynamic mechanical thermal analysis (DMTA) [16, 17]. For thermoplastic polyurethanes, it is usually difficult to observe the melting peaks in the DSC curves. Moreover, the values of the glass transition temperature ( $T_g$ ) of thermoplastic polyurethanes detected by DSC and DMTA are similar [1, 15]. Therefore, we have applied DMTA to detect the thermal transitions of the PEUs. For the LDI-based PEUs, if the chain extenders are monomeric diamines, e.g., bDA or iDA, the  $T_g$  values of the PEUs as deduced from



**Figure 1** Monitoring of the conversion of the reaction between bDA and urea by  $^1\text{H-NMR}$  spectroscopy (solvent:  $\text{DMSO-}d_6$ ).

**Table 1** Compositions, appearance and molecular weights of the obtained PEUs.

Entry <sup>a</sup>	DI	CE	$\text{HSC}_{\text{th}}^{\text{b}} \%$	$\text{HSC}_{\text{cor}} \%$	State	$M_n^{\text{d}}$ kg/mol	$\text{Đ}^{\text{d}}$
PLb	LDI	bDA	37.8	9.1	Soft <sup>e</sup>	28.8	1.70
PLi	LDI	iDA	40.1	12.5	Soft <sup>e</sup>	25.9	1.98
PLb <sub>2</sub>	LDI	b <sub>2</sub> DA	42.4	15.8	Elastic	24.8	1.86
PLi	IIDI	iDA	37.6		Elastic	32.4	1.71

<sup>a</sup> The names of the entries indicate: DI-CE (taking PLb as an example: L = LDI; b = bDA. The other symbols indicate: I = IIDI; b<sub>2</sub> = b<sub>2</sub>DA).

<sup>b</sup> The theoretical hard segment contents  $\text{HSC}_{\text{th}}$  are calculated as follows:

$$\text{HSC} = \frac{M_{\text{CE}} + 2M_{\text{DI}}}{M_{\text{CE}} + 2M_{\text{DI}} + M_{\text{PDMEA}}} \times 100\%, \text{ regarding that the entries of LDI are in the hard segments.}$$

<sup>c</sup>  $\text{HSC}_{\text{cor}}$  are the hard segment contents corrected by counting the LDI moieties as part of the soft segments.

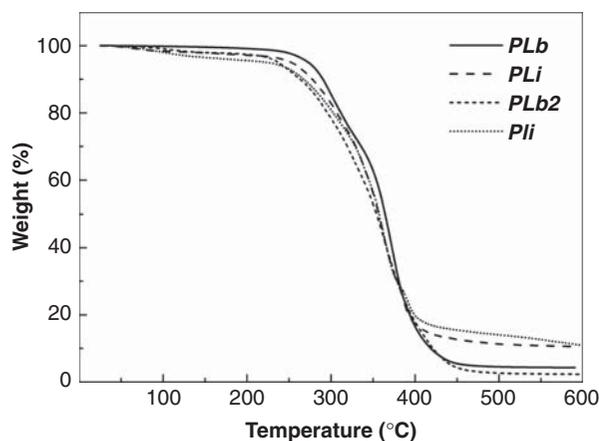
<sup>d</sup> The number average molecular weight  $M_n$  and the polydispersity index  $\text{Đ}$  of the PEUs were measured by HFIP-SEC, using PMMA standards;

<sup>e</sup> These materials can flow slowly at room temperature.

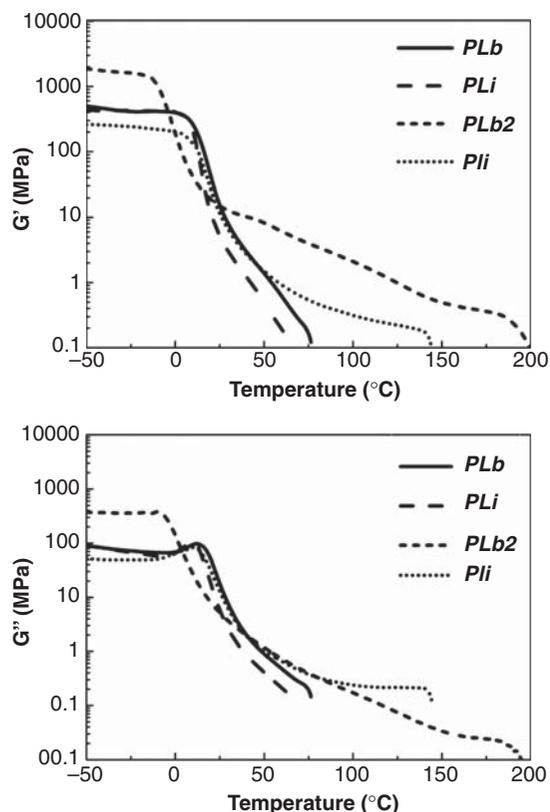
DMTA measurements (see Table 2 and Figure 3) are as low as 80°C. These relatively low flow temperatures, which are well below the degradation temperature of urethane linkages (approx. 170°C) facilitated the processing of these materials by compression molding rather than by casting. Since the  $T_g$  values of the PEUs are around 10–25°C, the width of the application window between  $T_g$  and  $T_{\text{fl}}$  is only about 50°C. Therefore,

it is found that these PEUs start to flow almost directly after the glass transition and there is hardly any rubbery plateau observed in the DMTA curves.

When comparing the HDI-based PEUs to the LDI-based counterpart (PLb), it is clear that their chemical structures are quite similar. The soft segments originate from the same polyester diol and the hard segments are almost the same, except for the DI moieties. The  $T_{\text{fl}}$



**Figure 2** TGA traces of the PEUs obtained. (Heating rate: 10°C/min).



**Figure 3** Dynamic mechanical thermal analysis portraits of the PEUs.

of the sample PLb observed in Figure 3 is only 75°C, which is far below that of its HDI-based counterpart, for which the  $T_g$  was found to be around 250°C in our previous work [15]. The large difference in the  $T_g$  values between the HDI- and LDI-based polymers is due to the less regular structure of LDI compared to HDI.

In the LDI-based PEUs, the existence of the pendant ester group in the LDI residue (see Scheme 1) might enlarge the distance between the individual polymer chains and therefore hinder the hydrogen-bond formation in the HSs. As a result, the self-organization of the HSs is disturbed so that the phase separation of the HSs and the SSs in these LDI-based PEUs may be less pronounced than that in the HDI-based polymers. Hence, LDI residues seem to be embedded more in the SSs than in the HSs. In this case the HSCs of the PEUs, calculated by assuming that the LDI residue is part of the SSs, need to be corrected. The values were recalculated ( $HSC_{cor}$ ) and are listed in Table 1. The practical values of the hard segment content are probably in between the theoretical values  $HSC_{th}$  (calculated assuming that the LDI residue is part of the HS) and the corrected values  $HSC_{cor}$  (assuming that the LDI residue is totally embedded in the SS). The values of  $HSC_{cor}$  seem to be more in line with the observed soft character of the LDI-based PEUs.

To increase the interchain interaction of the HSs and to further improve the mechanical properties of the LDI-based PEUs, a urea-containing dimeric diamine named di(4-aminobutyl) urea ( $b_2DA$ , chemical structure see Scheme 1) was employed as a chain extender. As mentioned above, the introduction of  $b_2DA$  might enhance the hydrogen-bonding density in the HSs of the PEUs. When comparing the DMTA curves (see Table 2 and Figure 3) of PLb<sub>2</sub> (based on  $b_2DA$ ) to that of PLb (based on bDA), we can conclude that PLb<sub>2</sub> does not only have a lower  $T_g$  ( $T_g$  of PLb = 13.7°C vs.  $T_g$  of PLb<sub>2</sub> = -13.1°C) and a higher  $T_{fi}$  ( $T_{fi}$  of PLb = 75.3°C vs.  $T_{fi}$  of PLb<sub>2</sub> = 201.8°C), but also exhibits a higher storage modulus. The differences in the thermo-mechanical properties between PLb and PLb<sub>2</sub> indicate that the application temperature range of the  $b_2DA$ -based PEU as an elastomer is wider than that of its bDA-based counterpart, and in addition, the  $b_2DA$ -based PEUs are stiffer. Clearly, the introduction of the urea-containing dimeric diamine improves the self-organization of the HSs and enhances the phase separation of the LDI-based PEUs. Another way to improve the interchain interaction of the HSs in PEUs is to introduce a more symmetric DI than LDI into the PU chains. As shown in Scheme 1, the structure of another renewable diisocyanate, namely IIDI, is more symmetric and less flexible than that of LDI. Might this help to improve the phase separation and properties of the PEUs? The PEUs PLi and Pli were selected to study the difference between using LDI and IIDI. As shown in Table 2 and Figure 3, the glass transition temperatures of PLi and Pli are quite similar while the  $T_{fi}$  of Pli is about 80°C higher than that of PLi. Interestingly, the  $T_{fi}$  of Pli is about 150°C, which is still below the degradation temperature of polyurethanes,

**Table 2** Thermal and mechanical properties of the PEUs obtained.

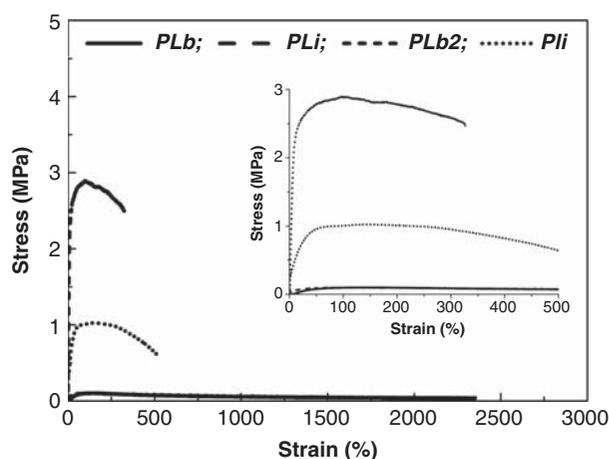
Entry	TGA		DMTA		Tensile testing	
	$T_{d,max}$ °C	$T_g$ °C	$T_{fl}$ °C	E-modulus MPa	Strain at break %	
PLb	369.3	13.7	75.3	$0.5 \pm 0.3$	$2400 \pm 250$	
PLi	362.0	9.9	63.3	$1.0 \pm 0.3$	$2400 \pm 150$	
PLb <sub>2</sub>	364.5	-13.1	201.8	$21.2 \pm 4.5$	$320 \pm 90$	
PLi	365.1	11.5	143.7	$3.4 \pm 1.3$	$490 \pm 70$	

thus this polymer can be processed in the melt without degradation. However, a broad glass transition in the DMTA curve of PLi indicates the occurrence of phase mixing. The phase separation of PLi is obviously less pronounced than that of PLb<sub>2</sub>.

### Mechanical Properties

Asplund *et al.* [12] has reported the LDI-based poly(urethane urea)s (PUUs) with water as a chain extender. In their materials, the HSs are composed of approximately 4.5 repeating lysine units. The authors found that all the materials, regardless of the SS used, exhibit a high elongation at break (from 1600 up to 4700%) and a low E-modulus (2.1 to 6.1 MPa), except one PUU which is based on poly(caprolactone-co-D,L-lactic acid) (E-modulus = 140 MPa) as this particular polymer is a glassy material at room temperature ( $T_g = 43^\circ\text{C}$ ).

In this study, the mechanical properties of the PEUs were also measured via tensile testing. The results of the testing are listed in Table 2 and the stress-strain curves are shown in Figure 4. The HS lengths ( $L_{HS}$ ) of the PEUs in this study are designed to be 4U (for PLb and PLi, with a HS sequence of "ULUXULU" in which L = lysine moiety; X = B, butylene moiety, or = I: isoidide moiety) or 5U (for PLb<sub>2</sub>, with a HS sequence of "ULUBUBULU"). It is found that the PEUs with a  $L_{HS}$  of 4U are soft, non-elastic materials exhibiting high strains at break (> 2000%) and low E-moduli (around 1 MPa or even less). The stress-strain curves of PLb and PLi are so similar that they cannot be distinguished from each other in Figure 4. The values of the E-moduli of these two materials are different, but the difference can be explained by the higher error of the tensile testing machine when measuring such soft materials with such low E-moduli. As discussed above, the lysine residues from LDI might be embedded more in the



**Figure 4** Stress-strain curves of the PEUs. Inset: zoomed-in portrait of the stress-strain curves.

SSs than in the HSs thus the value of the HSC may be closer to that of  $HSC_{cor}$  (see Table 1), where the HSCs calculated are between 9% and 13% for the PEUs with a  $L_{HS}$  of 3U.

For the PEUs with a  $L_{HS}$  of 5U (PLb<sub>2</sub>), the HSC increases to 15~20% ( $HSC_{cor}$ ). As a result, the E-modulus increases significantly to 21 MPa, but at the same time the strain at break decreases to 300%. However, a strain at break of 300% still meets the requirements for many applications. Indeed, the additional "B-U" moieties in the HS do not only help to broaden the application temperature range but also improve the mechanical properties of these LDI-based PEUs.

By introducing a more symmetric and less flexible IIDI, instead of LDI, in the HS, the E-modulus of PEU increases as well. This becomes obvious when comparing PLi and PLi. The E-modulus of PLi is around 3.4 MPa, which is higher than that of PLi. However, it is still much lower than that of a similar HDI-based PEU (E-modulus = 14.9 MPa) [1] which

has a similar composition except for the DI residues. This may be due to the fact that the interaction and the self-organization of the kinky isoidide residues are still less pronounced than for the hexamethylene residue.

#### 4 CONCLUSIONS

A series of fully renewable poly(ester urethane urea)s (PEUs) were synthesized based on a novel, renewable polyester diol poly(1,2-dimethylethylene adipate). When incorporating the renewable L-lysine diisocyanate (LDI) in the PEUs, its combination with the monomeric diamine chain extenders (1,4-diaminobutane bDA or diaminoisoidide iDA) does not lead to readily crystallizable hard segments. As a result, good phase separation is not achieved and the polymers show relatively poor mechanical properties. The materials are soft and exhibit high strain at break (> 2000%) with low E-moduli (around 1 MPa). A urea-containing dimeric diamine di(4-aminobutyl)urea (b<sub>2</sub>DA) was then employed as the chain extender to prepare LDI-based PEUs. It appears that the incorporation of b<sub>2</sub>DA in the PEU indeed increases the flow temperature (from approx. 80°C to approx. 200°C) and the stiffness (the E-modulus increases to above 20 MPa) of the PEUs. The PEU based on isoidide diisocyanate (PIi) exhibits a higher E-modulus (the E-modulus of PIi is 3.4 MPa) than the corresponding LDI-based polymer (the E-modulus of PLi is about 1.0 MPa), but it is still less stiff than the b<sub>2</sub>DA-based PEUs. In conclusion, fully renewable PEUs were prepared and after optimization of the chemical structures, satisfactory properties of these renewable PEUs have been successfully achieved.

#### Acknowledgements

This work forms part of the research program of the Dutch Polymer Institute (DPI project #653). The authors are grateful to Dr. Reinoud J. Gaymans for the productive discussions.

#### References

1. D. Tang, B.A.J. Noorder, R.J. Sablong, and C.E. Koning, Metal-free synthesis of novel biobased dihydroxyl-terminated aliphatic polyesters as building blocks for thermoplastic polyurethanes. *J. Polym. Sci. Part A Polym. Chem.* **49**, 2959 (2011).
2. Y.H. Zhang, A.Q. Wang, and T. Zhang, A new 3D mesoporous carbon replicated from commercial silica as a catalyst support for direct conversion of cellulose into ethylene glycol. *Chem. Commun.* **46**, 862 (2010).
3. I. Meynial-Salles, S. Dorotyn, and P. Soucaille, A new process for the continuous production of succinic acid from glucose at high yield, titer, and productivity. *Biotechnol. Bioeng.* **99**, 129 (2008).
4. Z.G. Qian, X.X. Xia, and S.Y. Lee, Metabolic engineering of *Escherichia coli* for the production of putrescine: a four carbon diamine. *Biotechnol. Bioeng.* **104**, 651 (2009).
5. J. Schneider, K. Niermann, and V.F. Wendisch, Production of the amino acids L-glutamate, L-lysine, L-ornithine and L-arginine from arabinose by recombinant *Corynebacterium glutamicum*. *J. Biotechnol.* **154**, 191 (2011).
6. F. Fenouillot, A. Rousseau, G. Colomines, R. Saint-Loup, and J.P. Pascault, Polymers from renewable 1,4:3,6-dianhydrohexitols (isosorbide, isomannide and isoidide): A review. *Prog. Polym. Sci.* **35**, 578 (2010).
7. H.R. Kricheldorf, "Sugar diols" as building blocks of polycondensates. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **C37**, 599 (1997).
8. S. Thiyagarajan, L. Gootjes, W. Vogelzang, J. Wu, J. van Haveren, and D.S. van Es, Chiral building blocks from biomass: 2,5-diamino-2,5-dideoxy-1,4-3,6-dianhydritol. *Tetrahedron* **67**, 383 (2011).
9. S. Thiyagarajan, L. Gootjes, W. Vogelzang, J. van Haveren, M. Lutz, and D.S. van Es, Renewable rigid diamines: efficient, stereospecific synthesis of high purity isohexide diamines. *ChemSusChem* **4**, 1823 (2011).
10. A. Gandini, The irruption of polymers from renewable resources on the scene of macromolecular science and technology. *Green Chem.* **13**, 1061 (2011).
11. M.S. Lindblad, Y. Liu, A.C. Albertsson, E. Ranucci, and S. Karlsson, Polymers from renewable resources. *Degradable Aliphatic Polyesters* **157**, 139 (2002).
12. J.O B. Asplund, T. Bowden, T. Mathisen, and J. Hilborn, Synthesis of highly elastic biodegradable poly(urethane urea). *Biomacromolecules* **8**, 905 (2007).
13. G. Holden, H.R. Kricheldorf, and R.P. Quirk: *Thermoplastic Elastomers*, Hanser, Munich (2004).
14. G. Odian: *Principles of Polymerization*, Wiley, Hoboken (2004).
15. D. Tang, B.A.J. Noorder, R.J. Sablong, and C.E. Koning, Thermoplastic poly(urethane urea)s from novel, bio-based amorphous polyester diols. *Macromol. Chem. Phys.* **213**, 2541 (2012).
16. G.J.E. Biemond, PhD thesis, University of Twente, Enschede, the Netherlands (2006).
17. G.J.E. Biemond, J. Feijen, and R.J. Gaymans, Segmented block copolymers with monodisperse hard segments: The influence of H-bonding on various properties. *Macromol. Mater. Eng.* **294**, 492 (2009).

