Tailoring the Properties of a Shape-Memory Polyurethane via Nanocomposite Formation and Nucleation

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Abstract: Thermoplastic polyurethanes (PUs) can display shape-memory (SM) characteristics if their microphase-separated structure, consisting of domains formed by hard blocks and soft segments, respectively, is complemented with the ability of the soft segments to partially crystallize, so that the third phase thus formed can serve as the switching element for the shape-memory effect. While property modifications of SMPUs usually require de novo synthesis, we show at the example of a commercially available poly(ester urethane) consisting of crystallizable poly(1,4-butylene adipate) soft/switching segments and hard segments composed of 4,4-methylene diisocyanate and 1,4-butanediol that the thermomechanical properties can also be modified by formulating nanocomposites and/or influencing the crystallization of the soft/switching segments via the addition of a nucleating agent. The incorporation of cellulose nanocrystals (CNCs) by simple melt-mixing allowed increasing the tensile storage modulus from 150 MPa (neat polymer) to 572 MPa (15% w/w CNCs) while the shape fixity at a specific fixing temperature was increased from 47 to 75%. The temperature at which good fixity (>97%) could be rapidly achieved was increased from 10 to 25ºC upon addition of 1% w/w dodecanoic acid, which served to nucleate the poly(1,4-butylene adipate) crystallization.

Keywords: Shape-memory polymer, poly(ester urethane), cellulose nanocrystals, melt-mixing, mechanical reinforcement, nucleation.
**Introduction**

Shape-memory polymers (SMPs) represent an emerging class of materials that can be deformed during application of an external stimulus such as heat, light, a specific chemical or electric or magnetic fields into a temporary shape, which can be fixed upon removal of the stimulus until the renewed exposure to the stimulus causes the return to the original shape.\textsuperscript{1-9} SMPs require the combination of rubber elasticity with a switchable fixing element that can be controlled to allow or thwart deformation. The switching elements can be designed to be responsive to different stimuli, including light, a pH change, or hydration, but the most widely used stimulus for SMPs is heat.\textsuperscript{2, 10-18} SMPs are potentially useful for applications in a wide range of fields such as biomedical devices, aerospace, textiles, energy, electronic engineering and household products.\textsuperscript{4,19-20} One approach for the design of materials with shape-memory effect is the formation of composites of an elastic matrix and micro/nano-sized fillers, whose mechanical properties and/or interactions can be switched in response to an external stimulus.\textsuperscript{21-23} In this case, the SM effect is an emergent property, which is absent in the constituting components. The framework thus permits creating new SM polymers from existing building blocks by readily scalable mixing processes, without the need for the synthesis of new polymers. Shape-memory composites thus have broadened the design and application fields of shape-changing materials\textsuperscript{24-26} and a plethora of different shape-memory composites containing fillers such as fibers, particles or crystals responsive to different stimuli have been reported.\textsuperscript{27-31}

Alternatively, the switching element can be covalently incorporated into a rubbery polymer. This design approach has been exploited with many polymer families, including for example polyurethanes, polystyrene- or epoxy-based polymers.\textsuperscript{32-38} In particular thermoplastic polyurethanes (PUs) are attracting great interest as shape-memory materials, on account of their
rubber elasticity that is imparted by a microphase-separated morphology consisting of hard blocks that serve as physical cross-links and a low-glass-transition phase formed by soft segments. If the latter are able to partially crystallize, the crystalline domains formed can serve as the switching element for the shape-memory effect. The shape-memory properties of such materials can \textit{a priori} be tailored by changing the constituents or varying the composition of the various building blocks.\textsuperscript{14, 33-34} While the \textit{de novo} synthesis is certainly an acceptable framework in academic research, the approach is less attractive when it comes to tailoring the properties of SMPs in a technological setting. The formation of composites, for example by introducing a reinforcing filler, represents an alternative approach to tailor the properties, notably the strength and stiffness, of polymers with intrinsic shape-memory behavior. In this context, several nano-fillers such as carbon nanotubes (CNTs), graphene, and magnetic nanoparticle have been integrated into various PUs and the resulting composites displayed property matrices that significantly broadened the parameter space accessible by the neat PUs.\textsuperscript{39-43} Cellulose nanocrystals (CNCs) represent another filler type that is increasingly used to reinforce polymers, primarily on account of the intriguing mechanical properties,\textsuperscript{44-45} renewable nature,\textsuperscript{46} and demonstrated low toxicity.\textsuperscript{47-50} CNCs have been used either as a switching element\textsuperscript{51-54} or to reinforce polymers with intrinsic shape-memory effect, including a few polyurethanes.\textsuperscript{55-56}

We here report tailoring the properties of a commercially available\textsuperscript{57-60} and widely investigated shape-memory poly(ester urethane)\textsuperscript{61-63} containing crystallizable poly(1,4-butylene adipate) soft/switching segments and hard segments composed of 4,4-methylene-diphenyl diisocyanate (MDI) and 1,4-butanediol. By formulating nanocomposites with CNCs and/or influencing the crystallization of the polyester segments via the addition of a nucleating agent we were able to increase the tensile storage modulus from 150 MPa (neat polymer) to 572 MPa, improve the
shape fixity at a specific fixing temperature from 47 to 75% and increase the fixing temperature from 10 to 25 °C. These property variations may be useful for potential applications in mechanical actuators, automobile parts, electronic parts or sporting equipment, which we speculate would benefit from an increased stiffness while the increased crystallization temperature might be particularly beneficial in biomedical devices, i.e. under conditions where fixation close to physiological temperature is desirable. Importantly, these modifications were achieved by an easily scalable processing approach and with readily available components.

**Experimental Section**

**Materials.** The PU based on crystallizable soft/switching segments of poly(1,4-butylene adipate) (PBA) and hard segments composed of 4,4-methylenediphenyl diisocyanate (MDI) and 1,4-butanol (BD) as chain extender was kindly provided by Covestro Deutschland AG as Desmopan DP 2795 A. Phosphoric acid (ACS reagent, ≥85 wt% in H₂O) was used as received. Dodecanedioic acid was purchased from sigma Aldrich and used without further purification. The isolation of phosphorylated CNCs from MCC was previously reported. The freeze-dried CNCs used here had an average length \( l \) of 290 ± 110 nm, an average diameter \( d \) of 25 ± 5 nm, and the surface charge was 15 mmol/kg.

**Fabrication of PU/CNC Nanocomposites, Nucleated PU, and PU/CNC/Nucleating Agent Nanocomposites.** The neat PU was dried at 70 °C for 3 h in an oven prior to the processing, while the freeze-dried CNCs were used as isolated. PU/CNC nanocomposites containing 5, 10, or 15% w/w of CNCs were prepared by melt mixing the PU and the CNCs using a roller blade mixer (RBM, Brabender® GmbH & Co. KG; mixer type 30EHT). The temperature and speed of the mixer were set to 180 °C and 70 rpm, respectively. The polymer was first introduced to the
RBM and processed until a homogeneous melt had formed (6 min). The CNCs were then added and mixing was continued for another 4 min. The total load of the RBM was kept fixed at 20 g. For example, to prepare the nanocomposite with 15% w/w CNCs, 17 g of the PU and 3 g of CNCs were used. The nanocomposite melt was then removed from the mixer and allowed to cool to room temperature. The compositions thus made were compression-molded between poly(tetrafluoroethylene) sheets in a Carver® press at 180 °C under a pressure of 4 metric tons for 5 min to produce films having a thickness of 200 μm. Reference films of the neat PU were also prepared by the same protocol. A mixture of the PU (19.8g) and 1% w/w dodecanoic acid (0.2 g) was prepared in an analogous manner, using identical processing parameters for the mixing and the compression molding step. Finally, a PU/CNC/dodecanoic acid nanocomposite containing 15% w/w CNCs and 1% w/w dodecanoic acid was prepared in the same manner, by combining 16.8 g PU, 3 g CNCs and 0.2 g dodecanoic acid. As a reference, a solution-cast film of PU/Dodecanoic acid 1% w/w was prepared by dissolving the PU (0.99 g) and Dodecanoic acid (10 mg) in warm THF (40 ml) and allowing the solvent to evaporate at room temperature in a poly(tetrafluoroethylene) Petri dish over a period of three days.

**Dynamic Mechanical Analysis (DMA).** The dynamic mechanical properties of the neat PU and PU/CNC nanocomposite films were characterized using a TA Instrument DMA Q800. The experiments were carried out in tensile mode with a strain amplitude of 15 μm and at a frequency of 1 Hz. Experiments were conducted in the temperature range of -50 to 200 °C, applying a heating rate of 5 °C·min⁻¹. The samples analyzed were prepared by cutting the compression-molded films into strips having a width of 5-6 mm and length of 10 mm. The mechanical data shown in Table 1 and values quoted for $E'$ in the text represent averages of 3–5 independent measurements ± standard deviation.
Differential Scanning Calorimetry (DSC). DSC measurements were performed using a Mettler-Toledo STAR system under N₂ atmosphere. The following sets of different experiments involving different heating and cooling cycles were performed on ~10 mg samples placed in standard DSC pans.

(i) A first set of DSC experiments was performed on the neat PU and the PU/15% w/w CNC nanocomposite. It consisted of three heating and cooling cycles in the temperature range of -50 to 200 °C; heating rates of 10 °C·min⁻¹ (1ˢᵗ, 2ⁿᵈ cycle) and 5 °C·min⁻¹ (3ʳᵈ cycle) and cooling rates of 10 °C·min⁻¹ (1ˢᵗ cycle), 5 °C·min⁻¹ (2ⁿᵈ cycle) and 2 °C·min⁻¹ (3ʳᵈ cycle) were employed to analyze the influence of the heating/cooling rate on the melting/crystallization transition.

(ii) A second set of experiments was also performed on the neat PU and the PU/15% w/w CNC nanocomposite; in this case heating and cooling cycles were carried out in the temperature range from 20 to 100 °C with heating and cooling rates used as in the first experimental set. After the cooling cycles, however, samples were kept isothermal at 20 °C for time intervals of 30 min (1ˢᵗ cycle), 60 min (2ⁿᵈ cycle) and 90 min (3ʳᵈ cycle).

(iii) The last set of experiments was performed on the PU/dodecanoic acid mixture and the PU/CNC/dodecanoic acid nanocomposite. Samples were analyzed in the temperature range from 0 to 100 °C with heating and cooling rates of 10 °C·min⁻¹ without any isothermal time intervals after the cooling cycles.

The melting temperature ($T_m$) was established from the maximum of the melting endotherm while the crystallization temperature ($T_c$) was established from the highest temperature point of cooling exotherm. The degree of crystallinity of the various samples was estimated from the melting enthalpy, using the melting enthalpy of 100% crystalline PBA (61.9 J/g) as reference.⁶⁷
**Shape-Memory Analysis.** The shape-memory behavior of films of the neat PU, the PU/dodecanoic acid mixture, the PU/CNC nanocomposites, and the PU/CNC/dodecanoic acid nanocomposite was analyzed using the same equipment and sample geometry employed for standard DMA experiments (see above). Experiments were conducted in controlled force mode. Cyclic stress-temperature-strain tests were carried out by first heating the sample to 70 °C and maintaining it at this temperature for 5 min. The sample was then uniaxially deformed by applying a force of up to 18 N with a rate of 0.8 N·min⁻¹ and a fixed strain limit of 40%. A strain abort step was utilized to achieve the targeted strain limit. The sample was maintained stretched at 70 °C for 5 min, before it was cooled to 0 (neat PU and PU/CNC nanocomposites), 10 (neat PU and PU/CNC nanocomposites), or 15, 20 or 25 °C (PU/dodecanoic acid mixture and PU/CNC/dodecanoic acid nanocomposite) at a rate of 5 °C·min⁻¹ and maintained at the respective fixing temperature for 5 min (all samples) or 15 min (samples fixed at 20 or 25 °C only). Monitoring the strain, the applied force was unloaded and the sample was maintained in this state for 5 min to establish the temporary shape. The sample was finally heated at a rate of 5 °C·min⁻¹ to 70 °C, and kept at this temperature for 10 min to recover the original shape. Three cycles were conducted for each sample and the fixity (%) and recovery (%) for each cycle was calculated according to Eqs. (1) and (2):

\[
\text{% Fixity} = \frac{\varepsilon_u - \varepsilon_l}{\varepsilon_s - \varepsilon_l} \times 100 \quad (1)
\]

\[
\text{% Recovery} = \frac{\varepsilon_u - \varepsilon_r}{\varepsilon_u - \varepsilon_l} \times 100 \quad (2)
\]

Where, \(\varepsilon_s\) is the strain after stretching, \(\varepsilon_u\) is the strain after unloading, \(\varepsilon_r\) is the recovered strain after heating, and \(\varepsilon_l\) is the initial strain.
**Size Exclusion Chromatography (SEC).** Size exclusion chromatography (SEC) measurements were carried out on an Agilent Technologies 1260 Infinity system equipped with a refractive index (RI) detector. The column system was composed of one guard column and two mixed bed PSS GRAM analytical linear 10 μm (300 mm × 8.0 mm), with a separation range from 100 to 10^6 Da, at 55 °C. DMF (LiBr 0.05M) was employed as solvent/eluent and the measurements were carried out at a flow rate of 0.5 mL/min. Data analyses were carried out on the PSS WinGPC Unchrom software and the mass-average molecular weight ($M_w$) and $M_n$ values were determined by comparison with poly(styrene) standards.

**Results and Discussion**

The shape-memory materials investigated in this study were based on (i) a commercially available poly(ester urethane) containing crystallizable poly(1,4-butylene adipate) (PBA) soft/switching segments and hard segments composed of 4,4-methylene diphenyl diisocyanate (MDI) and 1,4-butanediol (BD) as a chain extender;59-60 (ii) cellulose nanocrystals isolated from commercially available microcrystalline cellulose by ultrasonication in phosphoric acid;56 and/or (iii) dodecanoic acid as nucleating agent (Figure 1). The use of phosphorylated CNCs was motivated by the fact that these particles offer a combination of good dispersibility and high thermal stability.56, 68-69 The TEM micrograph shown in Figure 1c reveals that the CNCs used here are well-individualized and display the characteristic “rice-shape”, with an average length $l$ of 290 ± 110 nm and an average diameter $d$ of 25 ± 5 nm.56 The idea to use an aliphatic acid as nucleating agents was originally based on the finding that the incorporation of certain oleic acid-coated Fe₃O₄ nanoparticles into the PU under investigation appears to cause nucleation, although this effect was not further investigated.40 PU/CNC nanocomposites containing 5, 10, or 15% w/w of CNCs were prepared by melt mixing the PU and the CNCs using a roller blade mixer at 180
°C and 200 μm thin films were prepared by compression-molding at the same temperature (see Experimental Section for details). A mixture of the PU and 1% w/w of the nucleating agent and a PU/CNC/dodecanoic acid nanocomposite containing 15% w/w CNCs and 1% w/w dodecanoic acid were prepared in the same manner.

Figure 1. Chemical structures of (a) 4,4′-methylene diphenyl diisocyanate (MDI), 1,4-butanediol (BD) and poly(1,4-butylene adipate) and (b) phosphorylated cellulose. (c) Transmission electron microscopy image of phosphorylated CNCs (scale bar =1 μm).

We first investigated the mechanical characteristics of the neat PU and the PU/CNC nanocomposites by dynamic mechanical analysis (DMA) in a temperature range of -50 to 200 °C. Note that cooling the materials to sub-zero temperatures may increase the crystallinity of the PBA phase vis-à-vis samples that were merely cooled to ambient after processing (vide infra). Figure 2 shows representative measurements of the storage modulus $E^\prime$ against the temperature. The trace of the neat PU reveals a gradual decrease of $E^\prime$ as the temperature is increased from -50
(relaxations associated with the segmental motion of the PU network) to ca. 45-50 °C, where a sharp reduction related to the melting/relaxation of the crystalline PBA switching segments is observed. Furthermore it reveals a second relaxation associated with the dissociation of the polymer’s hard blocks around 175 °C. **Figure 2** reveals that the introduction of the CNCs shifts the DMA traces upwards, reflecting, as intended, a significant reinforcement of the PU over the entire temperature range. For instance at 25 °C, the storage modulus $E'$ increased from 150 MPa (neat PU) to 254, 308, and 572 MPa upon introduction of 5,10 and 15% w/w CNCs, respectively (**Table 1**). The DMA traces also reveal that the incorporation of the CNCs causes an extension of the rubbery plateau. Importantly, all nanocomposites also show the step-wise reduction in $E'$ associated with the melting of the PU’s PBA switching segments (**Figure 2**). This transition is exploited to create and fix the temporary shape (**vide infra**).

![Figure 2](image-url). Dynamic mechanical analysis (DMA) traces of films of the neat PU and PU/CNC nanocomposites containing 5, 10, or 15% w/w CNCs.
The thermal transitions of selected compositions were further studied by differential scanning calorimetry (DSC) experiments. Experiments were performed in different temperature ranges and with different heating/cooling rates, primarily with the goal to develop more insights about the crystallization and melting behavior of the PBA switching segments, although we note that such studies were in part already conducted for the neat PBA.\textsuperscript{70-74} It is important to point out that the neat PBA\textsuperscript{70-74} and also the PBA segments included in segmented polyurethanes\textsuperscript{61} exhibits polymorphism and a highly complex crystallization behavior. While a detailed discussion of these aspects is beyond the scope of this study, it is noted that the thermodynamically more stable $\alpha$ form and the kinetically preferred $\beta$ form are formed at different temperatures and slightly differ in their melting temperatures. In addition, recrystallization from the $\beta$ to the $\alpha$ form can occur and on account of crystal size variations the $\alpha$ form can give rise to two melting transitions. As a result, melting transitions are usually broad and both melting ($T_m$) and crystallization ($T_c$) temperature depend on the thermal history of a sample and also vary over time due to ageing. In a first set of DSC experiments, the neat PU (Figure 3a, b) and the 15% w/w PU/CNC nanocomposite (Figure 3c, d) were subjected to three heating and cooling cycles. The first heating cycle of the neat PU, recorded at a rate of 10 °C·min\textsuperscript{-1} (Figure 3a) shows a

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Table 1. Mechanical properties of the neat PU and PU/CNC nanocomposites.\textsuperscript{a}

| Composition          | $E'$ (MPa) 25 °C | $E'$ (MPa) 100 °C |
|----------------------|------------------|------------------|
| Neat PU              | 150 ± 50         | 2.2 ± 1.0        |
| PU/5% w/w CNCs       | 245 ± 44         | 6.9 ± 1.0        |
| PU/10% w/w CNCs      | 308 ± 24         | 8.5 ± 1.3        |
| PU/15% w/w CNCs      | 572 ± 31         | 12.0 ± 0.9       |

\textsuperscript{a}All data were collected by dynamic mechanical analyses and represent averages of $N = 3$–4 individual measurements ± standard deviation.
broad melting peak with a maximum temperature $T_m$ of 56 °C, indicative of the presence of mixture of $\alpha$ and $\beta$ polymorphs, recrystallization of the $\beta$ into the $\alpha$ form around 50 °C and melting of the $\alpha$ form above 55 °C.\textsuperscript{73} The first cooling trace (Figure 3b), recorded with a rate of 10 °C·min\textsuperscript{-1}, reveals a crystallization peak with a maximum temperature $T_c$ of 6 °C. The crystallization temperature $T_c$ shifted to higher temperatures when the cooling rate was decreased to 5 °C·min\textsuperscript{-1} (12 °C) and 2 °C·min\textsuperscript{-1} (16 °C), whereas neither a reduction in cooling nor heating rate changed the melting temperature much, although a slight reduction to ~52 °C vis-à-vis the as-prepared sample was observed. The DSC traces of the 15% w/w PU/CNC nanocomposite (Figure 3c, d) are virtually identical to those of the neat PU, suggesting that the introduction of CNCs in PU did neither nucleate nor stifle the crystallization. By contrast, under rapid cooling conditions (10 °C·min\textsuperscript{-1}) $T_c$ of the nanocomposite is reduced to 1 °C, perhaps on account of the viscosity increase imparted by the CNCs. In order to explore to what extent the PBA switching segment can be crystallized under ambient conditions, an additional set of DSC experiments was conducted in the temperature range of 20-100 °C (Figure S1c, S2c). The data show that the melting temperatures of both the neat PU and the 15% w/w PU/CNC nanocomposite are slightly reduced from around 55 to around 50 °C if the samples were never cooled below 20 °C. The data further refute the prospect that the crystallization of the PBA segments in the neat polymer and in the nanocomposite can be reasonably quickly achieved at 20 °C upon slow cooling and annealing the samples at this temperature; even after keeping the samples at 20 °C for 90 min, the crystallization process was incomplete.
Figure 3. DSC traces showing heating (a, c, e) and cooling cycles (b, d, f) of the neat PU (a, b), the 15% w/w PU/CNC nanocomposite (c, d), and the PU and 15% w/w PU/CNC nanocomposite nucleated with 1% w/w dodecanoic acid (e, f). Roman numerals indicate the sequence of heating and cooling cycles conducted with the heating/cooling rates indicated in the panels, whereas numbers indicate melting/crystallization temperatures.
Table 2. Melting ($T_m$) and crystallization ($T_c$) temperatures of the neat PU, a PU/CNC nanocomposite, and the corresponding materials with dodecanoic acid as nucleating agent.\textsuperscript{a}

| Composition                          | $T_m$ °C | $T_c$ °C | Crystallinity |
|-------------------------------------|----------|----------|---------------|
| Neat PU                             | 56       | 6        | 38%           |
| PU/dodecanoic acid (1% w/w)         | 47       | 15       | 45%           |
| PU/CNC (15% w/w)                    | 55       | 1        | 27%           |
| PU/CNC/dodecanoic acid (15% w/w, 1% w/w) | 44       | 9        | 33%           |

\textsuperscript{a}Determined by DSC at heating ($T_m$) and cooling ($T_c$) rates of 10 °C·min\textsuperscript{-1}.

With the goal to nucleate the crystallization of the PBA switching segment in order to achieve rapid fixing at ambient temperature, a small amount (1% w/w) of dodecanoic acid was incorporated into the neat PU and the effect on the crystallization, melting and degree of crystallinity was probed by DSC experiments (Figure 3e,f, Table 2). The data show that $T_c$ increased to 15 °C, which suggests that the switching element can be fixed at a higher temperature than in the neat PU (\textit{vide infra}). The melting temperature (44-47°C) was reduced in comparison to the neat PU, whereas wide-angle X-ray diffraction data reveal similar ratios of $\alpha$ and $\beta$ forms for nucleated and non-nucleated samples (Figure S3). Size exclusion chromatography traces reveal a substantial reduction of the number- and weight-average molecular weights from 110,000 to 20,000 and 229,000 to 66,000 Da, respectively (Figure S4), which suggests that the nucleation process is driven by chain scission and nucleation of the chain ends, as reported previously by others.\textsuperscript{75,76} Indeed, a solution-cast mixture of the PU and 1%w/w dodecanoic acid displays the same thermal behavior as the neat PU (Figure S5). We note that over the course of several months, $T_c$ and $T_m$ of the melt-processed PU/dodecanoic acid mixture increased to 20 °C and 52 °C, respectively, suggesting significant ageing.
Dodecanoic acid (1% w/w) was also incorporated into the 15% w/w PU/CNC nanocomposite. The DSC traces (Figure 3e,f) reveal clearly that nucleation occurs as intended; the melting temperature is reduced to 44 °C, whereas \( T_c \) is increased from 1 °C (nanocomposite without nucleating agent) to 9 °C (nanocomposite with nucleating agent). The fact that \( T_c \) is substantially lower than in the dodecanoic acid containing PU without CNCs (15 °C) is again likely related to the viscosity increase imparted by the CNCs, which leads to a reduced mobility of the PU chains and a lower crystallinity (Table 2). Also in this case, ageing of the sample for a few months caused an increase of \( T_c \) (13°C) and \( T_m \) (52°C).

To investigate the shape-memory behavior, cyclic thermomechanical tests were performed, using a DMA and conducting experiments in force-controlled mode, according to a previously reported protocol. Shape-memory experiments were carried out on thin strips of the neat PU, PU/CNC nanocomposites containing 5, 10, or 15% w/w CNCs, and the corresponding materials with dodecanoic acid as a nucleating agent. Representative experiments are shown in Figures 4, S6-S7 and the key data are compiled in Table 3.

As explained before, fixation of the temporary shape and triggering the shape recovery are related to crystallization of the switchable polyester segments and melting of these crystalline domains, respectively, and the parameters of the shape-memory experiments were chosen to validate the findings of the above-discussed thermal and mechanical data. Each shape-memory cycle consisted of four consecutive steps. First, the samples were heated to 70 °C (i.e., above the \( T_m \) of the PBA segments) and kept at this temperature for 5 min. While the temperature was maintained at 70 °C, the samples were strained until a strain of ~40% was reached by applying a force at a rate of 0.8 N·min\(^{-1}\). Keeping the stress constant, the samples were kept isothermal at 70 °C for 5 min (during this time the strain increased further) before they were cooled to 0, 10,
15, 20 or 25 °C, and kept at the respective temperature for 5 min (and in some cases longer) before the stress was removed and the samples had adopted their temporary shapes. The shape recovery was subsequently triggered by heating the samples to 70 °C and keeping them at this temperature for 10 min. This cycle was repeated at least 3 times. All data sets reveal a significant hysteresis between the first and the subsequent cycles, i.e., partial recovery after the first cycle. This effect is related to irreversible deformation of the PU matrix and has been previously observed in other TPUs.\textsuperscript{9, 51, 56, 61, 77} The shape fixity ratio, $R_f$, and the shape recovery ratio, $R_r$, were therefore established from the data acquired in the 2\textsuperscript{nd} and 3\textsuperscript{rd} shape-memory cycles, using Eqs. 1-2 (See Experimental Section).
Shape fixation – 0 °C, 5 min

(a) [Graph showing strain vs. temperature and stress for shape fixation at 0 °C, 5 min]

Shape fixation – 10 °C, 5 min

(b) [Graph showing strain vs. temperature and stress for shape fixation at 10 °C, 5 min]

Shape fixation – 0 °C, 5 min

(c) [Graph showing strain vs. temperature and stress for shape fixation at 0 °C, 5 min]

Shape fixation – 15 °C, 5 min

(d) [Graph showing strain vs. temperature and stress for shape fixation at 15 °C, 5 min]

Shape fixation – 20 °C, 15 min

(e) [Graph showing strain vs. temperature and stress for shape fixation at 20 °C, 15 min]

Shape fixation – 20 °C, 15 min

(f) [Graph showing strain vs. temperature and stress for shape fixation at 20 °C, 15 min]

Shape fixation – 25 °C, 15 min

(g) [Graph showing strain vs. temperature and stress for shape fixation at 25 °C, 15 min]

Shape fixation – 25 °C, 15 min

(h) [Graph showing strain vs. temperature and stress for shape fixation at 25 °C, 15 min]

Shape fixation – 0 °C, 5 min

(i) [Graph showing strain vs. temperature and stress for shape fixation at 0 °C, 5 min]

Shape fixation – 10 °C, 5 min

(j) [Graph showing strain vs. temperature and stress for shape fixation at 10 °C, 5 min]
**Figure 4.** Shape-memory stress-strain-temperature curves (three consecutive cycles) of the neat PU (a,b), the 15% w/w PU/CNC nanocomposite (c,d), the PU nucleated with 1% w/w dodecanoic acid (e, g, i) and the 15% w/w PU/CNC nanocomposite nucleated with 1% w/w dodecanoic acid (f,h,j). Experiments were conducted with a fixing temperature of 0 °C (a, c), 10 °C (b, d), 15 °C (e, f), 20 °C (g, h) or 25 °C (i, j). All cycles started with programming at 70 °C; after the samples had been kept at this temperature for 5 min the samples were strained until a strain of ~40% was reached by applying a force at a rate of 0.8 N·min⁻¹. Keeping the stress constant, the samples were subsequently cooled to and kept at the respective fixing temperature for 5 min or 15 min (for nucleated materials at 20 or 25 °C) before the stress was removed and the samples had adopted their temporary shapes. The shape recovery was subsequently triggered by heating the samples to 70 °C and keeping them at this temperature for 10 min.

**Table 3.** Shape-memory characteristics of the neat PU, the PU/CNC nanocomposites, and the corresponding materials with nucleating agents fixed at the temperature indicated and released at 70 °C.¹

| Shape fixing temperature (°C) | Shape fixity (%) | Shape recovery (%) |
|------------------------------|------------------|--------------------|
| Neat PU                      | 0                | 98 ± 0.2           |
| Neat PU                      | 5                | 98 ± 0.4           |
| Neat PU                      | 10               | 47 ± 1.3           |
| Neat PU b                    | 10               | 98 ± 0.16          |
| PU/1% w/w Dodecanoic acid    | 15               | 96 ± 0.7           |
| PU/1% w/w Dodecanoic acid b  | 20               | 58 ± 1.2           |
| PU/1% w/w Dodecanoic acid b  | 20               | 98 ± 0.4           |
| PU/1% w/w Dodecanoic acid b  | 25               | 97 ± 0.5           |
| PU/5% w/w CNCs               | 10               | 70 ± 1.0           |
| PU/10% w/w CNCs              | 10               | 70 ± 0.8           |
| PU/15% w/w CNCs              | 10               | 98 ± 0.2           |
| PU/15% w/w CNCs              | 10               | 75 ± 6.2           |
| PU/15% w/w CNCs/1% w/w Dodecanoic acid | 15 | 97 ± 1.0 |
| PU/15% w/w CNCs/1% w/w Dodecanoic acid | 20 | 61 ± 0.3 |

¹
| PU/15% w/w CNCs/1% w/w Dodecanoic acid$^b$ | 20 | 99 ± 0.2 | 97 ± 0.9 |
|-------------------------------------------|----|----------|----------|
| PU/15% w/w CNCs/1% w/w Dodecanoic acid$^b$ | 25 | 55 ± 2.3 | 97 ± 1.5 |

$^a$All data were extracted from the experiments shown in Figure 4 and Figure S6-7 and represent averages of 2nd and 3rd cycles of N=3 individual measurements ± standard error measurements. The fixation time was 5 min. $^b$The fixation time was extended to 15 min.

The shape-memory cycles of the neat PU reveal that the fixity is excellent (98%) if the fixing is carried out at 0 or 5 °C (Figure 4a, Figure S7, Table 3), indicating that at this temperature the PBA crystallization proceeds well, as expected on the basis of the DSC experiments. This is also reflected in the DMA traces, which reveal an increase of strain in the cooling step between 10 and 0 °C, which is diagnostic of the crystallization event. By contrast, a much lower fixity (47%) was achieved when the temporary shape was programmed at 10 °C (Figure 4b); however, the fixity could be increased to 98% when the fixation time at 10 °C was increased to 15 min (Figure S7). Notwithstanding the hysteresis observed in the first cycle, excellent recovery (97%) was observed for all fixing conditions, indicating that the PU hard blocks serve as highly robust cross-links. The shape-memory cycles of the 15% PU/CNC nanocomposite (Figure 4c,d), and also those of the nanocomposites with lower CNC content (Figure S6) mirror to a large extent the ones for the neat PU, although the strain required to achieve a comparable stress is higher, on account of the higher modulus. In addition, the fixity of samples programmed at 10 °C is increased from 47 to 70-75% vis-à-vis the neat PU, which is likely due to reinforcement of the CNCs and not nucleation, as shown in the DSC experiments discussed above. As in the case of the neat PU, near perfect fixity (98%) is observed for samples programmed at 0 °C. Gratifyingly, the introduction of the CNCs does not change the recovery properties, indicating that the CNCs, at least at the recovery temperature, do not form a stabilizing network.
As suggested by the DSC experiments, samples comprising dodecanoic acid as a nucleating agent display a markedly higher crystallization temperature than the neat PU or the PU/CNC nanocomposites without dodecanoic acid, suggesting that shape fixing could be achieved at a higher temperature. Thus, we investigated the shape-memory characteristics of the PU and the 15% w/w PU/CNC nanocomposite with 1% w/w dodecanoic acid, selecting fixing temperatures of 15, 20, and 25 °C (Figure 4e-j), as the crystallization sets in at ~20 °C in case of the nucleated PU and ~15 °C in case of the nucleated PU/15% w/w CNC nanocomposite (Figure 3). Gratifyingly, the fixity and recovery values are excellent (97% or higher) if programming is either carried out either at 15 °C or even at 20 °C if the fixing time is extended to 15 min (Table 3). The PU nucleated with dodecanoic acid also displayed an excellent fixity (97%), when the shape fixing temperature was increased to 25 °C and the fixing time was kept at 15 min, while the 15% w/w PU/CNC nanocomposite containing 1% dodecanoic acid showed limited fixity (55%) under these conditions (Table 3). Thus, the data confirm clearly that the fixing temperature can be pushed upwards by 15 degrees by way of nucleation. Importantly, this seemingly small difference has transformed the material such that it is possible to achieve excellent shape fixing at room temperature in timeframes that are useful for consumer applications.

Conclusions

In summary, we have demonstrated that the thermomechanical properties of a commercially available shape-memory poly(ester urethane) with crystallizable soft/switching segments can be modified by formulating nanocomposites and/or influencing the crystallization of the soft/switching segments via the addition of a nucleating agent. The incorporation of cellulose nanocrystals (CNCs) is feasible by simple melt-mixing and allows increasing the tensile storage modulus virtually at will from 150 MPa (neat polymer) to up to 572 MPa. Equally important is
the fact that the temperature at which good fixity can be rapidly achieved could be increased from 10°C to room temperature upon addition of a nucleating agent, which appears to be very useful from a technological point of view.

**Supporting Information**

Additional DSC data for neat PU and PU/15% w/w CNCs with slower cooling rates over temperature range of 20-100 °C, DSC data for PU nucleated with dodecanoic acid, WAXS spectra of dodecanoic acid nucleated PU and 15% w/w PU/CNC nanocomposite, shape-memory graphs of PU with 5% or 10% w/w CNCs, PU mixture with 1% w/w dodecanoic acid and 15% w/w PU/CNC nanocomposite with 1% w/w dodecanoic acid.

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