Reversible transition between anisotropic and isotropic thermal conductivity in elastic polyurethane foams

Mokit Chau[†], Bernd Kopera[†], Vanessa R. Machado, Sepehr Mastour Tehrani, Mitchell A. Winnik, Eugenia Kumacheva^{*}, and Markus Retsch^{*}

Synthesis and characterization of polyurethane (PU)

Materials: Isophoronediisocyante (IDPI), dimethylolpropionic acid (DMPA), triblock copolymer of polycaprolactone and polytetrahydrofuran (PCL-b-PTHF-b-PCL) ($M_w = 1850$ g/mol) with O-H end-groups, carbon nanofibers (CNFs), and *N*-(3-Dimethylaminopropyl)-*N*'ethylcarbodiimide hydrochloride (EDC) were purchased from Sigma Aldrich. Acetone was purchased from Caledon Laboratories Ltd. Deionized water was prepared using a Milli-Q purification system. Cellulose nanocrystals (CNCs) were purchased from Forest Products Laboratory (FPL)-University of Maine. Conductive-grade carbon black (CB), VXC 72, was generously donated by Cabot.

Synthesis of water-dispersible polyurethane (PU): PCL-b-PTHF-b-PCL (45.5 g) and DMPA (1.8 g) were added to a 1 L jacketed-three-necked round-bottom flask, which was then heated to 60 °C overnight under vacuum. The round-bottom flask was fitted with a condenser, nitrogen inlet, and nitrogen outlet. The content of the round-bottom flask was stirred with an overhead stirrer at 400 rpm throughout the reaction. The flask was heated to 85 °C. To form the prepolymer, 11.9 g of IPDI was added. The reaction was monitored using an attenuate total reflectance-Fourier transform infrared (ATR-FTIR) spectrometer (Vertex 70, Bruker Corp.) with a single reflection diamond ATR crystal (MIRacle, Pike Technologies). When the intensity of the isocyanate peak at 2260 cm⁻¹ ceased decreasing, the temperature was lowered to 60 °C, 200 mL of acetone was added, and the prepolymer was chain extended using 0.8 g of ethylene diamine.

Scheme S1. Synthesis of water-dispersible PU, in which x=5, y=12. The M_n and polydispersity index of the polymer are 59,000 g/mol and 1.8, respectively.



Infrared (IR) spectroscopy measurements of the PCL-*b*-PTHF-*b*-PCL oligomer and PU polymer was performed on an ATR-FTIR spectrometer (Vertex 70, Bruker Corp) with a single reflection diamond ATR crystal (MIRacle, Pike Technologies). For the PU spectrum, a drop of the aqueous PU dispersion was placed on the ATR crystal and left to dry before the measurement was taken.



Figure S1. IR spectra of the PCL-*b*-PTHF-*b*-PCL oligomer and the PU polymer.

IR spectra of the resulting polymer and PCL-*b*-PTHF-*b*-PCL oligomer are shown in **Figure S1**. The peak at 1731 cm⁻¹, observed in both the PCL-*b*-PTHF-*b*-PCL oligomer and PU spectra, was attributed to the ester C=O stretching vibrations from the polycaprolactone component. In the IR spectrum of the PU polymer, a shoulder at 1650 cm⁻¹ was related to the H-bonded C=O stretching vibrations of the polycaprolactone esters. The IR spectrum of the PCL-*b*-PTHF-*b*-PCL oligomer showed a broad peak at 3350-3600 cm⁻¹, attributable to the OH stretching vibration of the alcohol end groups. This peak was missing from the PU spectrum, which implied that the OH end groups had reacted during the reaction. A peak in the PU spectrum at 3200-2400 cm⁻¹, not present in the spectrum of the oligomer diol, was attributed to the N-H stretching vibration from urethane and urea groups. In addition, a peak at 1526 cm⁻¹ in the PU spectrum was attributed to the C=O stretching vibration of the addition of the IR spectra suggested the successful formation of the desired PU product.

Gel permeation chromatography (GPC) characterization of the PU polymer was conducted at 85 °C (Perkin Elmer Oven Column Selector) using a 1.0 g/L solution of lithium chloride in *N*-methylpyrrolidone (NMP) as eluent, at a flow rate of 1.0 mL/min through two Agilent PLgel 5µm MIXED-C columns equipped with a Perkin Elmer Refractive Index Detector. Poly(methyl methacrylate) (PMMA) standards were used for calibration. The polyurethane (PU) was dissolved at 2 mg/mL in the GPC eluent (**Figure S2**).



Figure S2. GPC trace of the PU polymer.

The nominal number average molecular weight, M_n , was found to be 59,000 g/mol with a polydispersity index of 1.8, based on the PMMA calibration.

Dispersal of PU in water and characterization of the PU dispersion

Dispersal of PU in water: The PU was dispersed by stirring the polymer in an acetone/triethylamine mixture (1.2 equiv. TEA per 1 equiv. DMPA) at 700 rpm, while adding 140 mL of water drop-wise. The acetone was subsequently removed by rotatory evaporation under reduced pressure. The concentration of the dispersion was found to be 22.4 wt% by gravimetric analysis.

Cryogenic transmission electron microscopy (cryo-TEM): A drop of dilute PU dispersion in water was placed on a copper grid coated with a lacey carbon film. The water was then removed with a filter paper. Immediately after, the grid was instantly shock-frozen by plunging it rapidly into liquid ethane. The sample was cooled to approximately 90 K by liquid nitrogen in a temperature-controlled freezing unit (Zeiss Cryobox). The frozen specimen was inserted into a cryogenic transfer holder (CT3500, Gatan) and transferred to a Zeiss EM922 Omega energy-filtered TEM instrument. The sample was imaged with an acceleration voltage of 200 kV and temperatures of ~90 K. The particle size was determined using the ImageJ software.



Figure S3. Cryo TEM images of the PU dispersion (scale bar: 100 nm).

Electrokinetic potential characterization of PU particles: The electrokinetic potential of the PU particles in the dispersion, diluted to 0.1 wt% using deionized water, was determined using a Malvern Zetasizer Nano ZS instrument.

Freeze-cast setup

The setup for freeze-casting samples at -20 °C is shown in **Figure S4**. The setup consists of an aluminum rod (2 inches in diameter and 12 inches tall, McMaster-Carr 8974K552), topped with six circular polyimide round heaters (Omega Product Number KHR-2/10) with each heater spaced by copper plates (Figure S5). Above the heaters was a copper cylinder (2 inches in diameter and 1 inch tall, McMaster-Carr 9103K2). The assembly was contained in a stainless steel container, which was filled with liquid nitrogen. The temperature of the heaters was controlled using a proportional-integral-derivative controller connected to a thermocouple embedded in the copper cylinder.



Figure S4. Setup for freeze-casting samples at -20 °C.

Two types of molds were used for freeze-casting. When freeze-casting samples for imaging and mechanical testing, smaller, polycarbonate cuboidal tubes (outer width and length of 1/2" and 1/2", and wall thickness of 1/16", McMaster-Carr) were used. When freeze-casting samples for thermal measurements, larger, chemical-resistant PVC cuboidal tubes (outer width = 3/4", length = 3/4" and wall thickness = 0.060", McMaster-Carr) were used. In either case, the molds were closed at one end with a 0.9 mm-thick copper bottom lid.

Microstructural dimensions of PU foams

The thicknesses of the lamellae and inter-lamellar distances of the PU foams used in this work are shown in **Table S1**. The lamellar thicknesses were $\sim 5 - 10 \ \mu\text{m}$ and were statistically similar for all samples. Their inter-lamellar distances were on the order of $\sim 10 - 30 \ \mu\text{m}$. The broad inter-lamellar distance distribution may have been due to the high viscosity of the 20 wt% PU dispersion, which may have impeded the regular ice growth.

Table S1. Thicknesses of the lamellae, inter-lamellar distances, and c_p (at 25 °C) for various PU foams.

Sample name	Lamellae thickness* (µm)	Inter- lamellar distance* (µm)	Density (gcm ⁻³)	κ _∥ /κ⊥ vacuum	κ _{ll} /κ _⊥ air	κ _∥ /κ⊥ helium	$(J g^{-1} K^{-1})$
PU _{pure}	7 ± 4	12 ± 9	0.288 ± 0.006	5.1	2.0	1.2	1.87
PU _{CNC}	8 ± 3	21 ± 18	0.281 ± 0.009	4.3	1.8	1.1	1.85
PU _{CNC-CB}	8 ± 3	18 ± 12	0.258 ± 0.028	2.2	1.4	1.0	1.94
PU _{CNC-CNF}	6 ± 2	17 ± 11	0.217 ± 0.003	2.7	2.1	1.6	1.68
*D-41.	CEM	00	- 4 -				

*Determined from SEM using 100 measurements

Low-magnification SEM images of PU foams

Low-magnification SEM images of the cross-sections and side-views of various PU foams are shown in **Figure S5**.



Figure S5. Low-magnification SEM images of various PU foams cut in the plane normal to the (a—d) parallel and (e—h) perpendicular direction of ice-growth. Scale bars are 400 μ m. The red lines emphasize the regular spacing of short, rail-like protrusions of PU_{pure} caused by dendritic ice. The red arrows mark the strut-like bridging features in PU_{CNC-CB} and PU_{CNC-CNF}.

Differential scanning calorimetry measurements of PU foams

Heat capacity of the PU foams was determined by differential scanning calorimetry (DSC) on a Mettler Toledo DSC 2 according to ASTM E1269 standard testing method. The sample masses ranged between 10 and 15 mg. The measurements were performed under a nitrogen flow of 50 mL min⁻¹ at a heating rate of 20 K min⁻¹. Two heating-cooling cycles between 0 °C and 150 °C were performed for each sample. The second heating cycles were used for the calculation of the specific heat capacity (c_p) at constant pressure. The c_p 's are reported in Table S1.

DSC measurements for microstructure determination of the PU foams were performed at a heating and cooling rate of 5 K min⁻¹ before and after annealing at 90°C for 8 h (**Figure S6**). In order to assess the thermal transitions of the PU foams, the first heating cycles of each sample are shown.



Figure S6. DSC curves measured at a heating rate of 5 K min⁻¹ for a) PU_{pure} , b) PU_{CNC} , c) PU_{CNC-CB} , and d) $PU_{CNC-CNF}$ before (red curves) and after (blue curves) annealing at 90 °C for 8 h.

All DSC traces featured a monotonic increase in heat flow with increasing temperature, which was attributed to the increase in specific heat capacity, c_p . No melting peaks or glass transition temperatures can be inferred. The differences in absolute heat flow between annealed and non-annealed samples were attributed to a lack of contact between the polymer sample and the DSC aluminum pan during the first heating cycle. For all annealed samples, a small and very broad endothermic contribution between 60 to 90 °C could be caused by the breakage of hydrogen bonds between the hard segments of PU. These hydrogen bonds may have formed during the thermal annealing step^[1]. Nevertheless, such hydrogen-bonded regions were very broadly distributed and constituted only a small fraction of the overall sample. Overall, these DSC measurements indicated an amorphous polymer structure^[2, 3].

X-ray diffraction measurements for PU foams, CNCs, and CNFs

X-ray diffraction (XRD) measurements were performed on a X'Pert MPD Pro Powder Diffractometer from PANalytical in reflection geometry with Cu-K α radiation filtered with a nickel filter. The scattering beam stop was on the primary and secondary side 1/8 °. The diffraction angle range was 2 to 60 ° (2 θ). The X-ray diffractograms for PU foams, CNCs, CNFs are shown in **Figure S7**. X-ray diffractograms for all foams showed only a broad peak with a maximum at 2 $\theta \approx 19$ °, which can be attributed to the amorphous halo of noncrystalline polymer materials^[2]. No sharp peaks were associated with a potential crystallization between the soft-segment or hard-segment blocks of the PU polymer^[4, 5]. The shallow and broad diffraction peak at ~45 ° could be attributed to the presence of amorphous hard segment domains containing hydrogen bonded polyurea segments^[6].

No diffraction peaks from the CNCs were observed in the X-ray diffractograms of the composite foams, likely because the concentration of CNCs (2.5 wt%) was too low. In addition, the crystalline CNC components did not induce the formation of ordered domains in the PU matrix^[6]. The addition of 5 wt% CB did not appear to affect the XRD pattern of PU_{CNC-CB} when compared to that of PU_{CNC}. Though CB may contain varying amounts of graphitic domains depending on the CB source^[7], XRD peaks were not observed for PU_{CNC-CB} possibly because the concentration of CB in the foam was not sufficient. Carbon nanofibers are cylindrical nanostructures composed of graphene layers arranged in stacked cones^[8]. The X-ray diffractogram of CNFs have been reported to possess a sharp Bragg peak at 27 °, which corresponded to the $d_{002} \sim 3.28$ Å of graphene layers in the CNFs^[9]. Our X-ray diffractogram of PU_{CNC-CNF} also showed a sharp Bragg diffraction peak at 27 °, which likely arose from the CNFs^[10]. Overall, the XRD measurements, agreed with the conclusions from DSC measurements, in that the PU had an amorphous structure.



Figure S7. X-ray diffractograms of PU_{pure}, PU_{CNC}, PU_{CNC-CB}, PU_{CNC-CNF}, CNCs, and CNFs.

Preparation and characterization of CNCs

The concentration of the CNC suspension was 11.8 wt% as received from FPL University of Maine. The CNC suspension was diluted to 2.5 wt% with deionized water and then dialyzed against deionized water using regenerated cellulose membrane with a 12 kDa molecular weight cut-off (Sigma Aldrich). The volume ratio of the suspension to dialysate was 1:100 per volume change. The water was changed a total of 10 times at 1 h, 2 h, 6 h, and subsequently at 12 h intervals. After dialysis, the CNC suspension was filtered using No. 41 and 42 Whatman filter papers and finally using 0.45 μ m syringe filters (Starstedt Filtropur, PES-membrane). The CNC suspensions were re-concentrated by centrifugation for 10 h at 14 000 x *g* (Thermo Scientific, Heraeus Multifuge X1R Centrifuge) and the supernatant was discarded. The final concentration of the sample was 8.3 wt%, as determined by gravimetric analysis.

The size of the CNCs was characterized by transmission electron microscopy (TEM) (**Figure S8**). A drop of CNC suspension, diluted to 0.1 wt% with deionized water, was dried on a carbon-coated grid (Ted Pella Inc.). A 2 wt% aqueous uranyl acetate solution at pH = 4.2 (adjusted by HCl) was used as a negative stain. The CNC was imaged using a Hitachi H-7000 Transmission Electron Microscope. The dimensions of the CNCs were determined using ImageJ software.



Figure S8. TEM image of the purified CNC (scale bar: 250 nm)

For the dialyzed CNC suspensions, inductively-coupled plasma atomic emission spectroscopy (ICP-AES) were performed on a Optima 7300 ICP-OES spectrometer, Perkin Elmer. The CNCs were found to consist of 1.86 ± 0.02 wt% Na and 2.67 ± 0.06 wt% S per dry weight of CNC.

Electro kinetic potential measurements for the CNC suspensions (diluted to 0.5 wt% with deionized water) were performed using a Malvern Zetasizer Nano ZS instrument.

Characterization of carbon black (CB) and carbon nanofibers (CNF)

X-ray photoelectron spectroscopy (XPS) spectra of CB and CNF were obtained on a ThermoFisher Scientific K-Alpha XPS system (ThermoFisher Scientific, E. Grinstead, UK). The samples were attached to the sample plate using conductive, double-sided tape. A monochromatic Al K α X-ray was used with a nominal spot size of 400 μ m. Following the collection of survey spectra (pass energy (PE) - 200 eV), high energy resolution spectra (PE – 25 eV) were obtained for C1s and O1s peaks. Relative atomic percentages were obtained from the C 1s and O 1s peak areas using the supplied sensitivity factors (modified Scofield – 1.000 and 2.881 respectively). Charge compensation was applied using the combined e-/Ar+ floodgun. The energy scale was not adjusted. All data acquisition and work-up were performed with the supplied software (Advantage v5.949 and v5.926 respectively).

To determine the amount and type of carbon and oxygen on the surface of each graphitic material, the C1s and O1s spectra for CB and CNFs are shown in **Figure S9a**—d. For the O1s spectra of CB, the high binding energy of the O1s peaks suggested that the O1s spectra were affected by differential charging. However, the peaks in the C1s spectra did not appear to be affected by differential charging, which implied that O1s contained contributions from oxygens, which were not bound to carbon, potentially from adsorbed moisture. Therefore, we did not further interpret the peaks from the O1s spectra. The C1s spectra for CB and CNFs were fitted and the resulting peaks and assignments are shown in **Table S2 and S3**, respectively.



Figure S9. High resolution XPS spectra of the C1s peak for a) CB and b) CNF. High resolution XPS spectra of the O1s peak for c) CB and d) CNFs.

Table S2. Peak fits and assignments from the C1s spectra of CB.

Peak label	Peak BE	Atomic %	Assignment
Cls A	284.43	58	Carbon sp ²
C1s B	285.31	24	Carbon sp ³ /C-O
C1s C	287.12	5	Possibly satellite structure
C1s D	289.26	3	π to π^* transition
C1s E	290.19	10	π to π^* transition

Table S3. Peak fits and assignments from the C1s spectra of CNF.

Peak label	Peak BE	Atomic %	Assignment
C1s A	284.55	83	Carbon sp ²
C1s B	285.35	3	C-C sp ³
C1s C	286.43	3	C-0
C1s D	291.28	11	π to π^* transition/loss structure

The CB had O1s peaks with binding energies (BEs) between 522.6 to 537.9 eV and contributed to 6 % of the atomic profile. The remaining 94 % was attributed to the C1s peaks

between BE 284.5 to 291.27 eV. Carbon nanofibers had fewer oxygen containing functionalities with an atomic profile of 99 % from C1s and 1 % from O1s. It is important to note that these atomic percentages are approximations and the O1s peak may also contain contribution from moisture.

Dispersion of graphitic components using CNCs

To assess the ability of CNCs to disperse CB and CNFs, the graphitic materials in water with and without CNCs were compared. Carbon black or CNFs were weighed in a vial to which a 4 wt% CNC suspension or deionized water was added. The suspension was vortexed for 30 s and then sonicated for 30 mins. Next, the suspension was vortexed again time for 30 s and then sonicated for 30 mins. Then, water was added such that the final concentration of graphitic material was 5 wt% and the final concentration of CNC, if present, was 2.5 wt%. The dispersions were vortexed again for 30 s and photographs of the vial were taken. These suspension were diluted by a factor of 1000 with deionized water. The samples were subsequently deposited on carbon-coated copper TEM grids (Ted Pella Inc.) and imaged using TEM (Quanta FEI 250 Electron Microscope).







Figure S10. a—d) Photographs and e—h) TEM images of CB and CNF with and without CNCs. Scale bars for the TEM images are 500nm.

The photographs in **Figure S10a**—d show that the CB and CNFs in water settled to the bottom of the vial, when no CNCs was added, while the presence of CNCs facilitated the dispersal of CB and CNFs into a homogenous and stable dispersion. The TEM images (Figure S10e) of the corresponding samples show that CB aggregated into clusters without the

addition of CNCs. The TEM images of CB dispersions containing CNCs (Figure S10f) shows the CB particles in clusters (~ 200 nm) surrounded by CNCs, which likely acted as stabilizers via their hydrophilic and hydrophobic facets. These clusters are consistent with the literature which describes CB existing as the clusters between 10—500 nm the indivisible units of quasi-spherical particles that are fused together[11]. It has been demonstrated that CNCs have hydrophobic facets to which hydrophobic molecules are able to bind[12, 13, 14]. Similarly, the TEM images (Figure S10e and f) of the CNFs without CNCs showed that the CNFs were highly entangled, while CNFs with CNCs were more evenly distributed.

Structural characterization of composite PU foams



Figure S11. Comparative structural characterization of pure PU and composite PU foams. a) – d) Photographs of the foam monoliths, the direction of ice growth points up (scale bar: 2.5 mm). e) –h) Corresponding top view SEM images showing the orientation of the lamellae parallel to the ice-growth direction (scale bar: 50 μ m). i) – l) Corresponding side-view SEM images showing the orientation of the lamellae perpendicular to the ice-growth direction (scale bar: 50 μ m).

Microstructural features in PU_{CNC-CNF} foams

The PUCNC-CNF foams exhibited more structural variability compared to the other PU foams. **Figure S12** shows SEM images of PUCNC-CNF with various microstructural features. Most of the CNFs were embedded inside the PU matrix of the lamellae, while some inter-lamellar CNF bridges and strut-like PU bridges were also present (Figure S12a). In several regions, a high concentration of CNFs resulted in a closure of the pores along the ice-growth direction (Figure S12b). Regions of high CNF content (Figure S12c) and bundles of pure CNFs (Figure S12d) also bridged between the lamellae. These CNFs may have phase-separated during the freeze-cast process into the pores of the foams.



Figure S12. SEM images of the same $PU_{CNC-CNF}$ foam show various structural features including a) CNFs embedded within the lamellae, inter-lamellar CNFs, strut-like PU bridges, b) blocked pores, c) pores bridged by a high concentration of CNFs, and d) isolated bundle of CNFs.

Transition from the free gas regime to the Knudsen regime

The mean free path of a gas is given by

$$MFP = \frac{\mu}{P} \cdot \sqrt{\frac{\pi \cdot k_B \cdot T}{2 \cdot m}}$$

For Helium:

Symbol	Description	Value / Unit
μ	Dynamic viscosity of Helium	$19 \cdot 10^{-6} Pa \cdot s$
Р	Gas pressure	N/m^2
k _b	Boltzmann's constant	$1.38 \cdot 10^{-23} J/_{K}$
Т	Thermodynamic temperature	283 K
m	Mass of a Helium atom	$6.64 \cdot 10^{-27} kg$



Figure S13. Mean free path of pure helium as a function of pressure. The orange regime indicates the inter-lamellae distance in our freeze-cast foams. Above the orange regime, the mean free path in the pores is bounded by the inter-lamellae distance.

Switching between anisotropic and isotropic thermal transport modes in PU foams

Figure S14a—d shows κ_{para} and κ_{perp} for various PU foams when the surrounding atmosphere was cycled between helium (1000 mbar) and vacuum (< 1 mbar). The PU_{pure}, PU_{CNC}, and PU_{CNC-CB} were switched between anisotropic and isotropic states of heat conduction by changing the pressure. For PU_{CNC-CNF}, the mismatch in κ between the solid and helium (at 1000 mbar) led to the retention of the thermal anisotropy regardless of pressure.



Figure S14. Thermal switching for various PU foams between helium (1000 mbar) and vacuum (< 1 mbar) atmosphere.

Determination of Young's modulus of PU foams



Figure S15. Compression testing of PU foams along the parallel (blue) and perpendicular (red) axis. a) – d) Compression testing was performed up to a compressive strain of 50 %. The Young's modulus was obtained via a linear fit to the initial loading regime (< 5 % strain).

The stress increased linearly for a strain < 10 %, which is attributable to the bending of the lamellae oriented parallel to the loading direction. Increasing the strain further led to a plateau, where the stress was largely independent of strain. This plateau was associated with the collapse of the pores by elastic buckling of the lamellae. Further increase in strain beyond the plateau region yielded a steep increase in stress as a result of densification, in which the lamellae were forced into contact and further buckling was not possible.

Compression-decompression cycles on PU foams

The foams were pre-compressed to 20 % of the original dimension. Samples were then subjected to 20 compression-decompression cycles up to 20 % compressive strain. The compression rate was 3 mm/min with 2 min between compressions for sample relaxation.

Stress-strain curves are shown in **Figure S16** for twenty compression-decompression cycles on various PU foams with compressive strain up to 20 %. The shift in the compression curves towards higher strains with increasing cycles, particularly with the first several cycles, was likely a result of compression set.



Figure S16. Stress-strain curves from the compression-decompression cycles on PU_{pure} (a, e), PU_{CNC} (b, f), PU_{CNC-CB} (c, g), and $PU_{CNC-CNF}$ (d, h). Note that the scales of the compressive stress for the perpendicular cases (right) are significantly lower than those in the parallel plots (left).

References

- [1] T. K. Chen, T. S. Shieh, J. Y. Chui, *Macromolecules* 1998, 31, 1312.
- [2] Y. Yanagihara, N. Osaka, S. Murayama, H. Saito, *Polymer* 2013, 54, 2183.
- [3] R. W. Seymour, S. L. Cooper, *Journal of Polymer Science Part B: Polymer Letters* 1971, 9, 689.
- [4] B. Bogdanov, V. Toncheva, E. Schacht, L. Finelli, B. Sarti, M. Scandola, *Polymer* 1999, 40, 3171.
- [5] K. K. Gupta, A. Kundan, P. K. Mishra, P. Srivastava, S. Mohanty, N. K. Singh, A. Mishra, P. Maiti, *Phys. Chem. Chem. Phys.* **2012**, *14*, 12844.
- [6] H. Xia, M. Song, J. Mater. Chem. 2006, 16, 1843.
- [7] T. Ungár, J. Gubicza, G. Ribárik, C. Pantea, T. W. Zerda, Carbon 2002, 40, 929.
- [8] R. L. Poveda, N. Gupta, *Carbon Nanofiber Reinforced Polymer Composites*, Springer International Publishing, **2015**.
- [9] D. Ponnamma, S. Thomas, *Non-Linear Viscoelasticity of Rubber Composites and Nanocomposites*, *Vol. 264*, Springer International Publishing, **2014**.
- [10] M. F. Sonnenschein, *Polyurethanes: Science, Technology, Markets, and Trends*, Wiley, **2014**.
- [11] P. J. F. Harris, Crit. Rev. Solid State Mater. Sci. 2005, 30, 235.
- [12] J. Lehtio, J. Sugiyama, M. Gustavsson, L. Fransson, M. Linder, T. T. Teeri, Proc Natl Acad Sci U S A 2003, 100, 484.
- [13] I. Kalashnikova, H. Bizot, B. Cathala, I. Capron, Biomacromolecules 2012, 13, 267.
- [14] A. G. Cunha, C. S. Freire, A. J. Silvestre, C. Pascoal Neto, A. Gandini, E. Orblin, P. Fardim, *Biomacromolecules* **2007**, *8*, 1347.