Polymer Nanocomposites with Cellulose Nanocrystals Made by Co-precipitation

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ABSTRACT: A premixing method to produce polymer nanocomposites with cellulose nanocrystals (CNCs) is reported. This method involves the dissolution and dispersion of a polymer and CNCs in an organic solvent, co-precipitation into water, and drying of the resulting particles, and subsequent melt processing. The key aspect of the method is that it allows the kinetic trapping of well-dispersed CNCs in the polymer. Although the nanocomposite must be dried before subsequent melt-processing, the organic solvent can be removed by extraction in water and recycled, leaving only residual water in the composite, which is easily eliminated. This process presents numerous advantages compared to the time-consuming solvent casting process, which often suffers from incomplete organic solvent evaporation. As a testbed, polyurethane (PU) composites with up to 30% of CNCs were prepared. These materials were either melt-processed as produced or used as a masterbatch, i.e., they were diluted via melt-mixing with neat polymer toward nanocomposites with lower filler content. All nanocomposites prepared using this approach had a homogeneous appearance. They displayed similar mechanical properties as the

corresponding reference materials made by solvent casting, and significantly better properties than materials prepared by direct melt mixing.

Keywords: cellulose nanocrystals, CNCs, nanocomposite, precipitation, procesing.

INTRODUCTION

The physical properties of polymers, such as mechanical, optical, and barrier characteristics, can be manipulated by the introduction of suitable filler materials. Various types of fillers are used to this end, for example metal oxides,[1] calcium carbonate[2], glass fibers,[3] carbon black[4] or graphene.[5] As a result of their low density, high mechanical strength, stiffness and aspect ratio, cellulose nanocrystals (CNCs) have emerged as an attractive reinforcing filler with the added benefits of low environmental impact and origin from renewable resources, thus contributing toward reducing global dependence on petrochemicals.[6-9] CNCs can be obtained by extraction from a wide variety of sources including wood,[10] cotton,[11] tunicates,[12] banana,[13] or bacterial sources,[7] among others. Both CNCs and cellulose nanofibers, obtained by mechanical treatment of macroscopic cellulose fibers, are already commercially available in large scale quantities, and therefore already industrially viable alternatives to traditional fillers, such as glass, stainless steel and other inorganic fibers.[14] A number of review articles summarize the outstanding properties and applications of CNCs.[8,9,15-21]

After Chanzy's group demonstrated the reinforcement potential of CNCs within synthetic polymer lattices via solvent casting from aqueous dispersions,[12] CNCs have been shown to enhance the mechanical properties of many other polar polymers such as poly(vinyl alcohol),[14] poly(vinyl acetate),[22] and poly(ethylene oxide).[23] Fabrication of nanocomposites with hydrophobic polymer matrices, such as

polyethylene, natural rubber or polypropylene remains, however, challenging, since CNC surfaces are hydrophilic and tend to form inter-CNC hydrogen bonds, which may result in aggregation in hydrophobic environments and thus a reduction of their reinforcement potential.[24] Various pathways of surface modification of CNCs have been shown to increase compatibility with hydrophobic polymer matrices, such as physical adsorption of surfactants,[25-27] attachment of non-polar molecules,[28-30] or covalent polymer grafting.[31,32] Nevertheless, surface modification increases the number of processing steps and often affords composites whose mechanical properties are lower than anticipated, possibly due to differences in filler-filler interactions, percolation threshold, and mechanical properties of the filler following surface modification.[33]

Various processing schemes have been used to reinforce both polar and non-polar polymer matrices with CNCs, such as direct melt-mixing,[34,35] solvent casting from a common solvent,[36,37] or the template approach.[38,39] The latter approach permits one to kinetically trap a percolating CNC scaffold by solvent-exchange from an aqueous CNC dispersion to an organic medium and impregnating the resulting organogel with a solution of a polymer of choice, which typically results in nanocomposites with exceptional mechanical properties in comparison to the other processing approaches. Solvent casting, for example from water, *N,N*-dimethylformamide (DMF), or dimethylsulfoxide (DMSO), is the laboratory method of choice to create nanocomposites in which the amount of CNCs necessary to achieve the desired mechanical properties is minimized; however, this process is not readily scalable for industrial exploitation and cannot be used to create 3-dimensional objects. Direct melt-mixing mixing, on the other hand, usually results in lower quality dispersion of

fillers, but the process is readily scalable, more economic, and more environmentally friendly.

Here we report a premixing method to produce polymer nanocomposites incorporating cellulose nanocrystals (CNCs). This method involves the dissolution and dispersion of a polymer and CNCs in an organic solvent, followed by precipitation into water and drying of the resulting material. The key aspects of the method are that it allows the kinetic trapping of well-dispersed CNCs within the polymer matrix, and that it permits subsequent melt processing into objects of any shape. To the best of the authors' knowledge, no similar process has been previously reported. The main limitations of the framework include the use of an (organic) solvent (which can, however, be recycled) and that it is limited to polymers that are soluble in solvents in which the CNCs form stable dispersions.

EXPERIMENTAL SECTION

Materials. PU (Texin 285, a polyurethane based on poly(tetramethylene glycol), butanediol, and 4,4′-methylenebis(phenyl isocyanate)) was obtained from Bayer Material Science (now Covestro). Dimethyl sulfoxide (DMSO) and N,N-dimethyl-formamide (DMF) were purchased from Sigma-Aldrich and were used as received. CNCs were extracted from Whatman No. 1 filter paper using sulfuric acid hydrolysis according to a procedure reported previously.[38] Their dimensions (220 ± 90 nm x 21 ± 4 nm, determined by the analysis of transmission electron microscopy (TEM) images) and surface charge (50 mmol/kg) were within the same range as previously reported.[40]

Preparation of PU/CNC nanocomposites by solvent casting. Solvent-cast PU/CNC nanocomposites were prepared, unless otherwise stated, by casting from

dimethylsulfoxide (DMSO), according to the procedure reported by Meesorn *et al.*[41] In brief, the polymer was dissolved in DMSO at a concentration of 100 mg/mL by stirring at 80 °C for 3 h. 10 – 30% w/w lyophilized CNCs (relative to the total weight of polymer + CNCs) were added and the mixture was vigorously stirred overnight. The suspension was then sonicated in a Sonoswiss SW3H ultrasonic bath for 4 h, cast into poly(tetrafluoro ethylene) Petri dishes, and dried in a ventilated oven at 70 °C for 72 h. Residual solvent was removed by further drying in a vacuum oven at 70 °C for 48 h. Films were placed between poly(tetrafluoro ethylene) sheets and compression-molded in a Carver press at 170 °C between spacers with a thickness of 0.4 mm, applying no pressure for the first 3 min and 5 bar of pressure for another 3 min. The films were then removed from the press and were allowed to cool to room temperature between the poly(tetrafluoro ethylene) sheets. The same procedure was followed for nanocomposites that were cast from dimethylformamide (DMF).

Preparation of PU/CNC nanocomposites by co-precipitation. The PU was dissolved in DMSO at a concentration of 100 mg/mL by stirring at 80 °C for 3 h. 10 - 30% w/w lyophilized CNCs (relative to the total weight of polymer + CNCs) were added and the mixture was vigorously stirred overnight. For example, to prepare a PU/CNC 10% w/w nanocomposite, 3.6 g PU were dissolved in 36 mL DMSO and 0.4 g CNC were added. The suspension was then sonicated in a Sonoswiss SW3H ultrasonic bath for 4 h, before it was dropped at a rate of ca. two drops per second into an excess of deionized water (1 L), which was stirred at 400 rpm. A 500 mL dropping funnel that formed drops with a diameter of ca. 3 mm was used and placed ca. 10 cm above the water surface to ensure that the spherical particles formed gravitationally accelerated past the air-water interface. After the addition was complete, the mixture was stirred for 20 min to exchange the solvent to water and

stabilize the PU/CNC particles. To ensure complete solvent exchange from DMSO to water, the water was changed every 20 min with fresh water for at least three times. The PU/CNC particles were isolated by filtration and unless otherwise stated dried in a ventilated oven for 24 h. This afforded spheres with a yellow appearance and a diameter of ca. 1 mm. The materials were compression-molded as described for the solvent-cast samples above or used as masterbatch (*vide infra*). Selected compositions were also prepared by co-precipitation from DMF using the same procedure.

Preparation of PU/CNC nanocomposites by dilution from a masterbatch. PU/CNC nanocomposites containing 20 or 30% w/w CNCs made by co-precipitation were diluted with neat PU to create 10% w/w PU/CNC nanocomposites by melt-mixing at 170 °C at 60 rpm for 10 min in a roller blade mixer (Brabender GmbH & Co. KG, Duisburg, Germany). For example, 6 g of the 30% w/w PU/CNC made by co-precipitation was mixed with 12 g of the neat PU to obtain a composite with a final CNC concentration of 10% w/w. Compression molding was carried out as described for solvent-cast samples above.

Preparation of PU/CNC nanocomposites by direct mixing. PU/CNC nanocomposites were also prepared by direct mixing in a roller blade mixer with a similar approach as described by Sapkota *et al.*[42] The same mixer and conditions were used as for the dilution from a masterbatch, however for the direct mixing approach, neat polymer was first molten, and then freeze-dried CNCs were slowly added to the polymer melt to a final concentration of 10% w/w. After the addition was complete, the melt was mixed for another 10 min, before the nanocomposite was removed from the roller blade mixer. Compression molding was carried out as described for solvent-cast samples above.

Gravimetric determination of CNC content in nanocomposites. 1 g of the PU/CNC nanocomposite was dissolved into 50 mL DMSO by stirring at 80 °C for 3 h, the mixture was cooled to room temperature, and the CNCs were separated from the polymer solution by centrifugation at 7000 rpm for 20 min. The sedimented CNCs were re-dispersed in 50 mL DMSO, stirred at 80 °C for 30 min and centrifuged again. This process was repeated two more times to ensure removal of the polymer. Finally, the CNCs were dried in a vacuum oven at 70 °C for 24 h before weighing. Average values were calculated from 2 samples per composition.

Materials Characterization. For differential scanning calorimetry (DSC) analysis, a Mettler-Toledo STAR system differential scanning calorimeter was utilized, and samples were heated and cooled with a rate of 10 °C/min. Thermogravimetric analyses (TGA) were performed on a Mettler-Toledo STAR system at a heating rate of 10 °C/min. Dynamic mechanical analysis (DMA) was performed on a TA Instruments Model Q800 with a frequency of 1 Hz, an amplitude of 15 µm, and a heating rate of 5 °C/min, using rectangular shaped samples (ca. 10 mm x 5.3 mm x 0.4 mm). The same instrument was used for stress-strain measurements, which were performed at 25 °C with a strain rate of 10%/min and dog-bone shaped samples (ca. 5 mm x 2.1 mm x 0.4 mm). Unless otherwise mentioned, stress strain measurements were performed with samples that were compression-molded and stored under ambient conditions for at least two days. In select cases, referred to as "... after cooling", samples were cooled to - 100 °C and heated back to room temperature at a rate of 5 °C/min, and equilibrated at room temperature for 30 min before the stress strain test was started. For DMA and stress strain measurements, values for mechanical properties are reported as averages of at least three measurements per composition. TEM images were acquired with a FEI Tecnai spirit electron

microscope, and samples were prepared by drop-casting 0.1 mg/mL dispersions of CNCs in water onto carbon-coated copper grids.

RESULTS AND DISCUSSION

As a testbed for this study, we prepared and investigated nanocomposites made from a commercial thermoplastic polyurethane (PU) based on poly(tetramethylene glycol), butanediol, and 4,4′-methylenebis(phenyl isocyanate) and up to 30% w/w of CNCs isolated by sulfuric acid hydrolysis from cotton.[38] The analysis of TEM images of the CNCs (**Figure S1**) revealed an average length of 220 ± 90 nm and an average diameter of 21 ± 4 nm. Conductometric titration (**Figure S2**) revealed a surface charge concentration of 50 mmol/kg, which is associated with presence of sulfate half ester groups that are introduced during hydrolysis. In addition to the samples prepared by the co-precipitation method, reference samples were prepared by solvent casting and direct melt-mixing of the PU and the CNCs. We also used the materials prepared by co-precipitation as masterbatches, which were diluted with neat PU by melt mixing. DMF has long been the dispersant of choice for CNCs,[34,43,44] but Meesorn *et al.* recently compared the mechanical properties of poly(ethylene oxide-*co*-epichlorohydrin)/CNC nanocomposites cast from DMSO and DMF, and found that composites cast from DMSO had a significantly higher stiffness than those prepared from DMF, presumably on account of better dispersion of the CNCs.[41] In the light of these findings, we selected DMSO as the primary solvent for this study and also conducted a few control experiments with DMF; as will be shown, DMSO affords indeed nanocomposites with better mechanical properties.

Figure 1 schematically illustrates the co-precipitation approach that was used to produce the nanocomposites. The PU was first dissolved in either DMSO or DMF at

a concentration of 100 mg/mL, before freeze-dried CNCs were added and the mixture was ultrasonicated. The polymer concentration was chosen so that precipitation into water yielded coherent spherical particles (or in the case of DMF larger strings, likely due to the higher viscosity of the DMF than the DMSO solution), from which the remaining solvent could be easily extracted by washing with water, before the material was eventually filtered off and dried. This method was based on the hypothesis that the rapid solidification achieved by co-precipitation would permit the kinetic trapping of well-dispersed CNCs in the polymer matrix. The gravimetric analysis of the CNC content (**Table S1**), which shows a perfect match between the CNC content in the dispersion and the precipitated materials, confirmed that the trapping is at least quantitative, i.e., virtually no CNCs remain in the aqueous phase. Thermogravimetric analysis (TGA) traces (**Figure S3, Table S2**) show a slightly reduced thermal stability of the nanocomposites prepared by co-precipitation with more than 10% CNCs compared to the neat polymer, however no significant weight loss was observed at temperatures below 270 °C. The nanocomposites thus prepared were either compression-molded into 400 µm thin films (**Figure 2A**), used as masterbatch, or injection-molded into test bars (**Figure 2E**).

The visual appearance of films of the neat PU and nanocomposites prepared by solvent casting (S), precipitation (P), or dilution of masterbatches (M) is documented by pictures shown in **Figure 2A.** All films showed a homogeneous appearance without any visible large-scale aggregates. In contrast to the neat PU (**Figure 2A**) and nanocomposites made from DMF (**Figure 2D**), which were all colorless, all nanocomposites prepared from DMSO were slightly yellow. A picture of the precipitate (before compression molding) reveals that the yellowing occurred already during the solvent casting process (**Figure 2B**). Yellowing of polymer/CNC

composites under elevated temperatures has been reported previously and is generally attributed to chemical degradation processes involving the sulfate half-ester groups on the surface of CNCs.[39] In fact, discoloration of thermoplastic composites incorporating macroscale unbleached cellulose fiber byproducts of Kraft pulping has also been observed.[45] Such color changes have also been associated with slight degradation of macroscopic cellulosic materials during high temperature processing, however are thought to improve fiber-matrix adhesion by rendering the filler surfaces more hydrophobic and thus improving overall mechanical properties. While the difference observed for composites prepared from DMF and DMSO, which were prepared under otherwise identical conditions, is not fully understood, we speculate that an oxidative process involving the DMSO and possibly the sulfate half-ester groups may be the culprit. Moreover, the acid-base equilibria of DMF and DMSO are dissimilar, which could also play a role in sulfate half-ester group reactivity during chemical degradation processes causing discoloration.[46,47] Any removal of sulfate half-ester groups from CNC surfaces that could have potentially occurred would have changed the thermal stability and ultimately alter the degree of discoloration.[48] We note, however, that the yellowing can be suppressed by freeze-drying the materials in lieu of drying at elevated temperature (**Figure 2B** and **C**) and that despite the yellowing, all materials processed from DMSO display superior properties than their counterparts made with other methods. These observations are in agreement with investigations of analogous composites incorporating macroscale cellulosic reinforcements, in which discoloration occurred.[45]

The mechanical properties of the neat PU and the PU/CNC nanocomposites prepared by the various processes were studied by dynamic mechanical analyses (DMA) and stress strain measurements. Representative measurements for each

composition are shown in **Figure 3** and **Figure 4**, respectively and key data are compiled in

Table 1. The analysis of the mechanical data reveals several interesting findings. Firstly, all PU/CNC nanocomposites prepared from DMSO (by both solvent casting and co-precipitation) show a substantially higher storage modulus, Young's modulus and stress at break than the corresponding nanocomposites prepared from DMF. For example, nanocomposites prepared by solvent casting or co-precipitation with 10% w/w filler content had a storage modulus of ca. 150 – 160 MPa at room temperature when DMF was used as a solvent, whereas the storage modulus was 350 – 360 MPa when DMSO was used. On the other hand, the neat polymer did not display any significant differences in mechanical properties when cast from DMF (44 MPa) or DMSO (40 MPa). These findings suggest that, for this particular polymer/CNC composite, the dispersion quality of CNCs is indeed higher in DMSO.

Secondly, PU/CNC properties for samples with the same CNC content and solvent used for nanocomposites prepared by solvent casting and co-precipitation exhibited nearly identical mechanical casting. The storage modulus at room temperature increased with the CNC content from 40 MPa for the neat PU up to 960 MPa for the 30% w/w PU/CNC nanocomposite by co-precipitation and 1050 MPa for the same composition made by solvent casting. The Young's modulus of both the solvent-cast and the co-precipitated nanocomposite increased by an order of magnitude vis-à-vis the neat PU, while the strain at break remained constant up to a CNC content of 10% w/w. The latter finding is quite remarkable, since in most cases, CNC addition leads to embrittlement. At higher CNC content, the strain at break is typically reduced due to the high stiffness of CNCs having an ever increasing effect on the overall mechanical properties of the nanocomposites. The stress at break was largest for compositions with a CNC content of 10% w/w and it decreased for higher concentrations along with the strain at break. The similarity of the mechanical

properties of the precipitated and solvent-cast nanocomposites is striking and supports the conclusion that kinetic trapping by precipitation indeed permits maintaining good dispersion of CNCs within the PU matrix. On the other hand, the 10% w/w PU/CNC nanocomposite made by directly mixing the components in a roller blade mixer displayed much lower storage (130 MPa at room temperature) and Young's moduli (32 MPa) than the corresponding nanocomposites prepared by solvent casting and co-precipitation, suggesting that the melt mixing process was not capable of inducing a comparable level of dispersion. Previously reported direct mixing of a different grade of polyurethane with CNCs confirm this suggestion, as an increase of the storage modulus at room temperature from the neat PU (940 MPa) to the PU with 10% w/w CNCs (1330 MPa) of only 40% was observed.[32]

Thirdly, the dilution of PU/CNCs nanocomposites containing 20% w/w or 30% w/w CNCs with neat PU to create nanocomposites with 10% w/w CNCs (M20-10 and M30-10) was readily achieved by melt-mixing in a roller-blade mixer. Gratifyingly, the mechanical properties of the materials made by this masterbatch approach are virtually identical to those of 10% w/w nanocomposites made by solvent-casting or co-precipitation. Together with the facts that the stiffness of the samples increases up to a CNC content of 30% w/w and the finding that direct melt-mixing affords materials with inferior properties (*vide supra*) this suggests that even at a high CNC content of 30% w/w the CNCs appear to be well-dispersed and that this level of dispersion can be maintained upon dilution with the neat polymer under low-shear conditions.

Finally, cooling of the PU/CNC nanocomposites to well below room temperature (a temperature of -100 °C was routinely selected) caused the PU's soft segment to crystallize, and the crystallinity was maintained when the samples were heated back to room temperature. This causes a change of the mechanical properties, as

reflected by the DMA trace shown in **Figure S4**, which displays the storage modulus of a PU/CNC 10% w/w nanocomposite (prepared by co-precipitation), which was cooled from 25 °C to -100 °C, heated back to 25 °C and then maintained at this temperature for several hours. After this treatment, the storage modulus increased from 58 MPa (never cooled sample) to 300 MPa. Upon storage at ambient temperature the storage modulus slowly decreased to a value of 180 MPa after 6h. To confirm that the increase in storage modulus was indeed due to an increase of the soft segment crystallinity, DSC measurements (**Figure S5**) were made. While the DSC traces clearly confirm the absence of crystalline domains for never-cooled samples, they reveal small endothermic peaks between 20 and 60 °C for samples that had been cooled. These signals are characteristic of crystallized poly(tetramethylene glycol) segments.[49] Values for crystallinity estimated from the DSC curves, which were calculated based on the reported enthalpy of fusion for a theoretically 100% crystalline poly(tetramethylene glycol), are given in **Table S3**. The crystallinity of nanocomposites prepared by co-precipitation and which had been previously cooled slightly decreased with increasing CNC content. For example, the neat PU had a crystallinity of 6.4%, whereas the crystallinity of the 30% PU/CNC composite was only 1.6%. The increasing presence of CNCs likely hampered the crystallization of the soft PU segments and thus decreased the enthalpy of fusion. The decreased crystallinity of PU/CNC nanocomposites with high CNC content compared to nanocomposites with low CNC content can give information about the interactions between CNCs and PU. Compared to PU nanocomposites with functionalized CNCs, for which an increase in crystallinity has been reported, the interactions between CNCs and PU in the current work are believed to be weak, mainly based on van der Waals forces and some degree of hydrogen bonding.[50] The

main reason for the reinforcement effect of CNCs is their formation of a percolating network, which is hold together by strong hydrogen bonds of adjacent CNCs.

On account of the above-discussed crystallization of the PU's soft segment upon cooling, the standard DMA experiments shown in **Figure 3** lead to an overestimation of the modulus vis-à-vis never-cooled samples. Thus, the nanocomposites were also measured utilizing a different protocol in which samples were never cooled. The dashed lines in **Figure 3A** and **Figure 3B** and the values in

Table 1 marked as “never cooled” show the DMA curves and the mechanical properties of samples that were never cooled, i.e. measured from room temperature up to 180 °C. In fact, the mechanical properties of all compositions were lower compared to samples which had been measured starting from -100 °C. For example, the storage modulus, measured after cooling, for a nanocomposite with 10% w/w CNC content prepared by co-precipitation and solvent casting was 360 and 350 MPa, respectively, while the storage modulus of the same compositions, which had never been cooled, was 110 and 140 MPa. The same trend was observed for stress strain measurements. In this case, most “standard” measurements were performed with never-cooled samples, while the dashed lines (**Figure 4A)** indicate that the samples were cooled to -100 °C before the experiment. As expected, the mechanical properties of cooled samples (e.g. a Young’s modulus of 78 MPa for a 10% w/w PU/CNC nanocomposite prepared by co-precipitation) were significantly higher than never-cooled samples (a Young’s modulus of 48 MPa for the never-cooled, otherwise same composition).

CONCLUSIONS

In summary, a series of PU/CNC nanocomposites was prepared and studied, with the goal to demonstrate that co-precipitation is an attractive process to create such materials. The key aspects of the method are that it allows the kinetic trapping of well-dispersed CNCs within the polymer matrix, and that it permits subsequent melt processing into objects of any shape. Nanocomposites made by the co-precipitation process showed mechanical properties comparable to those of the corresponding compositions made by solvent casting, with the added benefits of both facile and rapid processing conditions. Materials with up to 30% filler content were made, which

displayed considerable improvements in strength and stiffness, while at the same time maintaining high elongation at break. Dilution of masterbatches with high CNC content via melt-mixing was readily possible and resulted in nanocomposites which had identical mechanical properties as materials with a lower filler content that were directly prepared by solvent casting or co-precipitation.

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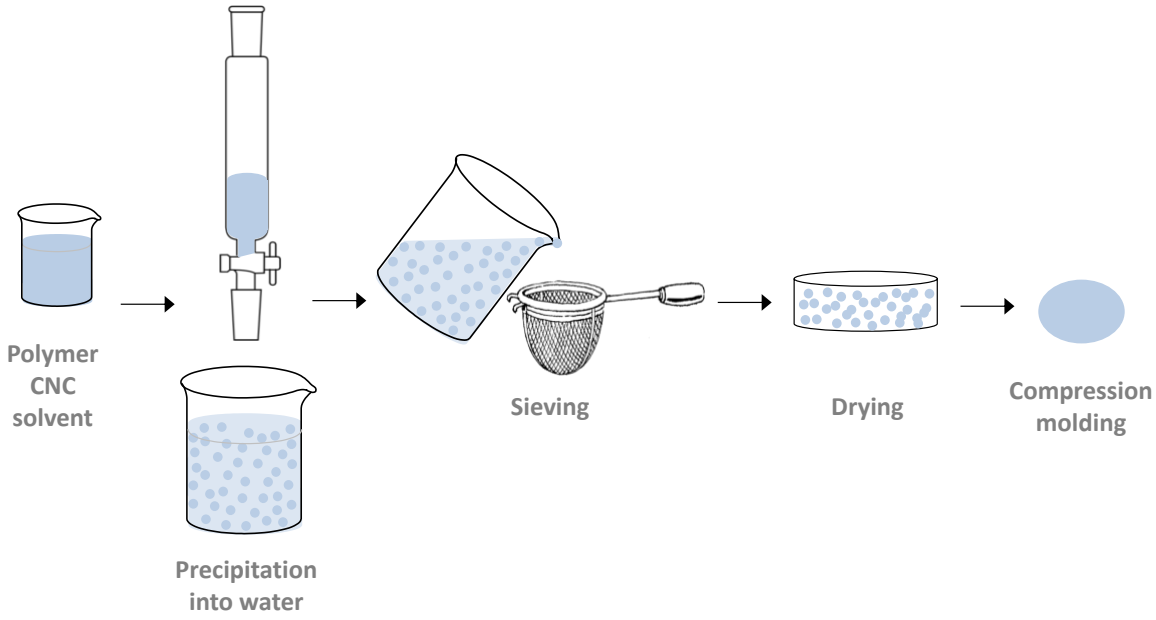


Figure 1. Schematic representation of co-precipitation process used to prepare PU/CNC nanocomposites.

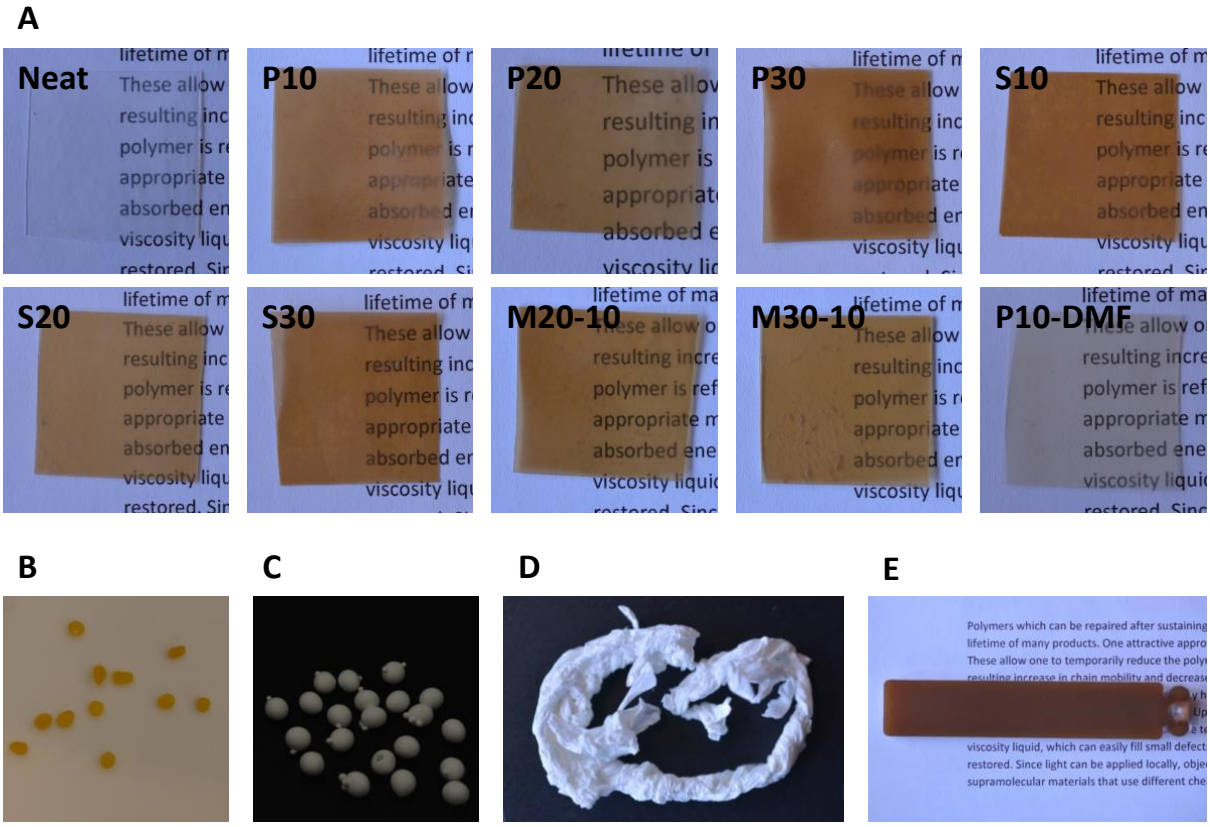


Figure 2. (A) Photographs of compression-molded films of the neat PU and PU/CNC nanocomposites. Sample codes indicate the preparation method (S = solvent cast, P = co-precipitated, M = diluted masterbatch), the CNC concentration, and the solvent employed if different from DMSO. Masterbatches were diluted from P20 or P30 with neat PU to 10% w/w and are referred to as M20-10 and M30-10, respectively. Also shown are photographs of a 10% w/w PU/CNC nanocomposite precipitated from DMSO after freeze-drying (B) or oven-drying at 70 °C (C) and a 10% w/w PU/CNC precipitate from DMF after oven-drying at 70 °C (D). (E) Picture of an injection-molded piece of the 10% w/w PU/CNC nanocomposite shown in (C).

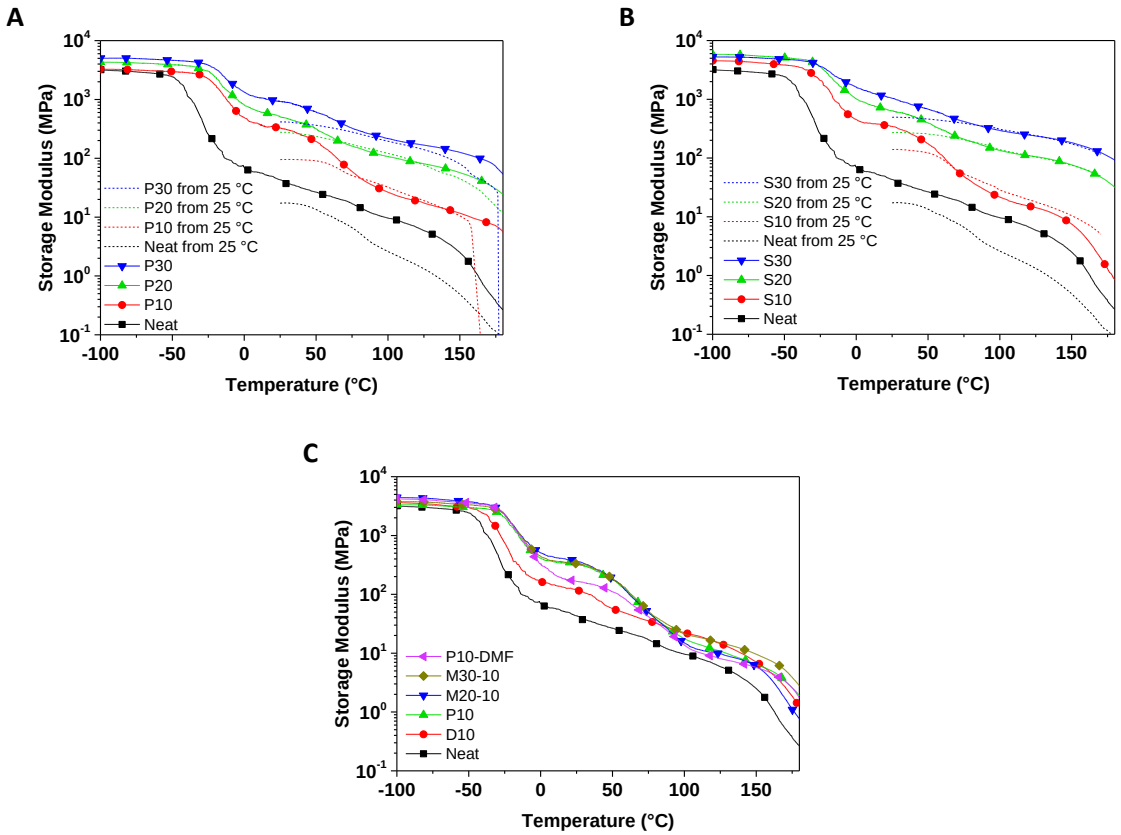


Figure 3. DMA curves of the neat PU and the PU/CNC nanocomposites. Sample codes indicate the preparation method (S = solvent cast, P = co-precipitated, M = diluted masterbatch; D = directly mixed), the CNC concentration, and the solvent employed if it was different to DMSO. Masterbatches were diluted from P20 or P30 with neat PU to a CNC content of 10% w/w and are referred to as M20-10 and M30-10, respectively. (A) Samples prepared by co-precipitation; the dashed lines are measurements of samples that were never cooled below room temperature to inhibit the crystallization of the PU's soft segment. (B) Samples prepared by solvent casting. (C) Comparison of the neat PU with and 10% w/w PU/CNC nanocomposites made by the different preparation methods.

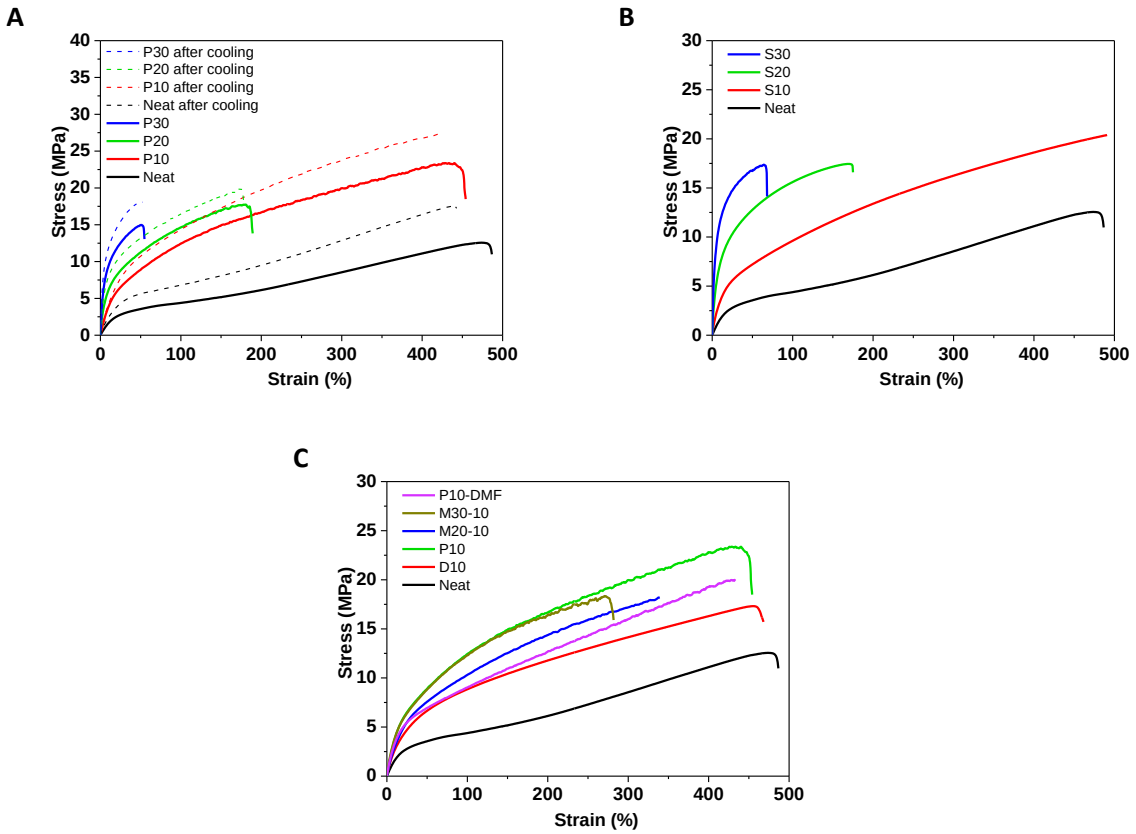


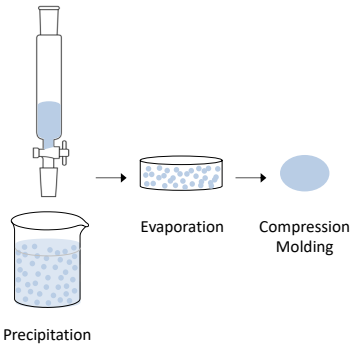
Figure 4. Stress strain curves of the neat PU and the PU/CNC nanocomposites. Sample codes indicate the preparation method (S = solvent cast, P = co-precipitated, M = diluted masterbatch; D = directly mixed), the CNC concentration, and the solvent employed if different from DMSO. Masterbatches were diluted from P20 or P30 with neat PU to a CNC content of 10% w/w and are referred to as M20-10 and M30-10, respectively. (A) Samples prepared by co-precipitation; the dashed lines are measurements of samples that had been cooled to -100 °C before to induce crystallization of the PU's soft segment. (B) Samples prepared by solvent casting. (C) Comparison of the neat PU and 10% w/w PU/CNC nanocomposites made by the different preparation methods.

Table 1. Mechanical properties of neat PU and PU/CNC composites prepared by co-precipitation, solvent casting, direct mixing, and dilution from a masterbatch.

Sample Code	Nanocomposite	Storage Modulus at 25 °C after cooling (MPa)[a]	Storage Modulus at 25 °C never cooled (MPa)[b]	Young's Modulus never cooled (MPa)[c]	Young's Modulus after cooling (MPa)[d]	Strain at Break (%)[c]	Stress at Break (MPa)[c]
Neat	Neat PU solvent casting from DMSO	40 ± 8	16 ± 3	17 ± 1	31 ± 3	470 ± 30	10 ± 2
D10	10% w/w PU/CNC direct mixing	130 ± 30	n/a	32 ± 3	n/a	410 ± 60	16 ± 2
P10	10% w/w PU/CNC co-precipitation from DMSO	360 ± 10	110 ± 10	48 ± 2	78 ± 6	450 ± 20	24 ± 2
P20	20% w/w PU/CNC co-precipitation from DMSO	590 ± 60	280 ± 10	93 ± 6	140 ± 10	190 ± 10	18 ± 1
P30	30% w/w PU/CNC co-precipitation from DMSO	960 ± 50	410 ± 20	170 ± 10	230 ± 20	58 ± 10	15 ± 1
S10	10% w/w PU/CNC solvent casting from DMSO	350 ± 10	140 ± 10	47 ± 3	n/a	460 ± 30	23 ± 2
S20	20% w/w PU/CNC solvent casting from DMSO	570 ± 50	270 ± 10	100 ± 2	n/a	190 ± 10	17 ± 1
S30	30% w/w PU/CNC solvent casting from DMSO	1050 ± 40	460 ± 30	150 ± 20	n/a	62 ± 6	16 ± 2
M20-10	10% w/w PU/CNC diluted masterbatch from P20[e]	340 ± 20	n/a	56 ± 7	n/a	290 ± 40	17 ± 3
M30-10	10% w/w PU/CNC diluted masterbatch from P30[e]	330 ± 10	n/a	57 ± 8	n/a	250 ± 30	18 ± 1
Neat-DMF	Neat PU solvent casting from DMF	44 ± 6	n/a	16 ± 3	n/a	450 ± 50	11 ± 1
S10-DMF	10% w/w PU/CNC solvent casting from DMF	150 ± 20	n/a	34 ± 5	n/a	380 ± 50	15 ± 2
P10-DMF	10% w/w PU/CNC co-precipitation from DMF	160 ± 20	n/a	37 ± 2	n/a	410 ± 40	19 ± 2

[a] Based on DMA measurements at 25 °C upon heating from -100 °C (standard DMA measurements).
[b] Based on DMA measurements at 25 °C with never-cooled samples.
[c] Based on stress-strain measurements at 25 °C with never-cooled samples (standard stress strain measurements).
[d] Based on stress-strain measurements at 25 °C with samples that had previously been cooled to -100 °C.
[e] Dilution was performed by melt-mixing with neat PU (see details in Experimental Section).
All data represent averages from at least three samples per composition.

Graphical Abstract



REFERENCES

1. Ng, L. Y.; Mohammad, A. W.; Leo, C. P.; Hilal, N. *Desalination* **2013**, *308*, 15-33.
2. Chan, C.-M.; Wu, J.; Li, J.-X.; Cheung, Y.-K. *Polymer* **2002**, *43*, 2981-2992.
3. Saheb, D. N.; Jog, J. P. *Adv. Polym. Tech* **1999**, *18*, 351-363.
4. Reddy, K. R.; Sin, B. C.; Ryu, K. S.; Noh, J.; Lee, Y. *Synthetic Metals* **2009**, *159*, 1934-1939.
5. Choi, S. H.; Kim, D. H.; Raghu, A. V.; Reddy, K. R.; Lee, H.-I.; Yoon, K. S.; Jeong, H. M.; Kim, B. K. *J. Macromol. Sci., Part B: Phys.* **2012**, *51*, 197-207.
6. Endes, C.; Camarero-Espinosa, S.; Mueller, S.; Foster, E.; Petri-Fink, A.; Rothen-Rutishauser, B.; Weder, C.; Clift, M. *Nanobiotechnology* **2016**, *14*, 78.
7. Eichhorn, S. J.; Dufresne, A.; Aranguren, M.; Marcovich, N. E.; Capadona, J. R.; Rowan, S. J.; Weder, C.; Thielemans, W.; Roman, M.; Renneckar, S.; Gindl, W.; Veigel, S.; Keckes, J.; Yano, H.; Abe, K.; Nogi, M.; Nakagaito, A. N.; Mangalam, A.; Simonsen, J.; Benight, A. S.; Bismarck, A.; Berglund, L. A.; Peijs, T. *J. Mater. Sci.* **2010**, *45*, 1-33.
8. Mariano, M.; El Kissi, N.; Dufresne, A. *J. Polym. Sci., Part B: Polym. Phys.* **2014**, *52*, 791-806.
9. Moon, R. J.; Martini, A.; Nairn, J.; Simonsen, J.; Youngblood, J. *Chem. Soc. Rev.* **2011**, *40*, 3941-3994.
10. Beck-Candanedo, S.; Roman, M.; Gray, D. G. *Biomacromolecules* **2005**, *6*, 1048-1054.
11. Revol, J. F.; Godbout, L.; Dong, X. M.; Gray, D. G.; Chanzy, H.; Maret, G. *Liq. Cryst.* **1994**, *16*, 127-134.
12. Favier, V.; Chanzy, H.; Cavaille, J. Y. *Macromolecules* **1995**, *28*, 6365-6367.
13. Mueller, S.; Weder, C.; Foster, E. J. *RSC Adv.* **2014**, *4*, 907-915.
14. Trache, D.; Hussin, M. H.; Haafiz, M. K. M.; Thakur, V. K. *Nanoscale* **2017**, *9*, 1763-1786.
15. Azeredo, H. M.; Rosa, M. F.; Mattoso, L. H. C. *Ind. Crops Prod.* **2017**, *97*, 664-671.
16. Brinchi, L.; Cotana, F.; Fortunati, E.; Kenny, J. *Carbohydr. Polym.* **2013**, *94*, 154-169.
17. Domingues, R. M.; Gomes, M. E.; Reis, R. L. *Biomacromolecules* **2014**, *15*, 2327-2346.
18. Dufresne, A. *Molecules* **2010**, *15*, 4111-4128.
19. Eichhorn, S. J. *Soft Matter* **2011**, *7*, 303-315.
20. Habibi, Y.; Lucia, L. A.; Rojas, O. J. *Chem. Rev.* **2010**, *110*, 3479-3500.
21. Shanmuganathan, K.; Capadona, J. R.; Rowan, S. J.; Weder, C. *Prog. Polym. Sci.* **2010**, *35*, 212-222.
22. Garcia de Rodriguez, N. L.; Thielemans, W.; Dufresne, A. *Cellulose* **2006**, *13*, 261-270.
23. Azizi Samir, M. A. S.; Alloin, F.; Sanchez, J.-Y.; Dufresne, A. *Polymer* **2004**, *45*, 4149-4157.
24. Ben Azouz, K.; Ramires, E. C.; Van den Fonteyne, W.; El Kissi, N.; Dufresne, A. *ACS Macro Lett.* **2012**, *1*, 236-240.
25. Bondeson, D.; Oksman, K. *Compos. Interfaces* **2007**, *14*, 617-630.
26. Kim, J.; Montero, G.; Habibi, Y.; Hinestroza, J. P.; Genzer, J.; Argyropoulos, D. S.; Rojas, O. J. *Polym. Eng. Sci.* **2009**, *49*, 2054-2061.
27. Salajkova, M.; Berglund, L. A.; Zhou, Q. *J. Mater. Chem.* **2012**, *22*, 19798-19805.

28. Ávila Ramírez, J. A.; Fortunati, E.; Kenny, J. M.; Torre, L.; Foresti, M. L. *Carbohydr. Polym.* **2017**, *157*, 1358-1364.
29. Bendahou, A.; Hajlane, A.; Dufresne, A.; Boufi, S.; Kaddami, H. *Res. Chem. Intermed.* **2015**, *41*, 4293-4310.
30. Frone, A. N.; Berlioz, S.; Chailan, J. F.; Panaitescu, D. M.; Donescu, D. *Polym. Compos.* **2011**, *32*, 976-985.
31. Cao, X.; Habibi, Y.; Lucia, L. A. *J. Mater. Chem.* **2009**, *19*, 7137-7145.
32. Ljungberg, N.; Bonini, C.; Bortolussi, F.; Boisson, C.; Heux, L.; Cavaillé *Biomacromolecules* **2005**, *6*, 2732-2739.
33. Pereda, M.; Kissi, N. E.; Dufresne, A. *ACS Appl. Mater. Interfaces* **2014**, *6*, 9365-9375.
34. Nicharat, A.; Sapkota, J.; Weder, C.; Foster, E. J. *J. Appl. Polym. Sci.* **2015**, *132*, 42752.
35. Nicharat, A.; Shirole, A.; Foster, E. J.; Weder, C. *J. Appl. Polym. Sci.* **2017**, *134*, 45033.
36. Biyani, M. V.; Foster, E. J.; Weder, C. *ACS Macro Lett.* **2013**, *2*, 236-240.
37. Grunert, M.; Winter, W. T. *J. Polym. Environ.* **2002**, *10*, 27-30.
38. Capadona, J. R.; Van Den Berg, O.; Capadona, L. A.; Schroeter, M.; Rowan, S. J.; Tyler, D. J.; Weder, C. *Nat. Nanotechnol.* **2007**, *2*, 765-769.
39. Sapkota, J.; Jorfi, M.; Weder, C.; Foster, E. J. *Macromol. Rapid Commun.* **2014**, *35*, 1747-1753.
40. Natterodt, J. C.; Sapkota, J.; Foster, E. J.; Weder, C. *Biomacromolecules* **2017**, *18*, 517-525.
41. Meesorn, W.; Shirole, A.; Vanhecke, D.; de Espinosa, L. M.; Weder, C. *Macromolecules* **2017**, *50*, 2364-2374.
42. Sapkota, J.; Natterodt, J. C.; Shirole, A.; Foster, E. J.; Weder, C. *Macromol. Mater. Eng.* **2017**, *302*, 1-6.
43. Samir, M. A. S. A.; Alloin, F.; Sanchez, J. Y.; El Kissi, N.; Dufresne, A. *Macromolecules* **2004**, *37*, 1386-1393.
44. van den Berg, O.; Capadona, J. R.; Weder, C. *Biomacromolecules* **2007**, *8*, 1353-1357.
45. Urreaga, J. M.; Matias, M. C.; De la Orden, M. U.; Munguia, M. A. L.; Sanchez, C. G. *Polym. Eng. Sci.* **2000**, *40*, 407-417.
46. Jiang, F.; Esker, A. R.; Roman, M. *Langmuir* **2010**, *26*, 17919-17925.
47. Trummal, A.; Lipping, L.; Kaljurand, I.; Koppel, I. A.; Leito, I. *J. Phys. Chem. A* **2016**, *120*, 3663-3669.
48. Lin, N.; Dufresne, A. *Nanoscale* **2014**, *6*, 5384-5393.
49. Liu, L. Z.; Yeh, F. J.; Chu, B. *Macromolecules* **1996**, *29*, 5336-5345.
50. Cao, X.; Habibi, Y.; Lucia, L. A. *Journal of Materials Chemistry* **2009**, *19*, 7137-7145.
51. Samir, M. A. S. A.; Alloin, F.; Sanchez, J.-Y.; Dufresne, A. *Polymer* **2004**, *45*, 4149-4157.