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COMMUNICATION

Omnidispersible poly(ionic liquid)-functionalized cellulose nanofibrils: surface grafting and polymer membrane reinforcement

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Cite this: DOI: 10.1039/x0xx00000x
Accepted 00th January 2014

DOI: 10.1039/x0xx00000x

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We report a facile one-step route to graft poly(ionic liquid) (PIL) onto cellulose nanofibrils (CNFs). The dispersibility in water and various organic solvents of the PIL-functionalized CNF could be tuned by the choice of PIL-binding anion. We demonstrate that such omnidispersible PIL@CNF hybrids can be used to reinforce porous poly(ionic liquid) membranes.

Nanocellulose is a renewable nanomaterial with outstanding properties that is attracting rapidly growing scientific and technological interest with applications such as composites, barrier films, scaffold materials, and multifunctional foams and aerogels.¹⁻³ Nanocellulose combines a versatile chemical-modification capacity, low thermal expansion, and excellent mechanical properties with a high surface area. There are three major forms of nanocellulose: cellulose nanofibrils, cellulose nanocrystals, and bacterial cellulose, that mainly differ with respect to dimensions and flexibility. Cellulose nanofibrils (CNFs) are long, slender and flexible rod-like particles with diameters of ~5-60 nm and lengths up to several μm . Due to the high aspect ratio, CNF dispersions are prone to gelation and display pronounced viscoelastic properties even at low concentrations.² CNFs are currently employed (or being introduced) in the food, hygiene, and packaging industry, as an additive in cosmetics and tablets, and scaffold material in tissue engineering.^{2, 4} They were also used to produce mechanically strong films (nanopaper) with tensile strengths up to 250 MPa.²

To achieve good material properties CNFs need to be well dispersed in a suitable medium. Current manufacturing of CNFs typically results in materials with high surface charge, which are dispersible in water but aggregate easily in organic media. This limits the application scope of CNFs in fields where material processing in organic media is unavoidable. To improve dispersibility in organic solvents and/or polymeric matrixes, adsorption or grafting of surfactants, polymers and coupling agents⁵⁻⁸ as well as corona treatment have been used.⁹⁻¹¹ CNFs have also been hydrophobized by acetylation, silylation or "click chemistry".¹²⁻¹⁴ However, many of these

routes have a limited versatility and some of them, e.g. silylation methods, may damage the fibrillar structure of CNFs.¹⁵ This highlights the necessity for facile and versatile surface modification methods for the preparation of *omnidispersible* CNF that can be easily processed in a wide range of solvents.

Poly(ionic liquid)s (PILs) are strong polyelectrolytes obtained from ionic liquid monomers.^{16, 17} PILs retain some features of ILs while showing enhanced mechanical stability and processability due to their polymeric nature. Bearing a high density of IL moieties in the polymeric chain brings new opportunities to combine IL chemistry with polymer research and materials design.¹⁸⁻²⁰ For instance, PILs show tunable anion-dependent solubility, which could be related to the binding strength of anions and for particular systems could be presented in a form of Hofmeister series.²¹⁻²⁸ They also appear to be effective stabilizers for nanomaterials, such as carbon nanotubes, graphene, hydrothermal carbons, and inorganic nanoparticles.^{23, 29-33} Especially PIL-stabilized single-walled and multi-walled carbon nanotube dispersions in water are noteworthy due to high achieved concentrations (up to 1.37 wt% and 17 wt% of carbon material, respectively), which may be of great importance in further practical applications.^{34, 35} Recently, our group has demonstrated the potential of PILs as components of polyelectrolyte membranes, which has attracted attention in both science and industry due to the multitude of possible applications of such systems (e.g., gas separation, controlled release, sensors or catalyst support). We have developed a straightforward pathway for preparation of porous membranes by triggering ionic complexation between PIL and poly(acrylic acid) (PAA) blend.³⁶ However, reinforcing of the as-prepared systems is required in order to face the problem of their unsatisfactory mechanical properties.

Herein, we report a versatile method to disperse CNFs in water and organic solvents (with different dielectric constants) via one-step grafting of PIL onto CNFs (PIL@CNF). The PIL@CNF hybrids are then exemplarily applied to reinforce the

mechanical properties of porous PIL membranes. The overall synthetic scheme is illustrated in Fig. 1.

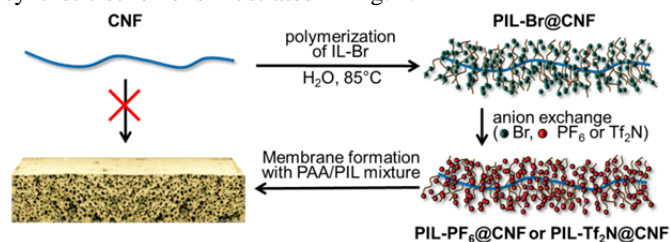


Fig. 1. Synthetic route to CNF-reinforced porous PIL membrane via one-step surface grafting of PIL onto CNF (IL-Br: ionic liquid monomer with Br⁻ anion).

CNFs were first sonicated in water to reach a suspension of untangled fibers. PIL chains were grafted onto the negatively charged surfaces of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl)-oxidized CNFs, by *in situ* polymerization of an ionic liquid, 1-ethyl-3-vinylimidazolium bromide (IL-Br) in water (at a weight ratio of IL-Br:CNF=40:1, $c_{CNF} \sim 0.05$ wt%). A gel-like state was reached during polymerization. After polymerization the hybrids were purified to remove the free polymer and were concentrated (to 0.1 wt% of CNF) by ultrafiltration (pore size: 50 nm) using water as eluent. We confirmed by atomic force microscopy (Fig. S1, Supplementary Information) that the bundle-free fiber morphology of CNFs is well-preserved after the polymerization and no degradation of the fibers due to their dissolution in reaction media occurred. Moreover, Fourier transform infrared spectroscopy (FTIR) was used in order to confirm the co-existence of PIL-Br and CNFs in the hybrid material (PIL-Br@CNF). The spectra (Fig. 2 A) show peaks at 1050 cm⁻¹ (C-O stretching vibration of CNF), at 1160 and 1550 cm⁻¹ (C-N stretching of imidazolium rings and ring in-plane asymmetric stretching, CH₂(N) as well as CH₃(N)CN stretching vibrations, respectively), which verifies the presence of both components in the hybrid product.³⁷

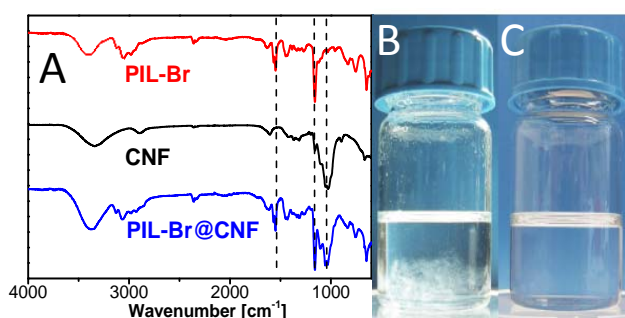


Fig. 2. A) FTIR spectra of PIL-Br, CNF and PIL-Br@CNF hybrid; Photos of dispersions of B) CNF and C) PIL-PF₆@CNF hybrid in acetone.

The successful grafting of PIL on the surface of CNFs expands the hydrodynamic radius and inverts the surface charge of CNFs. Dynamic light scattering measurement proves that the size of the CNFs increases from 500 to 700 nm after grafting of PILs. Zeta potential measurements verified that negatively charged CNFs (-45.4 ± 4.7 mV) became positive (37.3 ± 4.2

mV) after polymerization. This indicates that a cationic PIL brush layer is created on the CNF surface during the reaction. The CNFs to PIL weight ratio in the hybrid was determined by elemental analysis to be 1 to 2.5 according to the C/N weight ratio. The presence of ca. 70 wt% of PIL in the hybrid confirms the effective growth of PIL onto CNFs via the current one-step grafting method.

Thermogravimetric analysis was conducted to determine the thermal stability of CNFs before and after PIL functionalization. The electrostatic grafting of PIL chains onto the CNF surface does not cause any deterioration in the thermal stability of CNFs (Fig. S2). The temperature needed to create a 10 wt% mass loss of the CNFs is increased by 20°C after grafting of PIL. Furthermore, the residual mass between 330-900°C is higher for PIL-Br@CNF than that of pure PIL but lower than for CNFs, verifying again the presence of both components in the hybrid.

The *in situ* polymerization-introduced stabilization requires no surface pre-functionalization of CNFs. It should be noted that via direct mixing of aqueous solution/dispersion of PILs and CNFs, nondispersible aggregates were formed even upon sonication. This aggregation is caused by electrostatic interaction between these two oppositely charged species. In our *in situ* polymerization route, we suspect that after addition of several monomeric units to the radical, the short polymer chains adsorb onto CNFs due to electrostatic interaction. The short length of oligomeric PIL chains at this step is the reason, why interaction with individual CNF are preferred rather than crosslinking CNFs into an intermolecular network. Due to sorption of short PIL chains, the surface charge of CNFs is first neutralized and then becomes positive with further propagation of the PIL chain polymerization. This induces electrostatic repulsion between particular hybrids as well as between hybrids and free PIL chains in the solution and prevents undesired crosslinking.

The number-average molecular weight (M_n) of the free PIL chains was determined by gel permeation chromatography to be 35 kg/mol (using pullulan standards). It was assumed that M_n of both grafted and free PILs obtained during the *in situ* stabilization of CNFs are comparable, which allows us to roughly calculate grafting density of the polymer chains on CNF surface (detailed information in Supporting Information). The calculated grafting density amounted to 0.15 chain/nm². Thus PIL@CNF hybrid could be considered as moderate density brush.³⁸

One reason for grafting PILs onto CNFs is to control and enable the dispersibility of CNFs in a wide range of organic solvents via the well-known anion-effect of PILs.^{28, 39} For example, Br⁻ anions in PIL-Br@CNF were exchanged to hydrophobic PF₆⁻ and TF₂N⁻ anions in order to form PIL-PF₆@CNF and PIL-TF₂N@CNF hybrids, respectively. The dispersibility tests of the anion-exchanged hybrids were performed and summarized in Table 1. The PIL-Br@CNF hybrid is dispersible in water but only partially in DMSO. The PIL-TF₂N@CNF hybrid is hydrophobic and only dispersible in DMSO. Interestingly, the PIL-PF₆@CNF hybrid is fairly

dispersible not only in DMSO but also in acetone and methanol, which are poor solvents for pure, unmodified CNFs (Fig. 2 B, C). Hence, without changing the polymer backbone type, the hybrid can be dispersed in a range of solvents, showing that PIL grafting can produce an omnidispersible material.

Table 1. Dispersibility tests of CNF and PIL@CNF hybrids with different anions in various solvents.

Material	Water	MeOH/ EtOH	DMSO	Acetone
CNF	+	-	+	-
PIL-Br@CNF	+	-	+/-	-
PIL-PF ₆ @CNF	-	+	+	+
PIL-TF ₂ N@CNF	-	-	+	-

The tunable dispersibility of the hybrid in organic solvents together with high charge density of this novel material open new application possibilities for CNFs, such as in enhancing the mechanical strength of polyelectrolyte-based materials. In this work, we examined the effect of mechanical reinforcement by incorporating PIL@CNF hybrids into porous PIL membranes, prepared via electrostatic complexation triggered by aqueous ammonia.³⁶ For the membrane preparation, the PIL-PF₆@CNF hybrid was added to a mixture of PAA and poly(1-cyanomethyl-3-vinylimidazolium PF₆) in DMSO to form a stable dispersion. This mixture was then cast onto a glass plate, dried and immersed in aqueous ammonia to form a CNFs-reinforced porous membrane. Details on the pore formation mechanism can be found in our previous report.³⁶ As shown in the scanning electron micrographs (SEM) (Fig. 3), three-dimensionally connected porous structures were formed in both CNF-free and CNF-containing membranes. The CNF-free membrane and the reinforced membrane display a two-zone morphology (see white lines in Fig. 3A, 3C) consisting of a top zone with micropores and a bottom bulk zone with pores of 150 ± 50 nm for the CNF free (Fig. 3B) and 250 ± 40 nm for the reinforced membrane (Fig. 3D).

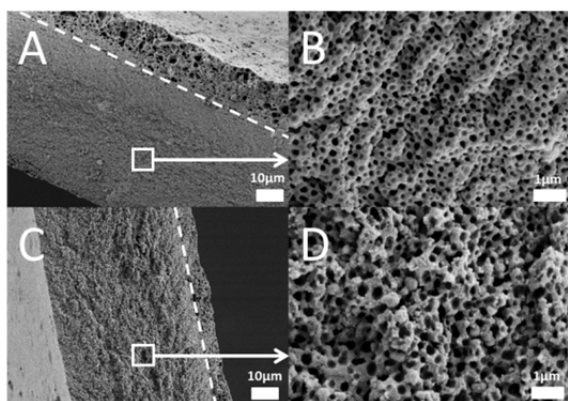


Fig. 3. SEM images of membranes containing: A,B - 0%; C,D - 5 wt % of PIL-PF₆@CNF.

In order to evaluate the reinforcement of the porous membranes by PIL-PF₆@CNF hybrids, the mechanical properties of membranes were tested in the wet state. Thin strips of membrane (14 x 2 x 0.1 mm, n>5) were stressed in tension in a custom-made device. Due to the reinforcement Young's modulus and stress at failure increased from ~470 to ~610 MPa and from ~7.8 to ~10.4 MPa respectively (Fig. S5, Fig. S6). The results show that the incorporated PIL@CNF hybrid, although only 5 wt%, can substantially improve the mechanical performance of the porous PIL membrane. In addition, the reinforced membrane exhibits satisfactory mechanical properties, outrunning stress at failure and Young's Modulus values of comparable porous membranes composed of polyethersulfonate, polysulfone, or other polyelectrolyte complexes (Table S1).

In conclusion, we demonstrated an efficient method for facile functionalization of CNFs by PILs in a simple *in situ* polymerization step. The as-synthesized PIL@CNF hybrids display excellent, tunable via simply anion exchange dispersibility in water and various organic solvents. The omnidispersibility of the PIL-functionalized CNFs enables processing in organic media. Furthermore we could show that the addition of PIL@CNF hybrids substantially reinforces porous PIL membranes. The PIL-functionalisation offers a versatile and facile route to create omnidispersible nanoparticles, which opens new avenues to process new composite materials from previously incompatible components.

Acknowledgements

The authors acknowledge financial support from the Max Planck Society and the Marie Curie Actions of EU's 7th Framework Programme under REA grant agreement no 289347. The authors thank the HINT-COST action MP1202. BW, TP and LB acknowledge the Wallenberg Wood Science Centre for funding. LB also acknowledges the Humboldt foundation for financial support.

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Electronic Supplementary Information (ESI) available: See DOI: 10.1039/c000000x/

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