

Supplementary Information

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

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Instrumentation and Materials

Materials

Potassium hexafluorophosphate (99%) was purchased from Alfa Aesar and used without further purification. Bromoethane (Aldrich 98%), 1-bromobutane (99%, Sigma-Aldrich), lithium bis(trifluoromethylsulfonyl) imide (99%, Io-li-tec), sodium tetrafluoroborate (98%, Sigma Aldrich), 1-vinylimidazole (Aldrich 99%) and 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (Wake Chemicals) were used as received. Poly(acrylic acid) (PAA, solid powder, MW=1800 g/mol) was purchased from Sigma-Aldrich. 1-Cyanomethyl-3-vinylimidazolium bromide (CMVImBr), and 3-ethyl-1-vinylimidazolium bromide was synthesized according to our previous methods (Chem. Mater. 2010, 22, 5003–5012 and ACS Macro Lett., 2012, 1 (1), 84–87) (Figure S3). Poly(3-cyanomethyl-1-vinylimidazolium hexafluorophosphate (PCMVImPF₆) was prepared by anion exchange of PCMVImBr (Figure S4) with KPF₆ salt in aqueous solution. Green muscovite mica obtained from AXIM Enterprises (New York, US) was used in the AFM (Atomic Force Microscopy) studies. Polyethylenimine (PEI) with a molecular weight of about 60 000 g/mol (supplied by Arcos organics, US) was used as received. All used solvents were of analytic grade. TEMPO oxidized cellulose nanofibers (CNFs) were obtained from a defibrillation process of soft wood pulp. [Wågberg, L. et al. The Build-Up of Polyelectrolyte Multilayers of Microfibrillated Cellulose and Cationic Polyelectrolytes. Langmuir 24, 784-795 (2008).] In brief, an aqueous suspension of pulp from Norwegian spruce was subjected to an enzymatic pre-treatment to liberate wood fibers followed by a TEMPO-mediated oxidation step to render carboxylated fibers (600 mmol/g charge). Subsequent subsection of the fibers to mechanical disintegration using a high-pressure microfluidizer equipped with a 100 µm chamber (Microfluidizer M-110EH, Microfluidics Corp., USA) provides fully defibrillated cellulose nanofibers. This mechanical treatment renders a highly viscous CNF

dispersion with a concentration of about 1 wt%. The CNFs are long and flexible fibers with a thickness of 5 nm and 1-2 μm in length (Figure S1A).

Instrumentation

Proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were recorded at room temperature using a Bruker DPX-400 spectrometer operating at 400.1 MHz. $\text{DMSO-}d_6$ was used as a solvent for all measurements.

Thermogravimetric analysis (TGA) experiments were performed under nitrogen flow at a heating rate of 10 K min^{-1} using a Netzsch TG209-F1 apparatus.

Elemental analysis was accomplished as a combustion analysis using a Vario Micro device. Fourier-transform infrared (FT-IR) spectroscopy was performed at room temperature with a BioRad 6000 FT-IR spectrometer equipped with a Single Reflection Diamond ATR. The determined C/N ratio of PIL-Br@CNF hybrid was 4.23. Moreover, it was confirmed that CNFs do not contain nitrogen ($<0.05\text{ wt}\%$). For the calculation of the amount of grafted polymer, C/N for the hybrid material was compared with the theoretical C/N value for pure PIL-Br polymer. The calculated weight ratio of grafted PIL-Br to CNFs was 2.45:1.

Scanning electron microscopy (SEM) was performed on a GEMINI LEO 1550 microscope at 3 kV acceleration voltage.

Gel permeation chromatography (GPC) was performed using TSK Gel Guard (50 x 7.5mm) + 6000 + 5000 + 4000 + 3000 (300x7.5mm, 10 μm) column with 0.2M Na_2SO_4 + 1% acetic acid solution in water (flow rate 1.00 mL/min, Pullulan PSS Polymer Standard Service 0.342kD – 710kD, equipped with UV-Detector Spectra System UV 2000 and double detector WGE SEC-3010).

Dispersibility tests were performed by mixing 20 mg of CNFs or PIL@CNF hybrids with 10 mL of different solvents followed by sonication for 30 sec using an ultrasonic finger at 50% of full amplitude.

Branson Digital Sonifier model W450D was used for further sonication treatment. A microtip (1/8'' in diameter) was immersed in the dispersion and the sonifier was run at different amplitudes. Dispersions were cooled in an ice bath during the whole process.

Tensile tests were performed using a custom-made instrument equipped with a video extensometer. For this purpose membrane strips (2 mm wide, 60-140 μm thick and around 2.5 cm long) were glued onto metal plates (distance between metal plates was in the range 1.3-1.5 cm), which were fixed on the tensile tester by a pin and hole assembly to allow for sample alignment in the strain direction during the tensile test. Samples were kept in the wet state during whole process of sample preparation as well as during stress/strain measurement.

Atomic Force Micrographs were taken using Nanoscope MultiMode 8 atomic force microscope (Bruker, Santa Barbara, CA) equipped with an E-scanner operating in tapping mode using a Tap150 cantilever (Bruker, Camarillo, CA). As substrate, freshly cleaved mica was used immersed in 0.02% sample solution, 10 sec for the PIL-Br@CNF hybrids and for the CNF the mica was first immersed into 0.01g/dm³ PEI for 1 second and after water rinse, immersed 60 seconds in CNF (0.02 % w/w) and, then rinsed with water and blown dry with a flow of filtered nitrogen gas.[ref, Ali Naderi, Tom Lindström, Torbjörn Pettersson, Cellulose, 2014, accepted for publication (manuscript number CELS-D-14-00070R1)] All measurements were performed in air at room temperature.

Experimental Details

In situ stabilization of CNFs and the anion exchange

10 g of 1 wt% CNF dispersion was diluted with 40 mL of water and sonicated using an ultrasonic horn (10 minutes of active working at 10% of full amplitude, 3 sec on/3 sec off cycles, followed by 10 minutes of active working at 50% of full amplitude, 3 sec on/3 sec off cycles). Afterwards, additional 120 mL of water were added and the dispersion was sonicated for another 10 min. (at 50% of full amplitude, 3 sec on/3 sec off cycles). During sonication the sample was cooled in an ice bath. 4.0 g of monomer (19.70 mmol of 1-ethyl-3-Vinylimidazolium bromide) was dissolved in 20 mL of MiliQ® water and 80 mg (0.277 mmol) of VA86 initiator solution in 10 mL of water were added dropwise to vigorously stirred CNF dispersion. Dispersion was charged into a 250 mL Schlenk flask followed by 5 cycles of degassing – filling with argon. The polymerization reaction was carried out under argon at 85 °C for 20 h. The product was purified by the ultrafiltration method (filters with 50 nm pores). For the anion exchange, one batch of stabilized CNF dispersion (amount of 100 mL of suspension) was dispersed using an ultrasonic horn (10 minutes of active working at 50% of amplitude, 3 sec on/3 sec off cycles) and 400 mg of KPF_6 (2.17 mmol) solution in 50 mL of water or 624 mg (2.17 mmol) of LiTF_2N solution in 50 mL of water was added dropwise into vigorously stirred CNF suspension. The mixture was stirred for 1 hour and purified by ultrafiltration (filters with 50 nm pores).

Membranes preparation

1.0 g of PCMVImPF_6 PIL was dissolved in 9.0 g DMSO. 2.58g of poly(acrylic acid) (PAA) (MW: 1800 g/mol) was dissolved in 10.0 g of DMSO. 1.258 g of PAA solution was added to PIL solution and stirred for 1 h. Then 1.5 g of the solution was cast onto a clean glass plate. The liquid film on the glass slide was dried in air at 80°C for 3h, and soaked in 0.2 wt% aqueous ammonia (pH=10.8,

20°C, 2 h). After 2 h, a yellowish and flexible freestanding membrane was easily detached from the glass surface and washed with demineralized water.

Reinforced membranes were prepared in a similar manner, but in the first step 1.0 g PCMVImPF₆ PIL was dissolved in DMSO followed by addition of 63 mg of PIL-PF₆@CNF hybrid dispersed in a stock solution in DMSO (the concentration of PIL-PF₆@CNF hybrid in the stock solution was determined by TGA measurement) and tuning the overall amount of DMSO to 9.0 g. Then 1.258 g of PAA solution was added and mixture was dispersed using ultrasonic horn (10 minutes of active working, 50 % of full amplitude in 3 sec. on/3 sec. off cycles). During sonication mixture was cooled down in an ice bath.

Characterization of free-standing polymer

For the characterization of free-standing polymer, the filtrate obtained from ultrafiltration process was concentrated using a rotary evaporator and dried for 24 h at 40°C. Afterwards, the number-average molecular weight (M_n) and polydispersity index of the free PIL chains were determined by gel permeation chromatography (using pullulan standards) to be 35 kg/mol and 1.5 respectively.

Calculation of grafting density

In the first step, surface area of CNFs in the sample of PIL-Br@CNF hybrid material (of weight m ; $m = m_{CNF} + m_{PIL}$; according to elemental analysis $m_{PIL} = 2.45 \cdot m_{CNF}$) was calculated according to the following equation:

$$A = \frac{2 m_{CNF}}{\rho \cdot r}$$

Where A is the surface area of CNFs, m_{CNF} the weight of the CNFs in the sample of hybrid material, ρ the density of nanocellulose (1.45 g · cm⁻³), and r is the radius of CNFs (5 nm, the value obtained from AFM image - Figure S1 A)

Then grafting density (σ) was calculated according to the following equation:

$$\sigma = \frac{2.45 \cdot m_{CNF} \cdot N_A}{A \cdot Mn} = 0.15 \text{ [chains} \cdot \text{nm}^{-2}\text{]}$$

Where $2.45 \cdot m_{CNF}$ is the weight of PIL-Br in the sample of PIL-Br@CNF hybrid material, N_A is the Avogadro number and Mn the number average molecular weight of PIL-Br

Figures and table

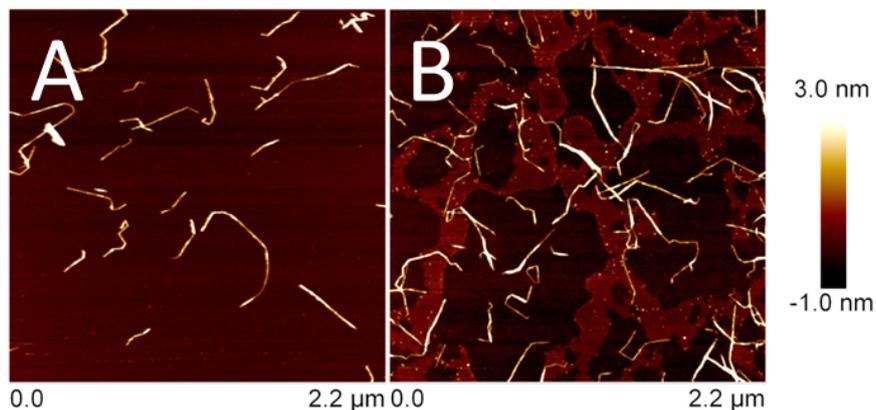


Figure S1. AFM height images of A) CNF; B) PIL-Br@CNF hybrid adsorbed from water suspensions and imaged in dry state.

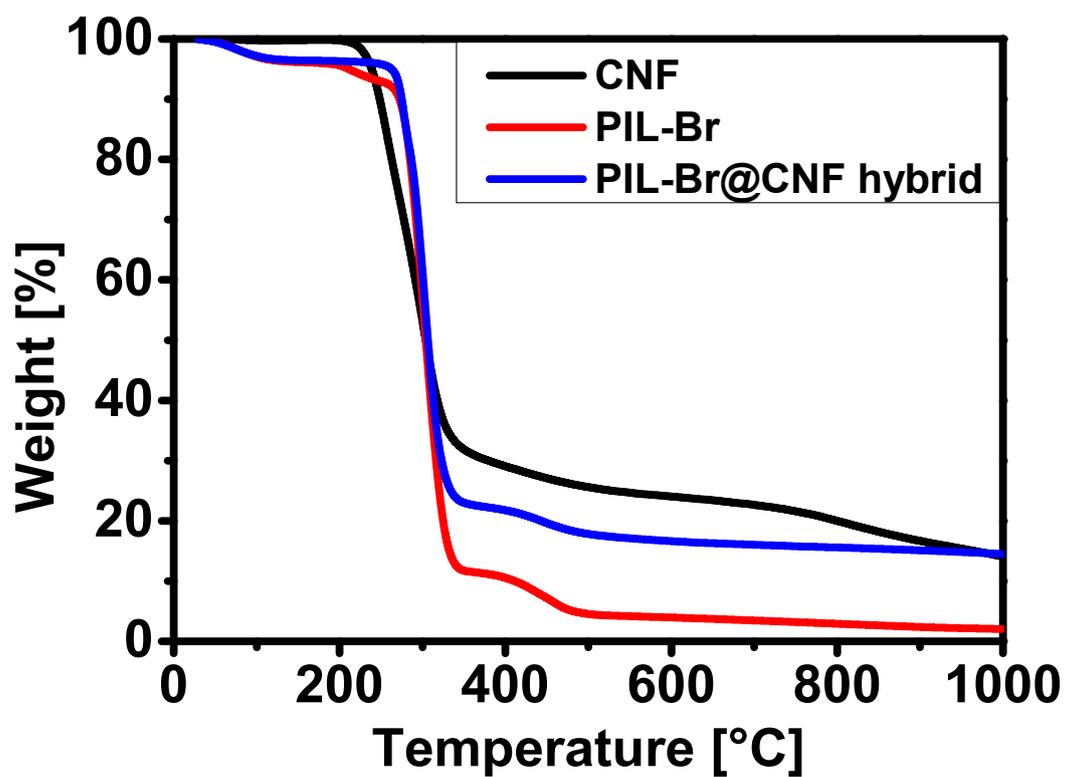


Figure S2. TGA curves of CNF, PIL-Br and PIL-Br@CNF hybrid

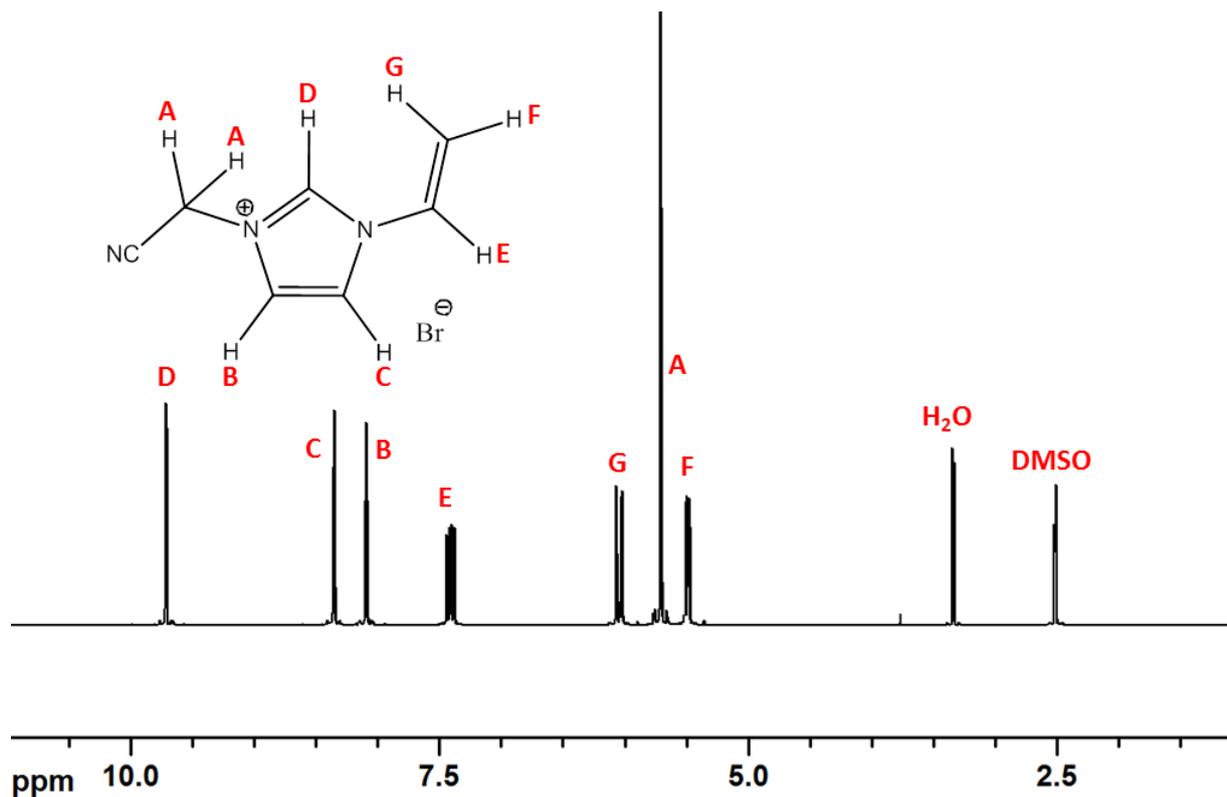


Figure S3. ¹H-NMR spectrum of 1-cyanomethyl-3-vinylimidazolium bromide

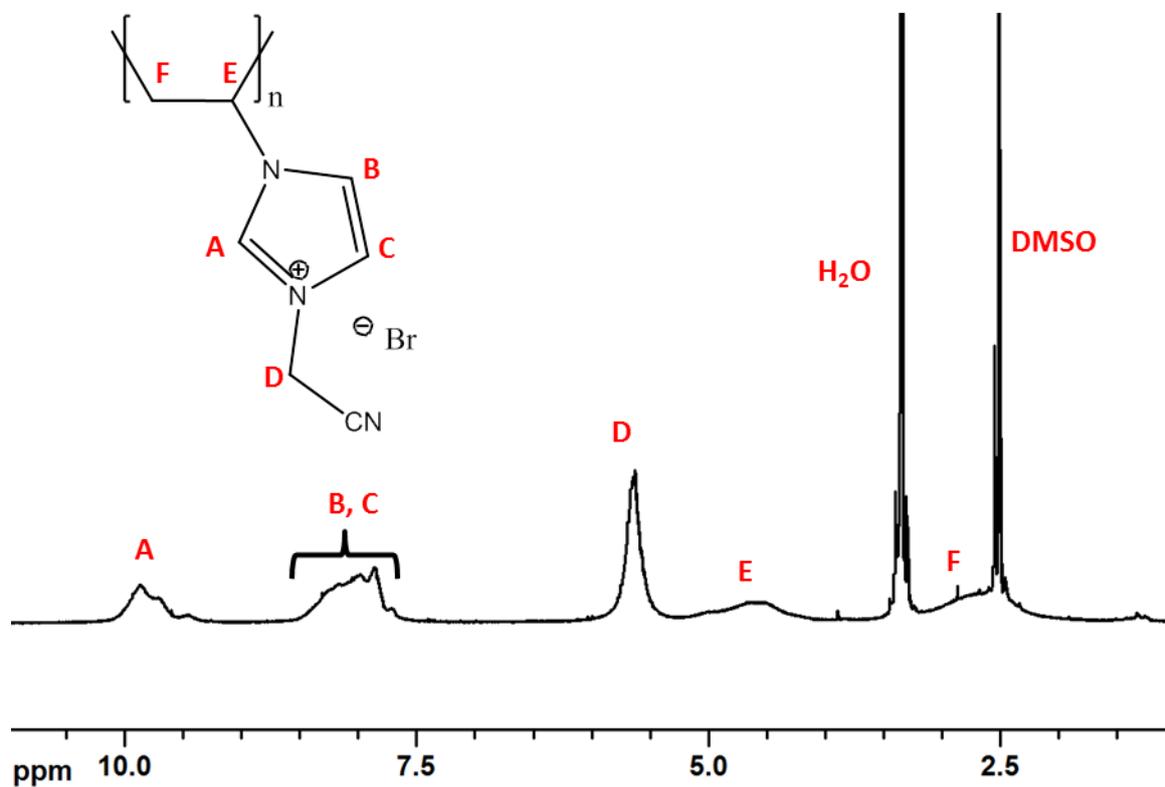


Figure S4. ¹H-NMR spectrum of poly(1-cyanomethyl-3-vinylimidazolium bromide)

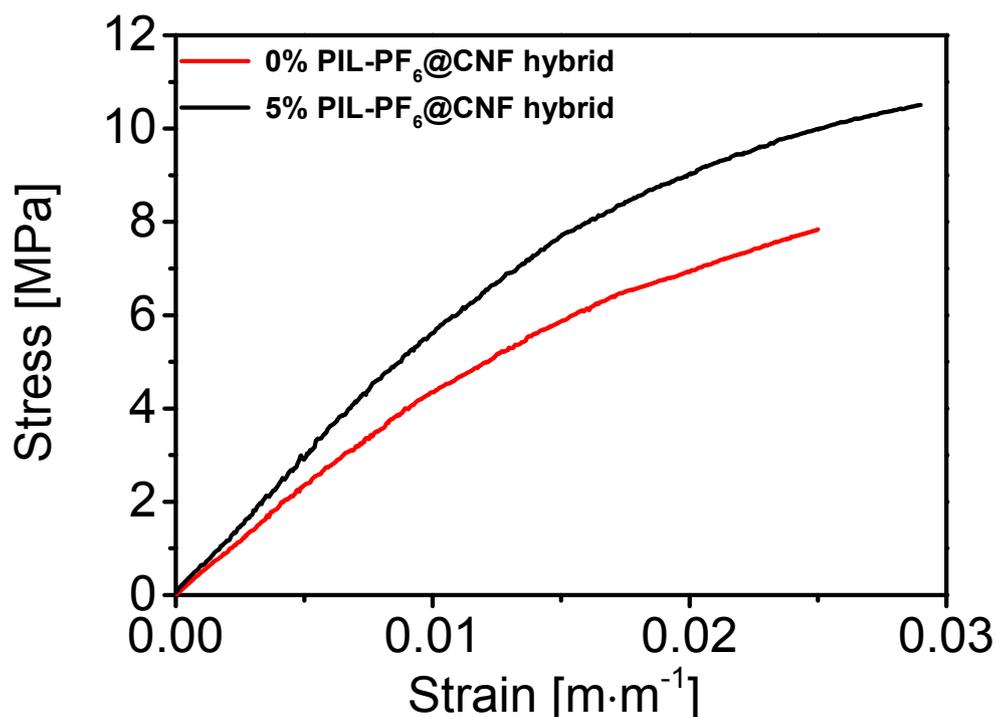


Figure S5. Average stress - strain curves of porous membranes composed of PCMVImPF₆/PAA matrix containing 0 wt% (red line) and 5 wt% (black line) of PIL-PF₆@CNF.

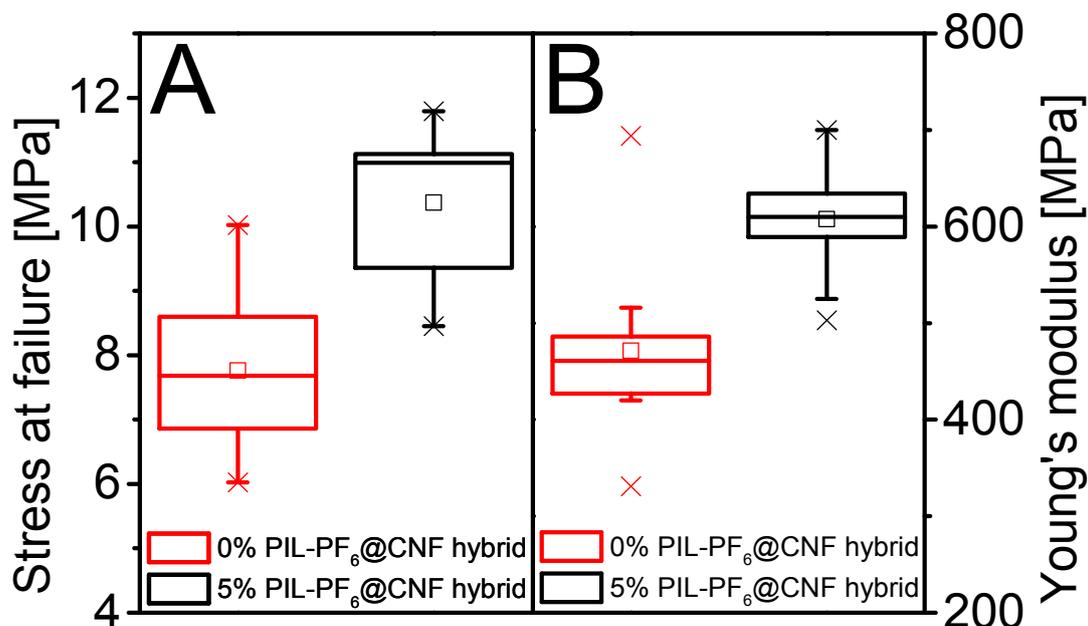


Figure S6. Box plots illustrating the data of the mechanical experiments: (A) stress at failure and (B) Young's modulus of porous membranes composed of PCMVImPF₆/PAA matrix containing 0 wt% (red) and 5 wt% (black) of PIL-PF₆@CNF hybrids (top and bottom lines of the box represent 25th and 75th percentile, medians are shown by the line inside the box, squares inside boxes represent average values, whiskers are 5th and 95th percentile and crosses represent maximum and minimum measured values).

Table S1. Literature values of stress at failure and Young's modulus of selected porous membranes (comparable to ours due to composition – polyelectrolyte complexes or application as supporting membranes)

Polymer	Stress at failure [MPa]	Young's modulus [MPa]
poly(vinyl alcohol) ¹	13.5	48
	4.3	110
Polyvinylidene fluoride ²	7,5	-
	17,7 (at 10% of porosity)	-
polyethersulfone ³	6.97 ± 0.23	228.30 ± 49.56
	5.88 ± 0.27	273.80 ± 21.58
polysulfone ⁴	6.04	194.9
poly(diallyldimethylammonium)-poly(styrene sulfonate) complex ⁵	6.0	-
cellulose acetate +poly(ether-ether-sulfone) ⁶	4.87	247.30
Chitosan-Alginate complex ⁷	1.54	-

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