SUPPORTING INFORMATION

Conducting, self-assembled, nacre-mimetic polymer/clay nanocomposites

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1. Materials

High conductivity grade poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) ("PEDOT:PSS") was purchased from Sigma Aldrich as an aqueous surfactant-free dispersion with 1.1 wt% polymer and was used as received.

Poly(*N*-ethyl-3-vinylimidazolium dicyanamide) (PIL) with an apparent molecular weight $M_n \approx 14$ kg/mol was synthesized by free radical polymerization. In detail, 5 g of IL monomer *N*-ethyl-3-vinylimidazolium dicyanamide and 100 mg of initiator VA86 were dissolved together in 50 mL of water. After removing the air by vacuum and back-filling the bottle with argon, the reactor was placed in an oil bath at 85 °C for overnight. After cooling down, the mixture was precipitated twice in THF. After drying at 60 °C under vacuum till constant weight, 3.5 g of polymer product was obtained. The PIL with a higher apparent molecular weigh $M_n \approx 78$ kg/mol was synthesized by cobalt-mediated radical polymerization (CMRP) of *N*-ethyl-3-vinylimidazolium bromide in water according to a procedure reported elsewhere (Cordella et al. ACS Macro Lett., 2014, 3 (12), 1276–1280). Briefly, *N*-ethyl-3-vinylimidazolium bromide was polymerized by an organocobalt(III) complex (R-$(CH_2$-CHOAc$)_{<4}$-Co$(acac)_2$; R = primary radical from the decomposition of V70) in water until high monomer conversion (96 %) at 30 °C. The polymerization was then quenched by the addition of a solution of TEMPO in tetrahydrofuran. The polymer was finally purified by dialysis in water (dialysis membrane: Spectrapor MWCO 1000 Da) before lyophilisation.

To replace bromide by dicyanamide as the anion, 1 g of poly(1-ethyl-3-vinylimidazolium bromide) was dissolved in 100 mL of Milli-Q water and 4.4 g of sodium dicyanamide (dicyanamide/Br molar ratio 10/1) were added. The mixture was stirred for 30 min. The polymer precipitates stick to the glass wall and the clean solution was decanted. The polymers were then directly re-dissolved in 100 mL of water. This procedure was repeated for 5 times to complete the anion exchange. The polymers were finally dissolved in Milli-Q water as 1.0 wt% solutions for preparation.

Synthetic Sumecton nanoclay was donated by Kunimine Industries and used as received. The cationic exchange capacity is CEC = 0.71 – 0.99 meq/g. Platelet thickness of 1 nm and aspect ratio of 140 were determined by statistical image analysis using scanning electron microscopy.

2. Methods

Sumecton nanoclay dispersions were prepared as 0.5 wt% mixtures in Milli-Q water and strongly stirred overnight. The resulting suspensions were then sedimented overnight. After discarding the sediment, dispersions of 0.4 - 0.5 wt% Sumecton (determined via gravimetry) were obtained.

To prepare the nanoclay/polymer core/shell nanoplatelets, the nanoclay dispersion was slowly added to a strongly stirred polymer solution until a weight ratio of 33/67 clay/polymer was achieved. After stirring for 1 h, excess polymer was removed through centrifugation at 10 000 rpm and redispersion of the resulting sediment. This core/shell nanoplatelet dispersion was then degassed in a rotary evaporator, cast into petri dishes and dried at 50°C overnight to obtain nacre-mimetic nanocomposite films.

3. Analysis

Size exclusion chromatography (SEC) was carried out in aqueous buffer solution of sodium acetate (0.1 M) with 20 % of methanol (flow rate: 1 mL min-1) at 25 °C on a Thermo-Fischer-Scientific p-100 equipped with a UV-detector UV-2000 and a Wyatt RI detector optilab-DSP-Interferometric

refractometer, and a NoVEMA column (300 mm x 8 mmx 10 µm). Poly(ethylene glycol) standards were used for calibration.

Field-emission scanning electron microscopy (SEM) imaging was done with a Hitachi S-4800 Field Emission (voltage: 3 kV). Samples were fractured by hand and sputtered with Au/Pt for 30 sec.

Wide-angle X-ray diffraction was conducted using an Empyrean setup from PANalytical. An Empyrean Cu-X-Ray tube LFF HR (line source of 12 × 0.04 mm^2) provided Cu-K_α-radiation with $\lambda = 1.542$ Å at a voltage of 40 kV and a current of 40 mA in Bragg-Brentano parallel-beam geometry.

Elemental carbon analysis was done with an Elementar varioEL.

Mechanical tensile testing was conducted with a DEBEN minitester equipped with a 20 N load cell at a strain rate of 1 mm/min (effective sample dimensions = 10 mm × 2 mm × 20 µm). Humidity was controlled to be 20 %, 60 % and 90 % by conditioning the samples in humidity chambers for 1 day, and measurement was also done in a humidity chamber at the respective humidity.

Electric resistance measurements for films containing PEDOT:PSS were done using a Keithley Model 2400 digital multimeter at a measurement current of 50 µA. The four point probe measurement setup was realized by attaching four steel wires (diameter 0.2 mm) as electrodes collinearly with a probe spacing of 3.5 mm onto 9 mm × 33 mm sample films with silver glue. In order to increase the conductivity, samples were tempered in a vacuum oven at 200 °C for 15 min. Measurement was done at 40% relative humidity after 1 day of conditioning for both thermally treated and untreated nanocomposites. The conductivity σ of the samples was calculated according to the following equation:

$$\sigma = \frac{1}{\rho} = \frac{1}{R} \cdot \frac{\ln\left(\frac{\mathrm{sinhyp}\left(\frac{d}{s}\right)}{\mathrm{sinhyp}\left(\frac{d}{2s}\right)}\right)}{d \cdot \pi} \approx \frac{1}{R} \cdot \frac{\ln 2}{d \cdot \pi}$$

where ρ is the resistivity, R is the measured resistance, d is the sample thickness and s is the electrode spacing on the sample.

Ion conductivity measurements were performed using a Solartron SI1260 Impedance/Gain Phase analyzer and a Solartron SI1287 electrochemical interface (AC amplitude: 200 mV, DC potential versus open circuit: 0 mV, frequency range: 10 MHz to 0.01 Hz). Thin layers of Au/Pd (Au:Pd ratio = 80:20) were deposited on the both sides of the thin film samples (cut into a disc shape with diameters of 6 mm) using BAL-TEC SCD 050 Sputter Coater device. Prior to the measurements, samples were conditioned at 25°C and 50 %RH for at least 24 h inside an ESPEC SH-641 Bench-top Type Temperature & Humidity Chamber. Subsequently, the measurements were performed using a two-electrode set-up at the above-mentioned conditions. The recorded spectra were analyzed using ZView 3.4c software. The conductivity σ was calculated from the resistance R (averaged value of three measurements for each sample) using the following equation:

$$\sigma = d \cdot (A \cdot R)^{-1}$$

where d is the thickness of the sample and A is the surface area of the sample. Thickness of the samples was determined independently for each disc using scanning electron microscopy (GEMINI LEO 1550 microscope at 3 kV acceleration voltage).