

Hierarchical Supramolecular Cross-Linking of Polymers for Biomimetic Fracture Energy Dissipating Sacrificial Bonds and Defect Tolerance under Mechanical Loading

Teemu T. T. Myllymäki^a, Laura Lemetti^b, Nonappa^{a*}, Olli Ikkala^{a*}

^a Department of Applied Physics, Aalto University, P.O. Box 15100, FI-00076 AALTO, Finland.

^b School of Chemical Technology, Aalto University, P.O. Box 16100, FI-00076 AALTO, Finland.

*E-mail: nonappa@aalto.fi, olli.ikkala@aalto.fi

1. Measurements and instrumentation

1.1. FT-IR spectroscopy

FT-IR spectra were measured with a Nicolet 380 spectrometer (Thermo Fisher Scientific) in ATR mode with a 2 cm⁻¹ resolution and averaged over 64 scans.

1.2. NMR spectroscopy

The NMR spectra (¹H and ¹³C NMR) were recorded on a Bruker Avance 400 MHz spectrometer with 5 mm probe at 400.13 MHz for ¹H and 100.62 MHz for ¹³C, respectively. In ¹H NMR measurements, number of scans was 64, a $\pi/2$ pulse length of 6.0 μ s, the flip angle 30°, with recycle delay 2 s, and 64 K data points in time domain was collected which was zero filled to 128 K prior to FT. The reference was set for 2.50 ppm for DMSO-*d*₅ quintet. In ¹³C NMR measurements, number of scans was 2048 and the spectra were processed with line broadening of 1 Hz before Fourier transform and the chemical shifts were referenced to DMSO-*d*₅ sextet (39.50 ppm). Sample was dissolved 5 mg/mL for ¹H NMR measurements and 10 mg/mL for ¹³C NMR measurements.

1.3. Scanning Electron Microscopy (SEM)

SEM images were obtained with Zeiss Sigma VP microscope at 2 kV voltage. The samples were fixed on a SEM pin stub on carbon tape. The samples were coated with Au/Pd under vacuum at 20 mA for 3 minutes prior to imaging.

1.4. Transmission Electron Microscopy (TEM)

TEM images were collected using FEI Tecnai G2 operated at 120 kV in bright field mode. TEM samples were prepared by drop casting dispersion (5 μ L) of the sample on Quantifoil R 2/1 Holey carbon film (Cu 200 Mesh) and the excess solvent was blotted with filter paper and let to evaporate to dry.

1.5. Mechanical testing

Mechanical testing was carried out with Kammrath & Weiss tensile tester. Samples were 2.25 mm wide and either 5 mm or 10 mm long. The thicknesses for evaporated films were between 200-400 μ m and for heat pressed films between 90-200 μ m. From each material, 5-9 samples were measured with elongation speed of 8.35 μ m/s. Films were equilibrated at 50 % humidity for 18 h before tensile testing. Humidity was maintained at 50 % (\pm 2 %) during the measurements.

1.6. Thermogravimetric analysis (TGA)

TGA were measured with TA instruments Q500 device. Samples were heated up to 800 $^{\circ}$ C with 10 $^{\circ}$ C/min heating rate, under nitrogen flow.

2. Experimental

2.1. Materials

All the syntheses were performed in clean and oven dried (120 $^{\circ}$ C) glassware. Reagents and solvents were purchased from commercial sources. 1,6-diisocyanatohexane (98 % purity), dibutyltin dilaurate (DBTDL, 95 % purity), polymers and MWCNTs were obtained from Sigma Aldrich. Technical/Analytical grade solvents (methanol, *N,N*-dimethylformamide) were purchased from Sigma-Aldrich. DMSO-*d*₆ was obtained from Sigma-Aldrich and used as received. Dialyses

were performed using Spectra/Por 7 Standard Regenerated Cellulose tubing (Mw cut-off 2000 Da). Ultrapure deionized water with resistivity of 18 MΩ/cm was used.

The multi-walled carbon nanotubes had following dimensions; outer diameter 10 nm ± 1 nm, inner diameter 4.5 nm ± 0.5 nm and length ~ 3 - 6 μm. These MWCNTs were made by catalytic chemical vapor deposition (CVD) method (CoMoCAT®). After oxidation the length was severely decreased.

Poly(2-hydroxyethyl methacrylate) (pHEMA) was purchased from Sigma Aldrich with two different molecular weights; 2×10⁴ g/mol and 1×10⁶ g/mol.

2.2. Synthesis of 2-(6-isocyanatohexylurea)-6-methyl-4[1H]pyrimidinone (UPy-NCO)

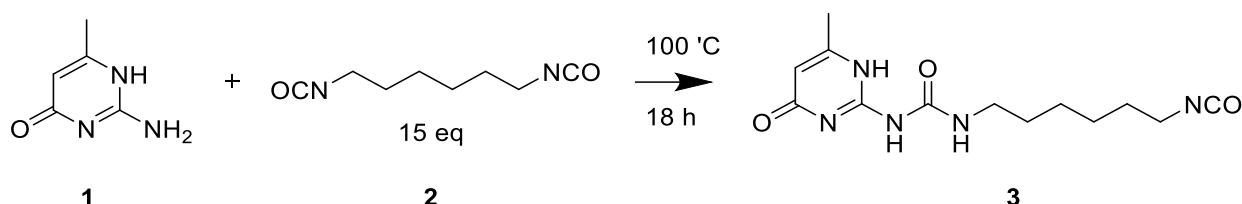


Figure S1. Synthesis of UPy-NCO

UPy-NCO (**3**) was prepared by adding 1.6 g of 2-amino-4-hydroxy-6-methylpyrimidine (**1**) and 18 mL 1,6-diisocyanatohexane (**2**) in a dry 250 mL 2-neck round-bottom flask equipped with stirring, condenser and nitrogen flow. After heating 19 h at 100 °C in an oil bath, the mixture was let to cool to room temperature. Mixture was transferred to 50 mL hexane, filtered with Büchner funnel and washed with 100 mL hexane. Clear white crystals were placed to vacuum oven at 50 °C to dry overnight. Yield: 3.33 g (84 %).

¹H NMR of **3** (400 MHz, CDCl₃): δ 11.86 (s, 1H), 10.19 (s, 1H), 5.81 (s, 1H), 3.28 (m, 4H), 2.23 (s, 3H), 1.63 (m, 4H), 1.40 (m, 4H).

¹³C NMR of **3** (100 MHz, CDCl₃): δ 173.22, 156.73, 154.83, 148.43, 120.55, 106.83, 77.16, 43.02, 39.92, 31.32, 29.45, 26.31, 19.10.

FT-IR of **3** (ATR) ν cm⁻¹: 3308, 2933, 2858, 2258, 1688, 1621, 1516, 1440, 1358, 1253, 1208, 1095, 862.9, 758.1, 660.5.

2.3. Synthesis of p(HEMA-co-UPyMA)

To partially derivatize pHEMA OH groups, 1 g of pHEMA (1 MDa) was dissolved in 40 ml of DMF in a dry 100 ml RB-flask. UPy-NCO was added (224 mg) and the mixture was stirred at 80 °C under nitrogen flow. 100 μ l dibutyltin dilaureate (DBTDL) was added and the mixture was heated at 80 °C for 24 h.

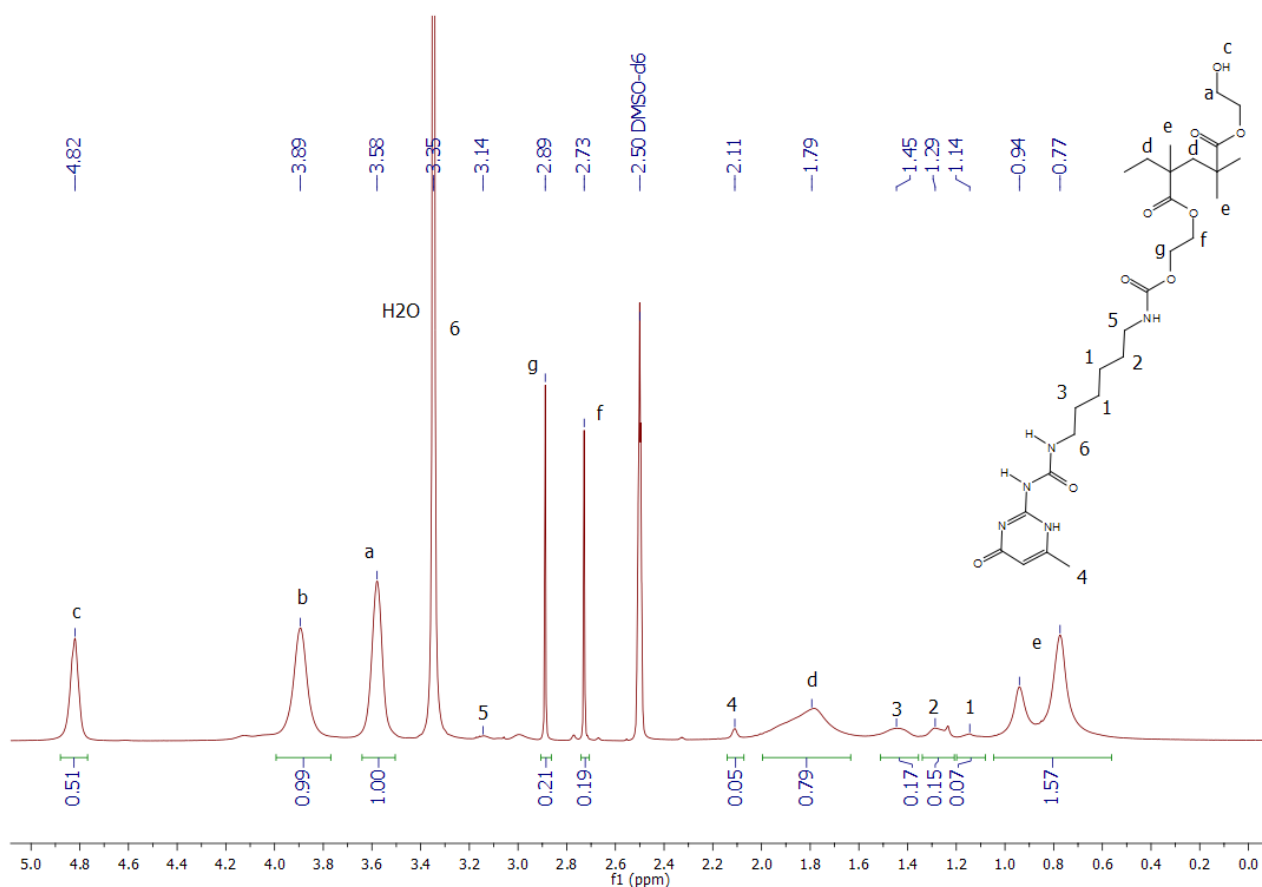


Figure S2. ^1H -NMR of pHEMA-UPy in DMSO- d_6

^1H -NMR of pHEMA-UPy (400 MHz, DMSO- d_6): δ 4.82, 3.89, 3.58, 3.14, 2.89, 2.73, 2.11, 1.79, 1.45, 1.29, 1.14, 0.94, 0.77

Comparing integrals between UPy methyl group (4) and pHEMA backbone protons (a), gives derivatization of 4 % of pHEMA hydroxyl groups with UPy.

FT-IR of pHEMA-UPy (ATR) ν cm^{-1} : 3369 (-OH, polymeric), 2935 (-CH₂-), 1698 (-CO₂-) and (RO-CONH-R), 1652 ((RNH)₂CO), 1557 (RO-CONH-R), 1455 (-CH₂-), 1387 (-CH₃), 1245 (-OH), 1149 (-CO₂-), 1070 (-CO₂-), 1021, 965, 898, 845, 746 (-CH₂-), 518, 471

2.4. Oxidation of MWCNTs

MWCNTs were oxidized with a 1:3 mixture of conc. HNO_3 and conc. H_2SO_4 . 1 g of MWCNTs were weighted in a 250 ml round bottom flask. Mixture of 50 ml conc. HNO_3 and 150 ml conc. H_2SO_4 was poured to the round bottom flask. The flask was equipped with a condenser and the mixture was heated to 80 °C and stirred vigorously. After 3 h the mixture was immediately cooled in an ice-water bath while stirring. The cold mixture was centrifuged and washed with water several times. When the mixture was not separating any more, the mixture was made acidic with HCl and the washing was continued until sulphates were no longer present in precipitation test with BaCl_2 . The ready product was a black viscous dispersion of OxMWCNTs in water. The solids content was 2 % and yield 30 %.

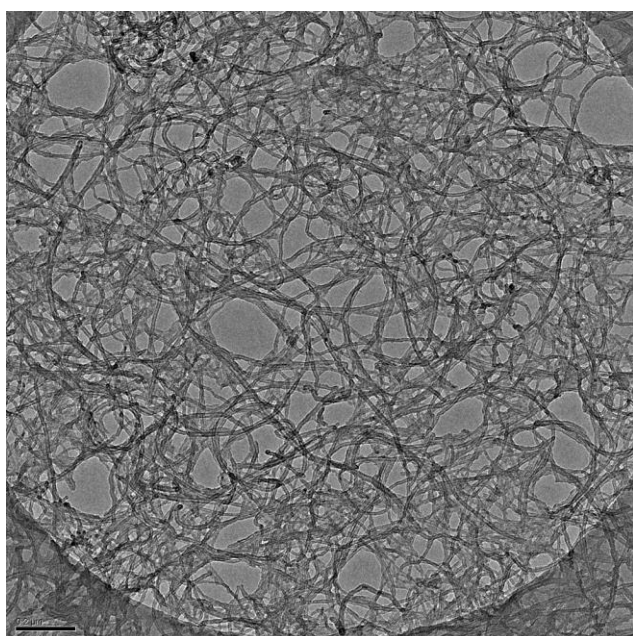


Figure S3. TEM image of oxidized carbon nanotubes dispersed in water

2.5. Synthesis of OxMWCNT-g-UPy

OxMWCNT dispersion in water was dialyzed against DMF for complete solvent exchange. UPy-NCO (100.5 mg) was added to OxMWCNT dispersion (amount of OxMWCNT 70 mg) in DMF while stirring under N_2 atmosphere. DBTDL (50 μL) was added as a catalyst and the mixture was heated to 80 °C for 24 h. Unreacted UPy-NCO and the catalyst were removed by dialysis in DMF.

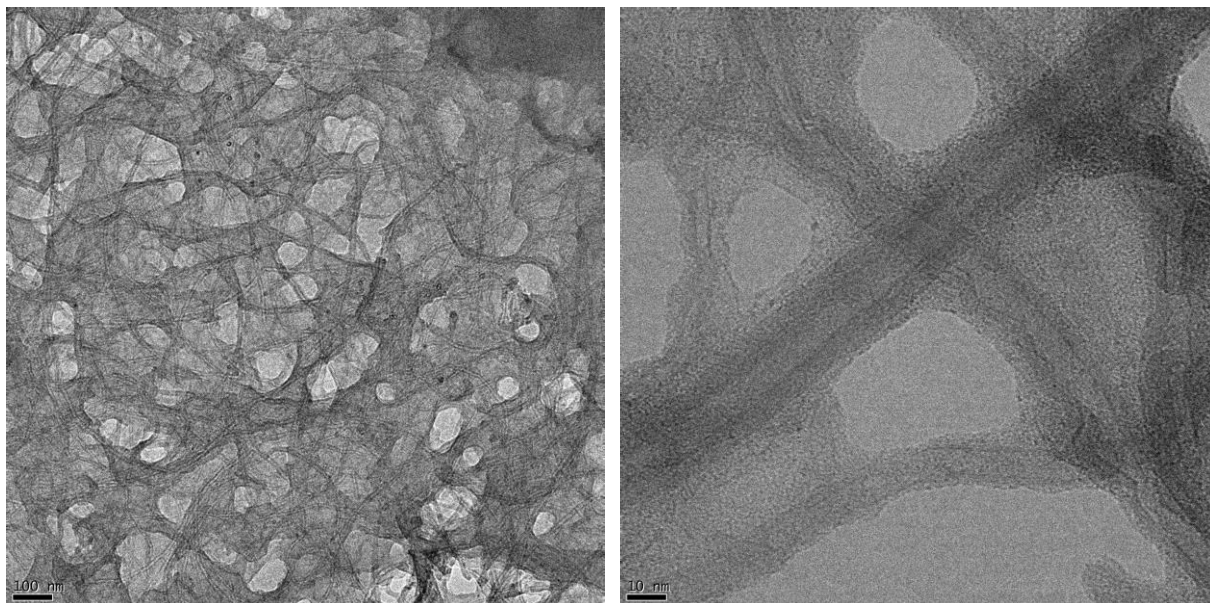


Figure S4. TEM images of a diluted sample of p(HEMA-*co*-UPyMA)/OxMWCNT-*g*-UPy 99/1 wt/wt.

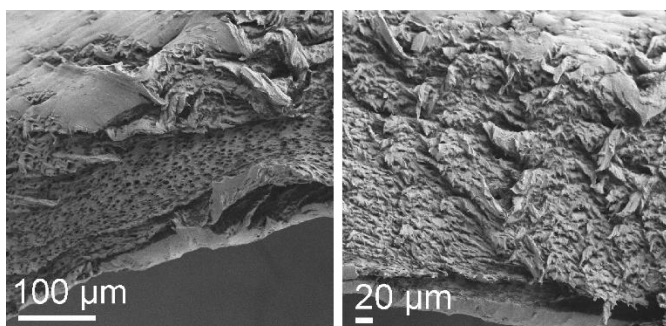


Figure S5. The SEM images of p(HEMA-*co*-UPyMA)/OxMWCNT-*g*-UPy 99/1 wt/wt composition fracture surfaces after fracture during tensile test shows the tortuous, rough surfaces after tensile test.

2.6. Thermogravimetric analysis (TGA)

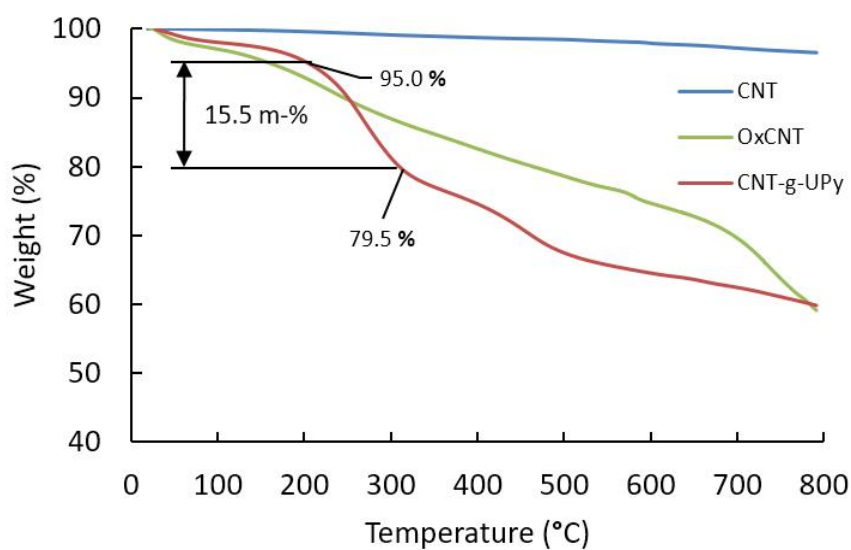


Figure S6. TGA of pristine CNTs, oxidized CNTs and CNT-g-UPy.

The TGA measurements in Figure S6 shows rapid weight loss from 95.0 m-% to 79.5 m-% for CNT-g-UPy, suggesting degradation of UPy from the surface of CNTs, giving 15.5 m-% UPy content on CNT surface.