Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supporting Information

Light-Stimulated Mechanically Switchable, Photopatternable Cellulose Nanocomposites

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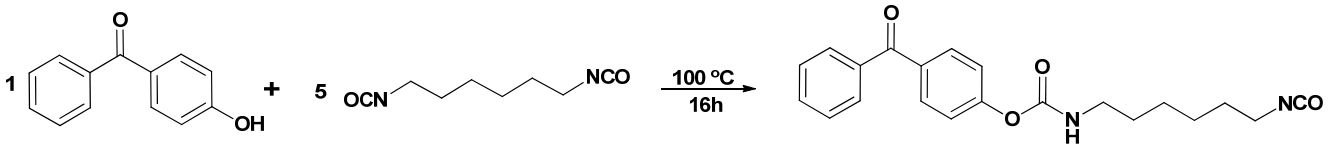
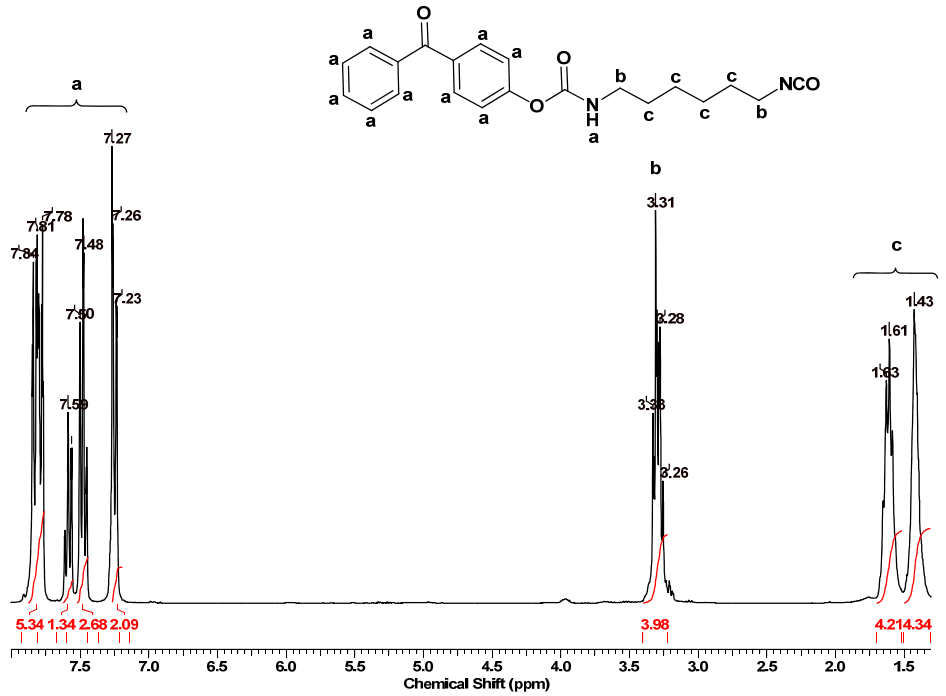
SI-Table 1. Swelling Data of EO-EPI/Bp-CNC nanocomposites before and after exposure to UV light after equilibrium swelling in deionized water for 48 h at 25 °C.

Sample	Swelling before UV irradiation (% w/w)	Swelling after UV irradiation[a] (% w/w)
Neat Bp-CNC film	93 ± 8	63 ± 7
EO-EPI/Bp-CNC 10% w/w	18 ± 3	5 ± 1
EO-EPI/Bp-CNC 20% w/w	20 ± 1	8 ± 1

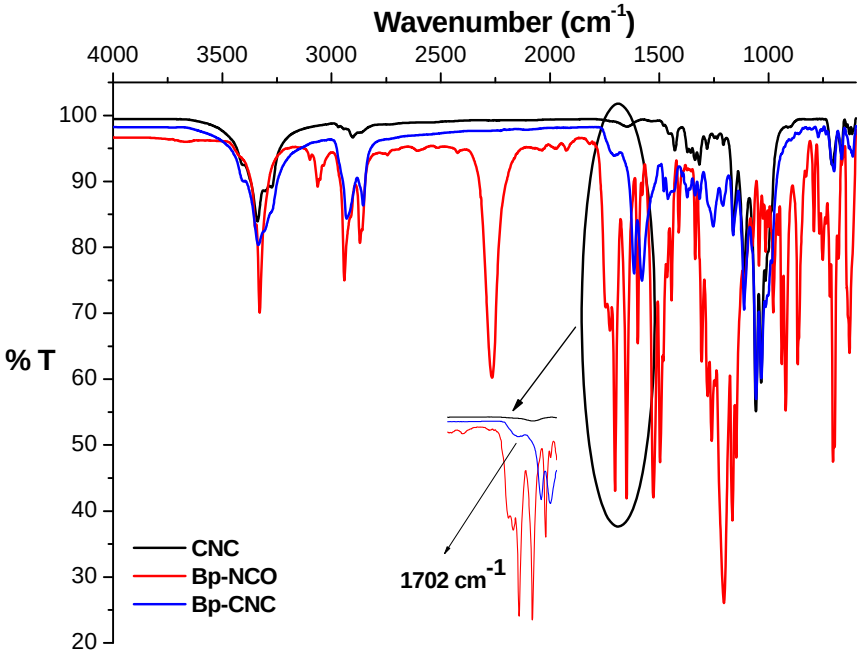
[a]All experiments were performed after 240 min of UV exposure (8W, 365 nm) at room temperature. Data represent averages of N = 4 experiments ± s.d.



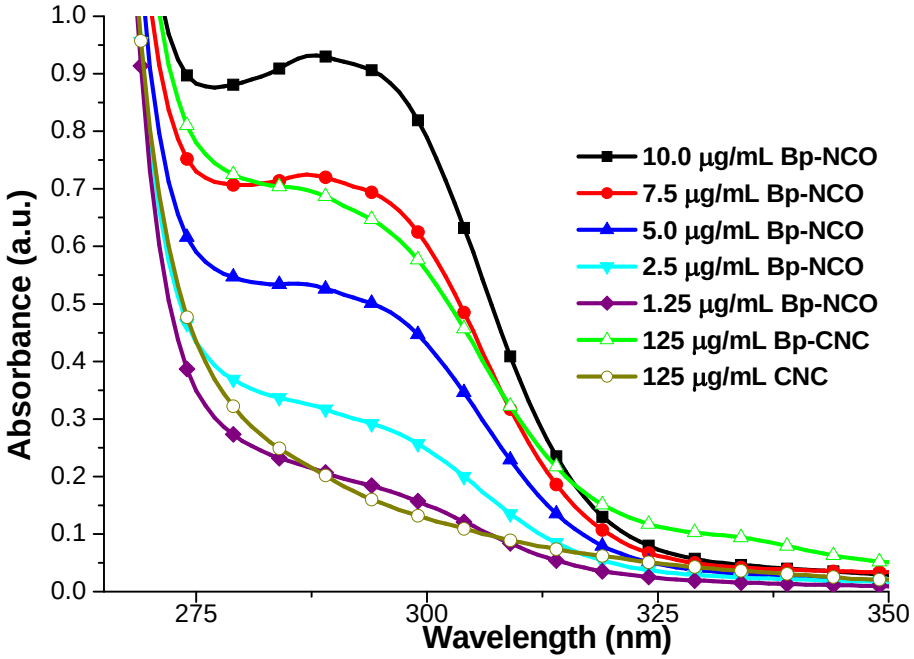
SI-Scheme 1. Reaction of 4-hydroxybenzophenone with hexamethylene diisocyanate.



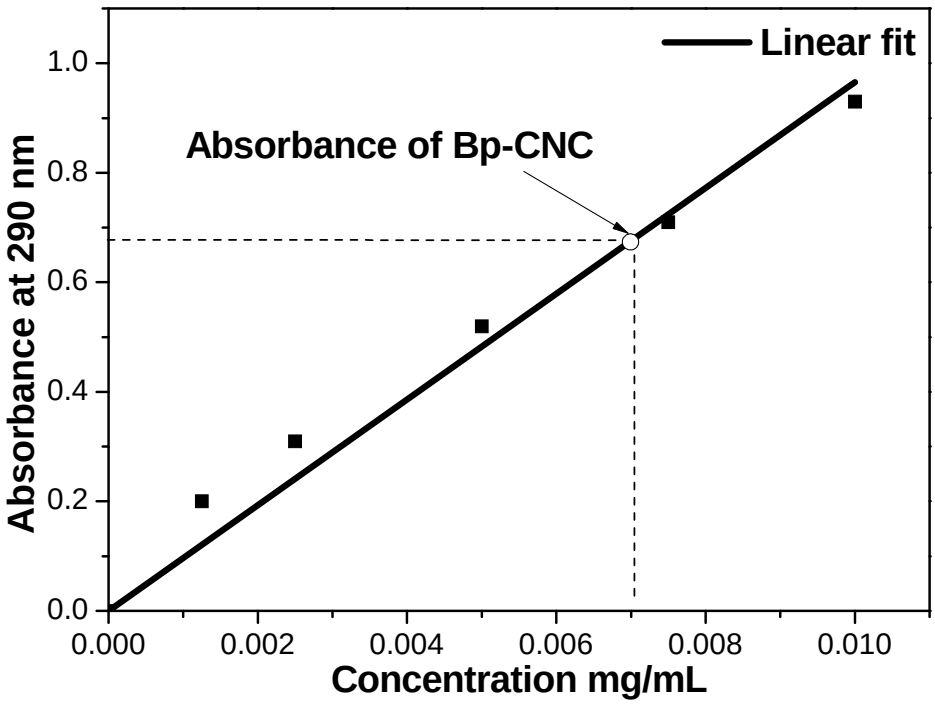
SI-Fig. 1. ^{1}H-NMR spectrum of 4-benzoylphenyl (6-isocyanatohexyl) carbamate (Bp-NCO) in $CDCl_3$.



SI-Fig. 2. ATR FT-IR spectra of unmodified CNCs, Bp-NCO, and Bp-CNCs. The spectrum of Bp-CNCs shows a characteristic peak at 1702 cm^{-1}, which corresponds to the urethane linkage after the reaction with Bp-NCO and is not observed in the spectrum of the neat CNCs. The spectrum also shows an increased transmission in the region of 2800-2950 cm^{-1}, due to alkyl chain vibrations.



SI-Fig. 3. UV-Vis absorption spectra of dispersions of unmodified CNCs, Bp-CNC (125 µg/mL) in DMF and solutions of Bp-NCO in DMF (concentration = 1.25-10 µg/mL). As seen from the spectra, the Bp-CNC and Bp-NCO shows an absorbance with maximum around 290 nm, which is characteristic of the benzophenone derivative; this absorbance peak was absent in the spectrum of the unmodified CNCs.



SI-Fig. 4. Plot showing the absorbance at 290 nm of Bp-NCO solutions as a function of Bp-NCO content (black, filled squares) and of a 125 µg/mL Bp-CNC dispersion (black, open circle). The data were used to determine the level of functionalization of Bp-CNCs.

Calculation for determining the Bp content on the Bp-CNC surface:

From the UV calibration curve of Bp-NCO, we determined a content of 7.2 µg of Bp present in 125 µg/mL of the Bp-CNC dispersion.

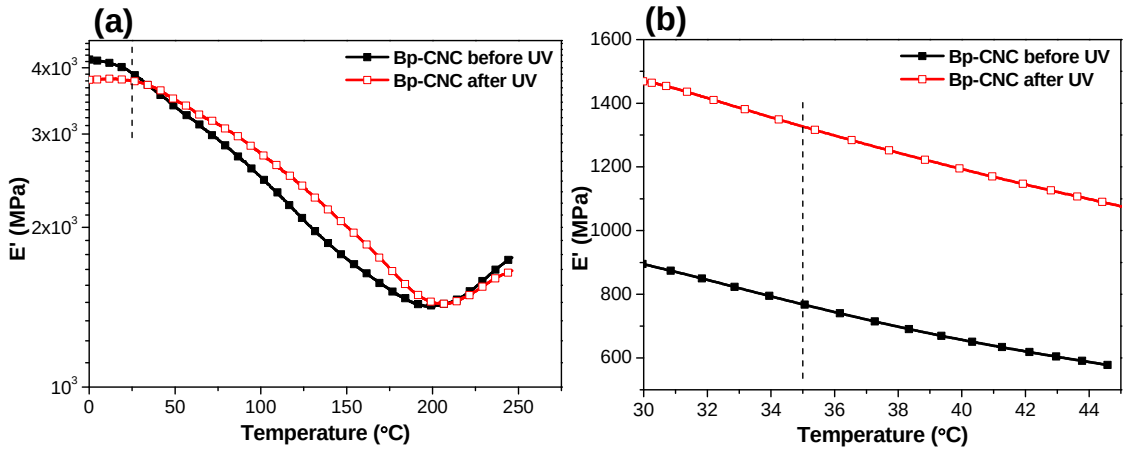
Therefore the amount of benzophenone present in 1 g/L of Bp-CNC = $7.2 \times 10^6 \times 8 = 57.6$ g

Concentration of benzophenone in mmol/kg = 57.6/molecular weight of Bp-NCO×1000

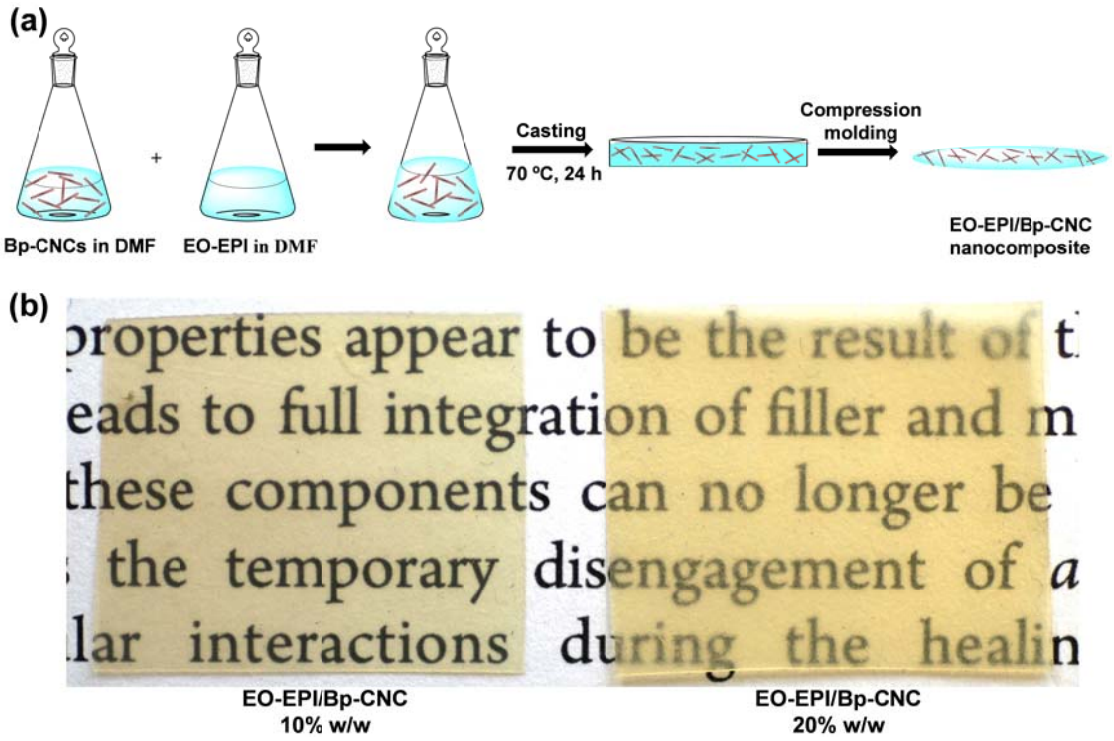
$= 76/366.16 \times 1000$

$= 157$ mmol/kg

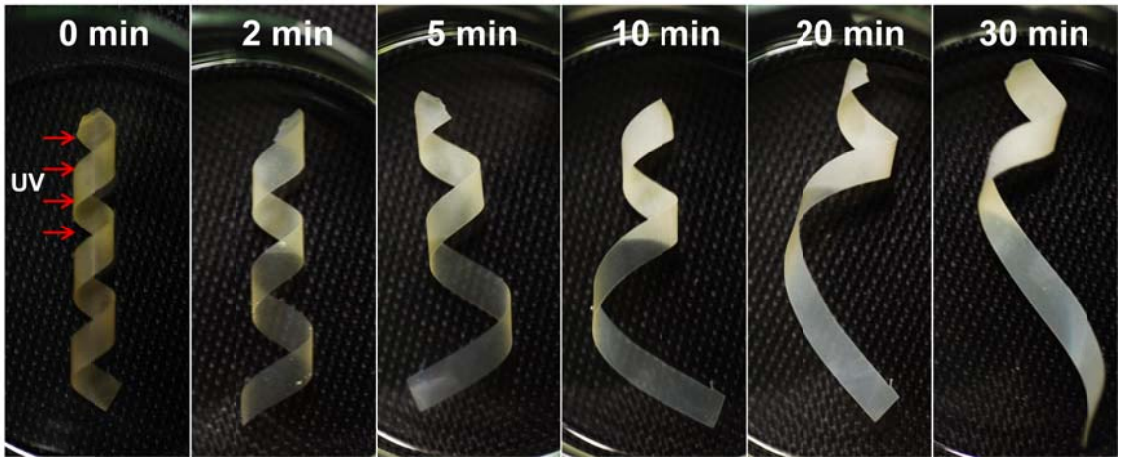
Therefore 157 mmol/kg of benzophenone is estimated for the Bp-CNC.



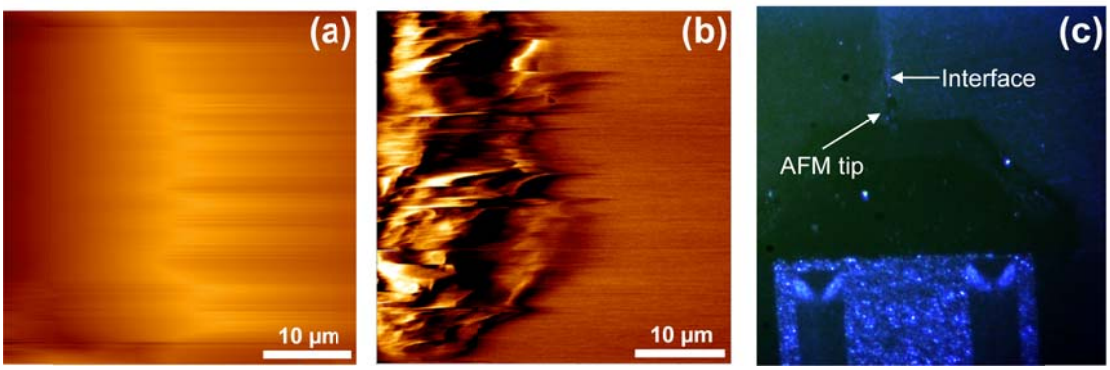
SI-Fig. 5. Dynamic mechanical analysis (DMA) traces of neat Bp-CNC films in the dry (a) and water-swollen (b) state, before (black curves) and after (red curves) exposure to UV light (302 nm, 8 W, 120 min, RT). Shown are plots of the storage modulus *E'* against temperature (note: in (a) Y axis is logarithmic and in (b) it is linear).



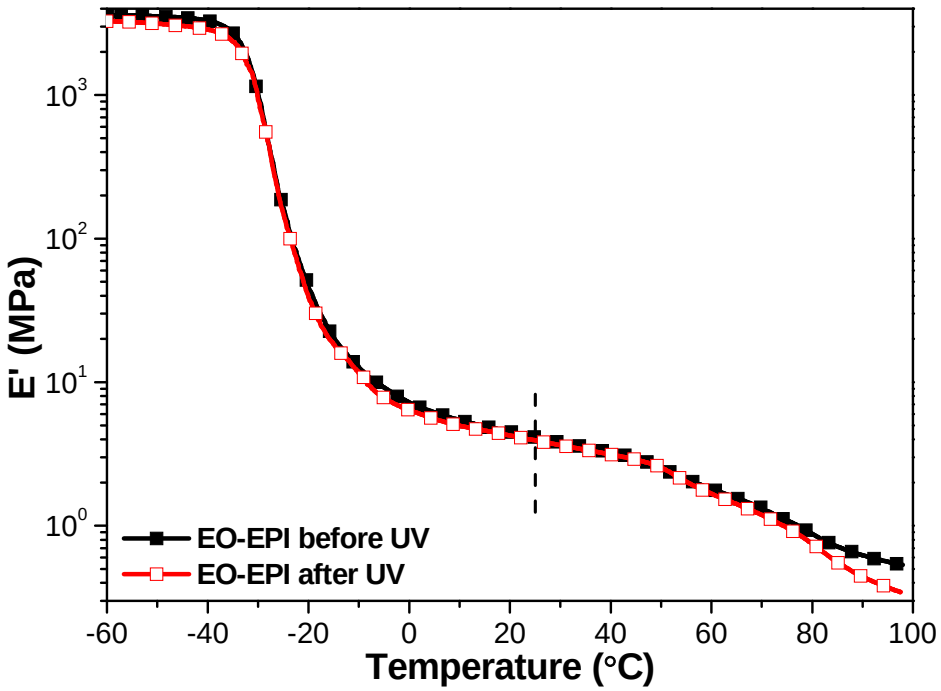
SI-Fig. 6. (a) Schematic representation of the process used to prepare EO-EPI/Bp-CNC nanocomposite films. (b) Pictures of compression-molded films of the nanocomposites.



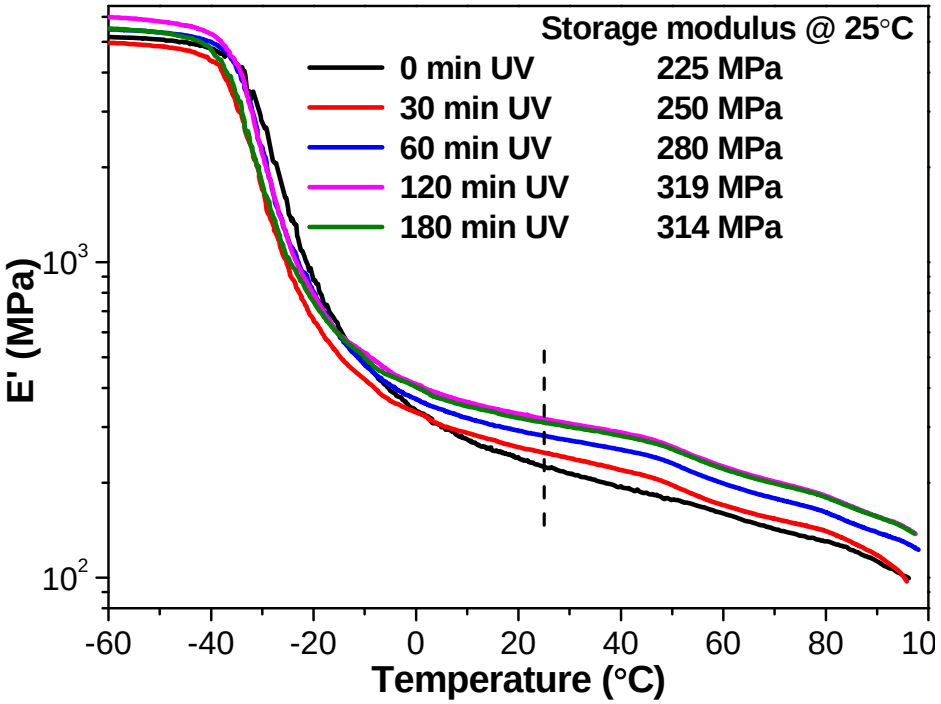
SI-Fig. 7. Pictures of a 10% w/w EO-EPI/Bp-CNC nanocomposite film, demonstrating shape memory and light-activated shape-fixing capabilities of the nanocomposite. The temporary shape shown at t=0 min was programmed by wetting the as-prepared sample, forming it into the desired shape, before drying it. The top half of the coil (a) was then exposed to UV light (302 nm, 8 W, 120 min, RT) while the bottom half was masked with during UV light exposure. The sample was subsequently immersion in water, which triggered relaxation only in the not-irradiated portion as shown in the images for t=2-30min.



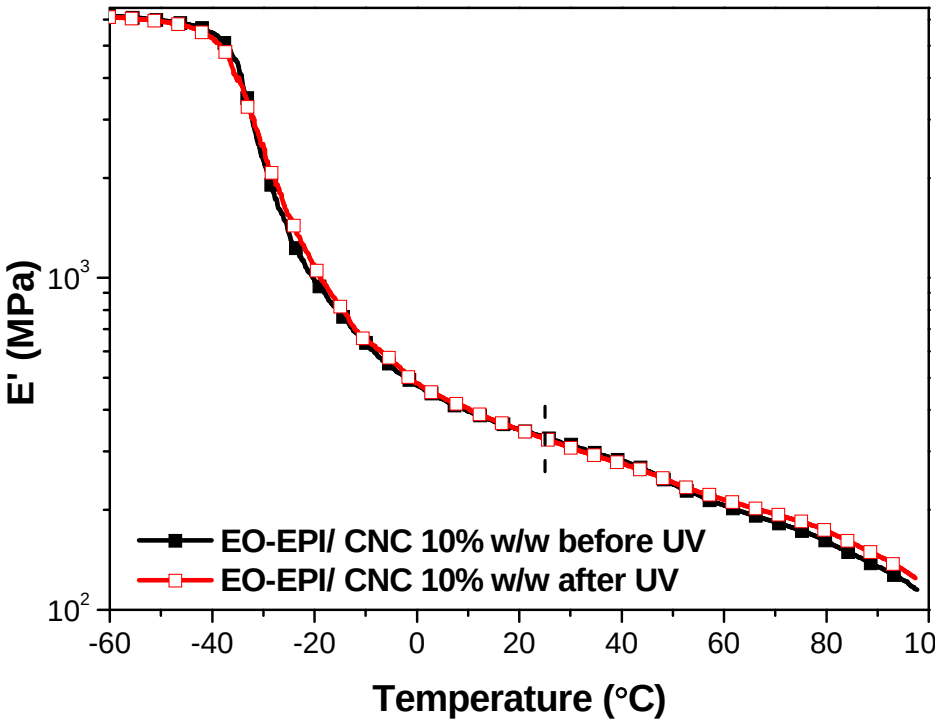
SI-Fig. 8. Atomic force microscopy (AFM) images in height (a) and amplitude (b) of EO-EPI/ Bp-CNC 10% w/w nanocomposite mode, as well as the corresponding cantilever AFM tip image (c) at the interface of soft and stiff segment. Height image was not evident to differentiate the interface between the stiff and soft state while, amplitude image clearly shows the difference in morphology in stiff segment (left part) and soft segment (right part).



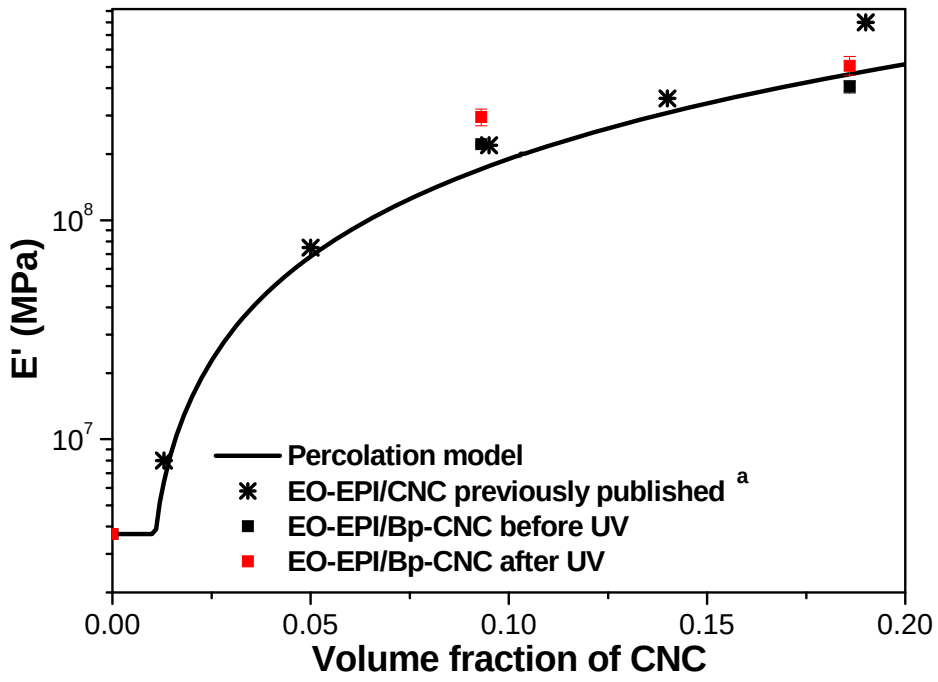
SI-Fig. 9. Dynamic mechanical analysis (DMA) traces of films of the neat EO-EPI before (black squares) and after (red squares) UV exposure (302 nm, 8 W, 120 min, RT). Shown are plots of the storage modulus E' against temperature.



SI-Fig. 10. Dynamic mechanical analysis (DMA) traces of films of nanocomposites of EO-EPI and 10% w/w Bp-CNC as a function of UV irradiation time (302 nm, 8 W, RT). Shown are plots of the storage modulus *E'* against temperature.



SI-Fig. 11. Dynamic mechanical analysis (DMA) traces of films of nanocomposites of EO-EPI and 10% unmodified CNCs, before (black squares) and after (red squares) exposure to UV light (302 nm, 8 W, 120 min, RT). Shown are plots of the storage modulus E' against temperature.



SI-Fig. 12. Tensile storage moduli of EO-EPI/Bp-CNC nanocomposite films as a function of Bp-CNC content at 25 °C in the dry state, before UV (black, filled squares) and after exposure to UV (red, filled squares, 302 nm, 8 W, 120 min, RT). The solid line shows values predicted by the percolation model in the dry state for EO-EPI/CNC nanocomposites. [a] Literature data (black, stars), taken from Capadona et al., *Science* **2008**, *319*, 1370), for EO-EPI/CNC nanocomposites with unmodified CNCs are included for reference purposes. DMA measurements represent averages N = 3-5 experiments ± s.d.