Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supporting Information

Photoswitchable Nanocomposites made from Coumarin-Functionalized Cellulose Nanocrystals

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

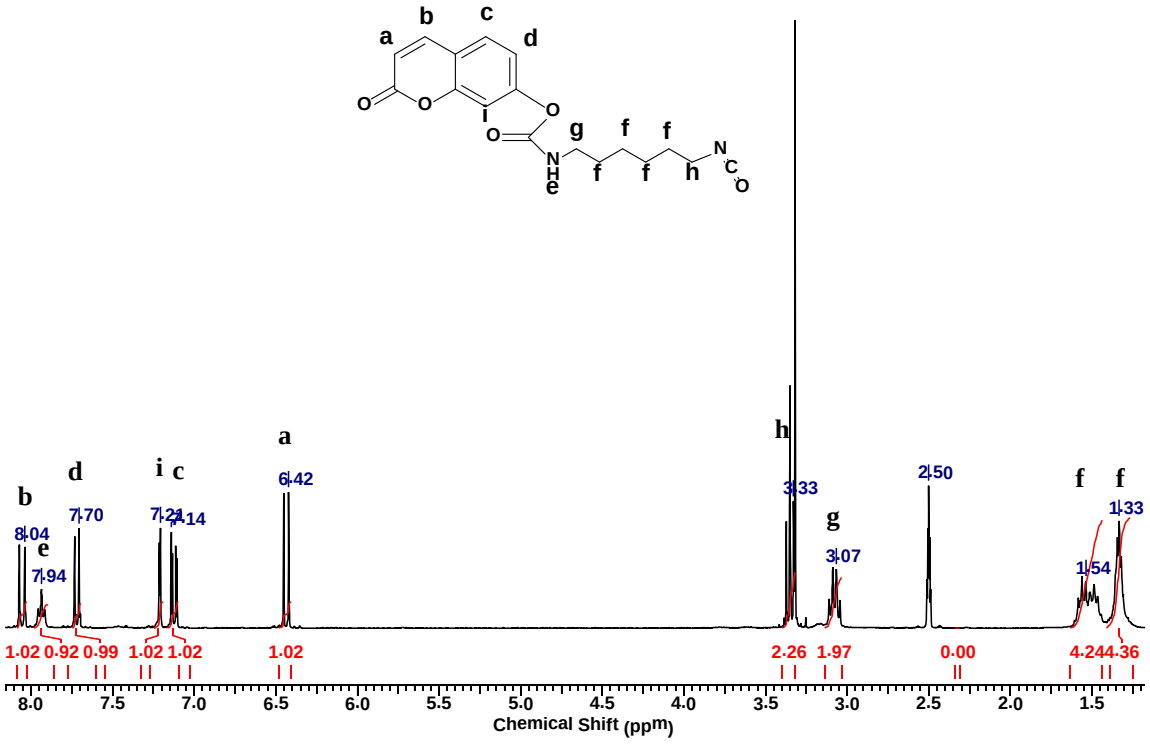
Sample	Before UV irradiation swelling % (w/w)	After UV irradiation [a] swelling % (w/w)
EO-EPI/Cou-CNC 10% w/w	22 ± 2	10 ± 2
EO-EPI/Cou-CNC 20% w/w	24 ± 2	11 ± 1

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

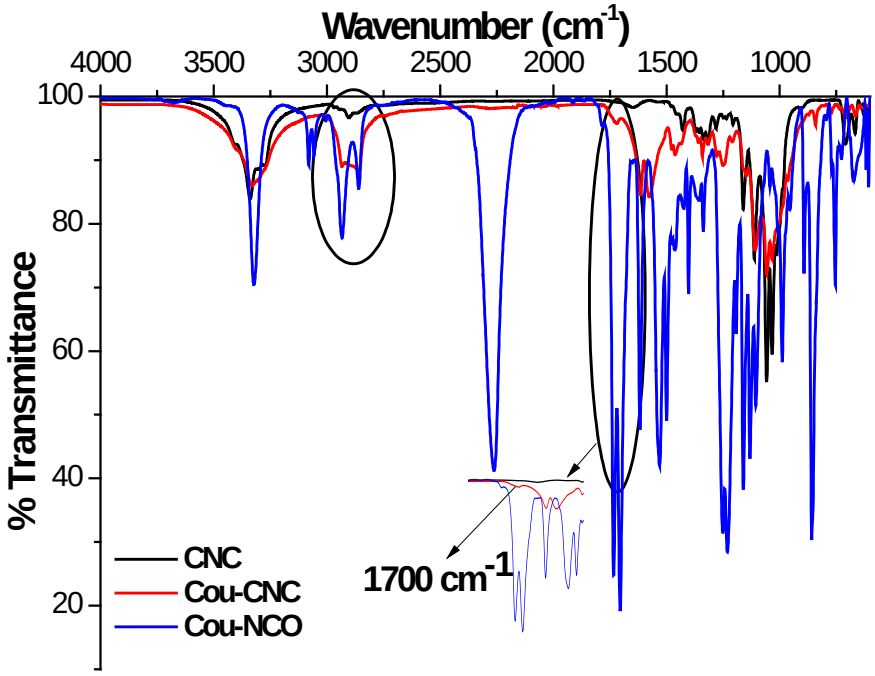
SI-Table 2. Summarizes weight and volume fraction of the CNCs present in nanocomposites.

Sample	Weight fraction of coumarin [a]	Weight fraction of CNC	Volume fraction of CNC
EO-EPI/Cou-CNC 10% w/w	0.007	0.093	0.091
EO-EPI/Cou-CNC 20% w/w	0.014	0.186	0.183

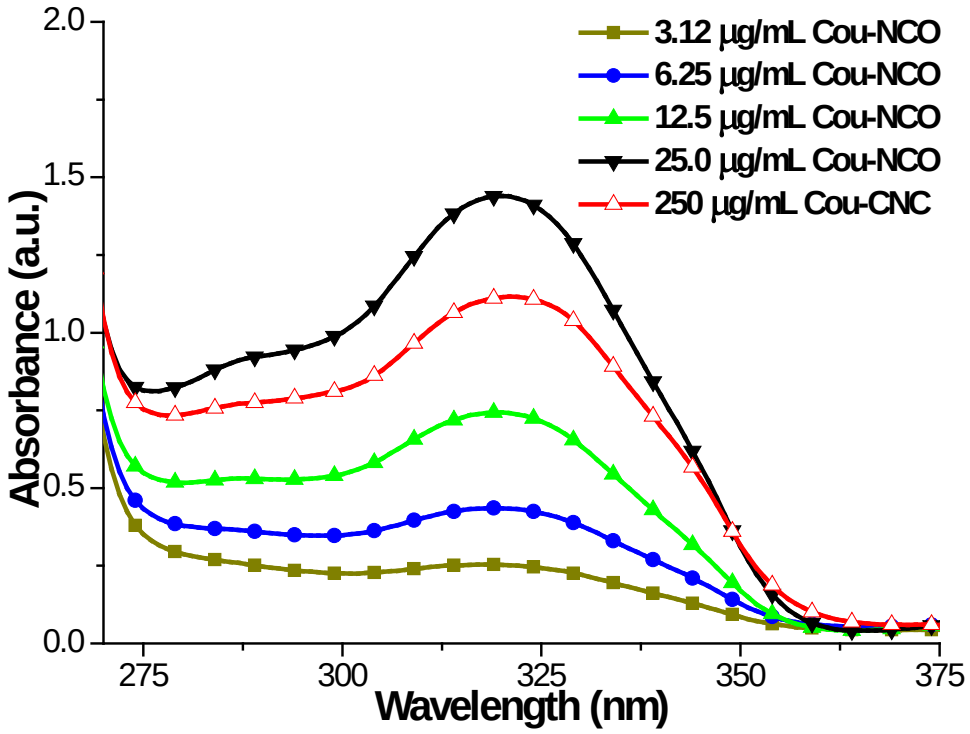
[a] Weight fraction of coumarin present in nanocomposites was determined by data obtained from SI-Fig. 4.



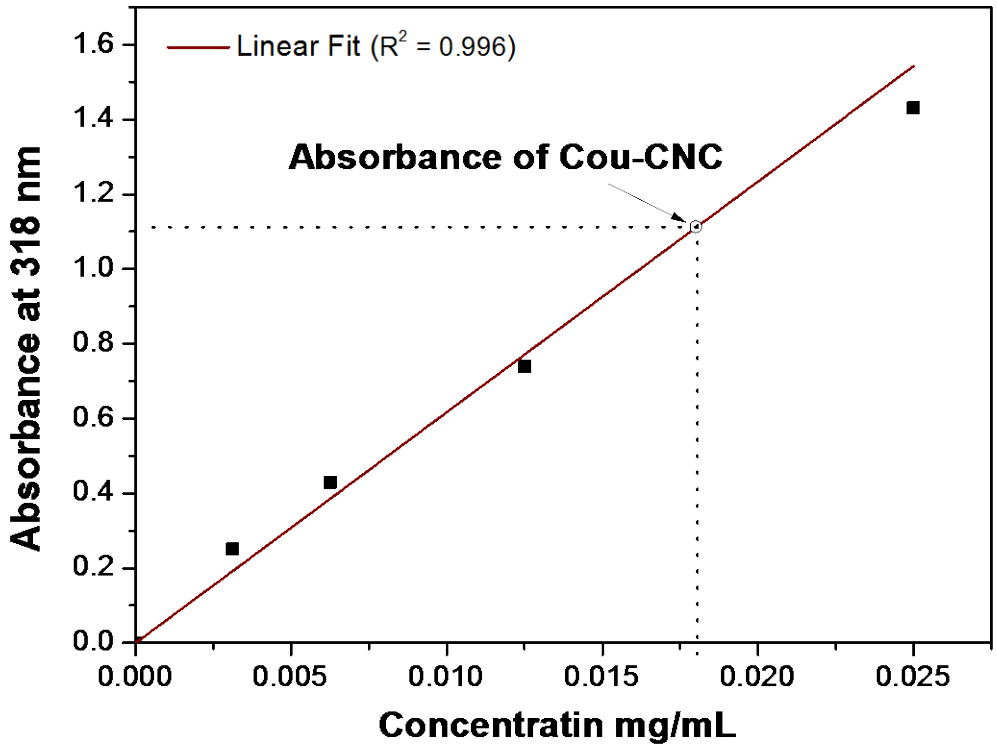
SI-Fig. 1. ^{1}H-NMR spectrum of 7-coumaryl-(6-isocyanatohexyl) carbamate (Cou-NCO) in DMSO-d_6.



SI-Fig. 2. ATR FT-IR spectra of neat CNCs, Cou-NCO, and Cou-CNCs. A comparison shows that the Cou-CNC spectrum feature a characteristic peak associated with the carbonyl group at 1700 cm^{-1}, which is absent in the spectrum of the neat CNCs, and also an increase of the bands between 2800-2950 cm^{-1} corresponding to alkyl chain vibrations.



SI-Fig. 3. (a) UV-Vis absorption spectra of a DMF dispersion of Cou-CNCs (concentration = 250 µg/mL) and solutions of Cou-NCO in DMF (concentration = 3.12-25.0 µg/mL). As can be seen from the spectra, both the Cou-CNCs and Cou-NCO show an absorbance with maximum around 318 nm, which is characteristic of the coumarin moiety.



SI-Fig. S4. Plot showing the absorbance of Cou-NCO solutions at 318 nm as a function of Cou-NCO content (black, filled squares) date extracted from the **SI-Fig. S3** and of a 250 µg/mL Cou-CNC dispersion (black, open circle). The data were used to determine the level of functionalization of Cou-CNCs.

Sample calculation for determining the coumarin content on Cou-CNC surface:

From the UV calibration curve of Cou-NCO, we determine 18 µg of coumarin present in 250 µg/mL of Cou-CNC dispersion.

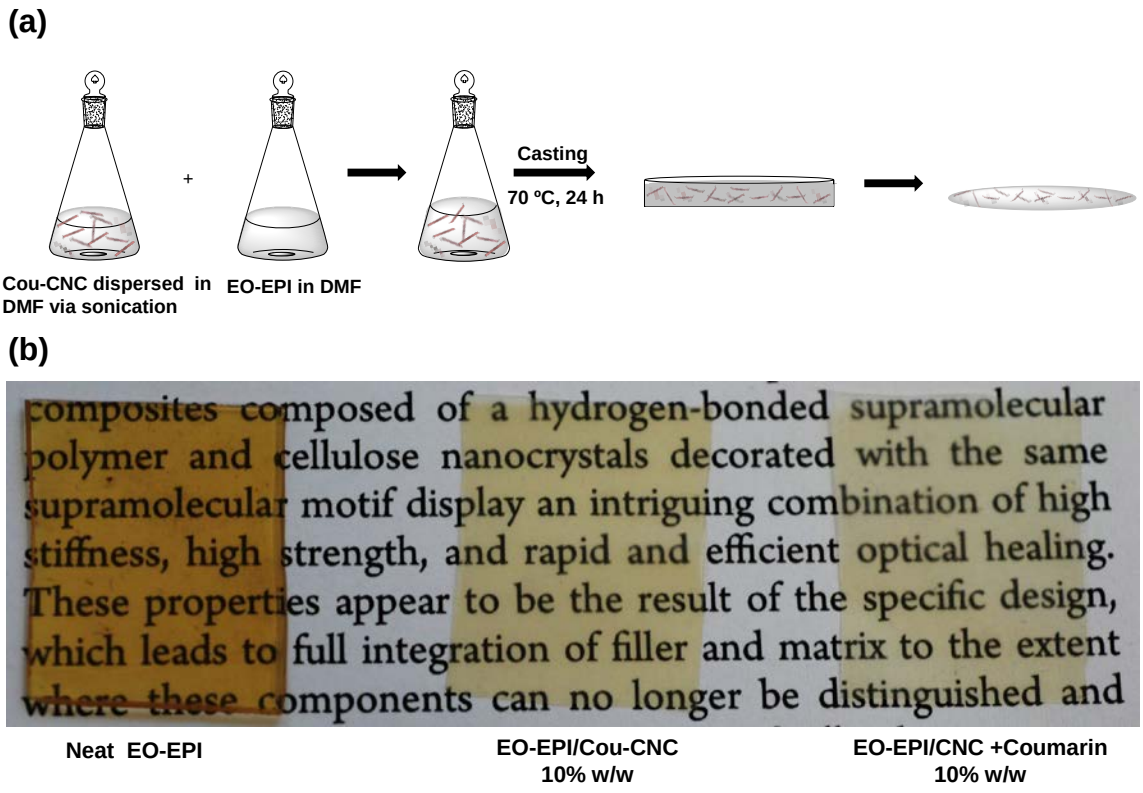
Therefore the amount of coumarin present in 1 g/L of Cou-CNC = $18 \times 10^6 \times 4 = 72$ g

Concentration of coumarin in mmol/kg = 76/molecular weight of Cou-NCO×1000

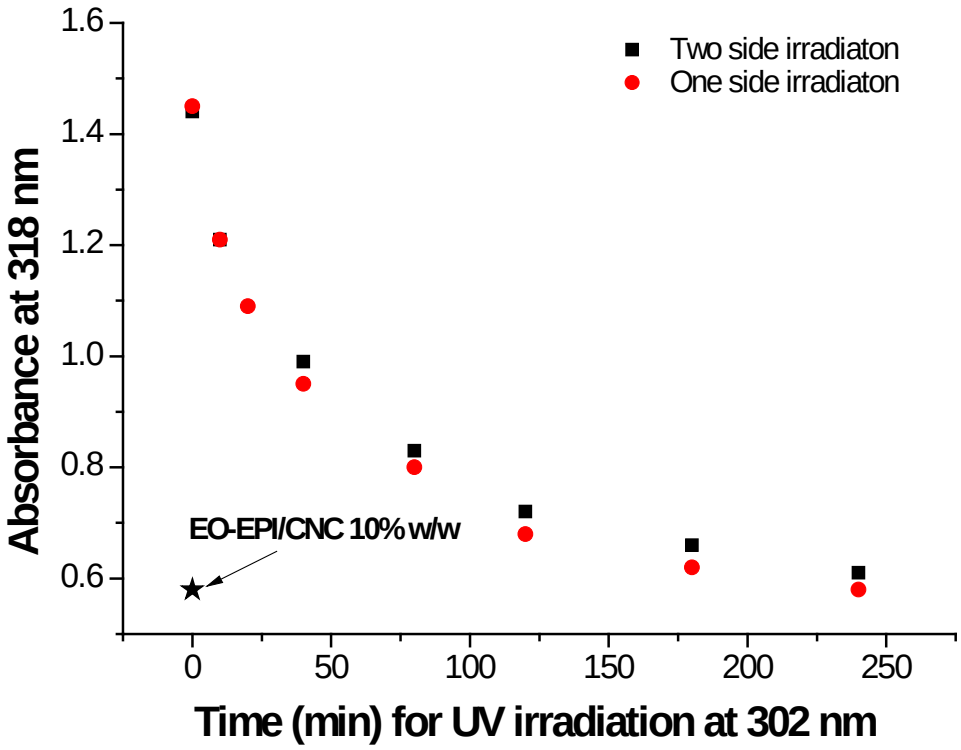
$= 76/330.34 \times 1000$

$= 217$ mmol/kg

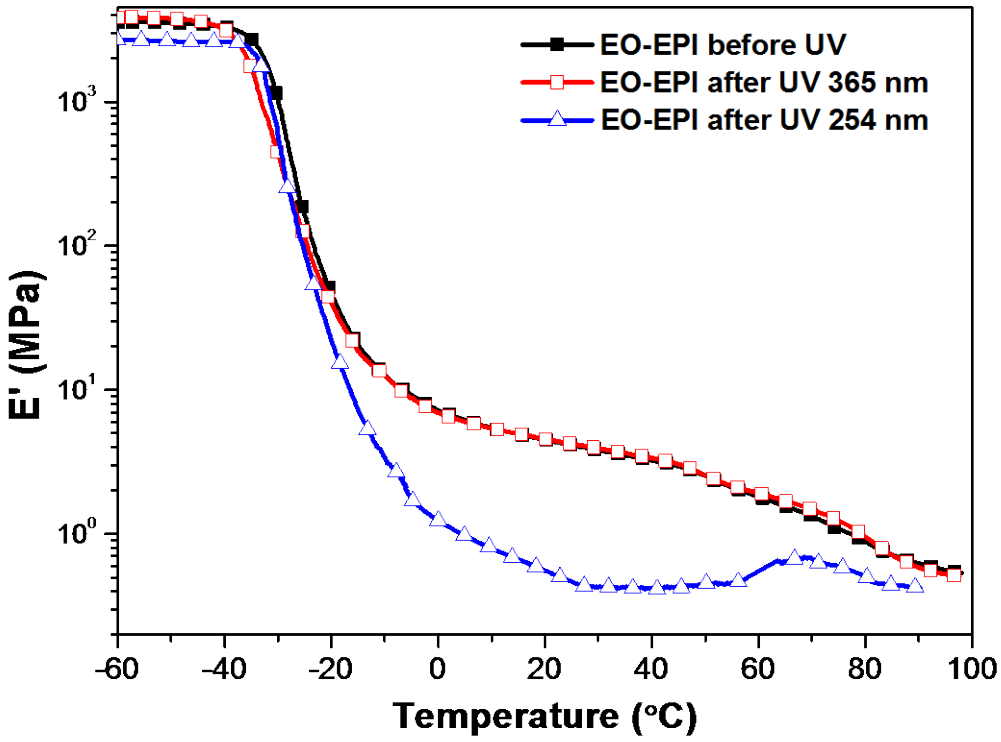
Therefore 217 mmol/kg of coumarin is estimated for the Cou-CNC.



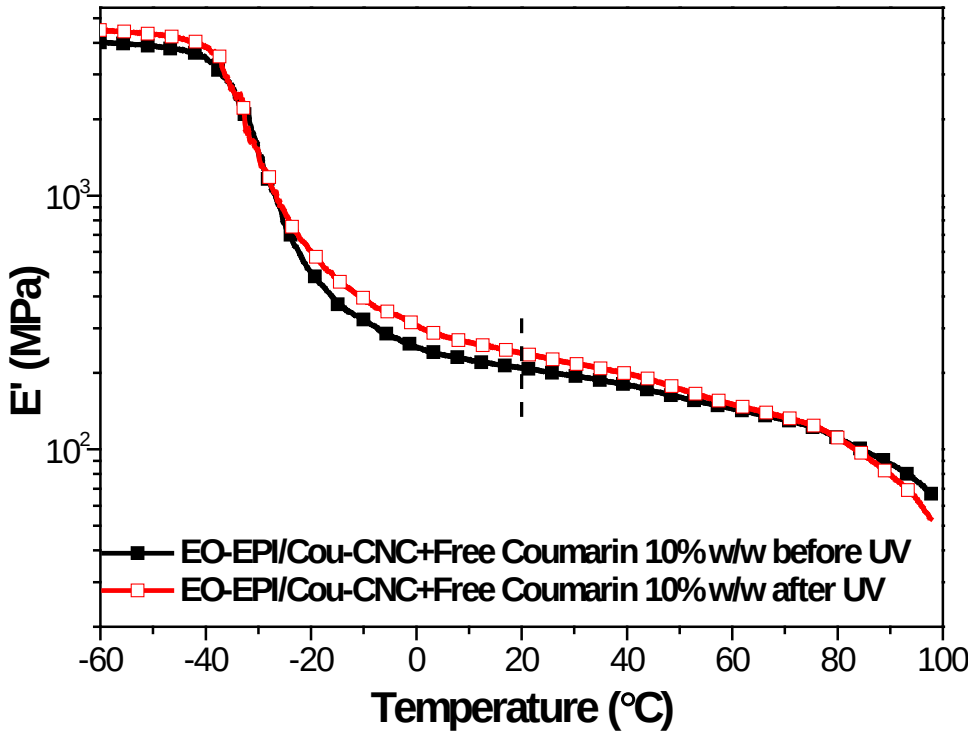
SI-Fig. 5. (a) Schematic representation of the preparation of EO-EPI/Cou-CNC nanocomposite films. (b) Photographs of films of the neat EO-EPI (600 µm) and nanocomposites of EO-EPI with 10% w/w Cou-CNCs (65 µm) or neat CNCs and unbound coumarin (50 µm).



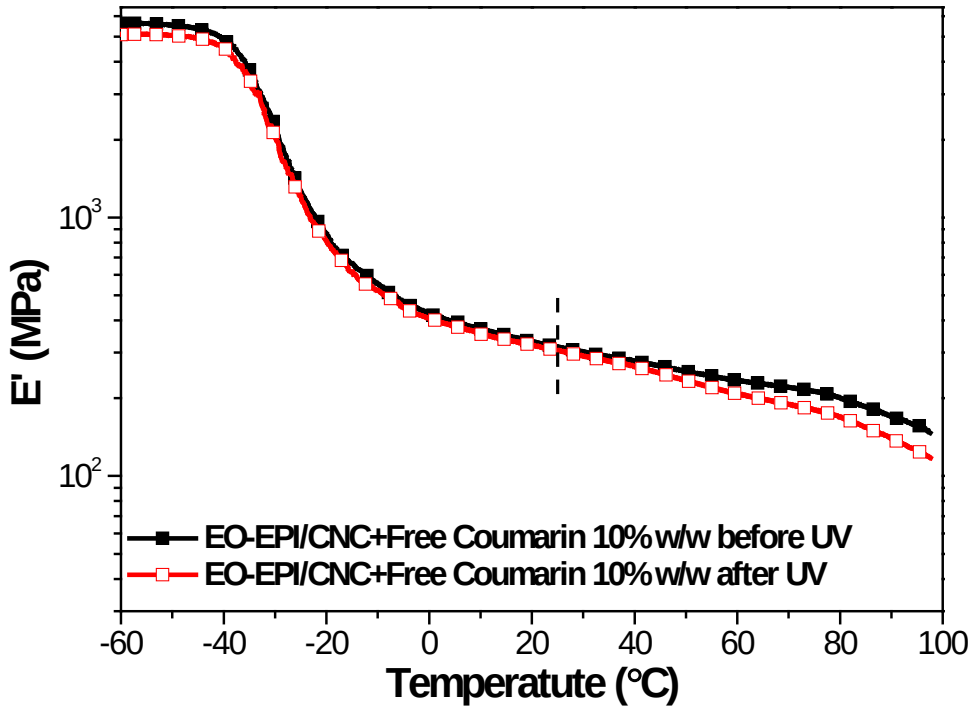
SI-Fig. 6. Plot showing the optical absorption of a 65 µm thick, 10% w/w EO-EPI/Cou-CNC nanocomposite film at 318 nm as function of exposure time to the light of one or two 365 nm UV lamps (8 W, RT). Black, filled squares represent data obtained upon irradiation with two lamps from both sides of the sample, whereas red, filled circles represent data acquired upon irradiation from one side only. Black, filled star represents the corresponding absorbance of a reference film made from a 10% w/w EO-EPI/CNC nanocomposite (*i.e.* with unmodified CNCs).



SI-Fig. 7. Dynamic mechanical analysis (DMA) traces of a neat EO-EPI reference film as a function of temperature before (black curve) and after exposure to UV light (8 W, 240 min, RT) at 365 nm (red curve), at 254 nm (blue curve).



SI-Fig. 8. Dynamic mechanical analysis (DMA) traces of films of a nanocomposite comprising EO-EPI, 10% w/w Cou-CNCs, and free coumarin 3.4% w/w (10 moles relative to the amount of coumarin on the Cou-CNC) in the as-prepared state (black, filled squares) and after irradiation (red, open squares) with light of a 365 nm UV lamp (8 W, 240 min, RT). Shown are plots of the storage modulus *E′* against temperature.



SI-Fig. 9. Dynamic mechanical analysis (DMA) traces of films of a nanocomposite comprising EO-EPI, 10% w/w unmodified CNCs, and free coumarin 3.4% w/w (10 moles relative to the amount of coumarin on the Cou-CNC) in the as-prepared state (black, filled squares) and after irradiation (red, open squares) with light of a 365 nm UV lamp (8 W, 240 min, RT). Shown are plots of the storage modulus *E'* against temperature.