Electronic Supplementary Information for

Nanocomposite Enhanced Hydrophobicity Effect in Biosourced Polyurethane with Low Volume Fraction of Organophilic CNC: Towards Solvent Absorbent and Porous Membranes

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Characterization Techniques

The full characterization of the cellulosic materials including microcrystalline cellulose (MCC), carboxylated cellulose nanocrystals (CNC-COOH) and organophilic cellulose nanocrystals were described in our previous study [1].

The chemical structure of the produced PU/CNC-ODA nanocomposite films was investigated by means of infrared spectroscopy using an Affinity-1S SHIMADZU instrument in transmission mode. To study the possible interfacial interaction between CNC-ODA and the biobased PU matrix, nanocomposite films were analyzed using infrared spectroscopy on an Affinity-1S SHIMADZU spectrometer equipped with a Golden Gate single reflection attenuated total reaction (ATR) accessory. FTIR Spectra were recorded in the range of 600-4000 cm^{-1} at a resolution of 32 cm^{-1}. All the spectra were obtained after an accumulation 92 scans. X-ray diffraction (XRD) measurements were performed on a Bruker D8 Discover diffractometer fitted with a Cu-Kα irradiation source ($\lambda = 1.5438$ Å) operating at 40 kV with a scan speed of 0.5°/min. The thermal stability of the as-prepared PU/CNC-ODA nanocomposites films was studied by thermogravimetric analysis (TGA) using TGA-Model Q500 (TA Instrument), by heating samples of about 35 mg from 25 to 700 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere at a flow of 90 mL min^{-1}. Differential Scanning Calorimetry (DSC) thermograms were recorded on a DSC-Q100 (TA Instrument). Samples of about 8 mg were heated under nitrogen atmosphere from -50 to 300 °C at a heating rate of 10 °C min^{-1}.

The surface morphology of the produced nanocomposite films was observed by Scanning Electron Microscopy (SEM) using an FEI Quanta 200-ESEM operating at an accelerating voltage of 20 kV. Before measurement, the sample was immersed in liquid nitrogen and then cryofractured for the cross-section observations.

Tensile properties of the prepared PU/CNC-ODA nanocomposite films were performed on a Shimadzu EZ-SX apparatus at a tensile speed of 20 mm/min. Measurements were performed upon rectangular specimens of 50 mm in length and 10 mm in width and 0.36 mm in thickness. Before being analyzed, specimens were conditioned at 60 °C for 4 h for complete removal of the adsorbed moisture. The reported tensile data are the averages of three measurements for each sample. The surface hydrophobicity of the films was evaluated by water contact angle using an automatic video contact-angle testing apparatus (OCA 40, DATAPHYSICS) by the sessile drop method. A drop of about 9 μL of distilled water was applied on the top surface of the film and the contact angle was determined from the video

camera images of the drop after approximately 10 s. Reported water contact angles are the average value of three measurements.

Solvent uptake (SU) capacity was determined by simple immersion of squared specimens of 20 mm, previously dried at 60°C for 24h and weighted (Wi), in a 30 mL test bottle containing 20 mL of the desired solvent over the duration of 24 hours. Specimens were periodically removed from the glass bottle, wiped to remove the excess solvent on their surface and quickly weighed (Wf), and then, immediately immersed into the test bottle. The drying and weighing procedure was conducted repeatedly until equilibrium swelling was reached for each test sample. The SU was calculated as follows:

$$SU\ (\%) = \frac{(Wf - Wi)}{Wi} \times 100 \quad (Eq.1)$$

The reusability of nanocomposites films was conducted by using THF as the representative of organic solvents. After saturated with THF, the sample was slightly compressed to squeeze the excess THF. Then put in oven at 60 °C for 2h. The whole process was cycled 20 times. The absorption of each film was measured for each cycle. The reusability was mainly evaluated with stability of THF absorption. The tests were repeated three times.

The diffusion properties described by Fick's laws was evaluated by weight gain measurements of pre-dried samples immersed in solvent by considering the slope of the first part of the weight gain curve versus square root of time [2]. The diffusion coefficient was determined using the following equation:

$$D = \pi \left(\frac{kh}{4Wm} \right)^2 \quad (Eq.\ 2)$$

Where, k is the initial slope of a plot of weight gain versus $t^{1/2}$, Wm is the maximum weight gain and h is the initial sample thickness in mm.

The diffusion coefficient characterizes the ability of solvent molecules to move among the polymer matrix segments. The sorption coefficients that are related to the equilibrium sorption is calculated as follows:

$$S = \frac{Qs}{Qt} \quad (Eq.3)$$

Where Qs and Qt are the molar percentages of solvent uptake at saturation time and at time t.

The permeability coefficient P (mm2/s), which implies the net effect of sorption and diffusion [3], is given by the equation :

$$P = D \times S \quad (Eq.4)$$

The crosslinking density of PU based nanocomposites films was obtained using the following method with slight modification [4]. Briefly, 0.1 g dried sample was soaked in 20 mL DMF for one week at 25°C. After swelling, the samples were removed from the DMF and the DMF on the sample surface was absorbed with filter paper, and weighed. The cross-linking density (v_c/V_0, mol/cm^3) was calculated according Flory-Rehner equation:

$$v_c/V_0 = -2(v + \chi v^2 + \ln(1 - v))/V_1(2v^{1/3} - v)$$ (Eq. 5)

where v_c is the effective moles number of cross-linking chains; the V_1 is the molar volume of DMF (76.87 ml/mol for DMF); the χ is the parameter of polymer–solvent ($\chi = 0.40$); the v is the volume fraction with respect to the polymer ($v = V_0/V_\infty$); the V_0 and V_∞ are the volumes of dry polymer (W_D/ρ_p) and swollen polymer ($W_D/\rho_p + (W-W_D)/\rho_S$), respectively. W_D and W are the weights of dry polymer and swollen polymer, respectively. The ρ_S is the density of the solvent (0.94 g/mL for DMF)

Table S1: Crosslinking density measurements of the elaborated films

Samples	v_c/V_0 (mol/cm^3)[a]
PUBCO	179.63± 2.12
PU/CNC-ODA 1	195.19± 3.66
PU/CNC-ODA 1.5	203.74± 2.74
PU/CNC-ODA 2.5	220.19± 5.82
PU/CNC-ODA 5	256.41± 6.37

[a] effective number of crosslinked chains (crosslinking density).*

References

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