Supporting Information

A simple method for the melt extrusion of cellulose nanocrystal reinforced hydrophobic polymer

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Experimental Section

Materials. CNC were prepared from cotton Whatman filter paper. The paper was milled with a laboratory milling device to obtain fine particulate substance. The cotton fibers were extracted in a 2 wt% aqueous NaOH solution (25 g fibers for 1 L solution) for 12 h at room temperature under mechanical stirring and then filtered and rinsed with distilled water. Acid hydrolysis was achieved at 45°C with 65 wt% sulfuric acid (preheated), for 45 min under mechanical stirring (25 g fibers for 500 mL solution). The suspension was diluted with ice cubes to stop the reaction and washed until neutrality by successive centrifugations at 10,000 rpm and 4°C for 20 min each step and dialyzed against distilled water. After dialysis, the dispersion of nanocrystals was completed by an ultrasonic treatment using a Branson sonifier, filtered and a few drops of chloroform were added to avoid bacterial growth.

Low density polyethylene (LDPE - Lacqtene 1008 FE 24) with a density of 0.924 $g.cm^{-3}$ and a melting point of 112°C was supplied by Atofina S.A. Polyoxyethylene (PEO) with average molecular weights $M_w = 3.5\times10^4$ and 5×10^6 $g.mol^{-1}$ was purchased from Fluka Chemika and Sigma Aldrich, respectively. Their melting point is around 65°C.

Processing of Nanocomposites. PEO solutions were prepared by adding 1.25% of the polymer in distilled water. The solution was protected against light by an aluminum foil and weakly stirred at 500 rpm for 4 days at room temperature. This procedure was shown to avoid degradation of the polymer.[16] The desired amount of cotton nanocrystals aqueous suspension was added to the solution and stirred for 30 min. The proper amount of distilled water was then added to reach a final PEO concentration in water of 1 wt% and the suspension was stirred for 1h. Rheometrical measurements were performed for these suspensions with different amounts of CNC which content was expressed on the basis of the PEO content.

Cotton nanocrystals reinforced LDPE films were prepared by extrusion. First, the CNC suspension with or without PEO was freeze-dried. LDPE and this lyophilisate were

introduced in the mixing chamber of a twin-screw DSM Micro 15 compounder and allowed to melt at 160°C. The mixing speed was 60 rpm for 10 min. Extrusion was carried out with a slit die of 0.6 mm in gap and 1 cm in length. The nanocrystal content ranged between 0 and 9 wt% (expressed on the basis of the LDPE + PEO content).

Experimental Methods.

Rheometry Measurements. The rheometrical measurements were performed using a rotational rheometer, the MCR, from Anton Paar. The cone and plate geometry, with a 50 mm diameter plate and an angle of 1°, was used. This geometry was chosen to allow obtaining accurate data for the low viscosities samples considered in this study. To prevent solvent evaporation during measurements, geometries were enclosed in a solvent trap which saturates the atmosphere. The lower plan was equipped with a Peltier thermoelectric device that insures a controlled temperature, fixed at 20°C ± 0.1°C for this study. Two kinds of rheometrical tests were performed.

First, steady shear measurements consisted in applying a rising shear rate ramp, between $0.1 s^{-1}$ and $30\ s^{-1}$. For a given shear rate, $\dot{\gamma}$, the transient shear viscosity versus time was measured and the steady-state viscosity values $\eta(\dot{\gamma})$ were determined as the limit, on long time scales, of the transient viscosity. The aim of these measurements was to determine the optimal conditions in terms of temperature and shear to process the nanocomposites.

Second, tests consisted in dynamic measurements using small amplitude oscillatory shear deformations. Firstly, the linear viscoelastic regime was determined by carrying out a strain sweep at a fixed frequency. The strain range varies from 0.1% to 100%. The frequencies used were fixed at 0.1 and 1 Hz. Then, isothermal frequency sweeps were carried out within the linear viscoelastic regime and the elastic and viscous modulus, G' and G", respectively, were measured as a function of the frequency of the oscillations ω. The complex viscosity $\eta^*(\omega)$ was deduced from these measurements. In many cases, this complex viscosity is found to be a

good evaluation of the shear viscosity $\eta(\dot{\gamma})$. Moreover, for viscoelastic materials, the empirical Cox-Merz rule is found to work very well. It allows to link η* and η according to the following relation:

$$\eta(\dot{\gamma}) = \eta^*(\omega) \qquad for \qquad \dot{\gamma} = \omega$$

the shear rate being expressed in s^{-1} and the frequency in $rad.s^{-1}$.

For the present study, these frequency sweeps were performed in the range 100-0.01 $rad.s^{-1}$ starting from the highest frequencies. By this way, less time is needed to obtain a higher number of data points and thermo-mechanical degradation of the fluid is minimized. It's worth noting that dynamic measurements using small amplitude oscillatory shear deformations are representative of the behavior of the sample at rest and allows for a characterization that is smooth regarding the internal structure of the fluid when it exists.

Microscopic Observations. An environmental scanning electron microscopy (ESEM) on a Quanta 200 FEI device (Everhart-Thornley Detector was used to investigate the morphology of the extruded nanocomposite films and dispersion of the filler within the matrix. The specimens were frozen under liquid nitrogen before being fractured and coated with gold/palladium. SEM observations of the fractured cross-section were obtained using 10 kV secondary electrons.

Thermogravimetric Analysis (TGA). TGA (STA 6000, Perkin Elmer Instruments model, USA) was carried out to determine the thermal stability of freeze-dried cotton nanocrystals and mixtures of CNC with PEO. Measurements were performed under nitrogen flow of 20 $mL.min^{-1}$. The samples were heated from 30°C to 600°C with a heating rate of $10°C.min^{-1}$. The sample weight was plotted as a function of temperature for all samples.