Simple Method for the Melt Extrusion of a Cellulose Nanocrystal Reinforced Hydrophobic Polymer

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Ⓢ *Supporting Information*

ABSTRACT: The rheological properties of a dispersion of cellulose nanocrystals (CNCs) in an aqueous solution of polyoxyethylene (PEO) have been investigated. A peculiar behavior is reported. Upon adding CNC, the viscosity of the suspension first decreases and then increases. Adsorption of PEO chains on the surface of the nanoparticles has been suspected. Freeze-drying of this PEO-adsorbed CNC dispersion was performed, and the ensuing lyophilizate was extruded with low density polyethylene. Compared to neat CNC-based nanocomposites, both improved dispersibility and thermal stability were observed. This simple and physical method constitutes an approach of choice for the melt processing of CNC-based nanocomposites with a hydrophobic polymeric matrix applicable at the industrial scale.
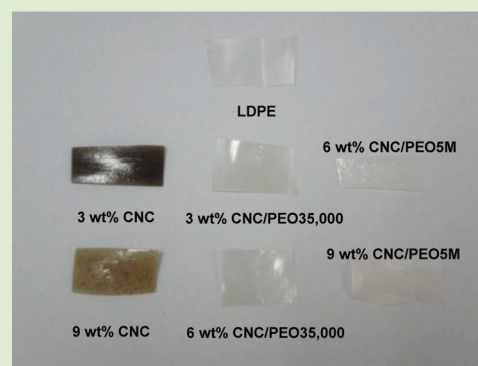
Impressive mechanical properties and reinforcing capability, abundance, low weight, renewability, and biodegradability make cellulose nanocrystals (CNCs) ideal candidates for the processing of polymer nanocomposites.[1−4] With a Young's modulus of over 100 GPa and a surface area of several hundred $m^2 \cdot g^{-1}$,[5] they have the potential to significantly reinforce polymers at low filler loadings. A broad range of potential applications of nanocellulose exist even if a high number of them remain unknown to date. Many scientific publications and experts show its potential even if most of the studies focus on their mechanical properties as a reinforcing phase and their liquid crystal self-ordering properties. However, as for any nanoparticle, the main challenge is related to their homogeneous dispersion within a polymeric matrix.

CNCs are obtained as aqueous suspensions, and most investigations focused on hydrosoluble (or at least hydrodispersible) or latex-form polymers.[1,3,4] They can be dispersed in nonaqueous media using surfactants or surface chemical grafting involving the high density of surface hydroxyl groups broadening the range of applicable polymeric matrices. However, dispersion in some nonaqueous solvent is possible by a variety of methods (direct dispersion in DMF, low dispersibility in DCM, or template approach).[6−9]

However, facilities for industrial-scale CNC production exist, and the recent announcement of their large-scale production requires the use of more industrial processing techniques. Melt-compounding such as extrusion, commonly used to process thermoplastic polymers, is infrequently employed for the preparation of CNC reinforced polymer nanocomposites because of inherent incompatibility and thermal stability issues. Indeed, the hydrophilic nature of polysaccharides causes irreversible agglomeration upon drying and aggregation in nonpolar matrices because of the formation of additional hydrogen bonds between the nanoparticles. Moreover, sulfuric acid prepared CNCs present low thermal stability when heated at moderated temperatures, which prevents their processing with methods involving heat.[10] This is ascribed to the dehydration reaction resulting from the presence of sulfate groups with negative charge on the surface of CNCs. All of these issues limit the processing of CNC-based nanocomposites to wet processing methods such as solution casting, which was extensively studied.

Functionalization of the surface of the nanoparticles is most of the time a necessary step to avoid irreversible agglomeration during drying and aggregation in nonpolar matrices.[11−13] However, this strategy is hardly compatible with an industrial application of these renewable nanoparticles. Therefore, the next challenge is to be able to prepare polymer nanocomposites using industrial processing techniques, thus avoiding the solvent methods and surface chemical modification of the nanoparticles. An attempt to use poly(vinyl alcohol) (PVA) as a compatibilizer to promote the dispersion of CNCs within the poly(lactic acid) (PLA) matrix was reported.[14] Two feeding methods of PVA and CNC were used, dry-mixing with PLA prior to extrusion or pumping as suspension directly into the extruder. However, due to the immiscibility of the polymers, phase separation occurred. The CNCs were primarily located in the discontinuous PVA phase, and only a negligible amount was

located in the continuous PLA phase, leading to poor performance of the nanocomposites. Melt processing (extrusion and injection molding) of CNC reinforced poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) was also attempted.[15] Despite using low molecular weight polyethylene glycol (PEG) as a compatibilizer, the nanoparticle agglomerates formed during freezing could not be broken and well dispersed by the extrusion process. PEG is miscible with PHBV, and a lack of strong interaction between PEG and CNC was suspected. Therefore, during high shear twin-screw compounding PEG could be removed from the nanoparticle surface and blended with the PHBV matrix. Without the shielding of the PEG coating, the nanocrystals could not be well dispersed as evidenced from microscopic observations.

In the present paper, we present an easy way to melt process nanocomposite materials from an apolar polymeric matrix (we choose low density polyethylene) and CNC using high molecular weigh polyoxyethylene (PEO).

Figure 1A shows the evolution of both G′ and G″ moduli obtained within the linear regime, as a function of the angular
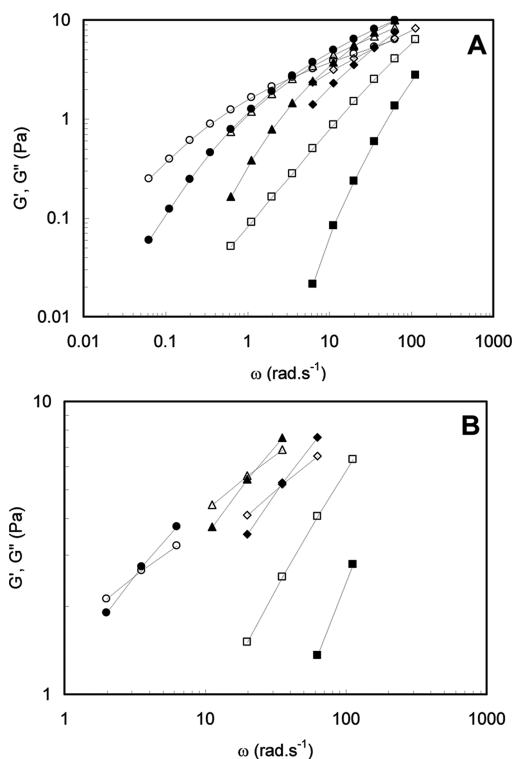

Figure 1. (A) Evolution of the storage (filled symbols) and loss (open symbols) shear moduli within the linear regime for the 1 wt % PEO ($M_w = 5 \times 10^6$ g·mol^{-1}) solution containing various amounts of CNC (on the PEO basis) as a function of the frequency: 0 wt % (●,○), 3 wt % (▲,△), 6 wt % (■,□), and 9 wt % (◆,◇). (B) Zoom on the experimental values surrounding the cross over zone.

frequency for the neat PEO solution and PEO/CNC suspensions with 3, 6, and 9 wt % cotton nanocrystals. It is worth noting that, as detailed in the Supporting Information, the PEO content was fixed at 1 wt % on the water basis for all solutions/suspensions and that the CNC content was expressed on the basis of the PEO content. Moreover, precautions were taken to limit degradation of PEO as detailed in the Supporting Information.[16] Focusing first on the viscoelastic behavior of the PEO solution, it is clear from Figure 1A that it

is typical of melt polymers with the onset of a terminal zone at low frequency and the beginning of a rubbery plateau at high frequency. It is separated by a G′−G″ cross over at intermediate frequency, indicating the transition from a viscous predominant behavior to an elastic predominant one. Figure 1B shows a zoom on the experimental values surrounding the cross over zone.

Considering now the viscoelastic response of the PEO/CNC suspensions, the main remark is related to the evolution of the frequency corresponding to the G′−G″ crossover. Except for the PEO solution filled with 6 wt % CNC for which the cross over is out of the experimental range, it is clear that it decreases with CNC content, indicating a molecular dynamic that is slowed down for higher CNC concentrations. This is in coherence with what is generally observed for encumbered systems and may be associated here to the presence of CNC in the solution. Moreover, a peculiar behavior is observed in Figure 1. A continuous decrease of both G′ and G″ is observed when increasing the CNC content up to 6 wt %, and then an increase is reported for the 9 wt % suspension compared to the 6 wt % suspension. This peculiar behavior will be explained in light of steady shear measurements.

In Figure 2A, the steady shear behavior for the neat 1 wt % PEO solution and with increasing CNC content up to 9 wt % is
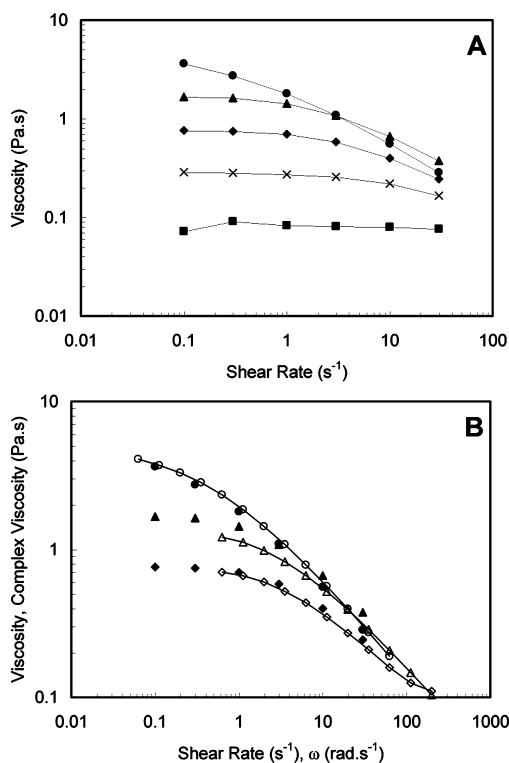
Figure 2. Steady shear viscosity and complex viscosity for the 1 wt % PEO ($M_w = 5 \times 10^6$ g·mol^{-1}) solution containing various amounts of CNC (on the PEO basis): (A) evolution of the viscosity as a function of the shear rate and (B) evolution of the viscosity as a function of the shear rate (filled symbols) and complex viscosity as a function of the frequency (open symbols): 0 wt % (●,○), 3 wt % (▲,△), 5 wt % (×), 6 wt % (■,□), and 9 wt % (◆,◇).

represented through the variation of the viscosity as a function of the shear rate. It shows that all solutions/suspensions exhibit a low-shear Newtonian viscosity, followed by a shear thinning behavior. Figure 2B shows the same data for the neat 1 wt %

PEO solution and solutions containing 3 and 9 wt % cotton nanocrystals as well as variation of the complex viscosity $\eta^*(\omega)$ calculated from G′ and G″ measurements. It is clear that it superimposes quite well with the steady shear viscosity, thus indicating that the Cox−Merz rule[17] is satisfied for those materials. As for the steady shear behavior (Figure 2A), an unexpected behavior is observed infirming the mechanical strengthening induced by the nanocrystals. Indeed, it is observed that the shear viscosity first decreases when the concentration of nanoparticles increases from 0 to 6 wt %. As cotton nanocrystal content still increased (9 wt %), typical suspension behavior is observed with a viscosity increasing as the concentration increases. However, the viscosity of the 9 wt % filler PEO solution remains lower than that of the unfilled solution. This peculiar behavior is summarized in Figure 3A
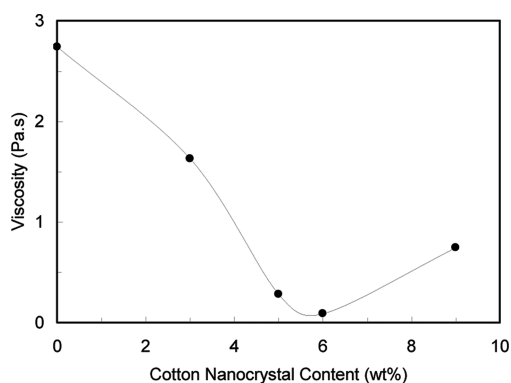
Figure 3. Steady shear viscosity measured for a shear rate of 0.3 s^{-1} for 1 wt % PEO (M_w = 5 × 10^6 g·mol^{-1}) solution as a function of CNC content.

which shows the evolution of the viscosity measured for a shear rate of 0.3 s^{-1} as a function of the cotton nanocrystal content.

Thus, it clearly appears that the viscosity first decreases, and this may be attributed to strong affinity between PEO chains and the cellulosic surface through interactions between the oxygen groups of PEO and hydroxyl groups of cellulose. These interactions were characterized in a previous work using heat flow calorimetry.[18] The affinity of water to cellulose surface as a competitive binder was higher, but the polymeric nature of PEO and possibility of wrapping have to be considered. Consequently, increasing nanoparticle content leads to an increase of the available specific area, and less free PEO chains are available in the solution. Interactions between CNC are hidden, and the behavior is close to that of water. In the present experimental conditions, it appears that a cotton nanocrystal concentration around 6 wt % corresponds to a critical concentration, sufficient to adsorb all the PEO chains available in the suspension. Obviously, this critical concentration should depend on the specific area of the nanoparticles, i.e., origin of cellulose and molecular weight of PEO. This aspect is currently under investigation. Above this critical value, the viscosity increases with filler content, and the suspension displays a typical suspension behavior with a viscosity increasing with the suspension concentration. However, in the range of nanoparticle concentration investigated, the viscosity remains lower than that of the neat PEO solution, and its evolution is completely controlled by the viscosity of the nanocrystal suspension in a semidilute regime.

The next step was to know if this localization of the polymer could be retained after freeze-drying and if this wrapping layer could be used to play the role of a compatibilizer with the polyolefin matrix through the ethylene moieties of PEO. Saturation of the cellulosic surface occurs for quite low nanocrystal content compared to the amount of PEO (around 6 wt %). It is therefore difficult to use such nanoparticles because the amount of PEO introduced in the composite would be very high. We decided to prepare suspensions consisting of 1 wt % PEO and 4 wt % cotton nanocrystals in water. Therefore, the ratio of cellulose-to-PEO is 80 wt %. It means that only part of the surface of CNC is covered with adsorbed PEO chains.

CNCs have been extruded with low-density polyethylene (LDPE) to prepare nanocomposite films. Before extrusion, the aqueous suspension of cotton nanocrystals with or without PEO was freeze-dried. When PEO was present in the suspension, the freeze-dried material consisted of 20 wt % PEO and 80 wt % CNC. The lyophilizates were optically investigated. The freeze-dried material obtained from the mixture of cotton nanocrystals and higher molecular weight PEO (5 × 10^6 g·mol^{-1}) forms a dense pad that tears upon stretching, forming very stretchable polymer-like threads. To be able to introduce this lyophilizate into the extruder, it was necessary to chop it into fine pieces. On the contrary, the freeze-dried material obtained from the mixture of cotton nanocrystals and lower molecular weight PEO (3.5 × 10^4 g·mol^{-1}) consists of a very fluffy powder, as for the pure cotton nanocrystal lyophilizate. This difference of appearance is probably ascribed to the possibility of entanglements between long enough adsorbed polymeric chains.

Figure 4 shows the appearance of extruded LDPE-based nanocomposites. The neat LDPE film is obviously translucent

Figure 4. Pictures of the extruded films: unfilled polyethylene (LDPE) matrix and LDPE reinforced with neat CNC and PEO-adsorbed CNC.

as any low thickness polymeric film with a relatively low degree of crystallinity induced by ramifications. When adding 3 wt % CNC, the film becomes homogeneously dark. This dark coloration of the film after extrusion is an indication of the degradation of the filler, despite the quite low extrusion temperature (160 °C). Cellulose is assumed to degrade at higher temperature, but it is well-known that sulfate groups resulting from sulfuric acid hydrolysis treatment decrease the thermal stability of cellulose because of the dehydration reaction.[10] When increasing the CNC content, it seems that the film is less dark and less homogeneous and becomes dotted with black. These dots probably correspond to nanoparticle

aggregates, as expected when trying to disperse hydrophilic nanoparticles within a highly hydrophobic matrix.

When using PEO-adsorbed CNC, the appearance of the film becomes similar to the one of the unfilled film, revealing probably a much more homogeneous material. This is a strong indication that the adsorbed polymeric layer probably plays the role of compatibilizer because of the hydrophobic moieties of the monomer unit of PEO. Moreover, the dark color observed for uncompatibilized samples disappears. It could be related to the protection of sulfate groups induced by the coating polymeric layer. Most probably, the use of a high molecular weight PEO is important to achieve this effect. Indeed, previous tests have proved unsuccessful because of the pulling out of the adsorbed polymer upon extrusion.[15]

To access the level of homogeneity of the samples, microscopic observations were carried out on extruded nanocomposites, and the thermal stability of the filler was determined from thermogravimetric analysis (TGA).

Figure 5 shows SEMs of LDPE-based extruded films. The freshly fractured surface of the neat LDPE film (Figure 5A) is
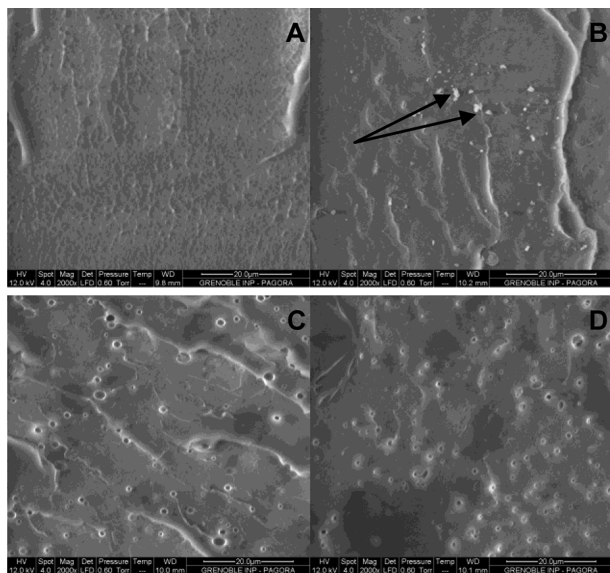
Figure 5. SEMs of (A) neat LDPE and LDPE reinforced with (B) 9 wt % CNC, (C) 6 wt % PEO-adsorbed CNC (3.5×10^4 g·mol^{-1}), and (D) 9 wt % PEO-adsorbed CNC (5×10^6 g·mol^{-1}).

smooth and uniform. For nanocomposites (Figures 5B−D), a slightly rougher aspect is observed. It is probably due to the brittle fracture under liquid nitrogen. The cellulosic nanoparticles are hardly distinguishable, but the presence of nanocrystal aggregates (spotted by arrows) is reported for the uncompatibilized sample (Figure 5B). This aggregation phenomenon is not observed for PEO-compatibilized nanocomposite films. However, the latter shows many air bubbles whose origin is unclear.

TGA experiments were carried out for freeze-dried neat as well as PEO-adsorbed CNC. Results are reported in Figure 6. For neat CNC, an initial weight loss is observed upon heating up to 100 °C. It corresponds to the removal of moisture in the material. At higher temperatures, a gradual weight loss in the range 200−400 °C is reported. It is well-known that small amounts of sulfate groups resulting from the sulfuric acid hydrolysis process induce a considerable decrease in degradation temperatures.[10] A complex behavior was reported, in
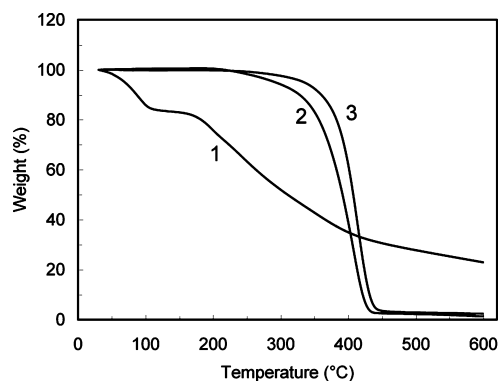
Figure 6. TGA curves of freeze-dried CNC: neat CNC (1) and PEO-adsorbed CNC (CNC:PEO 80:20) with 3.5×10^4 g·mol^{-1} (2) and 5×10^6 g·mol^{-1} (3).

which the lower temperature degradation process may correspond to the degradation of more accessible and therefore more highly sulfated amorphous regions, whereas the higher temperature process is related to the breakdown of unsulfated crystal. The char fraction was also found to increase upon acid hydrolysis and displayed a continuous increase upon prolonged hydrolysis times.[10] It was ascribed to the higher amount of sulfated groups acting as flame retardants.

For PEO−CNC mixtures, the thermal degradation behavior is significantly different. No low temperature weight loss is observed, probably because of the less hydrophilic nature of the material. Moreover, the main degradation process is shifted toward higher temperatures and occurs in a narrower temperature range. This effect is enhanced when using the higher molecular weight PEO. This is probably ascribed to a protection role of adsorbed PEO chains that hid the surface sulfate groups of CNC. It can explain the improved thermal stability and lower thermal degradation of LDPE-based nanocomposites processed from PEO-adsorbed CNCs.

This paper reports preliminary results showing the possibility to melt process nanocomposites consisting of cellulose nanocrystals and a hydrophobic polymeric matrix (low density polyethylene in this investigation). The simple and physical method reported in this study avoids the classical solvent methods and surface chemical modification of the nanoparticles. It therefore constitutes an approach applicable at industrial scale. The basic idea consists in wrapping the nanoparticles with polymer bearing moieties susceptible to interact physically with the cellulosic surface and with the apolar matrix. These interactions were evidenced from rheological measurements performed in aqueous suspensions. It is expected to overcome an important challenge aiming at melt processing this class of nanocomposites. This strategy could also be applied for example to the extrusion of polyvinyl alcohol using PEO as a buffer against degradation. However, further investigation is necessary to fully understand the phenomena involved and study the role of the specific area of the nanoparticles and molecular weight of the compatibilizing polymer. Moreover, the physical and mechanical characterization of extruded nanocomposite films should be performed. These experiments are in progress.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials, processing of nanocomposites, and experimental techniques. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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