Dispersion and percolation of nanocrystalline cellulose in polymers: percolation threshold

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ABSTRACT

Due to their high modulus, nanocrystalline cellulose may be used as reinforcing fillers in gels of solutions or melts of polymers provided that their concentration overcomes a mechanical percolation threshold. In this work, we demonstrate that empirical laws relating this threshold with volume fraction and aspect ratio can be explained by theoretical arguments based on the rotational volume of rods in comparison to the packing fraction. Illustrations in the case of cellulose nanocrystals dispersed by extrusion in polyether matrices having various molecular weights will be proposed.

INTRODUCTION

Because of their large aspect ratio, cellulose nanocrystals are known to enable the formation of gels when they are properly dispersed in solution or melts of polymers provided that their concentration overcomes a mechanical percolation threshold. Above this critical volume fraction, dynamic mechanical properties of the nanocomposites in molten or gel state show a plateau of the storage modulus at low frequency. Favier et al.[1] and Dufresne[2] show that the percolation threshold Φ_p can be well predicted by a simple equation:

$$\Phi_p = \frac{0.7}{p} \qquad (1)$$

where p is the aspect ratio of the CNC.

In this work, theoretical arguments are proposed to explain this relation. Conversely, these arguments can also be used to explain why orientation during extrusion can have a detrimental effect on the properties of polymer films made by this processing method in comparison to nanocomposites obtained by solvent casting. This will be illustrated in the case of CNC dispersed in polyether matrices having various molecular weights by solvent casting and extrusion.

MATERIALS AND EXPERIMENTS

Materials

Microcrystalline Cellulose (Avicel PH 105 NF, FMC BioPolymer). It was used to prepare cellulose nanocrystals (CNC) using the procedure described in the literature[3, 4].

Polyethylene oxide (PEO) (Polyox, Dow Chemical) with weight average molecular weight of 265000 g/mol and polyethylene glycol (PEG) (Sigma Aldrich) with weight average molecular weight of 20000 g/mol were used as matrices.

Nanocomposites

Films of nano-composites with filler content between 0 and 10 wt% (dry basis) were prepared by the well established procedure of solvent casting in de-ionized water after dispersion, sonication, casting and evaporation and the products were then used as a reference to compare with melt

process. Nanocomposite films were also prepared in a twin screw extruder either by adding dry CNC to the molten matrix or by a two-step method using freeze-dried master-batches prepared as for solvent casting.

TEM microscopy

The cellulose nanocrystals were observed in a transmission electron microscope (TEM), Hitachi H-800, at an acceleration voltage of 70 kV. A droplet of a dilute CNC aqueous suspension was deposited on a copper grid. The grid was immersed in a 2 wt% solution of uranyl acetate for 5 min to improve contrast.

Dynamical mechanical spectrometry in the molten state

Dynamical mechanical spectrometry of molten films was measured with a MCR301 from Anton Paar, operating under controlled stress conditions. The analyses were carried out at 70°C. The storage modulus G' and the loss modulus G'' were measured in the linear viscoelastic domain using a parallel plate geometry of 8 mm in diameter, with a gap adapted to the film thickness.

RESULTS AND DISCUSSION

Characterization of cellulose nanocrystals

Fig. 1 shows TEM micrographs of a diluted suspension of cellulose nanocrystals. The size was estimated on circa 100 CNC's over several images and found to be between 10 and 22 nm in diameter with an aspect ratio L/D of 15 ± 2.

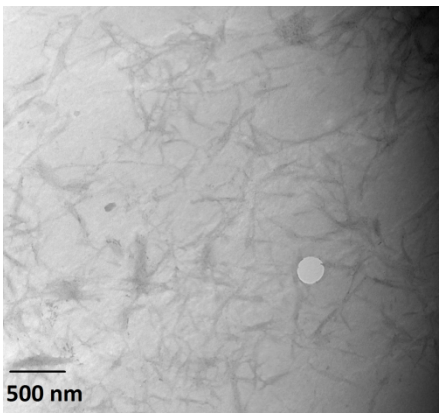

Figure 1. TEM picture of CNC in water.

Percolation threshold from rheology

Fig. 2 shows the storage and loss moduli as a function of the angular frequency for the nanocomposites films obtained by solvent casting and evaporation. An increase of the dynamical moduli is observed with the CNC concentration. At low frequencies, a plateau is clearly visible at concentrations higher than 6.5 wt% of filler. This plateau is the signature of a percolating network between fillers. The experimental value of the percolation threshold (5±1 vol%) agrees well with the calculation by Eq. (1) for the aspect ratio of 15.

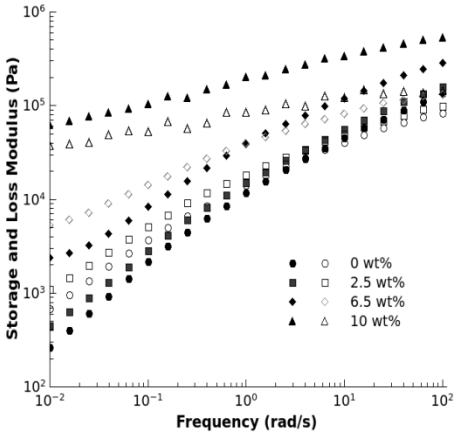

Figure 2. Storage (G', filled symbols) and loss (G'', open symbols) moduli versus angular frequency at 70 °C for the cast PEO nanocomposites.

Theoretical justification of Eq. (1)

The following arguments were proposed for the justification of Eq. (1). CNC were

assimilated to ellipsoids with large axis (L) and small axis (D). When the actual volume fraction, Φ_{eff}, occupied by the randomly oriented particles reaches the maximum packing fraction Φ_M, percolation occurs[5].

In thin 2D films, particles can be assumed to be confined in layers of thickness (e), therefore:

$$\Phi = \frac{n\pi LDe}{4V} \quad (2)$$

with V an arbitrary volume.

The situation is similar during shear flow where the vorticity confines the rotation of the fillers in a plane[6].

The actual volume fraction Φ_{eff}, occupied is larger because of steric hindrance:

$$\Phi_{eff} = \frac{n\pi L^2 e}{4V} \quad (3)$$

Therefore, these two fractions can be related to the aspect ratio p by:

$$\Phi_{eff} = p\Phi \quad (4)$$

This leads to a percolating volume fraction related to the shape factor according to the following equation:

$$\Phi_p = \frac{\Phi_M}{p} \quad (5)$$

From a quantitative point, the maximum packing volume is known to be between 0.62 and 0.74 for specific arrangements (random, body centred cubic or hexagonal or random). A broad size distribution, that contributes to fill the interstitial volume, increases this value until 0.84[7]. In this range of values, Eq. (5) is similar to Eq. (1).

Effect of orientation

Fig. 3 shows the storage and loss moduli as a function of the angular frequency for the nanocomposites films obtained by extrusion with the high molecular weight POE. The modulus of the composites are lower than for pure POE due to degradation of the polyether. The use of the freeze dried masterbatch (2-steps) increases the moduli in comparison to dry CNC (1 step). Nevertheless, percolation can not be obtained even at high CNC loading.

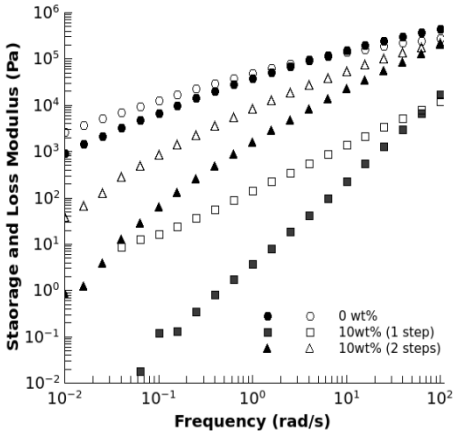

Figure 3. Storage (G', filled symbols) and loss (G'', open symbols) moduli versus angular frequency at 70 °C for extruded nanocomposites with PEO.

This was attributed to orientation during flow. Indeed for ellipsoids oriented in the flow direction (angle θ), using an analysis similar to that of the previous section, it can be easily shown that:

$$\Phi_p = \frac{\Phi_M}{psin\theta} \quad (6)$$

which explains the delayed percolation.

Reducing the orientation

In shear flow, the rotation period of an object with aspect ratio p was given by Jeffery[8]

$$T = \frac{2\pi}{\dot{\gamma}}\left(p + \frac{1}{p}\right) \quad (7)$$

Preferential alignment in the flow axis can hence be expected in a very short time especially when interactions with walls exist as it is the case in a flat die. Actually, the

ratio between residence time in the die and rotation period is a good indication of conditions for significant orientation. In the experimental extrusion conditions of this work, this ratio was larger than unity and orientation was expected.

It was proposed that the reduction of the orientation can be obtained by using a matrix with a small relaxation time that enables nanocrystal mobility and causes a quick disorientation.

To test this assumption, PEG with a low molar mass was used as a matrix. PEG films of nanocomposites with 10 wt% of CNC were extruded. Fig.4 reveals a plateau modulus at low frequencies for films of PEG with 10 wt% of CNC, indicating the desorientation and percolation of CNC.

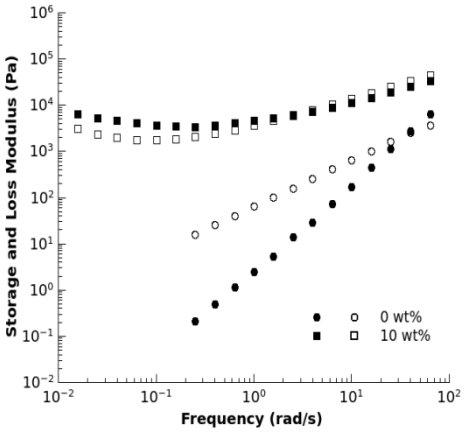

Figure 4. Storage (G', filled symbols) and loss (G'', open symbols) moduli versus angular frequency at 70 °C for extruded nanocomposites with PEG.

CONCLUSION

Theoretical arguments were proposed to elucidate the relation between the percolation threshold of CNC dispersed in a polymer matrix and the aspect ratio of these fillers. This also explains the deleterious effect of orientation on the CNC network during extrusion.

Experiments on CNC dispersed in polyethers using solvent casting or extrusion and polymers with a large difference in viscosity confirm these findings.

The same arguments can be used in other dispersion of fillers with large aspect ratio dispersed in polymer melts.

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