CELLULOSE MICROFIBRILS BIONANOCOMPOSITES. MECHANICAL AND RHEOLOGICAL PROPERTIES

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Abstract

The objective of this study is the development of bionanocomposites using cellulose microfibrils (CMF) as nanoreinforcement in two different biopolymers: poly(ethylene oxide) (PEO) and poly(vinyl butyral) (PVB). Nanocomposites were prepared using two different dispersion methods: dispersion in solvent and melt-extrusion. In order to study the state of dispersion, rheological, morphological and mechanical characterization were carried out. Rheological and morphological analysis showed that high dispersion of CMF was obtained though small differences were observed. Rheological results showed the formation of a CMF network at the rheological percolation (1.5-2 wt% CMF). Mechanical properties were also influenced by the presence of CMF, increasing with their content in the bionanocomposites.

1 Introduction

In the last years, there is a growing interest in developing green materials-based products due to ecological concern. In this aspect, polymer bionanocomposites have attracted a great attention due to the possibilities for enhancement of their material properties via nanoscale reinforcement but also for avoiding environmental problems. Among several nanosized reinforcements, cellulose microfibrils (CMF) can be converted in one of the most interesting since they present a unique combination of great versatility, light weight, renewability, biodegradability and processing advantages at favourable cost [1].

The overall objective of this work is to study mechanical and rheological properties of cellulose microfibrils-based bionanocomposites using two different biopolymers: polyethylene oxide (PEO), and polyvinyl butyral (PVB).

2 Experimental

2.1 Materials

Cellulose microfibrils (CMF) have been extracted from raw jute fibre (Celesa) using several chemical treatments: first alkalization process (NaOH solution, 130 ºC, 90 min), then an acetylation treatment (CH_3COOH and HNO_3 solution, 130 ºC, 30 min), and finally an acid hydrolysis treatment (H_2SO_4 solution, 45 ºC, 60 min) in order to solve the amorphous cellulose and extract CMF. The suspension was washed with water until neutrality was reached and submitted to a sonication treatment.

Two different matrices have been used: PEO from Sigma Aldrich (M_w=100000), PVB from Mowital (M_w=75000).

2.2 Nanocomposite preparation

Cellulose microfibrils suspension has been obtained after sonication for 15 min in water solution. Then, polymer powder have been added and stirred at room temperature during 24 h. Solid films have been obtained by casting this suspension on glass plates and then water evaporation at 40 ºC for a week. Finally, films have been maintained under vacuum for 28 h at 100 ºC.

2.3 Nanocomposite characterization

Dynamic rheological measurements have been performed in an ARES rotational rheometer, Rheometrics, using 25 mm diameter parallel plates with gap setting of about 0.7 mm. Prior to testing, specimens were subjected to thermal annealing at 10 ºC above T_m for 2 days (PEO) and at 120 ºC (for PVB) (the same temperature as tested after) to allow for complete microstructural equilibration. The following rheological measurements were carried out: (i) dynamic strain sweeps to asses the linear

viscoelastic region, (ii) dynamic frequency sweeps, and (iii) steady shear rate sweep tests.

The morphology of the samples has been examined by atomic force microscopy (AFM) (NanoScope III) For every sample, analysis HAS BEEN performed in TappingMode (TM) in air under moderate conditions for recording height and phase images. Silicon cantilevers with a resonance frequency of about 200-400 kHz and a spring constant of 12-103 N/m were used for imaging. The trace and retrace signals were set identical before image capture and no filtering was used during scanning. The images presented are raw, unprocessed data, except for flattening in some cases. Samples were cut from ultra-thin specimens using a Leica Ultracut UCT microtome.

Tensile tests have been carried out in a miniature material tester MiniMat 2000 (Rheometric Scientific) using a load cell of 200 N and a cross-head speed of 3 mm/min. The length between gaps has been fixed at 30 mm. At least 5 samples for each material have been tested.

3 Results and discussion

AFM micrograph of CMF used for nanocomposite preparation is shown in Fig. 1, being 20-30 nm in diameter and 200-300 nm length. Depending on the source and the extraction procedure used, CMF dimensions and consequently the reinforcing ability can vary [2]. In the context of mechanical properties, this aspect is crucial as CMF of lower crystalline order will be less stiff since the cross-sectional density of covalent bonds is lowered [2-3]. The extent of stabilizing interchain hydrogen bonds will also influence mechanical properties [2].
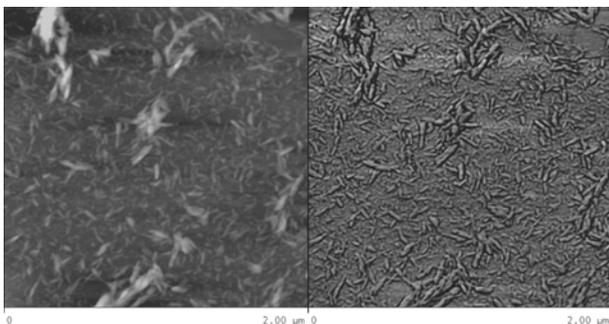
Fig. 1. TM/AFM micrograph of CMF used.

Although, the degree of exfoliation and dispersion of nanoreinforcements in the

nanocomposites is usually investigated by means of X-ray scattering and transmission electron microscopy, these methods fail in detecting the three-dimensional superstructure of nanocomposites. A good approach to obtain such information is the analysis of rheological behaviour, which is very sensitive to elastic properties of network-like superstructures as described by Krishnamoorti et al. [4]. Generally, the rheological behaviour of polymer nanocomposites melts strongly depends on their nanostructure, their state of dispersion-distribution and their interfacial properties [4].
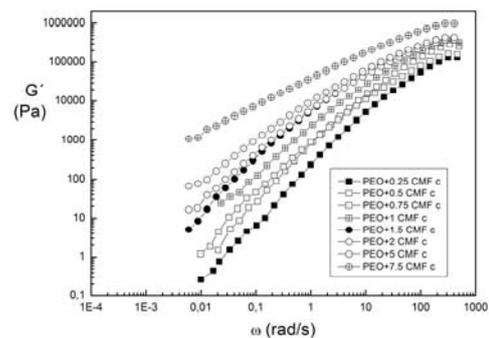
Fig. 2. Frequency sweep test, storage modulus vs. frequency for PEO/CMF nanocomposites.

Results concerning frequency sweep tests for PEO/CMF nanocomposites are summarized in Fig. 2, where complex modulus is represented vs. frequency (first, dynamic strain sweep tests have been carried out in order to limit the linear viscoelastic range). Similar behavior can be observed in all cases as storage modulus decreases with frequency lowering. Low CMF content nanocomposites exhibit the terminal behavior typical of homogeneous polymers where G´ slope is near 2 [5-7] but a change in the frequency dependence in particular at low frequencies is visible when increasing CMF content. The increase of G´ at low values of frequency is attributable to the increased surface area due to an enhanced dispersion since when CMF are better dispersed in the polymeric matrix, the surface area of CMF is expected to markedly increase [6,7]. Non-terminal behavior is an indication of solid-like elastic response, with a long relaxation time [8]. Similar solid-like behavior has been observed for other nanoreinforced composites [7-10]. The critical particle loading can be calculated with the help of percolation theory [9]. In this case, PEO/CMF nanocomposites exhibit an important slope change for 1.5 wt % CMF, thus this value can be considered the rheological percolation threshold.

The variation of steady shear viscosity as a function of shear rate is presented in Fig. 3 for PEO/CMF nanocomposites. Nanocomposites show increased viscosities and more shear thinning with higher CMF loadings, especially at low shear rates, increasing monotonically at a given shear rate. Moreover, the plateau of viscosity at low shear rates gradually disappears with increasing CMF concentrations especially after 1-1.5 wt % CMF addition. This enhancement is related to the interactions and dispersion of CMF in the polymer matrix that would slow down the movement of the polymer chains due to larger resistance to flow is produced [10].

Moreover, unlike a typical polymer, which exhibits a low shear rate Newtonian plateau region [10], well dispersed nanocomposite display a shear thinning behaviour at low shear rates. This observations are supported by other studies on nanocomposites that showed increases in the shear viscosity at low shear rates [10-13]
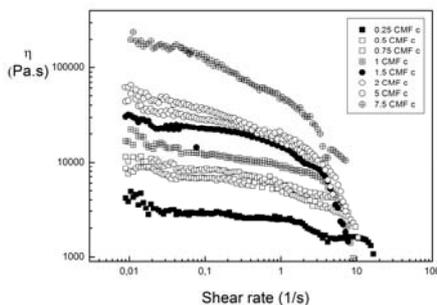
Fig. 3. Shear viscosity vs. shear rate test for PEO/CMF nanocomposites.

Additionally, rheological characterization of PVB/CMF nanocomposites has also been studied and a similar behaviour has been observed. Both dynamic frequency sweep test and steady shear rate test indicate good dispersion of CMF in the polymeric matrix and also rheological percolation threshold is in the same range.

In Fig. 4, AFM micrograph of PEO/1 wt % CMF nanocomposite is reported. In this case, considering that CMF can be observed as light rod-like structures, uniform distribution of CMF and no agglomerations are detected. Increasing CMF content some agglomerations are observed for CMF contents beyond 2 wt %. Finally, mechanical properties of nanocomposites have been evaluated by tensile tests. Tensile strength and Modulus for PEO nanocomposites filled with CMF are reported in Fig. 5. The increase in both tensile modulus and strength is directly attributed to the reinforcement effect of CMF. The non-linear growth shown in Fig. 5 suggests that both parameters are affected not only by the CMF content, but also by the strong interaction of CMFs with the PEO matrix [14]. When good dispersion of CMF is achieved, thus restrict the mobility of polymer chains during tensile loading. The network-like structure of CMF can provide very high surface area, which reduces stress concentration in the matrix with better stress distribution [14].
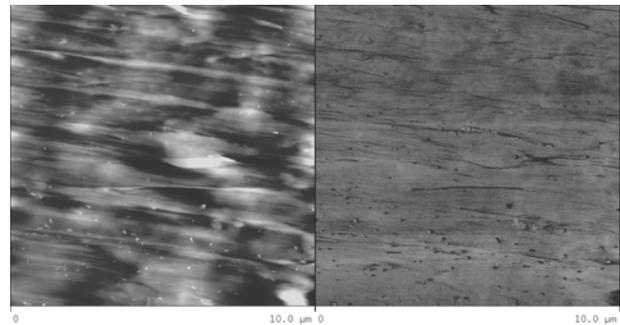
Fig. 4. TM/AFM micrograph for PEO/1 wt % CMF nanocomposite (10 µm x 10 µm).
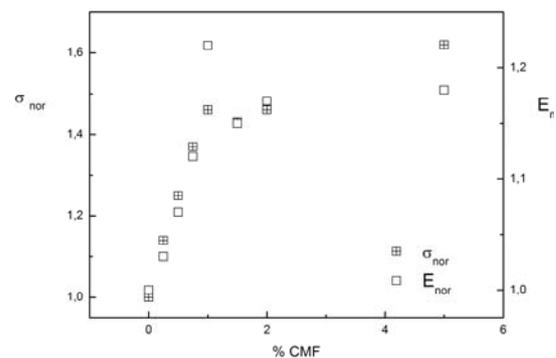
Fig. 5. Tensile properties of PEO/CMF nanocomposites.

4 Conclusions

Bionanocomposites with different polymeric matrices and cellulose microfibrils have been obtained. Uniform distribution of CMF in the polymeric matrix has been observed by AFM, which also results in an improvement in mechanical

properties. Probably the formation of a three dimensional network-like by hydrogen bonding structures [1] is the consequence of these data, that is supported by both AFM and mechanical results.

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