INFLUENCE OF CELLULOSE NANOCRYSTALS ON POLYVINYL(PYRROLIDONE) GRAPHITE COMPOSITES

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In this work, composites with poly vinyl(pyrrolidone), PVP, and graphite reinforced with cellulose nanocrystals, CNCs, were made. The CNCs had a nanometric size, with a hydrodynamic radius of 52 nm. FTIR analysis confirmed the presence of the characteristic functional groups of cellulose nanocrystals in the spectrum of pure CNCs. The PVP-graphite-CNC composites showed the characteristic peaks of PVP and graphite on the FTIR spectra, without the characteristic peaks of CNCs, which is explained by the incorporation of a small quantity of CNCs into the composites. However, the presence of CNCs increased the storage modulus of the composites by 70%, compared to the blank sample. The composites showed a glass transition temperature, attributed to PVP, and a tendency to increase with increasing CNC content; the highest CNC content caused a complex behaviour of glass transition temperature. To conclude, the addition of CNCs enhanced the mechanical properties of the composites.

Keywords: cellulose nanocrystals, composites, poly vinyl(pyrrolidone), graphite

INTRODUCTION

Cellulose nanocrystals (CNCs) are a versatile material, widely used in engineering. CNCs derive from cellulose, a natural material found in plants, marine animals, bacteria, algae and fungi.[1,2] As CNCs are obtained from cellulose, they are non-toxic and biodegradable.[1] CNCs can be obtained from cellulose via many methods, forming a highly crystalline material,[1] which confers the material high mechanical properties. For this reason, CNCs are used as reinforcement in polymer science.[3-5]

CNCs have been reported to be used as binders in capacitors;[6,7] along with cellulose nanofibers (CNF), which are a commonly used binder in energy applications.[6] CNCs have been also used as dielectric paper,[8,9] as well as dielectric material in capacitors.[9] CNCs and CNFs are thus effective binders with potential to be used in applications such as capacitors and supercapacitors.

CNCs have been used to reinforce polyvinyl(pyrrolidone) (PVP) films.[10,11] CNCs were added to increase the mechanical properties of the fabricated films. In a reported study,[10] PVP films were reinforced with varying amounts of CNCs, and the films were produced by the solution casting method. The authors found that the tensile strength increased by 283% when the films contained 39.9 wt% of CNCs, while the Young's modulus increased by 913% with the same amount of CNCs. The elongation at break decreased by 62%. The glass transition temperature (T_g) increased from 180 °C, for the pure PVP films, to 199 °C for the films reinforced with 37.9 wt% of CNCs. The elongation at break and T_g suggested an increase

in the rigidity of the films. The degradation temperature of the PVP/CNC films decreased from 240 °C for the films with 6.7 wt% of CNCs, to 155 °C for the films loaded with 37.9 wt% of CNCs.

In another study,[11] PVP and CNC films and aerogels were successfully prepared. It was found that, with increasing CNC content, the particle length also increased. The aerogels could be redispersed in water, with no changes in particle size and surface charge after redispersing.

As stated above, CNCs can be used as binding agent in capacitors and in electrodes made of activated carbon[7] and graphite. When used binders in energy storage devices, CNCs are known to enhance the mechanical properties and give cohesion to the electrodes, preventing crumbling.[7] To the best of the authors' knowledge, no works have been found in the literature studying the effects of the use of CNCs as binder in composites of PVP and graphite on their mechanical properties. Evaluating these effects is important to understand the binding properties of CNCs in graphite based capacitors, and to have numerical data regarding the expected improvement of mechanical properties. Although graphite can increase the mechanical properties of some composites, the role of CNCs is not only to increase the mechanical properties of the composites, but also to give cohesion to the materials. Therefore, in this study, we examine the effects of various CNC loadings in composites based on PVP and graphite on the mechanical properties of the obtained materials.

EXPERIMENTAL

Materials and methods

Polyvinyl pyrrolidone was acquired from Sigma-Aldrich, with a M_n of 40,000. Graphite (Aldrich, powder, synthetic, pore <20 mm) was used in the films.

The CNCs were fabricated using the sulfuric acid method.[12,13] Namely, a solution of 64 wt% sulfuric acid (Analytyka) was prepared, and 1 gram of a-cellulose (Sigma) was suspended in this solution. The suspension was vigorously stirred for 45 min at 45 °C. Then, the reaction was quenched by diluting 10-fold with cold distilled water.[12] The suspension was briefly stirred for 5 min, then it was allowed to settle for 2 h, decanted and the supernatant was discarded, and the suspension was diluted again with cold distilled water, stirred for 5 min and let to settle overnight and the suspension was decanted again, with the supernatant being discarded.[13] Then, the suspension was sonicated 15 for min with a 200 W sonicator. Then, the suspension was filtered using Millipore filter (450 nm of pore size),[14] to eliminate impurities. Then, the suspension was dialyzed using distilled water as buffer. The dialysis was stopped when the effluent achieved neutral pH. The concentration was measured gravimetrically, measuring 10 mL aliquots thrice, which were dried ad 105 °C,[15] and the average was taken; the measured concentration was 0.1497 wt%.[15] The suspension was treated with Dowex 50WX8 ion-exchange beads to ensure the CNCs were fully protonated and in the acid form. The beads were previously washed with ethanol and dried in a furnace at 65 °C. The suspension was gently stirred at room temperature for 2 days. Then, the suspension was filtered using with Millipore glass microfibers to remove the beads. Finally, the suspension was spiked with a drop of toluene, to avoid bacterial growth.

Table 1
Concentrations of CNCs

Sample	CNC concentration, wt%
Blank	0.0
CNC1	0.1
CNC2	0.2
CNC3	0.5
CNC4	1.0
CNC5	2.0

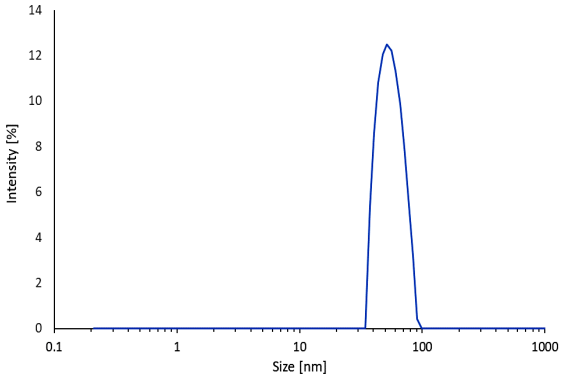

Figure 1: DLS of pure CNCs

Table 2
CNC parameters

Parameter	Value
Mean size	52 nm
Polydispersity index	15.7%
Mean zeta potential	45.9 mV

Fabrication of films

The films were prepared by diluting PVP in a concentration of 5 wt% in water, then adding graphite in a concentration of 1 wt%. Then, the CNC suspension was added dropwise until the desired concentration was achieved. The solution was stirred vigorously for 1 h at 25 °C, and, after this, it was sonicated in an ultrasonic bath for 5 min to avoid bubble formation. Then, it was poured on a Teflon Petri dish and allowed to dry at 80 °C for 2 days. The concentration of PVP and of graphite remained constant in the experiment, the concentration of CNCs was varied as shown in Table 1, in order to study the effect of CNC concentration on the properties of PVP-graphite films.

Characterization

Both the CNCs and the films were characterized by several analytical techniques. The hydrodynamic radius of the CNCs was measured by Dynamic Light Scattering (DLS), using an Anton Paar Litesizer 500 Analyzer.

Fourier Transform Infrared Spectroscopy (FTIR) was performed on the samples. For the analysis, a small volume of the CNC suspension was dried at 50 °C to avoid desulfation of the sample. The dried CNC film and PVP-Graphite-CNC films were characterized using a Perkin Elmer Spectrophotometer, model Spectrum 100, which included an attenuated total reflectance (ATR) device with a diamond tip. The spectra were obtained with the average of 12 scans, and a resolution of 4 cm^{-1}.

Dynamic Mechanical Analysis (DMA) was carried out on the samples, using a TA Instruments DMA model Q800 equipment. The analysis was done in the temperature range of 25 to 200 °C, the heating rate was 5 °C/min, using a fixed frequency of 1 Hz, and a dual cantilever clamp.

The cellulose nanocrystals were observed with Atomic Force Microscopy (AFM), using an Asylum Research-Oxford Instruments AFM, model MFP-3D Infinity. The scannings were performed in tapping mode, using an OPUS cantilever, model 240AC-NA. The CNC sample was put on a mica substrate. The mica was cleaved with tape, it was treated with a drop of poly-L-lysine for 5 minutes, then, it was rinsed with distilled water, and allowed to dry. When the treated substrate was partially dry, a drop of the CNC suspension was deposited on the substrate, and was allowed to dry in a powder free environment.

RESULTS AND DISCUSSION

The hydrodynamic radius of CNCs was determined by DLS (Fig. 1). The size and parameters are given in Table 2. The radius of CNCs was 52 nm, indicating that nanoparticles were formed; this value is similar to those reported in the literature – of approximately 50 nm.[16] Other authors reported that the same technique yielded larger nanoparticles, ranging from 80 nm to 100 nm.[11,17] It should be noted that the hydrodynamic radius for CNCs is higher than the diameter of CNCs.

Figure 2 shows the FTIR spectrum of CNCs. The spectrum reveals the characteristic bands of cellulose. The peaks located in the region around 1430-1317 cm^{-1} confirm that the presence of polymorph I cellulose.[18] The two peaks at 3300 cm^{-1} are characteristic of CNCs and nanocellulose in general. At 2900 cm^{-1} the peaks of the glucopyranosic ring are present.[14] There are no peaks in the 1750-1700 cm^{-1} region, indicating that the CNCs are not in an oxidated form, or that there are no carboxylic groups. This also confirms the absence of lignin in the sample. At 1000 cm^{-1}, the peaks attributed to C-O-C of the glucopyranosic ring are located.[14]

Figure 3 shows the FTIR spectra of the PVP-graphite-CNC composites. The peaks and their assignments, made according to the literature, are given in Table 3.[10,14] The functional groups present correspond mainly to PVP. The C-N assignment appears in two positions. A C-O stretching is present at 932 cm^{-1}, attributed to stretching C-O due to graphite.[19] It can be noted that all the spectra exhibit the same peaks. As the PVP was sampled dry, the bands at 3430 cm^{-1} are not broad, contrary to works where broad bands were found in PVP-water containing samples.[10] As the quantity of CNCs was small in the composites, no peaks attributable to CNCs are found, as the peaks are almost identical to those of the blank. This can be explained by the small quantity of CNCs used, maximum 2 wt%. Moreover, as mentioned previously in the literature, the interactions between PVP and CNCs are weak,[10] resulting in small changes in the positions of the peaks.[10]

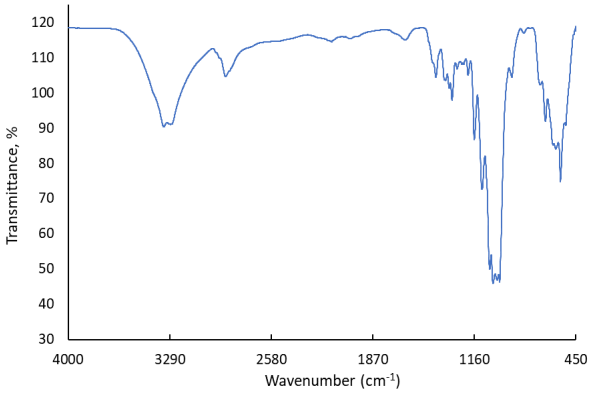

Figure 2: FTIR spectrum of pure CNCs

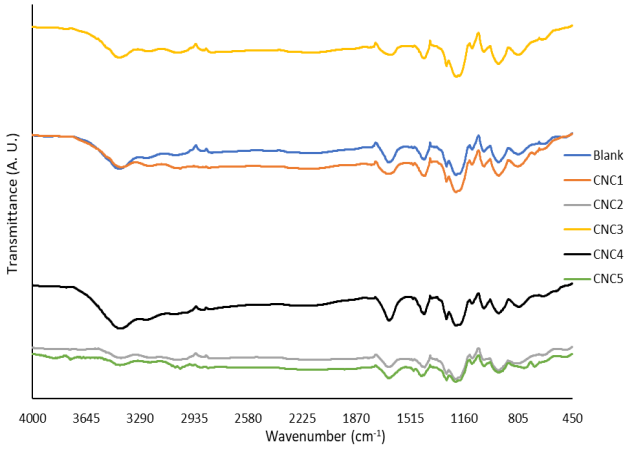

Figure 3: FTIR spectra of PVP-graphite-CNC composites

Table 3
FTIR assignments of composite samples

Peak	Assignment
3430 cm^{-1}	nOH
2880 cm^{-1}	n_aCH
1655 cm^{-1}	nC=O
1418 cm^{-1}	nC=C
1282 cm^{-1}	nC-N
1217 cm^{-1}	g_wCH
1057 cm^{-1}	nC-N
932 cm^{-1}	nC-O

The mechanical properties were analyzed by means of dynamic mechanical analysis. This is a powerful technique that analyzes mechanical properties, showing transitions in samples.

Figure 4 presents the DMA curves of the composites. According to the results obtained, the blank presented a storage modulus (StM) of 418 MPa, decreasing for CNC1 – 378 MPa, and then CNC2 – 313 MPa. Starting with CNC3, the StM started to increase – 406 MPa, reaching the highest level in CNC4 – with a value of 649 MPa. Finally, CNC5 dropped to the lowest value, with a StM of 223 MPa. Thus, as shown by DMA, an increasing content of CNCs improved the value of the storage modulus until a maximum of 649 MPa is achieved, with an increase of 55%, but after this level, the storage modulus suddenly deteriorated to 223 MPa. In relation to CNC1, an increase of 71% was recorded. Thus, the optimum concentration of CNCs was found as 1 wt%.

The initial decrease in StM, upon the addition of CNCs, is indicative of insufficient filler loading. Lower filler loadings, compared to the optimal one, lead to smaller values of storage modulus, but the modulus increases with increasing CNC content. On the other hand, overly high CNC loadings cause a drop in storage modulus, likely because of increased stiffness of the composites and agglomeration of CNCs. In the literature, it has been reported that the Young's modulus and tensile strength of PVP films increased with the addition of CNCs,[10] and the mechanical properties increased until an optimum loading was achieved at 29.2 wt%, then, the mechanical properties decreased. The maximum values were recorded as: 43.8 MPa for tensile strength, and 1755 MPa for Young's modulus. The elongation at break decreased with the addition of CNCs, suggesting that the addition of CNCs increased the brittleness of the films,[10] similarly to the findings in our work.

The addition of CNCs also increased the thermal stability of the samples. CNC3, CNC4 and CNC5 showed a decrease in the storage modulus with increasing temperature, and then a plateau is reached, where no changes of modulus occurred, even with an increase of temperature. The plateau started at 49 °C for CNC3, 71 °C for CNC4 and 79 °C for CNC5. Thus, an increasing temperature tendency for reaching the plateau, with a rising CNC content in the composites is noted. Considering this, as well as the mechanical properties of the composites, allows concluding that, overall, the addition of CNCs had beneficial effects on the characteristics of the composites, by improving their mechanical properties. Table 4 summarizes the DMA results of the composites.

CNFs have been often reported in the literature as binders for many applications, due to the fact that they form hydrogen bonding with the matrix material.[6] Other cellulosic materials, such as carboxymethyl cellulose (CMC), are also commonly given the role of a binder in composites.[20] The inter- and intra-molecular hydrogen bonding, characteristic of cellulose, stabilizes the material, conferring it high mechanical properties.[1] The hydrogen bonding among CNCs, and between the CNCs and the O of PVP stabilized the composite, including the graphite. Figure 5 shows the proposed network formed.

Table 4
DMA results of the composites

Sample	Storage modulus, MPa	T_g, °C
Blank	418	182
CNC1	378	184
CNC2	313	190
CNC3	406	185
CNC4	649	180
CNC5	223	188

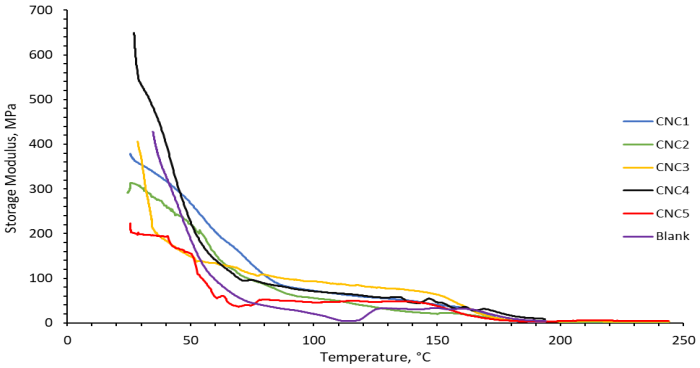

Figure 4: DMA curves of PVP-graphite-CNC composites and of the blank sample

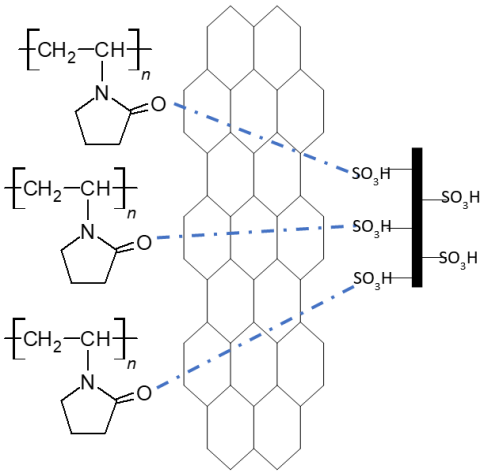

Figure 5: Proposed network formed (blue dotted line: hydrogen bonding)

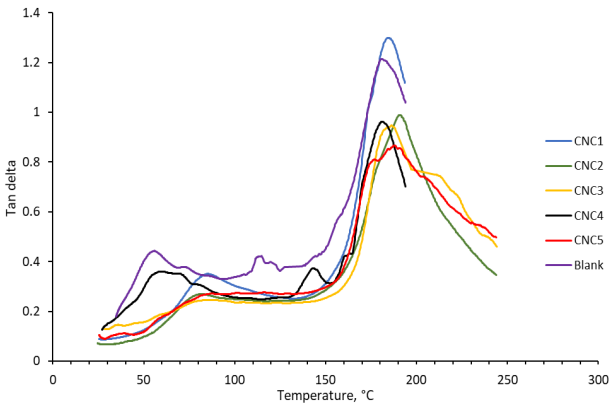

Figure 6: Tan delta curves of the composites

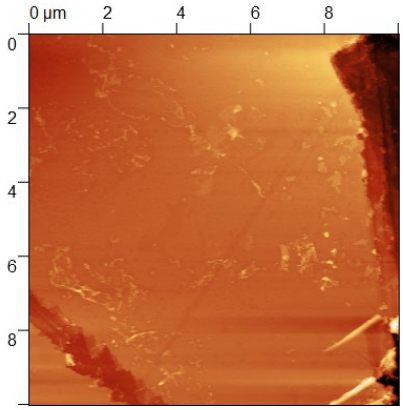

Figure 7: AFM micrograph of CNCs

Figure 6 shows the tan delta curves of the composites and of the blank sample. The glass transition temperature, T_g, of the samples is indicative of the PVP. Other peaks are seen at lower temperatures, due to the effect of graphite, acting as a plasticizer among the chains of PVP. There is no clear correlation between the T_g and the CNC content in the materials. However, the general tendency is: the higher the CNC content, the higher the T_g. The highest T_g values were recorded as 190 °C for CNC2 and 188 °C for CNC5. This last sample, CNC5, showed a complex peak, formed of two close peaks, with measured values of 178 and 188 °C. This

suggests an association of PVP chains enhanced by the presence of CNCs.[10] This effect and the tendency to increase temperature in T_g may be ascribed to the macromolecular confinement provided by the CNC surface in the composite.[21] This confinement may contribute to the observed increase of mechanical properties with increasing CNC content.[10]

Figure 7 shows the AFM micrograph of CNCs, which gives an insight into the colloidal arrangement of CNC particles.[15] The nanocrystals have an elongated form. They look like whiskers, which is a common form of CNCs.[1] Some aggregation of the CNCs may be noticed, caused by the attraction among the nanocrystals. The measured dimensions showed the length of 311.7±68.4 nm, and a diameter of 17.6±1.8 nm. The length is higher than that those reported for CNCs in other publications,[7,14] due to agglomeration of the nanocrystals.

CONCLUSION

The CNCs obtained in this work had a hydrodynamic radius of 52 nm. The addition of the optimum loading of CNCs improved the mechanical properties of PVP-graphite composites. The optimum concentration was 1 wt%, while values smaller or higher than the optimum caused a decrease in the storage modulus of the composites. The nanometric size of the CNCs contributed highly to the enhancement of the mechanical properties of the composites, with increases of up to 70%. The T_g of the composites in the range of 178-190 °C indicates the presence of PVP. The evolution of T_g was also influenced by the increasing CNC content. The sample with 2 wt% of CNC exhibited a complex T_g behaviour, with two T_g peaks observed. The FTIR analysis identified the cellulose nature of the obtained CNCs by the expected functional groups. The absence of characteristic peaks of cellulose in the spectra of the composites can explained the small quantity of CNCs in their composition.

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