

Conductive nanocomposites based on TEMPO-oxidized cellulose and poly(N-3-aminopropylpyrrole-co-pyrrole)

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Abstract

In this paper, conductive composite films were synthesized based on oxidized cellulosic nanofibres (CNFo), 1-(2-cyanoethyl)pyrrole and pyrrole. The 1-(2-cyanoethyl)pyrrole was reduced into N-(3-aminopropyl)pyrrole before being grafted on carboxyl groups of CNFo. Oxidative polymerization of polypyrrole (Ppy) was conducted in an iron (III) chloride (FeCl_3) solution, onto the N-(3-aminopropyl)pyrrole grafted. The resulting composite films were characterized by FTIR-ATR Spectroscopy, scanning electron microscopy (SEM) equipped with energy-dispersive x-ray spectroscopy (EDX), tensile strength measurement, thermogravimetric analysis (TGA), wettability and electrical conductivity measurements. The grafting of 1-(2-cyanoethyl)pyrrole played a leading role in improving these properties by increasing potential connections between chains of conducting polymer and cellulose fibres. The outcomes show that the PPy nanoparticles coating on the grafted films increase a lot of characteristics of our composite such as wettability, mechanical properties, thermal protection and more importantly the electrical conductivity which was improved by a 10^5 factor in comparison to

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the uncoated films. In this condition, this nanostructure could be considered in the design of high-performance electrodes for supercapacitor, battery and sensor applications.

Keywords : Oxidized cellulosic nanofibres, Polypyrrole, 1-(2-Cyanoethyl)pyrrole, Grafting

1. Introduction

Considering the growing interest and demand for new technologies with high performance materials in the past 10 years, researches have been driven toward novel functional nanoscale materials with superior properties. In that way, conducting polymers are promising because of their functional properties, allowing them to be used in many application fields such as batteries, sensors, antistatic coating, among others (Ambade et al., 2013; Wang Z. et al, 2014). Lately, polyacetylene, polyaniline, polythiophene or polypyrrole have been massively studied but, it appears that PPy is one of the most promising conducting polymers for most of the applications, such as electronics (supercapacitor) and biomedical (biosensors, blood purification...). This is due to its biocompatibility, environmental and thermal stability and its high electrical conductivity (Molina et al. 2010; Vaitkuviene & Kaseta, 2013). However, PPy presents poor processability and mechanical properties who limit its commercial applications (Sangawar & Moharil, 2012).

In order to overcome these physicals problems, considerable attention has been focused on a possible reinforcement of the matrix with natural fibres such as bacterial and algal cellulose, dextrin, carboxymethylcellulose, chitosan (Cabuk et al., Ding et al., 2010; Ionescu et al.,2006; 2014; Otero & Vasquez, 1995; Sasso et al.,2010; Zare et al., 2014). Among them, cellulose who is the most abundant natural polymer on earth present a great interest. Indeed, using cellulose-based materials is advantageous since cellulose is renewable, unlimited and biodegradable. The wood nanocellulose fibres of this study are obtained by a TEMPO oxidation reaction that is a region-selective reaction that will chemically modify the primary carboxylic

groups of the cellulose (Paquin et al., 2013; Rattaz et al., 2011). Among advantages of using oxidized cellulose fibres is their large specific surface area, their microporous structure and surface charges for good adherence and their high mechanical properties (Syverud & Stenius, 2009). The polymerization of PPy on the surface occurs when the cellulose nanofibres are dip in a solution of iron chloride in presence of pyrrole. Usually, the bonds obtained between the PPy and the reinforcement are a weak electrostatic interactions (Jradi et al., 2012). The main goal of the current study was to graft 1-(2-Cyanoethyl)pyrrole on CNFo before performing the deposition of PPy as describe above. The 1-(2-Cyanoethyl)pyrrole offers the possibility of creating covalent bonds (amide) between carboxylic groups and the conducting polymer (Lee & Schmidt, 2010). Thus the cellulose was first grafted (PyCNFo) before the synthesis of the final composite (p(PyCNFo)) via polymerization of polypyrrole using FeCl_3 .

2. Experimental section

2. 1. Materials

Pyrrole ($\text{C}_4\text{H}_5\text{N}$), iron III chloride (FeCl_3), 1-(2-Cyanoethyl)pyrrole ($\text{C}_7\text{H}_8\text{N}_2$) and all others chemicals were purchased from Sigma Aldrich and used as received. A commercial never-dried bleached Kraft wood pulp was used as the cellulose sample for the production of CNFo through the TEMPO oxidation and sonication treatments (Rattaz et al., 2011) which confer a carboxyl rate of 1600mmol/kg. The width and length of nanofibres are estimated at 3.5 ± 1.0 and 306 ± 112 nm nevertheless a small proportion of microfibrillated cellulose is still present.

2. 2. Methods

Synthesis of PyCNFo

In order to graft the 1-(2-cyanoethyl)pyrrole onto the CNF, it needs to be reduced in N-(3-aminopropyl)pyrrole. The product was formed in agreement with with the data gathered in the literature (Naji et al., 2003; Rajesh et al., 2005). A yellow oily product was obtained and stored at 4°C for further uses. The reduction was confirmed by ^1H NMR and FTIR analysis. Yield

about 90 % (Abu-Rabeah et al., 2005; Naji et al., 2003). δ H(400MHz; CDCl₃): 1.90 (2H, quint, CH₂-2), 2.70 (2H, t, CH₂-3), 3.96 (2H, t, CH₂-1), 6.15 (2H, d, CH- β), 6.66 (2H, d, CH- α). FTIR spectrum (cm⁻¹) give 3364 and 3300 (NH) while Rajesh et al. (2005) have reported 3370 and 3295.

To synthesize PyCNFo, a part of N-(3-aminopropyl)pyrrole was introduced in a pH 7 buffer solution containing CNFo at a concentration of 0,5 % and mixed for 10 minutes. In order to start the grafting, N-Hydroxysuccinimide (NHS) and 1-ethyl-[3-(dimethylamino)propyl]-3-ethylcarbodiimide HCl (EDC) were added (Abu-Rabeah et al., 2005). The quantities of N-(3-aminopropyl)pyrrole, NHS and EDC have been calculated to graft 10, 20 and 50 % of the carboxylic groups of the CNFo (1600 mmol/Kg). The solution was stirred for 3 hours before being placed in a dish and dried in a forced air oven for two days. The casted films were analysed with FTIR and EDX to confirm that the grafting did occur.

Chemical polymerization of p(PyCNFo)

A transparent film was prepared from PyCNFo suspension at the concentration of 0.5 %. The film was dipped in a solution of FeCl₃ at 0.2 M for 10 min at room temperature. Then 2 ml of pyrrole was added and dispersed over the entire film. After 30 min of polymerization, the film was black and completely coated with PPy nanoparticles. The composite was thoroughly rinsed with distilled water and placed into a solution of HCl at 0.1 M, according to the literature (Hu et al., 2011) to enhance the conductivity. Finally, the film was dried between two hot plates at 80°C.

Characterization

FTIR-ATR Spectroscopy: Effects of modification treatments on surface chemistry of CNFo were examined by FTIR. The spectra were obtained at room temperature on a Nicolet IS10 FT-IR spectrometer (ThermoScientific) equipped with a Diamond/ZnSe crystal. Each spectrum was

acquired in the range of 600–4000 cm^{-1} from 16 scans with the resolution of 4 cm^{-1} . Duplicates of each sample were analyzed at five different points.

Scanning electron microscopy: The surface morphology of samples was studied using scanning electron microscopy (SEM) with a JEOL JSM T300 microscope equipped with EDX analysis. Only the samples PyCNFo (10, 20, 50 %) were gold coated using an Instrumental Scientific Instrument PS-2 coating unit, since the p(PyCNFo) composites (10, 20, 50 %) are conductors. The operation was conducted in secondary electron mode at a beam current of 100 μA with an accelerating voltage of 15 kV.

Tensile strength: The tensile strength of the PyCNFo (10, 20, 50 %) and p(PyCNFo) (10, 20, 50 %) were measured on a universal testing machine (Instron 4201) at room temperature. Elongation at break and Young's modulus of these samples were, therefore, measured. Samples 30 mm in length, 15 mm in width, and approximately 0.08 mm in thickness were cut from the casted film and used in these measurements. The average value of six replicates for each sample was collected.

Wettability: Static distilled water contact angles have been carried out on PyCNFo (10, 20, 50 %) and p(PyCNFo) (10, 20, 50 %). The contact angles were determined by measuring the angle between the samples surface and the tangent to the drop at the solid–liquid air point using a Contact angle system OCA20 (DataPhysics). At least 5 drops (2 μl) of water were deposited onto each substrate and a total 300 images were captured within 30 second for each drop. The investigation was carried out with an accuracy of $\pm 1^\circ$ at a temperature of 25°C.

Thermogravimetric analysis: Thermal stability analysis of the samples was carried out in a Perkin-Elmer (Pyris Diamond) Thermoanalyzer. Samples of CNFo, PyCNFo (10, 20, 50 %) and p(PyCNFo) (10, 20, 50 %) were heated in open alumina pans from 25 to 600°C, under a nitrogen atmosphere, at a heating rate of 10°C/min. Then, samples were heated from 600 to 950°C under air at a heating rate of 15°C/min.

Electrical conductivity measurements: The electrical conductivity of the samples was measured at room temperature by a four-point probe method with the ResTest apparatus from Jandel Engineering Ltd. The probe was equipped with four tungsten carbide needles having a diameter of 100 μm and spaced 1 mm apart. Sheet resistance (R_s , ohms per square) and thickness (t , cm) were used to calculate the specific resistivity, $\rho = R_s \times t$ and the corresponding conductivity, $r = 1/\rho$ ($\text{S}\cdot\text{cm}^{-1}$).

3. Results and discussion

To obtain a functionalized CNFo that can be conjugated with polypyrrole, we first reduced 1-(2-Cyanoethyl)pyrrole in N-(3-aminopropyl)pyrrole using LiAlH_4 in anhydrous ether. Then, PyCNFo was synthesized by coupling N-(3-aminopropyl)pyrrole to carboxylic groups on CNFo via EDC/NHS chemistry (figure 1). In a second step, we have polymerized polypyrrole onto PyCNFo, from pyrrole by using FeCl_3 as oxidant (figure 1). Analysis by FTIR indicated that the coupling between N-(3-aminopropyl)pyrrole and CNFo was a success.

Figure 1: Chemical structure of the p(PyCNFo) composite.

The figure 2 shows the FTIR spectrum of the PyCNFo and p(PyCNFo) samples in the range of 4000 to 600 cm^{-1} . The absorbance of the $-\text{OH}$ bands about 3280, 1420 cm^{-1} of CNFo appear on the two spectras. The band at 1380–1310 cm^{-1} is attributed to the antisymmetric COO^- stretching or aliphatic C–H deformation (Araki et al., 2001). Spectrum from PyCNFo reveal that both surface modification treatments have succeeded in coupling N-(3-aminopropyl)pyrrole with CNFo carboxyl groups. Several of the bands originating from both materials are shared on the spectra, thus indicating the co-existence of the two starting materials in the modified products. Among them, the peaks at 3334 and 1532 cm^{-1} could be attributed to the N–H stretching vibrations of secondary amides and N-H bending. A band at 1242 cm^{-1} results from interaction between N-H bending vibrations and C-N stretching (Clothup et al., 1990).

Moreover the band at 1330-1310 cm^{-1} demonstrates the C-H and C-N in-plane deformation vibration, respectively. The peak at 1050 cm^{-1} is attributed to C-N stretching of tertiary amine (N-(3-aminopropyl)pyrrole). The carbodiimide-mediation clearly resulted in the generation of amide bonds as shown by the presence of amide II (combination of N-H deformation and C-N stretching near 1250 cm^{-1}) and N-H stretching (3334 cm^{-1}) bands. Additionally, the spectrum of p(PyCNFo) shows a small peak at 1634 cm^{-1} that is attributed to the C=C stretching of polypyrrole (Aguilar-Hernandez & Potje-Kamloth, 1999).

Figure 2: FTIR absorbance spectra of PyCNFo and p(PyCNFo).

To further investigate the grafting, EDX analyses were performed on the surface of PyCNFo (10, 20 and 50 %) samples and have confirmed the presence of N on surface. Has no nitrogen is found in the CNFo, that was used as confirmation of the presence of the N-(3-aminopropyl)pyrrole on the surface. The quantitative analysis of the elements C, O, N and others elements was performed and listed in the Table 1. Note that each samples spectrum were acquired onto all area from the SEM micrograph, not a single point. In Table 1, it is also possible to note an increase in nitrogen percentage with increasing grafting percentage of the N-(3-aminopropyl)pyrrole, which reinforces the idea that the chemical reaction was a success.

Table 1: Atomic percent of element of PyCNFo (10-20 and 50 %).

In order to visually study the behavior of grafted fibres, scanning electron microscopy (SEM) images of PyCNFo and p(PyCNFo) were analyzed. The SEM images attest that the surface of grafted and polymerized CNFo exhibits compact, wrinkled and homogeneous mud-like morphology due to the polymerization of PPy (figure 3b) contrary the nanostructure that more developed on the surface of grafted CNFo. Many visible aggregate (regular sphere) on the surface of the PyCNFo (figure 3a) could be attributed to N-(3-aminopropyl)pyrrole grafted. Indeed this aggregate are not present on the cellulose fibres ungrafted (figure 3c). Thus the presence of aliphatic chains in the surface, changes the behavior of the fibres together,

particularly with the presence of sheets on the surface as demonstrated in figure 3a. With the polymerization of polypyrrole, the structure appears denser and the fibres are completely covered by polypyrrole nanoparticles. However, some PPY aggregates are visible on the surface. The layer of PPy explains the electric conductor character of our composite. These structural differences have a direct influence on the mechanical properties of the samples as we have seen during tensile strength tests.

Figure 3: SEM micrograph of PyCNFo (a), p(PyCNFo) (b) and CNFo (c).

The thermogravimetric curves of PyCNFo and p(PyCNFo) are presented in figure 4. The analysis has been realized from 60°C and 600°C with a ramp of 10°C and 600 to 950° with a ramp at 15°C. There are two major weight losses. The first one occurring around 180°C, was attributed to the destruction of crystalline region of the CNFo and decomposition of amorphous CNFo into a monomer of D-glucopyranose. The second one, occurring around 640°C, was attributed to the destruction of carbon chains. We can observe that the p(PyCNFo) have a better thermal resistance than the PyCNFo, in generality. If we look closer to the thermal degradation curves of grafted and polymerized CNFo samples, it's visible that the 50 % grafted composite is better except for the temperature between 180°C et 360°C, where the 20 % grafted is the best. Thus, the thermal stability of the composite seems to be increased until 600°C by the presence of PPy. The aliphatic chains of polypyrrole confer thermal protection to the cellulose fibres. Regarding PyCNFo samples, it's possible to observe the same improvement to the thermal stability which could be attributed to the grafted N-(3-aminopropyl)pyrrole which offer thermal processing advantages. This improvement can be potentially extended if we increase the grafting degree of aliphatic chains.

Figure 4: Thermogravimetric analysis of PyCNFo and p(PyCNFo) (solid line: samples at 50 %; dash dot line: samples at 20 %; dot line: samples at 10 %).

The mechanical properties of PyCNFo and p(PyCNFo) are obtained after a clear breaking of samples and shown in Table 2. It is important to note that the mechanical properties of pure PPy are very poor due to the chemical polymerization which gives PPy powder form and thus, no film can be casted. Results from Table 2 demonstrate that increasing the degree of grafting on the cellulose fibres, leads to a decrease of strength for the unpolymerised PyCNFo. The presence of aliphatic chains affects the mechanical properties of films as this decrease can be attributed to the loss of interactions, inter- and intra-molecular hydrogen bonding between fibres. These interactions result of the presence of free carboxyl groups. Therefore a degree of 50 % of grafting of carboxyl group causes a greater loss of cohesion of the fibres and lower mechanical properties. The elongations at break (%) at different grafting degree of grafted CNFo are similar. In this context, Young's modulus values of the PyCNFo confirm a lower stiffness of the samples, which is conferred by the presence of grafted N-(3-aminopropyl)pyrrole.

Table 2: Mechanical properties, conductivity and contact angle of PyCNFo and p(PyCNFo) samples.

It is interesting to note that in presence of polypyrrole, the mechanical properties of the samples are very much improved (multiplied by 2). In the current literature, the polypyrrole have not yet be recognized to improve the mechanical properties of any composites (Jardi et al., 2012). To explain this improvement due to the presence of PPy, it is possible to think of the establishment of covalent bond between the cellulose fibres through the intermediary of polypyrrole chains which polymerize onto the grafted pyrrole molecule (figure 5). This hypothesis seems to be confirmed since the mechanical properties and elongation at break seem to increase with the grafting degree of fibres and more evidently for the 50 % grafted. Thus, stastically, the percentage of formation of these intermolecular bonds should growth with increased presence of grafted pyrrole.

Figure 5 : Chemical structure and proposed pathway of the covalent bond formation between the PyCNFo fibres via the polymerization of polypyrrole.

In conclusion, the improved mechanical properties of p(PyCNFo) compared to PyCNFo that were observed could be explained by the contribution of the polymerization of polypyrrole. However the decreased behavior of grafted CNFo could be attributed to the weakened inter- and intra-molecular hydrogen bonding of cellulose nanofibres caused by the incorporation of grafted N-(3-aminopropyl)pyrrole. Therefore, it's interesting to note that the polypyrrole increases the mechanical properties of composite.

Beyond increasing the mechanical properties, the presence of polypyrrole in the composite increases the hydrophobic character. The values of the contact angle measured with distilled water are shown in Table 2. The grafting of N-(3-aminopropyl)pyrrole gave the expected increase in hydrophobic character (75.8°), which is explained by the presence of the aliphatic chain from the pyrrole derivative. With only 10 % of grafting, the behavior is quite hydrophilic due to the lower presence of aliphatic chains and the higher presence of free carboxyl group. The addition of polymerization of polypyrrole on the surface achieve the same degree of hydrophobicity that PyCNFo 50 % whatever the degree of fibres grafted. These result can be explain by a layer of polypyrrole on the surface which completely cover fibres, thus concealing any difference in grating percentage.

Electrical conductivities of the samples were determined and the results were shown in Table 2. It was observed that the conductivity is very low for the grafted CNFo ($6.51E-05$ S/cm), whatever the degree of grafting. This result can be explain by the insulating character of cellulose and the presence of aliphatic chains which don't have a conjugated systems to allow the delocalization of electrons. For the grafted and polymerized CNFo samples, the conductivity is multiplied by $10E5$ (20S/cm). This behavior is attributed to the formation of a continuous conducting PPy layer that homogeneously coat the surface of PyCNFo. As

expected, the insulating character of cellulose was inhibited by a PPy layer and the grafted N-(3-aminopropyl)pyrrole. The effect of the grafting degree is significant because an increase in conductivity by four with 50 % grafted was found. These results obtained are superior to those obtained by Zhang *et al.* with tunicate cellulose and PPy via the in situ oxidative chemical polymerization ($10E-3$ S/cm) (Zhang D. *et al.*, 2013) or those obtained by Xu *et al.* with bacterial cellulose (3.9 S/cm) (Xu *et al.*, 2013). To confirm the good conductivity of our samples polymerized, we have realized a simple installation with a battery (12V) and a light emitting diode (LED). The sample is included in the circuit between the white and red wires (bottom) and it is easy to see the powered LED (figure 6) and the magnitude of the light intensity. Even if the conductivity is not in the range of metals yet (over $10E2$ S/m), it is clear from figure 6 that our composite exhibit some conductive properties.

Figure 6: Demonstration of conductivity of the p(PyCNFo) by light emitting diode (LED).

4. Conclusions

In conclusion, the grafting of N-(3-aminopropyl)pyrrole was a success as confirmed by the FTIR and EDX results. The several analysis performed on the PyCNFo and p(PyCNFo) at different grafting degrees have shown that the deposition of PPy nanoparticles onto the surface of PyCNFo has increased its mechanical properties (stress and elongation at break), particularly at high grafting percentage. This is the first time in the literature that the PPy is accounted as a mechanical reinforcement for a composite. From our proposed mechanism, the grafting of 1-(2-cyanoethyl)pyrrole played a leading role in improving these properties since allowing for the connection between chains of conducting polymer and cellulose fibres. The polypyrrole also allowed improving the thermal resistance and the hydrophobic character of the films by forming a protective layer. The combination of polypyrrole and 1-(2-cyanoethyl)pyrrole also allowed obtaining a high conductivity (about 20S/cm), never achieved by simple use of natural fibres and a semiconductor polymer. Such nanostructure can be foreseen in the design of high-

performance electrodes for supercapacitor, battery and sensor applications from a renewable source.

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6. Notes and references

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