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Advancement in conductive cotton fabrics through in situ polymerization of polypyrrole-nanocellulose composites

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ABSTRACT

Current research was undertaking with a view to innovate a new approach for development of conductive – coated textile materials through coating cotton fabrics with nanocellulose/polypyrrole composites. The study was designed in order to have a clear understanding of the role of nanocellulose as well as modified composite thereof under investigation. It is anticipated that incorporation of nanocellulose in the pyrrole/cotton fabrics/$FeCl_3$/H_2O system would form an integral part of the composites with mechanical, electrical or both properties. Three different nanocellulosic substrates are involved in the oxidation polymerization reaction of polypyrrole (Ppy) in presence of cotton fabrics. Polymerization was subsequently carried out by admixing at various ratios of FeCl3 and pyrrole viz. Ppy1, Ppy2 and pp3. The conductive, mechanical and thermal properties of cotton fabrics coated independently with different nanocellulose/polypyrrole were investigated. FTIR, TGA, XRD, SEM and EDX were also used for further characterization. Results signify that, the conductivity of cotton fabrics increases exponentially with increasing the dose of pyrrole and oxidant irrespective of nanocellulose substrate used. While, the mechanical properties of cotton fabrics are not significantly affected by the oxidant treatment.

1. Introduction

By virtue of their excellent electrical and optical properties conductive polymers have been extremely studied (Carrillo et al., 2013; Hazarika & Kumar, 2014, 2016; Mondal & Sangaranarayanan, 2015; Tabačiarová, Mičušík, Fedorko, & Omastová, 2015). One of the intrinsic conducting polymers is Polypyrrole (Ppy). It has evoked the interest of researches because of their electrical, optical, biological and medical areas of applications. It is characterized by a good electrical conductivity and its straightforward polymerization, cytocompatibility, environmental stability and electrical conductivity that can be controlled by changing the doping degree (Müller, Rambo, Recouvreux, Porto, & Barra, 2011). Polymerization of pyrrole can be induced by electro-chemical oxidation on metallic substrates or by chemical oxidation (Molina, del Río, Bonastre, & Cases, 2009; Sasso et al., 2010, 2011).

Recently, composite materials with potential application in many fields have been developed, which the conductive polymer–coated textiles are now a part of that family (Bober et al., 2015; Lin, Wang, Wang, & Kaynak, 2005; Mičušík et al., 2007). Demands in coated fabrics are stimulated by growth in many industrial areas. These fabrics are used for industrial applications, such as filters, as well as home and business applications, including electrostatic dissipating and electromagnetic interference shielding, flooring, ceiling materials, de-electrifying clothes, and dust- and germ-free clothing. The microwave absorption characteristics of these fabrics are also highly desirable, thus allowing these materials to be used in military applications such as camouflage and radar protective fabrics for stealth technology. Considering support materials for conductive additives, cellulose nanofibers is by far the most promising. This is unequivocally due to high strength and stiffness along with renewability, biocompatibility and biodegradability of cellulose nanofibers among other important properties (Kamel, 2007; Klemm et al., 2006; Plackett et al., 2010; Xu et al., 2013).

These outstanding properties make nanocellulose a good candidate in various advanced materials for biomaterials and electronic devices (Hebeish, Farag, Sharaf, & Shaheen, 2014c; Hebeish, Farag, Sharaf, & Shaheen, 2015b; Luong et al., 2011). Much research and development effort has been devoted recently to the production of cellulose nanocomposite with high electrical and mechanical performances to applied for such applications (Luong et al., 2013; Marins, Soares, Barud, & Ribeiro, 2013; Wang et al., 2015).

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Recently, Wang et al. demonstrated that Ppy-nanocellulose reinforced 3D Ppy can be readily manufactured and employed as free-standing paper-like electrodes for efficient capacitive storage devices using a facile, low-cost, *in situ* polymerisation method (Wang et al., 2014).

Current research work is taking all of these aforementioned unique physical and mechanical properties to develop new conducting nanocellulose-based materials through coating cotton fibers with cellulose nanoparticles/polypyrrole composite. Three nanocellulosic materials having different surface chemical modifications, are used. In our previous works, surface modifications had been conducted to impart polymeric and monomeric groups on the backbone of cellulose nanowhiskers (CNW) to produce CNW – Polyacrylamide (CNW-PAAm) copolymer as an example of polymeric groups (Hebeish, Farag, Sharaf, & Shaheen, 2014a) and nanocarbamoylethylated cellulose (NCEC) as an example of monomeric groups (Hebeish, Farag, Sharaf, & Shaheen, 2015a). CNW-PAAm was prepared through free radical graft polymerization reaction with polyacrylamide, whilst, NCEC was obtained through etherification reaction of CNW with acrylamide as a monomer. Both chemically modified; CNW – PAAm copolymer and NCEC, as well as CNW are allowed to be interact during polymerization of polypyrrole in situ cotton fabrics. Herein, the main objective brings into study the effect of enclosing of those cellulosic nanoparticles which having different groups attached on the cellulose nanowhiskers backbone.

2. Experiments

2.1. Materials

CNW (Hebeish, Farag, Sharaf, & Shaheen, 2014b; Hebeish, Farag, Sharaf, Rabie, & Shaheen, 2013), CNW – PAAm copolymer (Hebeish et al., 2014a) and NCEC (Hebeish et al., 2015a) were prepared according to our previous contributions. Sodium hydroxide, sodium borohydride, silver nitrate, copper acetate, ascorbic acid, ethylene glycol, iron chloride ($FeCl_3$) and pyrrole (purchased from SigmaAldrich) were all of laboratory grade chemicals. Mercerized and bleached cotton and polyester/cotton blend fabrics were provided from El-Nasr Company for Spinning, Weaving and Dyeing – El-Mahalla El-Kubra, Egypt.

2.2. Methods

2.2.1. Preparation of conductive fabrics via in situ polymerization of pyrrole

Herein, CNW, CNW – PAAm copolymer and NCEC are involved in the oxidation polymerization reaction of Polypyrrole (Ppy) in presence of cotton fabrics. Polymerization was subsequently carried out by admixing at various ratios of FeCl3 and pyrrole. In separate vessels, 0.3 g of CNW, CNW – PAAm copolymer and NCEC, are dispersed in 50 ml distilled water using high-energy ultrasonication. To each dispersion, pyrrole monomer was dissolved and the solution was completed to 100 ml. Then, the cotton fabrics (15 cm × 20 cm) were immersed into the latter solution for only 30 min before the polymerization reaction took place. $FeCl_3$ dissolved in 100 ml distilled water was, finally, poured dropwise onto the cotton fabrics to initiate the polymerization. The polymerization reaction was allowed to proceed for 120 min under gentle stirring at ambient temperature. Three different ratios of $FeCl_3$ and pyrrole monomer were used in these reactions as shown in Table 1. At the end, the loaded cotton fabrics are washed first with 100 ml of 0.1 M HCl and thereafter thoroughly with distilled water for several times and finally dried in oven at 70 °C. Blank sample was made with exclude of cellulose nanosized substrates.

Table 1
Chemical composition used for the preparation of Polypyrrole/nanocellulose composite coated cotton fabrics.

Sample ID	Pyrrole (ml)	$FeCl_3$ (gm)
Ppy-1	5.3	2.0
Ppy-2	8.0	3.0
Ppy-3	10.6	4.0

2.3. Testing and characterization

- Fourier-transformed infrared spectroscopy (FT-IR)

FTIR spectroscopy has been extensively used in cellulose research, since it presents a relatively easy method of obtaining direct information on chemical changes that occur during various chemical treatments. FT-IR spectra were recorded using a S-100 FT-IR spectrometer (Perkin Elmer) and scanned from 4000 to 400 cm^{-1} in ATR mode using KBr as supporting material. Characterization of samples using FT-IR technique was carried out to follow the change in the functionality of CNW as a result of grafting with acrylamide monomer.

- X-Ray Diffractometry (XRD).

X-ray diffraction (XRD) patterns of finely coated fabrics with metals were recorded on a Philips PW3040 X-ray diffractometer system by monitoring the diffraction angle from 5° to 80° (2θ) at 40 keV.

- Thermo Gravimetric Analysis (TGA).

The TG measurements were carried out using 8–10 mg of the samples at a heating rate of 283 K min^{-1} in an N_2 atmosphere using a TGA/SDT Q600 analyzer. The TG was conducted with the compounds placed in a high-quality nitrogen (99.5% nitrogen, 0.5% oxygen content) atmosphere with a flow rate of 20 ml min^{-1}, to avoid unwanted oxidation. Each sample was scanned over a temperature range from 298 to 1073 K.

- Scanning electron microscopy (SEM):

SEM was studied using a scanning electron – JSM-5400 instrument (Jeol, Japan). The specimens in the form of fabrics were mounted on the specimen stabs and coated with thin film of gold by the sputtering method.

- Energy dispersive X-ray analysis (EDX).

The elemental analysis was performed using EDX, which is an attachment to thescanning electron microscopy. The spectra obtained during EDX studies were used for carrying out the quantitative analysis.

- Weight increase

The amount of Ppy/cellulose nanoparticles deposited on the cotton fabrics was determined by weighing the cotton samples before and after the polymerization reaction under standard conditions of temperature (20 °C) and relative humidity (65%). The percentage weight increase (W%) was calculated as follows:

$$W\% = \frac{Wf - Wi}{Wi} \times 100$$

Where *Wi* and *Wf* are the initial and final weight, respectively.