

PPy Covered Cellulosic and Protein Fibres Using Novel Covering Methods to Improve the Electrical Property

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Abstract: This paper is about the adjustment and improvement of some properties of fibers for creating super properties and special applications that have always been considered. One of instances has been to create filament yarns with electrical conductive property. Preparation of fibers from blended polymers (by ways of melt spinning and wet spinning) and yarn spinning from different mixed fibers have been among cases to be studied in this research, but few cases of research on fibers coating have been met by the past researches. In this study, first we have done a pretreatment on cellulosic fibers (e.g. cotton) and a protein fiber (e.g. silk), after going and activation stages, then we coated them with conductive polymers such as pyrrole and aniline by two methods: Vapor and liquid phases. In these two methods we studied value of penetration of conductive polymer fibers by Scanning Electron Microscope (SEM) and we have continued with assessing physical properties and optimizing value and percent of coating by these properties. Electrical properties of produced fibers have evaluated by Four Probe Method. We finally obtained optimized value of properties and suitable conductivity. Electronic images of SEM showed that vapor and gas coating is more desired and gas penetration into fibers has been done better and polymer conductivity after several washing has shown 6.4×10^{-4} S/cm for cellulose fiber and 3.2×10^{-4} S/cm for silk fiber. Heat studies of Differential Scanning Calorimetry (DSC) also showed increase in both heat resistances for both coated fibers. The study demonstrates that conductive-coated fibers improve conductivity and the physical properties remain fixed nearly.

Key words: Covering . electrical property . cellulosic and protein fibers . PPy . continuous vapour-phase polymerization . electro-active polymer

INTRODUCTION

Several works have been devoted to the coating of fibers or fibrous materials with Conducting Electroactive Polymers (CEP). All these works involve a vapour-phase treatment of oxidant-containing carriers with the monomers [1]. Polymers with conjugated π -electron backbones can be oxidized or reduced more easily and more reversibly than conventional polymers. Dopants, which act as charge transfer agents, affect this oxidation or reduction process and render these polymers conductive. The ultimate goal of electrically conductive polymer research is to combine the processability of polymers with the electronic properties of metal or semi-conductors [2]. Unfortunately, most of these conductive polymers are intractable and cannot be processed into useful articles. This is particularly true for polypyrrole (PPy) and

polyaniline (PANi), which are preferred for their high conductivity and stability under environmental condition [3, 4].

Metal coated fabrics [5] and carbon filled or copper sulphide textile fibers are used to impart various degrees of conductivity to polymer structures [4]. A PPy-carbon fiber composite with a carbon fiber content of 15-20% was prepared by the chemical polymerization of pyrrole [6]. The resulting composite has tensile strength and good thermal stability and can be used as a cathode material for a rechargeable battery, where carbon fibers act as an electrically conductive skeletal electrode for current collection with a specific capacity of 91 mA h/g [6]. Electrically conductive composites have been prepared by treating with oxidizing agents and exposing them to pyrrole, depositing a substantial amount of conductive polymer within the interstices of the material [7]. This process

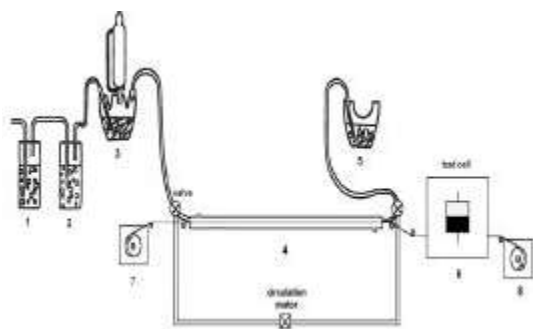


Fig. 1: A scheme of coating system with evaporation method in which: (1) the first gas wash (containing pyrogallol solution), (2) second gas wash (containing concentrated sulphuric), (3) 25 mL three-necked flask contain monomer, (4) bi-layer glass pipes with the inlet and outlet in the second wall, (5) two-necked flask, (6) conductivity measurement cell, (7) bobbin of prepared string, (8) bobbin of coated strings [13, 10]

pipe. This glass pipe has a water inlet and outlet that for pyrrole hot water flows in the second wall till homogeneous. So, we would have suitable environment in heat terms being established. The monomer sits on the surface of fibers smeared with oxidizers and the polymerization takes place on fibers. We could control the passing time or polymerization time in polymerization process by different valves. To have a better performance of both functions, two valves have been fixed in the beginning and ending points of the bi-layer glass pipe (1) and (2) and connect them to the circulator motor via a glass pipe. After entry of gas into the bi-layer glass pipe, the valve (1) is closed and after passage of monomer, the valve (2) would be closed. The gas circulates in the closed path through circulator motor for a few minutes till a homogeneous polymerization takes place on the fiber. Finally, all gases remained enter into the two-opening balloon containing concentrated sulphuric acid which has been employed at the environment to prevent diffusion of pyrrole gas. Then by motion of bobbin (8), the coated string moves and the direction conductivity path is measured by a four-point probe method and then collected on bobbin. This operation continues for production of necessary amounts of the coated strings.

RESULTS AND DISCUSSION

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC): DSC and TGA thermograms of cotton coated by PPY in vapor phase are given in Fig. 2 and 3, respectively. Figure 4 shows

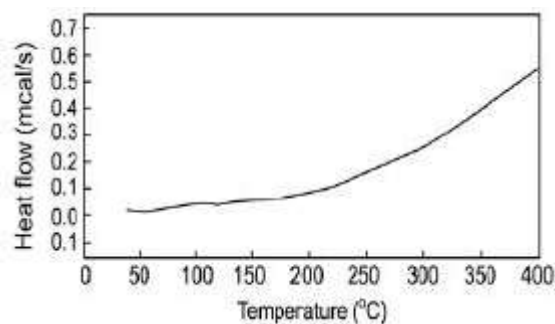


Fig. 2: DSC Thermogram of cotton coated by PPY

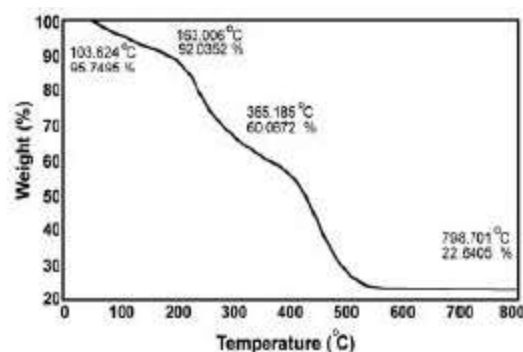


Fig. 3: TGA Thermogram of cotton coated by PPY

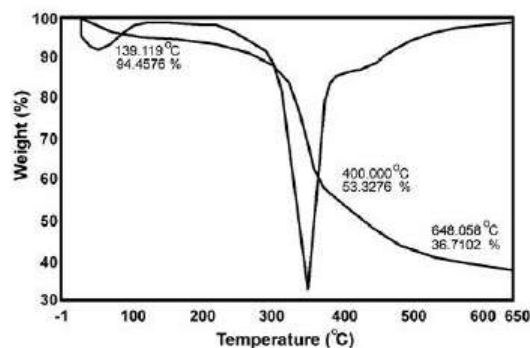


Fig. 4: STA (DSC and TGA) Thermogram of silk coated by PPY

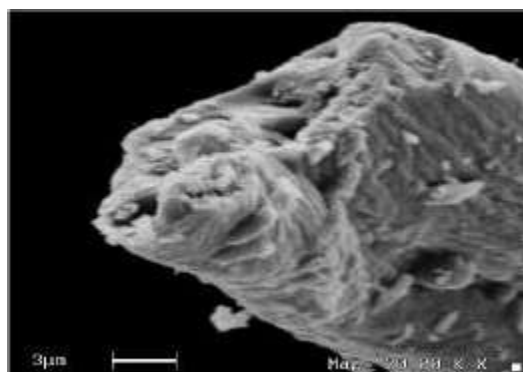
STA (DSC and TGA) thermograms for silk coated by PPY. As it is shown in all coated fibres no exothermic peak is observed, but an endothermic peak is produced at 120°C for cotton and at 50 and 350°C for PPY coated silk. The TGA of PPY coated cotton shows a weight loss in three stages. The first stage is range of 50°C and 163°C and shows about 8% loss in weight. This may correspond to loss adsorbed and bound solvent. The second stage of weight loss at 170°C and continued at 365°C during which there was a 40% of weight loss due to the first degradation of polymer. The third stage of weight loss starts at 370°C and continues to up



(a)



(b)

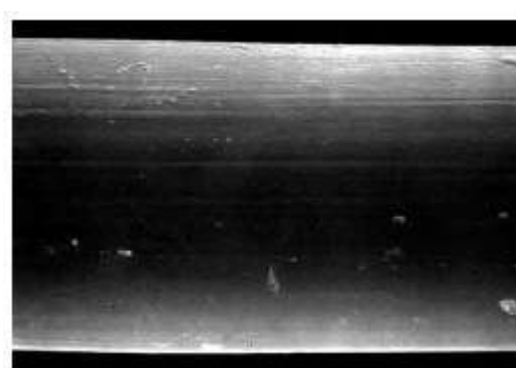


(c)

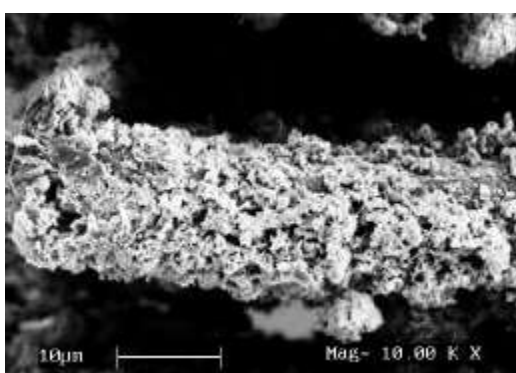
Fig. 5: SEM Micrographs of (a) cotton crude, (b) cotton coated by PPy and (c) cross-section cotton coated by PPy

500°C during which there was a 77.36% of weight loss due to the second degradation of polymer.

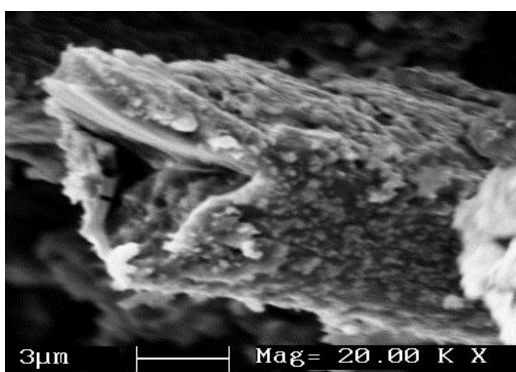
Therefore, TGA of coated silk by PPy shows a weight loss in three stages. The first stage range is between 40°C and 280°C and shows about a 5.54% loss in weight. This may correspond to a loss being adsorbed. The second stage of weight loss starts at 280°C and continues to 400°C during which there was a 46.68% of weight loss due to the first degradation of



(a)



(b)



(c)

Fig. 6: SEM Micrographs of (a) silk crude, (b) silk coated by PPy and (c) cross-section silk coated by PPy

polymer. The third stage of weight loss starts at 400°C and continues up to 600°C during which there was nearly a 70% of weight loss due to the second degradation process of polymer.

Scanning electron microscopy: Polymer structure and morphology are greatly affected by electro-synthetic conditions, such as electrode materials, solvent and electrolyte salts, oxygen and water content of the

Table 1: Conductivity of cotton and silk fibers coated (S/cm) with polypyrrole (PPy) before and after doping by gas and solution HCl, I₂ after 30 min exposed

PPy coated	Before doping	Doping by HCl (g)	Doping by HCl (l), 1 M	Doping by I ₂ (g)	Doping by I ₂ (l), sat.
Cotton	1.4×10^{-5}	2.1×10^{-4}	6.1×10^{-4}	6.2×10^{-3}	3.6×10^{-4}
Silk	3.1×10^{-5}	4.2×10^{-4}	7.2×10^{-4}	8.0×10^{-3}	6.5×10^{-4}

Table 2: ANOVA data of cotton and silk fibers coated by PPy

Code	Sum of squares	df	Mean square	Sig.
Between groups (Cotton coated by PPy)	710.7	1	710.719	0.572
Within groups (Cotton coated by PPy)	63054.7	29	2174.3.00	-
Between groups (Silk coated by PPy)	861080.7	2	430540.344	0.196
Within groups (Silk coated by PPy)	22588901.0	87	259642.540	-

Table 3: Paired samples statistics of cotton and silk fibres coated by PPy

Code	Paired differences			95% Confidence interval of the difference		Sig. (2-tailed)
	Mean	SD	Std. Error mean	Lower	Upper	
Cotton crude	-164.1935	46.1226	8.2839	-181.1100	-147.2750	0.000
Pair of cotton and cotton coated by PPy	13.4667	45.3041	8.2714	-3.4502	30.3835	0.114
Silk crude	3733.7000	492.3305	89.8868	-93.2000	-75.5304	0.000
Pair of silk and silk coated by PPy	168.3000	595.5218	108.7268	-54.0710	390.6713	0.132

system and the current density used for electropolymerization. Although a quantitative measure of these effects has not been established, some general observations have been made. Thin films generally appear smooth, whilst thicker samples have a much more uneven textured surface [13]. Lower current densities and potentials used during electropolymerization give rise to smoother films. Scanning Electron Microscopy (SEM) of figures shows a monotony and kind of phase and surface of polymers completely. SEM also shows that the doping/dedoping process is often accompanied by major changes in morphology, perhaps due to swelling caused by the insertion and removal of ions within the polymer matrix. The SEM results show polypyrrole is space-filling, i.e. non-fibrillar and non-crystalline [10] and a similar amorphous morphology is also as a typical polythiophene. However, in the case of polythiophene it indicates a basically granular or fibrillar structure. There is also an evidence to suggest that chemically synthesized polythiophene is crystalline. Figures 5a-c and 6a-c show the images of SEM for PPy coated on cotton and silk either along fiber surface or its cross section. Earlier studies on the surface morphology of fibers coated by PPy have demonstrated their smooth surface.

The cross-section of images of conductive fibers shows two phases of the fibers completely clear. So, these fibers have special characterization between fibers and conducting polymers.

Tenacity and conductivity measurements:

Conductivity of cotton and silk coated by PPy before and after I₂ and HCl doping vapors are listed on Table 1. According to Table 1 the conductivity of conductive fibers, is comparable with normal conductive polymers. Physical properties of two groups of fibers have been investigated together, such as, crude fibers and coated fibers by PPy. We have studied tensile strength of the prepared fibers and then statistical comparison is made by software SPSS 2002. Table 2 and 3 show ANOVA data and paired samples statistics of cotton and silk fibers coated by PPy, respectively. As shown in the Tables, the tensile strength of the coated fibers in comparison to the crude fibers, not only shows no changes but also in some of the cases it has increased as well.

CONCLUSION

Continuous vapour phase polymerization of pyrrole on silk and cotton yarns enabled production of uniformly coated yarns with low electrical resistivity.

The resistivities, tensile properties, longitudinal and cross-sectional views of continuous vapour deposited PPy-cotton and PPy-silk yarns were investigated.

The tensile strength of the crude silk is higher than crude cotton. The tensile strength of the conductive silk is better than cotton as well. Simple operation, low cost and sufficient conductivity are advantages of this method.

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