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ELECTRICAL PROPERTIES OF CONDUCTIVE POLYMERS: PET – NANOCOMPOSITES' FIBRES

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Abstract

Researches in the field of conductive polymers have attracted considerable attention for more then 20 years. Among the conductive polymers, polyaniline and polypyrrole have drawn considerable interest because of their economical importance, good environmental stability and satisfactory electrical conductivity when doped. On the other hand, electrically conductive materials such as aluminium powder, graphite and carbon nanotubes have very interesting conductive properties and are promising in the synthesis of new composite conductive materials. In almost all studies, conducting polymer films are developed and then electrical and mechanical properties are tested.

In our paper, the conducting polymer fibres have been obtained by melt mixing and chemical coating on the fibres. Different conductive materials have been used in order to obtain conductive polypropylene-based fibres with specific electrical and mechanical properties. The electric conductivity and morphological characteristics of these fibres have been investigated and the results are discussed.

The originality of our approach lies in our having created conductive fibres based on conductive polymers. These fibres are intended for use in creating conductive yarns and realising connections in smart clothing, or producing conductive fabrics which can be used as electromagnetic shields.

These developments have been carried out in order to create new multifunctional textile structures for different applications in the field of intelligent and communication apparel or other similar branches.

Key words:

conductive fibres, conductive polymers, polymers, polyaniline, polypyrrole, melt mixing, PRT fibres

1. Introduction

The conventional method for preparing electrically conductive polymer composites (CPCs) is by admixing conductive solid fillers such as metal particles, carbon black, graphite or carbon nanotubes into the common polymer [1-4]. On the other hand, conductive polymers were also expected to yield numerous potential applications over the last decade. Conductive polymers are a suitable replacement for inorganic materials since they exhibit extraordinary electrical properties and a wide variation in colour due to their conjugated double-bond chain structure, which derives from both their conducting or neutral (non-conducting) forms. However, they are inherently insoluble, infusible and non-processable due to their strong intermolecular interactions. Therefore, high-quality conducting blends with conventional polymers by melt mixing [5-9] or by solution casting [10-14] are still at the development stage.

Among the conjugated conducting polymers, polyaniline (PANI) and polypyrrole (PPy) have attracted much interest worldwide because of their high environmental, thermal and chemical stability and their high conductivities. The electrical conductivity of these polymers is between 10^{-5} S/cm and 10^{2} S/cm while being doped, whereas common insulators exhibit conductivities below 10^{-12} S/cm. With a simple protonation process in PANI and PPy [15-17], both solubility in common organic solvents and compatibility with various matrix polymers on the nanometer scale can be improved.

These conducting blends or composites have been developed with a wide range of exciting properties for applications in film, fibres, and coatings. Conducting polymers may therefore find applications in electromagnetic interference (EMI) shielding, transparent packaging of electronic components, solar batteries, nonlinear optical display devices, 'smart' fabrics and recording, and so on. Recently, electroluminescence from conjugated polymers was observed at Cambridge Display Technologies (CDT), and this extraordinary feature could open up potential markets for organic light-emitting diodes (OLED) [18-21]. This light-emitting polymer (LEP) technology is expected to provide an opportunity for the fabrication of flexible, full-colour displays with high luminescence, small power consumption and low-cost technology.

On the other hand, the Clemson, Furman, and Ga. Tech. laboratories have begun to conduct research into chameleon fibres that change the substrate colour upon application of an electrical field. These intelligent textiles based on conductive materials have been prepared by direct surface coating or by in-situ polymerisation on textile substrates [22].

Consequently, extensive control of the conductivity of CPCs is theoretically possible, and the construction of communication apparel such as wearable computer and micro-display applications will also become possible in the near future. From this viewpoint, the aim of our approach is to prepare conductive fibres in order to realise connections in smart clothing or to realise conductive fabrics which can be used as electromagnetic shields.

Until recently, many remarkable attempts at making electrically conductive blends were performed in the resulting film, but not in the field of fibre spinning. Here, in the first section of our research, doped PANI was chemically coated onto PET fibres. In section 2, conductive fibres of different conductive materials/polyolefins were prepared by using melt-processing techniques. In section 3, conductive fibre morphology and electrical conductivity were investigated due to their significant effect on the resulting electrical conductivity. Finally, a conclusion regarding future research projects is put forward in the forth section. The organisation of this paper should facilitate readability and comprehension.

2. Experimental

2.1 Materials

Leucoemeraldine salt form polyaniline (PANI-LES) and polypyrrole (PPy) were purchased from the Sigma-Aldrich Chemical Company. In addition, graphite (Carbon Nanotechnologies Inc.) was also used as conductive material.

Dodecylbenzene sulphonic acid (DBSA, Fulka) and camphor sulphonic acid (CSA, Aldrich) were used to simultaneously protonate the PANI and induce solubility of the PANI in the conducting form in common solvent. Here, xylene and m-cresol were used as solvents for the solution process. For the melt process, polypropylene (PP, Elf-Atochem.) and low-density polyethylene (LDPE) were used as matrix polymers.

2.2 Sample preparation

Method 1

The PANI series, graphite and matrix polymer were melt-mixed using a twin-screw extruder (Mini Lab., Thermo Haake, Germany) at 50 rpm for 15 min, at 150°C, 180°C and 200°C for LDPE, PMMA and PP respectively. The conductive materials' concentration range was from 1 to 40 wt%.

Method 2

The PANI-LES with excess DBSA was dissolved in hot xylene and was vigorously stirred for 3 hrs. Next, this solution was treated in an ultrasonic bath for 2 hrs at 50°C.
The PANI-DBSA polyblends in PP were prepared by mixing PANI-DBSA solution in hot xylene with 10% (w/w) solution of PP. The PANI-DBSA films and polyblends films were obtained by casting the corresponding solutions onto glass plates and then drying at 50°C for the solvent to evaporate. After drying, composite films were obtained by peeling them off the glass substrate. The PANI-CSA solution in hot m-cresol was prepared as previously reported [10] and was placed under a hood for 2 days.

Then, the PANI-DBSA, PANI-CSA reaction solutions were filtered off and washed with 0°C acetone to obtain the dark green powder.

PET fibres were absorbed into the PANI-DBSA/xylene solution and PANI-CSA/m-cresol solution, and dried at 50°C for 24h.

2.3 Morphological and electrical characterisation

The surface structures of the coating fibres were simply determined by reflected light optical microscopy with an Axioskop (Zeiss). Electric conductivities were determined using the 'two-probe test technique' and a Keithley 617 electrometer was used as an ammeter. The Keithley 617 electrometer generates a variable DC voltage power supply connected to the conductive fibres. At the same time it measures the electric current with the PA maximum precision. The electrometer is connected to a PC computer, which controls the voltage of the DC power supply and records the measured current. The measurement scheme is shown in Figure 1.

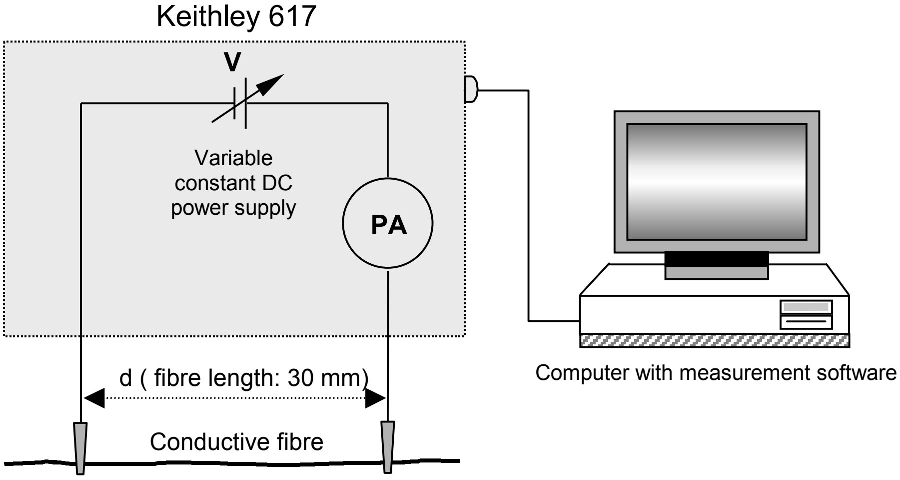

Figure 1. Schematic view of geometry and circuit for making the resistivity measurement

3. Results

In this section we present all the results concerning the conductivity of different fibres and their morphological structures. These results are presented for the fibre samples prepared by Method 1 and then by Method 2.

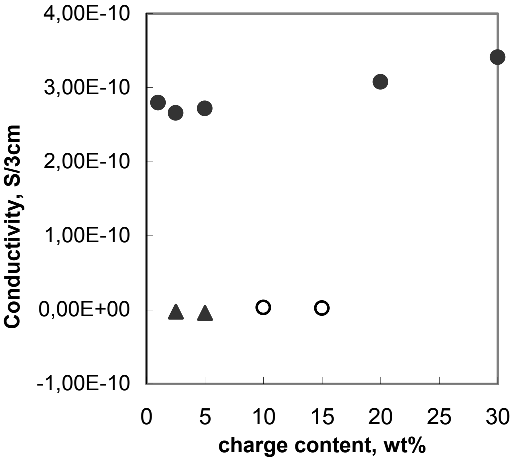

Figure 2. Electric conductivity of conductive materials/matrix polymer blends with twin screw extruder: (●) PANI-LES in PP, (▲) PANI-LES in LDPE, (○) graphite in PP

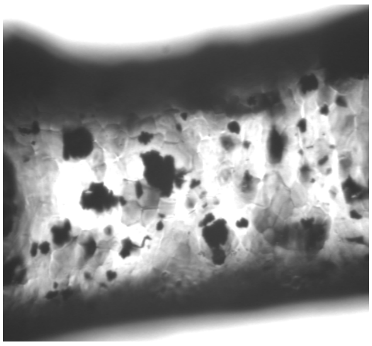

Figure 3. Morphology of 5 wt% PANI-LES in PP based blend, as revealed by bright field reflected light optical microscopy

Figure 2 shows the electric conductivity of conductive materials in PP or LDPE fibres obtained by Method 1. It is obvious that electric conductivity is very low. This can be explained by the non-homogeneous morphological structure of fibres presented in Figure 3. In this figure the fibre composite, 5 wt% of PANI-LES in PP, is analysed. The particles of PANI-LES are aggregated, and this configuration does not imply good conductivity.

Method 1 (melt mixing) has also been used in order to prepare fibre samples with PPy and PP, and the corresponding results (electric conductivity and morphological structure) are given in Figures 4 and 5. In this case, the problem is similar as in the previous situation. The electric conductivity is low and the fibre structure is not homogeneous. The conductivity increases as the PPy content increases, but even for 40% of PPy content in PP it remains very low.

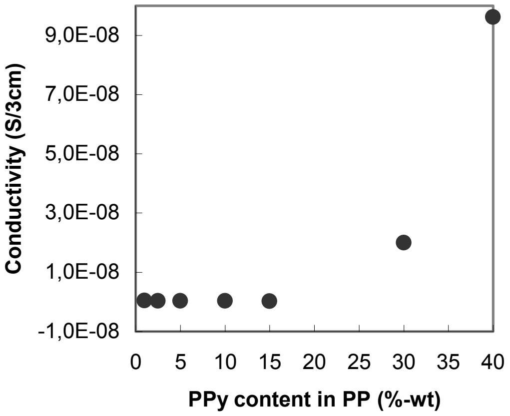

Figure 4. Electric conductivity vs. weight percentage of PPy in PP based blends

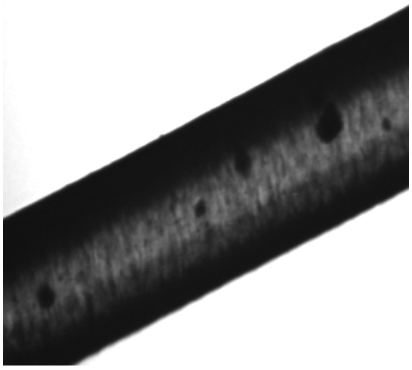

Figure 5. Morphology of 5 wt% of PPY in PP based blend

Because of the poor results obtained by the melt mixing method for sample preparation, we decided to use the second method. Therefore Figure 6 shows the electric conductivity of films obtained from 100% PANI-DBSA, PANI-CSA and fibres obtained by the chemical coating of PANI-DBSA and PANI-CSA on the PET fibres. The conductivity is much better and the morphological structure given in Figure 7 is more homogeneous.

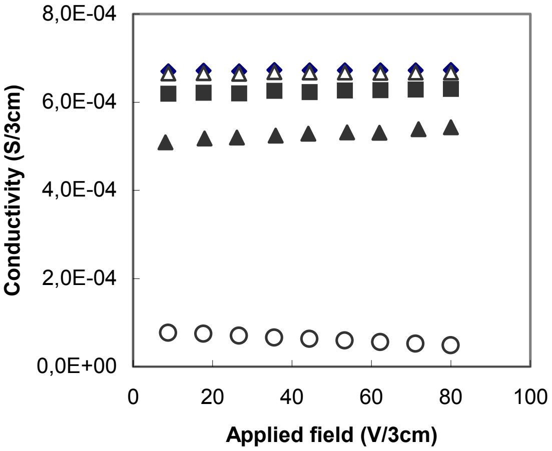

Figure 6. Electric conductivity of doped PANI series and PANI coated PET fibres: (♦) PANI-DBSA, (■) PANI-CSA, (▲) PANI-LES, (∆) PET-spun fibre, (○) PET filaments

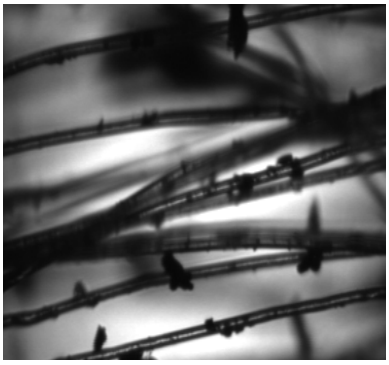

Figure 7. Morphology of PET fibres coated with PANI-DBSA solution, as revealed by bright field reflected light optical microscopy

4. Conclusion

The main conclusion of this study is that the melt mixing method using a twin screw extruder is not appropriate to preparation of fibre samples with conductive polymers. The conductivity of fibres obtained by this method is very low, due to problems of structure homogeneity and the aggregation of conductive polymers. The second method, based on coating fibres with dissolved conductive polymers, gives better results regarding electrical properties.

Nevertheless, the mechanical characteristics of the different conductive fibres have not been examined. The morphological structures of the samples lead to the conclusion that these mechanical properties may be modified, and we are currently investigating these modifications.

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