

Monofilament Composites with Carbon Nanotubes for Textile Sensor Applications

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ABSTRACT

The aim of this work was to develop polymer matrix/carbon nanotube composite monofilaments to incorporate in textile products, to be used as sensors. The carbon nanotube polymer composite (CPC) monofilaments were produced with the required electrical and mechanical properties for the development of a textile sensor of water vapor. The monofilaments selected were formed by polylactic acid (PLA), and were incorporated directly into the fabrics. The presence of water induced a variation on the electrical conductivity of the filaments.

A textile prototype, incorporating sensors and connectors, was produced with the CPC monofilaments developed.

KEY WORD

Carbon Nanotubes; Polymer Composites; Smart Textiles, Liquid Sensing.

INTRODUCTION

In order to provide people with personalized healthcare, technological advances should be brought closer to the subject by means of easy-to-use wearable interfaces between devices and human [1]. A healthier daily life, safer and more comfortable may be possible thanks to through multifunctional fabrics. Textiles are being developed in numerous types with various functions. As a result the so called smart fabrics or e-textile are under development. The final result is expected to be a smart human-machine interface.

The e-textiles are usually separated in two groups. In the first group, there are the transducers and circuit components attached off-the-shelf on fabrics [2] [3]. As an example, a research team from the University of Southern California, Virginia Tech and Raytheon has developed an acoustic beam forming array on textiles [4]. They used a textile fiber network in fabric containing discrete microphones. In the second group are the conductive yarns, conventional yarns modified with various functional materials, conducting polymer or carbon fiber, which are flexible materials developed to incorporate electronics and transducer yarns [5] [6]. Solutions based on textile materials are favorable for application in the medical field, or

in applications where the sensors are in contact with the skin of people. Areas of possible application are the detection of urine, for people suffering from urinary incontinence or the detection of sweat, for people performing sport activities.

A class of new materials that has been showing potential for application as sensors are carbon nanotubes. Since their presentation by S. Ijima in 1991 [7], carbon nanotubes (CNT) have been showing potential for application in numerous fields of science and engineering. The superlative mechanical, thermal and electronic properties attributed to them was never observed in previous materials. Researchers have envisaged taking advantage of their conductivity and high aspect ratio to produce conductive plastics with low percolation thresholds [8]. The diameter of the CNT varies from 1 to 100 nm and its length may reach the millimeter scale [9]. Their densities range from 1.3 to 1.8 g/cm³ and their Young's moduli are superior to all carbon fibers, with values near 1 TPa [10]. Its strength reaches values of 63 GPa [11].

The main objective of this work is to perform a smart textile which is able to respond with an intelligent answer when detecting humidity. Composite monofilaments formed by a specific polymer and CNT may change considerably their electrical response in the presence or absence of a conductive liquid. The monofilament should be able to sense water after it is incorporated into a fabric. The action of humidity on the electrical resistivity of the monofilament should be detectable. The work presented includes the production of poly(lactic acid)/CNT monofilaments, their mechanical and electrical characterization, and testing for changes in electrical resistivity in the presence of water vapor. Other sensors, combining different polymers and CNT could be able to detect other parameters, like temperature or strain.

EXPERIMENTAL

Materials

The polymer chosen for the composite production was poly(lactic acid) (PLA). The CNT composition was 4%. The description of the materials used for the production of carbon/polymer composites (CPC) for monofilament is detailed in Table I.

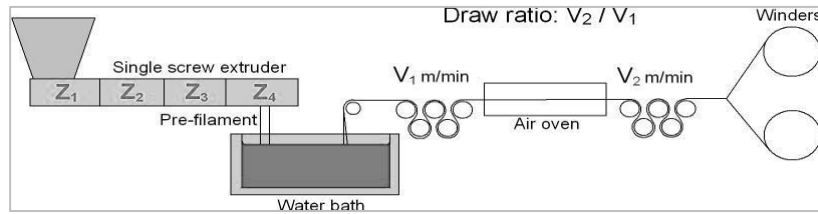


Figure 1 : Equipment setup for monofilament extrusion and drawing

Table I : CPC prepared by twin-screw extrusion

Materials	Origin	CPC prepared
CNT N7000	Nanocyl	-
PLA	Natureworks, sent by Nanocyl	-
PLA + 17% CNT	Nanocyl	Produce PLA + 4% CNT by dilution with PLA

Preparation of the CPC composites

The PLA + 4% CNT composite was prepared by melt processing, diluting the PLA/CNT masterbatch on a Coperion ZSK 27 MEGACOMPOUNDER modular co-rotating twin screw extruder fitted with the adequate screw configuration (See Table II). The polymer was cooled in water through, dried with blown air and cut into pellets by a suitable cutter. The operating conditions and extruder/die temperature profiles used for the PLA composites and the general extruder layout is schematically presented in Table II.

Table II: Operating Conditions and Temperature Profiles Used for Compounding

Composite	PLA / 4% CNT			
Operating conditions	Output = 16.5 Kg/h (gravimetric feeding), screw speed=300 rpm.			
	Screw profile: 6 mixing zones with kneading blocks staggered at 90° and 45°. Cold pelletizing			
Oven Temperature (°C)	Zone 1	160	Zone 6	180
	Zone 2	165	Zone 7	185
	Zone 3	165	Zone 8	185
	Zone 4	170	Zone 9	190
	Zone 5	175	Zone 10	180 (die)

Processing of the CPC monofilament yarns

Monofilament yarn was processed in a prototype extrusion line, consisting of a Periplast (Portugal) single screw extruder and downstream equipment comprising die, water tank, 1st set of pulling rolls, 1st oven (for extrudate orientation), 2nd set of pulling rolls (for drawing the filament at the required stretching ratio), 2nd oven (for extrudate relaxation or further orientation), 3rd

set of pulling rolls (for drawing or relaxation of the filament). In the experiments reported, only the first part of the extrusion line was used, i.e., no relaxation/second drawing were performed. The filament extrusion and drawing stage are schematically represented in Figure 1

The set temperature profile was optimized according to the characteristics of the material to be processed. Generally, the hopper throat was cooled with circulating water and the heaters were set at temperatures increasing in the downstream direction. Setting appropriately the die temperature of the first oven was critical, as it determined the stretchability of the material. Whenever possible, the first set of rolls was adjusted to provide the same stretching ratio of the emerging extrudates, while the second set of rolls was at increasing speeds, in order to obtain monofilaments with greater molecular orientation.

The optimized set of experimental conditions for monofilament processing is summarized in Table III. The draw ratio was maintained at minimum level, keeping $V_2/V_1=1.3$.

Table III : Processing Conditions for the Monofilament Yarn

Composition	Temperature profile (°C)	Oven Temperature (°C)
PLA / 4% CNT	185/185/180/175 (Die)	65 °C

Filament testing

The monofilament was tensile tested on a Instron 4505 universal testing machine. The filaments were stabilized in a temperature controlled environment at 23° C for at least 48 hours before tensile testing. At least five 100 mm long monofilament samples were cut and tested using a grip distance of 50 mm. The test speed was 5mm/min.

The volume resistivity of the samples was obtained by measuring the characteristic I-V curves at room temperature with a Keithley 6487 picoammeter/ voltage source. The voltage was varied from -10V to 10V, and the corresponding current was measured. The resistivity was calculated accounting for the geometrical factors of the filament. The filament length between contacts was approximately 65 mm. At least 3 samples were analyzed.

The water vapor sensing ability of the filaments was tested on a climatic chamber “Fitoclima 150 EDT” from ARALAB manufacturer.

RESULTS AND DISCUSSION

Tensile testing

The monofilament tensile test results are presented in Table IV

Table IV: Tensile test results for PLA/4% CNT

Material	Drawing Ratio	Modulus (MPa)	Tensile strength (MPa)	Strain at break (%)
PLA / 4% CNT	1,3	1407±554	39±3	2.0±0.3

Electrical characterization

The volume electrical resistivity measured for the monofilaments is presented in Table V, and compared with the electrical resistivity of bulk PLA. The incorporation of 4% of CNT in PLA originated a highly conductive composite filament.

Table V: Volume Electrical Resistivity Results Obtained

Material	Drawing Ratio	Diameter (mm)	Resistivity (Ω.m)
PLA	-	-	10 ¹⁴
PLA / 4% CNT	1,3	0.8±0.06	0.14±0.03

Linear density

The linear density of the monofilaments was measured according to the definition given by the international system of units. By definition, the linear density is the weight given in grams per kilometer of monofilament.

The linear density measurement was carried out by weighing 50 monofilament samples with approximately 50 cm length. Table VI summarizes the results and the corresponding statistical analysis.

Table VI : Linear Mass Density Results

	Lenght (cm)	Weight (g)	Linear Mass Density
Average	49,03	0,345	704
Standard Deviation	0,09	0,007	15
Coefficient of Variation	0,18	2,019	2

Sensitivity to water vapor

Water may be present in several states. The water vapor in the atmosphere, usually known as moisture, may be quantified as relative humidity considering the following definitions:

- Absolute humidity (Ha): specifies the amount of water vapor present per unit volume in a gas.
- Saturation humidity (Hs): refers to the maximum amount of water per unit volume of gas which is supported at a given temperature.
- Relative humidity (Rh%) is the ratio of absolute humidity and saturation humidity, described by the equation:

$$RH(\%) = \frac{Ha}{Hs} \times 100$$

The climatic chamber was programmed to perform cycles at 98% RH followed by drying at 30% RH. The experiment begins at the maximum saturation humidity and decreases the relative humidity until 30%. Between each step the relative humidity is maintained during a stipulated period of time. During the entire test the current intensity is acquired as depicted in Figure 3 and Table VII.

Table VII : Electrical resistivity variation with relative humidity

%Rh	Time (min)	ρ (Ω.m)
98,2	1	2,124
90,88	10	2,281
80,14	20	2,417
70,65	30	2,521
60,30	40	2,675
50,81	50	2,854
40,08	60	2,991
30,84	70	3,215

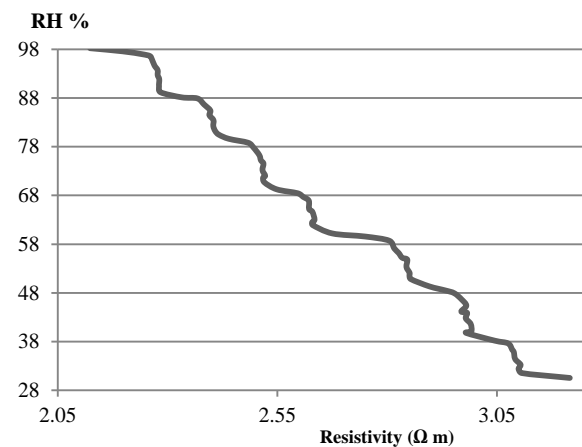


Figure 2 : Humidity Test Results

Conclusions

The monofilament of PLA / 4% CNT is sensitive to humidity as has been demonstrated. The target of this sensor is for textile applications (clothing or home textiles) where there is the need for early detection of humidity. Its applications in textile materials are still the most complicated stage of the process. The stiffness of the monofilaments is a limitation for their textile processing, but may be circumvented if the weaving machines where they are produced can be adapted.

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