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Investigations on coating durability and tenso-resistive effect of carbon black-coated polycaprolactam fibers

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Abstract A novel coating method (dissolving-coating method) is designed to provide electrically conductive fibers with lower electrical resistivity and permanent conductivity. In the dissolving-coating method, no adhesive was used, but a solvent of fiber substrate was used. Carbon black (CB)-coated polycaprolactam (PA6) fibers application for electrically conducting sensor were prepared by the new coating method. The durability of CB coatings on PA6 fibers was tested through washing and stretching test. To make a study on the electromechanical behavior of the CB-coated PA6 fibers under tensile load, the effects of various factors that are responsible that correlates the resistance change with the applied strain, strain rate (S.R), the environmental temperature, and the relative humidity (RH) were discussed.

Introduction

In the last few decades, electrical conducting sensor has attracted more and more attention due to it able to sense strain under tension and to assess the damage [1, 2]. Electrically conductive fibers (ECF) can be intrinsically conducting fibers (carbon fiber, metal fiber, et al.), or become conductive by coating or blending with electrically conductive materials [3–9]. One of the electrically conductive materials, carbon black (CB) is a widely used in preparing ECF because of its good electrical conductivity and cost-effective.

Carbon fibers represent a class of intrinsically conducting fibers. But, most carbon fibers possess a modulus of about 200 Gpa or more, while most textile fibers have a modulus in the magnitude of several Gpas. Introducing rigid carbon fibers into a textile structure may alter its strain field significantly. Besides, the measurement range of carbon fiber-based sensors is limited to small strains, while most textile fibers have an extensibility of over 10% [2]. The ECF prepared through blending CB with fiber forming polymer may overcome the deficiency of carbon fibers. Unfortunately, blends requiring a high concentration of CB are often result in bad spinnability and a decrease in the mechanical properties of the final fibers [10–12]. Post-treatment of the commercial fibers by a coating with CB can maintain the properties of fiber substrate, provide the fibers with lower electrical resistance and also have the characters of less costly and easy operation than melt spinning method. The traditional coating method is achieved by the use of an adhesive to produce a true coating on a fiber surface. However, such coatings are often found lacking in cohesion and the permanence of conductivity will fall with increased washing cycle [8–10]. Economy is achieved only through sacrifices in permanence of conductivity of the fiber. Therefore, it is desirable to explore new kinds of ECF to serve in these application.

The purpose of this article is to design a new coating method which can provide the conductive fibers applied to tensile strain sensor with the characters of low-cost, lower volume resistivity, yet durable. Fig. 1. presents the schematic diagram of traditional coating method

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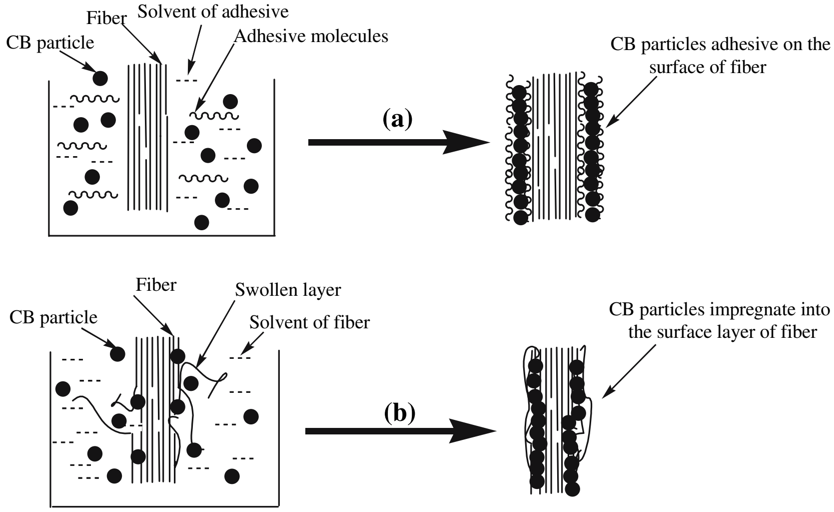


Fig. 1 Schematic diagram of (**a**) Traditional coating method; (**b**) Dissolving-coating method

and the new coating method (dissolving-coating method), respectively. As shown in Fig. 1(a), in the traditional coating method, adhesive was used and CB particles adhere to the surface of fiber on the basis of adhesive. In the dissolving-coating method of this research, there is no adhesive applied, but a true solvent of fiber substrate is chosen, in which CB are dispersed. As shown in Fig. 1(b), there is a true dissolution of the fiber surface and CB present as a dispersion in the solvent can suffuse uniformly into the surface of the fiber and CB become part of the structure of the fiber. Additional, the most important factor for the dissolving-coating method is that solvent of fiber must be removed before the structural integrity of the fiber being destroyed. In this paper, polycaprolactam (PA6) fibers were used as fiber substrate and CB-coated PA6 fibers were prepared by the dissolving-coating method and traditional coating method, respectively. The coating durability and the effects of various factors that are responsible for variations of tenso-resistive effect were studied.

Experimental

Materials

Electrically conductive CB was used as conductive particles, obtained from Huaguang Chemical factory, China. The primary particle of CB was 33 nm and the absorption of dibutyl phthalate (DBP) value was 380 ml/100 g, monofilaments of polycaprolactam (PA6) fibers (98 dtex) were supplied by Ruisheng Fiber Company of Wuxi City, China. Other reagents in the research were supplied by Tianjin Chemical Reagent Institute.

Preparation of CB-coated PA6 fibers

First, CB was pre-treated by titanate coupling agent under high-speed stirring while being heated to react for certain time. In the case of dissolving-coating method, no adhesive was used, but a solvent (formic acid) of fiber substrate was used. The coating mixture was prepared by dispersing 10 wt.% treated CB in formic acid/pure water solution. Then the coating mixtures were applied to PA6 monofilaments to prepare CB-coated PA6 fibers (ECF1#) on the coating machine shown in Fig. 2, which was designed in our laboratory. The coating machine has a grooved roll-type coating applicator for applying uniformly the coating mixture on the fiber surface. To ensure the structural integrity of the fiber being not destroyed, solvent was immediately removal by evaporation tube after the application. Then the coated fibers were washed within ultrasonic bath in order to eliminate the solvent probably remain on the surface of fiber.

To test the conductive durability of the CB-coated PA6 fibers prepared by the dissolving-coating method, the CB-coated PA6 fibers were also prepared by the traditional coating method (ECF2#). In the case of traditional coating method, polyurethane was used as adhesive. Polyurethane was diluted by dimethyl

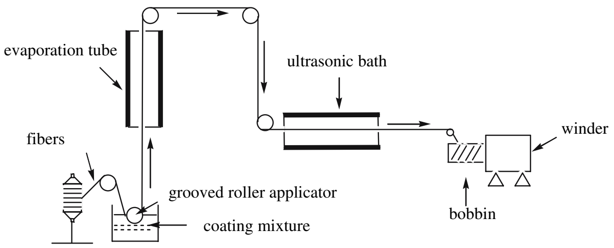


Fig. 2 Fiber coating machine in this research

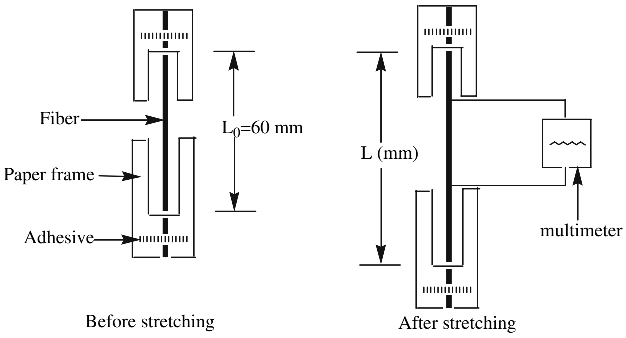


Fig. 3 Schematic stretching of fibers to be tested

formamide at the weight ratio of 1/4, in which 10 wt.% treated CB was dispersed. Then the coating mixture were applied on the same PA6 monofilaments.

Test and analysis

Mechanical properties measurement

Mechanical properties of fiber were measured with tensile test machine (PC/LLY-06, Laizhou Electron Instrument, China). Within the capacity of the testing facility, the drawing speed examined was 5, 10, 20, 40 (mm/min) respectively. All tested samples had the same gauge length (60 mm) and the corresponding strain rates (S.R.) were 0.0014, 0.0028, 0.0056, 0.011 (1/s). The tests were carried out at 20 °C and 65% relative humidity (RH). Under specified testing, the temperature is in the range from 20 °C to 100 °C and RH is in the range of 40–85%. All measurements were performed 3 times for an average.

Sensing of tensile strain

The electrical resistance of the CB-coated PA6 fibers was measured with a two-lead system while they were extended. The load and deformation were obtained and recorded on PC/LLY-06 mechanical testing system. A single fiber was attached vertically with adhesive to a piece of paper with a cut in the center (Fig. 3). L_0 and L are the length of fiber before and after drawing, respectively. R_0 and R are the electrical resistance of fiber before and after drawing, respectively.

Results and discussion

Coating durability of ECF1# and ECF2#

The CB coating durability on PA6 fibers was tested through washing with water and stretching. Table 1 shows the volume resistivity and mechanical properties of PA6 fiber substrate, CB-coated PA6 ECF1# and CB-coated PA6 ECF2#, respectively. We note that from Table 1 that both the traditional coating method and the dissolving-coating method can provide the fibers with satisfied electrical properties before washing. After 50 washing cycles, the coating of ECF1# was stable for a washing test. However, the volume resistivity of ECF2# increased from 1.20×10^1 to 3.58×10^8 Ω cm. Meanwhile, the datum of mechanical properties of Table 1 indicate that both ECF1# and ECF2# can maintain the excellent physical properties of the PA6 fiber substrate.

Meanwhile, the CB coating durability on PA6 fibers was tested through stretching test. And the ECF1# and ECF2# were stretched under the same condition. Figure 4 depicts the electrical resistance versus strain curves of coated ECF1# and ECF2# from the tests. R_0 and R are the electrical resistance before and after

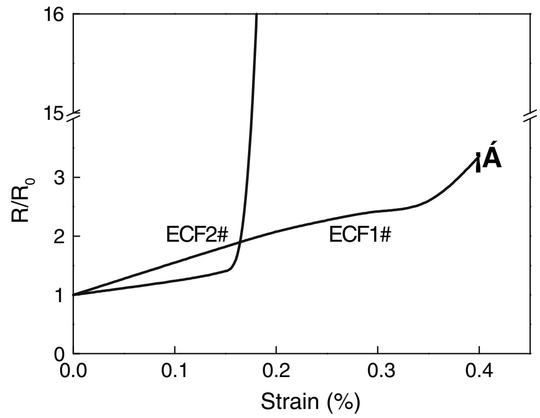
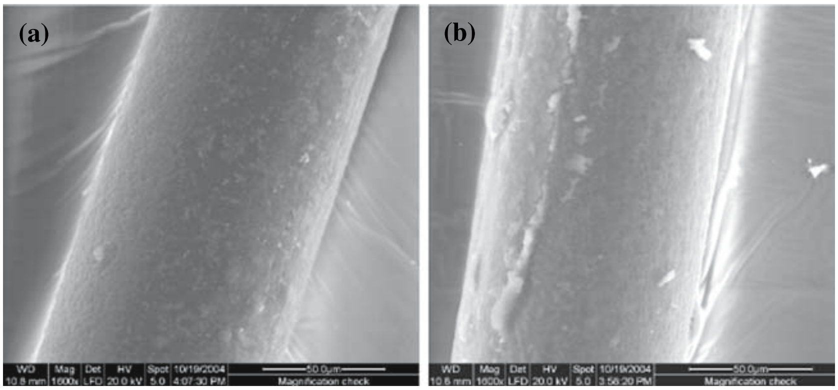


Fig. 4 Typical R/R_0 versus strain curves of ECF1# and ECF2# (drawing speed is 20 mm/min S.R.0.0056)

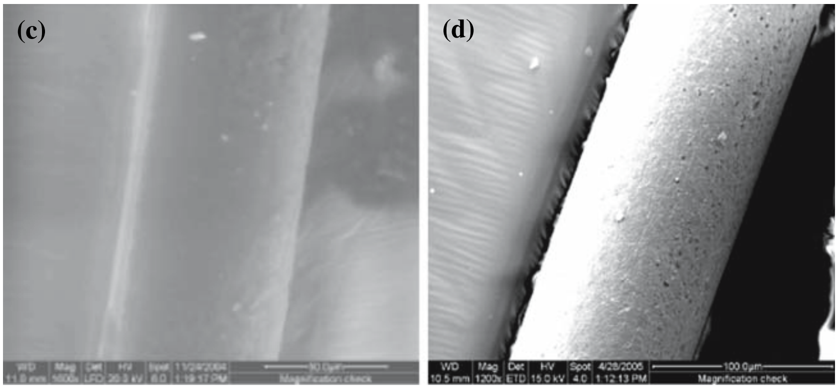
Table 1 Properties of PA6 fiber substrate, ECF1# and ECF2#

Sample	Volume resistivity (Ω cm)		Mechanical properties	
	Before washing	After 50 washing cycles	Breaking strength (cN/dtex)	Percentage of breaking elongation (%)
PA6 fiber Substrate	$>10^{12}$	$>10^{12}$	4.20	46.32
ECF1#	4.94×10^0	8.36×10^0	3.85	40.26
ECF2#	1.20×10^1	3.58×10^8	4.15	45.58

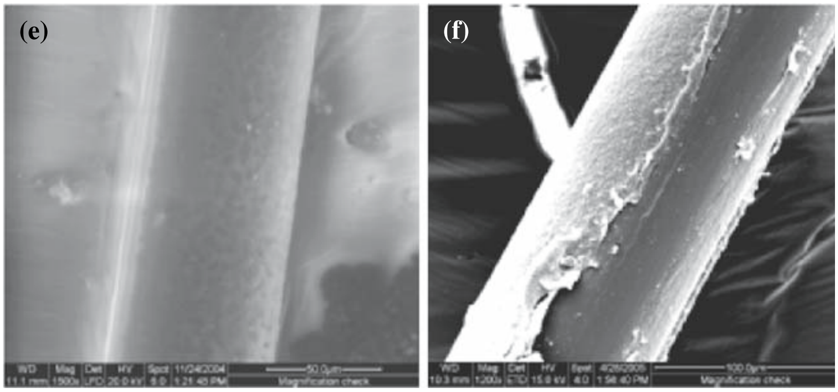
Fig. 5 SEM photographs of fibers



ECF1# ECF2#



ECF1# after drawing ECF2# after drawing



ECF1# after washing ECF2# after washing

stretching testing, respectively. For coated ECF1#, the electrical resistance increased with increased strain when the strain smaller than 35% and the relationship between R/R_0 and strain was almost linear under tensile loading. When the strain is larger than 35%, there is a nonlinearly increasing in the electrical resistance until fracture. This is because the CB particles would be pulled apart at larger strain and result in the destruction of the conducting network. However, for the coated ECF2#, the resistance change could be clearly divided into two phases and the phase changes at very lower strain (15%). In the initial phase (when strain is less 15%), the resistance increased gradually, followed by a second phase in which the resistance increased nonlinearly and rapidly. This phenomenon is result from the damage of coating layer.

SEM photographs of ECF1# and ECF2# are shown in Fig. 5. Before being stretched and washed, the surface of both ECF1# and ECF2# were uniformly coated with CB particles, which were observed from the Fig. 5(a) and (b). After being stretched, we see from the Fig. 5(c) and (d) that the coating surface of ECF1# is still smooth and coherent. But for ECF2#, the coating was partly peeled off and CB network on the fiber surface is become incoherent. This is the reason that R/R_0 of ECF2# increased nonlinearly and rapidly with strain in the second phase. The durability of the coating was tested through washing with water. As shown in Fig. 5(e) and (f), after the same condition washing test, coating of ECF1# is stable for washing test. However, the coating of ECF2# became even flaking.

The above washing and stretching test, and SEM photographs confirm that ECF1# prepared by the dissolving-coating method have the characters of high degree of durability comparing with ECF2# prepared by the traditional coating method. Besides the durability, as is well known that linearity between the input and output signals is one of the most important characters for strain sensors application. As seen from the experimental results in Fig. 4, ECF1# possess good sensing performance. However, ECF2# are not so promising for application as strain sensors in electrotextile. Meanwhile, it is evident that the conductivity of the ECF1# according to the dissolving-coating method is significantly enhanced and the tensile properties are not substantially diminished. We will discuss the effects of temperature, RH and stain rate on tenso-resistive effect of the ECF1# in the following section.

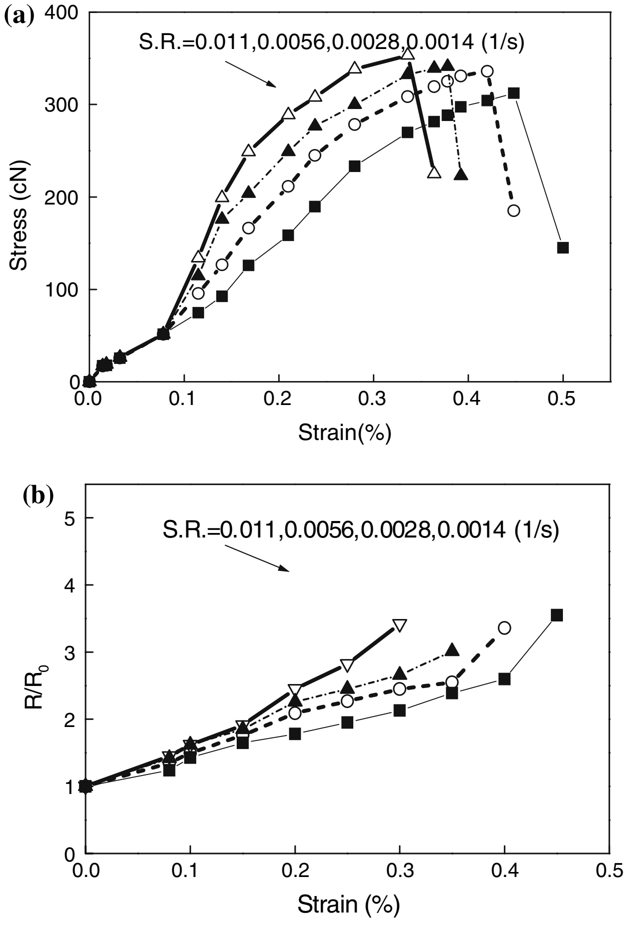


Fig. 6 (**a**) Load versus strain rate and (**b**) electrical resistance versus strain curves under different strain rate (S.R.)

Tenso-resistive effect of ECF 1#

Figure 6(a) and (b) are the typical stress–strain curves and electrical resistance versus strain curves at different S.R., respectively. Figure 6(a) displays that the Yong's modulus and the material strength are enhanced with the increased S.R., but the ultimate strain decrease. Figure 6(b) shows that under different S.R., the resistance change can be divided into two stages. In the first stage, the relationship between the measured resistance and the applied strain can be reasonably represented by a straight line before a percolation strain threshold, while the threshold appears earlier at higher S.R. The change in the slope of the straight lines reflects the effect of S.R. on the electrical resistance of the fiber. With the increased S.R., the slop of the straight lines increases, while the strain threshold decreases. After a linear range, the electrical resistance increases nonlinearly up to the rupture of the fibers. This nonlinearlity is a result of the destruction of the CB channel network.

For a given strain (20%), the effect of RH on the electrical resistance is shown in Figs. 7 and 8, respectively. In Fig. 7, the temperature was kept at 20 °C and the RH varied in the range from 40% to 85%. It is evident that the normalized resistance R/R_0 changes gradually with the variation of the normalized humidity in the range examined in this study. A linear relationship with a small slope can be assumed between the electrical resistance and the RH. The temperature dependence of the conductivity for ECF1# is shown in Fig. 8 at 65% RH. The normalized resistance R/R_0

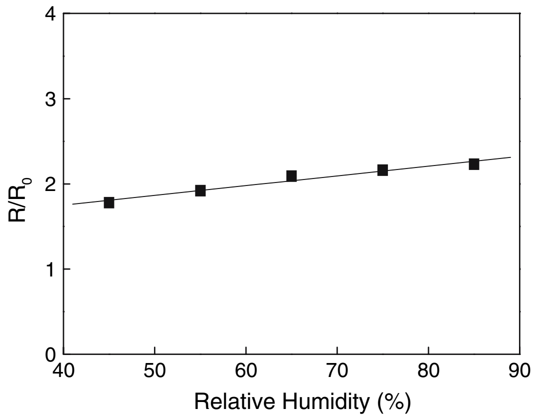


Fig. 7 Normalized resistance measured under different relative humidity

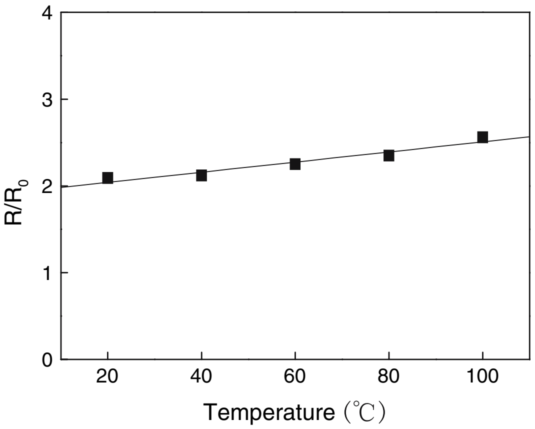


Fig. 8 Normalized resistance measured under different temperature

increases with increased temperature. However, it does not change significantly.

Conclusion

In this study, a novel coating method (dissolving-coating method) is designed to provide CB-coated PA6 fibers application for tensile strain sensor. The coating durability and the tenso-resistive effect of the CB-coated PA6 fibers were discussed and the following conclusions can be drawn:

(1) Conductivity of the ECF1# according to the dissolving-coating method is significantly enhanced and the tensile properties are not substantially diminished.

(2) Compared with ECF2#, CB-coated PA6 ECF1# prepared by dissolving-coating method have the durability of electrically conductivity.

(3) CB-coated PA6 ECF1# is more suitable to be used for the application in the tensile strain sensor. The tenso-resistive test shows that the relationship between the measured resistance and the applied strain can be reasonably represented by a straight line. Meanwhile, higher the S.R., the earlier the destruction of the conducting network and the normalized resistance R/R_0 are stable within the testing temperature and RH.

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