Polyaniline-Coated PET Conductive Yarns: Study of Electrical, Mechanical, and Electro-Mechanical Properties

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ABSTRACT: Intelligent and multifunctional yarns (textiles) have attracted interest because of their high potential in applications such as flexible displays, batteries, or sensors. The main objective of our research was to obtain the flexible and electrically conducting yarn based on the conductive polymer and polyethylene terephtalate (PET) yarns. Among the conductive polymers, polyaniline (PANI) is considered as a promising material and is well adapted for modifications of textile structure because of its excellent environmental, thermal, and chemical stability. Chemical PANI coating on PET yarns was performed by absorption of yarns through PANI solution. The electrical, mechanical, and electro-mechanical properties of PET conductive yarns prepared were investigated. The environmental effects on the electrical and mechanical properties of the obtained conductive yarns were also studied. These conductive yarns are expected to be used as fibrous sensors, connection devices in smart clothing, and for electromagnetic shielding applications. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1252–1256, 2006

Key words: polyaniline; PET conductive yarn; coating; electro-mechanical property; fibrous sensors

INTRODUCTION

The term "intelligent and multifunctional fibrous materials" describes a class of yarns or textiles that have active functions in addition to traditional textile properties. The novel functions and properties are obtained by modifying the textile materials or integrating the electronic devices into the textile structures. The textile industry has made considerable advances in the field of high valued textiles, mainly in the sectors of high performance textiles, yarns, and fibers.

In addition, the demand for the electrically conductive fibers and textiles is growing rapidly not only in relation to industrial needs such as the sensing, electrostatic discharge, corrosion protection, electromagnetic interference shielding, dust- and germ-free clothing, monitoring, data transfer in clothing but also for military applications such as camouflage and stealth technology.[1–8] For all the applications previously mentioned, the basic element is the textile fiber. It is important to modify the mechanical and electrical properties of fiber so as to obtain previously mentioned new functions.

The modification of fiber (yarn) using conductive polymers seems to be an interesting approach. Conductive polymers show the electrical properties due to their conjugated double bonded chain structures, which derive both their conducting or neutral (nonconducting) forms. However, they are inherently insoluble or infusible because of their strong intermolecular interactions. High quality conducting blends with conventional polymers by melt mixing[9–13] or by solution casting[14–17] are still in a development stage. Among the conjugated conducting polymers, polyaniline (PANI) has attracted much interest worldwide because of its excellent environmental, thermal, and chemical stabilities.[18–20]

Even though conducting polymers can be electrochemically produced in the fibers or film forms, they show weak mechanical properties disabling their application in traditional textile process. Considering this difficulty, thin coating or polymerizing using conducting solutions on the surface of textiles (fibers) should be a reasonable method to create conductive textiles fibers. Since polypyrrole-coated polyester textiles have been developed by Milliken Research Corp.,[21] many research groups are active in this field. In addition, PANI-coated or in situ polymerized on nonwoven fabric, nylon 6, cotton, polyester fabric, and Nomex fabric are recently reported.[22–25] Water soluble conductive polymers are also studied.[26,27]

The soluble conductive form of PANI may be obtained by protonation with functionalized protonic acid, denoted as H^+ (M^-—R).[28] H^+M^- is protonic

acid group and may be sulfonic acid, carboxylic acid, phosphonic acid, etc. The proton of the protonic acid reacts with imine groups of PANI and the M$^-$—R group serves as the counterion. R is an organic group that can be compatible with nonpolar or weakly polar organic solvents e.g., *N*-methyl-2-pyrrolidione, dimethylsulfoxide, xylene, and *m*-cresol. Efficient doping methods of PANI with dodecylbenzene sulfonic acid (DBSA) or camphor sulfonic acid were reported.[14–16,29] The PANI chains tend to form extended chain conformation in the presence of DBSA, thus the electron transport between the polymer chains should be enhanced. In the PANI/solvent system, the film-like agglomerates of PANI take place on the solution/solid interface when the solvent is removed. In our research work, this spontaneous molecular assembly has been used to coat conductive polymers on the material surface, and has been successfully applied to yarns and textiles.

In this paper a doped PANI has been used to obtain improved electrically conducting polyethylene terephtalate (PET) yarns, without modifying their textile properties. A comprehensive approach for preparing the conductive yarns has been developed by our research team based on a *sol–gel* coating process. In general, the sol–gel process involves the transition of a system from a liquid *sol* (mostly colloidal) into a solid *gel* phase. PANI coating was carried out during the impregnation of PET yarns in the PANI solution. The solvent has evaporated at the end and we obtained PANI-coated PET (PANI-PET) conductive yarns.

The electrical resistance of PET conductive yarns was measured for different yarn lengths and at different temperatures. In addition, various environmental effects, including ultra violet (UV) radiation, solvents, ageing, and thermal effects on the electrical and electro-mechanical properties were studied. The study of the mechanical properties is also important because the conductive yarns should be transformed in textile structure by weaving, knitting, or other manufacturing process.

EXPERIMENTAL

Materials

Emeraldine salt form polyaniline (PANI-ES) was supplied by Sigma-Aldrich Chemical Company. Dodecylbenzene sulfonic acid (DBSA, Fluka) was used as a dopant to obtain an homogeneous conducting PANI solution. Polyethylene terephtalate (PET) spun yarn (20 nm, Hyosung) was used after washing with the solution of 2 g/L of sodium carbonate and 1 g/L of Tinovetine at 70°C for 30 min.
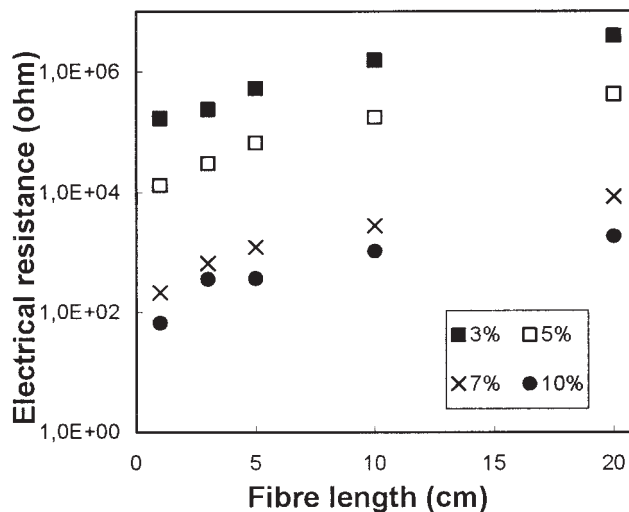

Figure 1 The electrical resistance of PET conductive yarns coated with PANT solution at different concentrations.

Solution preparation and coating process

PANI-DBSA mixtures (1 : 0.5, w/w in ratio) were dissolved in xylene to prepare the solutions going from 3 to 10 wt % of PANI. These solutions were stirred vigorously for 3 h at high temperature and treated in the ultrasonic bath for 2 h. The continuous sol–gel coating process has been performed using an experimental device, with a bath temperature control and a taken-up speed of yarns control. This device should be equipped with several bathes filled with PANI solution. PET yarns were withdrawn through the baths in the presence of a dry airflow along the coating surfaces to enhance solvent evaporation. The taken-up speed of yarn was controlled considering the drying dynamics during experimental procedure.

Characterization

The electrical resistance tests were performed using the "two-probe test technique" with Agilent 34401A multimeter at 25°C, 55.56 HR%. The measurements have been repeated 20 times for different yarn lengths from 1 to 20 cm and the mean values have been computed. Tensile strength test was performed using the MTS yarn tester with its software testworks® at 20°C, 65 HR%. The sample length was fixed at 50 mm and the speed of traction was 12 mm/min.

RESULTS

Electrical properties

All the electrical resistances of PANI-PET conductive yarns obtained by coating with different concentrations of PANI solutions are presented in Figure 1. The electrical resistance (Ω) of PANI-PET conductive yarns
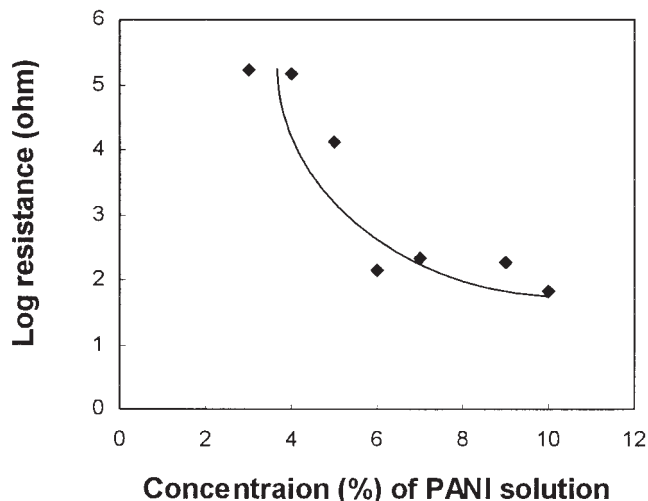
Figure 2 The effect of concentrations of PANI solutions on the electrical resistance (Ω) for 5cm of PANI-PET conductive yarns.

decreases as the concentration of solution increases and the yarn length between two electrodes increases. It is obvious that the concentration of PANI solution is important to obtain highly electrically conducting yarns. The electrical resistance (Ω) shows two different areas delimited by the PANI concentration as we can see in Figure 2. The electrical resistance (Ω) below 5% PANI solution coated PET yarns is significantly higher than that of PANI-PET conductive yarns coated with high concentration solution.

Another important phenomenon should be considered. In fact, the gelation of PANI solution at high concentration occurs very quickly. We pointed out that faster gelation occurs during the experimental procedure for over 7% of PANI solutions compared with the 3–6% of PANI solutions. This gelation of PANI could be considered as an obstacle to perform the homogeneous coating on fiber surface. The temperature of bath should also influence the solidification of PANI solution as well as evaporation of the solvent. To obtain a homogeneous conducting layer, the concentration of PANI solution, a yarn taken-up speed from a bath, and the temperature of a bath have to be considered carefully. Currently, we investigate all these parameters to optimize the whole process.

The environmental effects, including time, thermal, UV radiation, and solvent effects to electrical property for PANI-PET conductive yarns were studied. The ageing effect with time on the electrical properties of PANI-PET conductive yarns was studied under standard condition (at 25°C, 55.56 HR%). The electrical resistance for 5 cm of PE conductive yarn coated with 7% of PANI solution increases highly from 12 weeks (see Fig. 3). The external protection on the conductive yarns is proposed to improve their electrical stability.

The influence of the temperature on the electrical resistance of PANI-PET conductive yarns is shown in
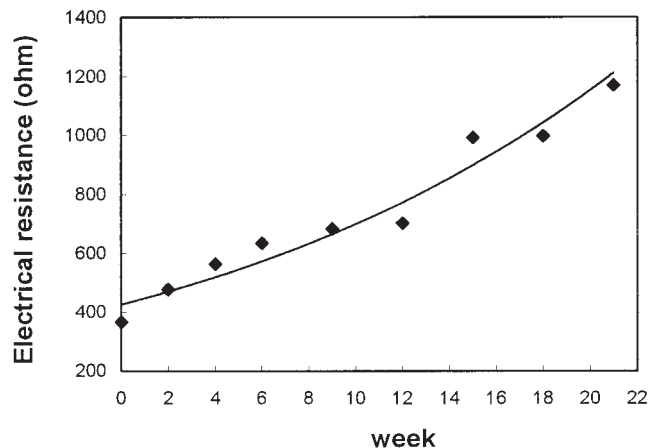

Figure 3 The time effect on the electrical resistance for 5 cm of PET conductive yarns coated with 10% of PANI solution.

Figure 4. The electrical resistance remains low until 55°C. For higher temperatures, the electrical resistance of conductive yarns increases quickly. It is possible to notice that our PANI-PET conductive yarns may be used below 55°C without change of the resistance. This phenomenon may be explained by the combined actions of the fiber substrate, the dopant, and/or the solvent on the conductive yarn.

Generally, incident UV light has sufficient energy to provoke a catalyze decomposition of the polymer. The active chain ends produced by photolytic degradation may react with the polymer structure, producing crosslinks that generate the brittleness of the polymer.[30] The UV sensibility study is important to determine the photo-degradation behavior of PANI-PET conductive yarns for the textile applications. PANI-PET 6 and 10% conductive yarns that have been exposed to UV radiation during 80 h show slight degra-
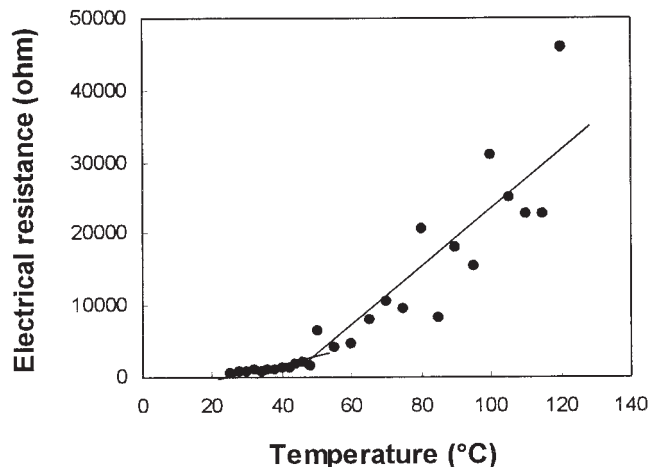

Figure 4 The thermal effect on the electrical resistance for 5 cm of PET conductive yarn coated with 9% of PANI solution.
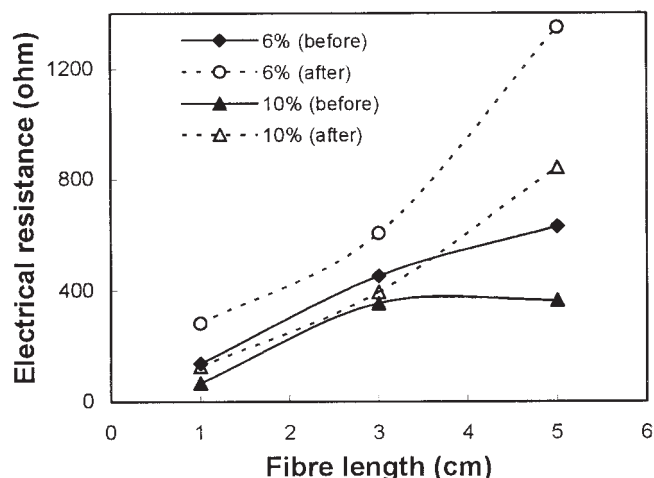
Figure 5 The UV treatment effect on the electrical resistance of PET conductive yarns coated with 6 and 10% of PANI solutions.

Figure 7 Electro-mechanical property for 5 cm of PANI-PET conductive yarns with different applied force and strain-stress curve (small figure).

dation (with increasing resistance (Ω)) as we can see in Figure 5.

Mechanical and electro-mechanical properties

Tensile test was performed to characterize the mechanical properties of conductive yarns. Before analysis, PET spun yarns were treated with solvent (xylene) for 20 min. At the molecular scale, the solvent attacks the polymer chains in amorphous regions, which are important to the mechanical properties. In Figure 6, it is possible to observe that the yarn modulus is reduced after the solvent treatment, comparing the untreated original PET yarn. On the other side, the coated PET yarn PANI-PET 10% shows better modulus than the original yarn does. These results can be
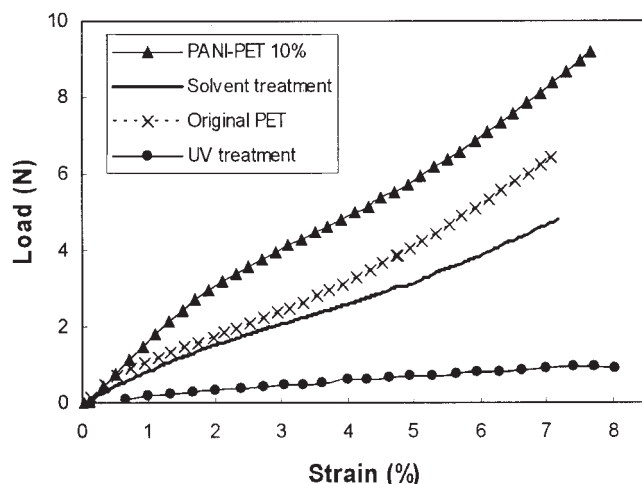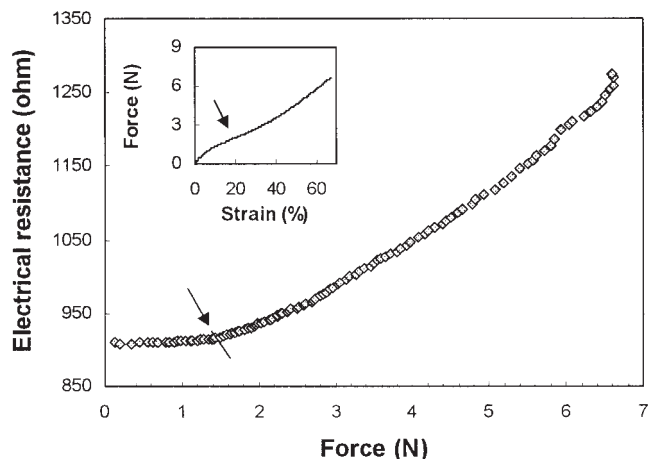

Figure 6 Stress–strain curves of original PET yarn, PET conductive yarn coated with 10% PANI solution (▲), solvent-treated (solid line), and UV treated (●) yarns.

explained by interforce of PANI conducting layers on the fiber–fiber regions of PET spun yarn. Inherently, spun yarns contain many discontinuous fibers showing the bulky structures with many interstices. Most of these interstices are filled with the PANI particles during the coating process; thus, the tensile properties are improved. The combined effect of these interforces may be more important than those of the solvent effect for PANI-coated PET spun yarn. The mechanical properties of conductive yarns are important for transforming them in textile structures by weaving, knitting, or for other applications. The electro-mechanical property of PANI-PET conductive yarns was also investigated. The relationship between the electrical resistance (Ω) and the load (N) applied to the yarn was studied and is shown in Figure 7. The electrical resistance increases highly from the yield point of conductive yarn. From the yield point, the deformation of conducting layers on the fiber surface is occurred in function of the load, then, the resistance should be increased.

The ability of conductive yarns to recover from deformation was studied by means of the strain recovery test vs. the electrical property and the results were shown in Figure 8(a,b). The electrical resistance was measured after four repeated cycles of stretch and recovery tests at 20% of breaking load and the fifth cycle was continued until breaking point. After repeated stretching actions, the conductive yarns show fewer electrical properties [see Fig. 8 (b)]. The electrical resistance lost is ~12–15% of the initial value. We think that it is possible to reduce this abrasion by improving the coating process. Electro-mechanical properties are very important to confirm the possibility of the applications of PET conductive yarns as fibrous sensors.
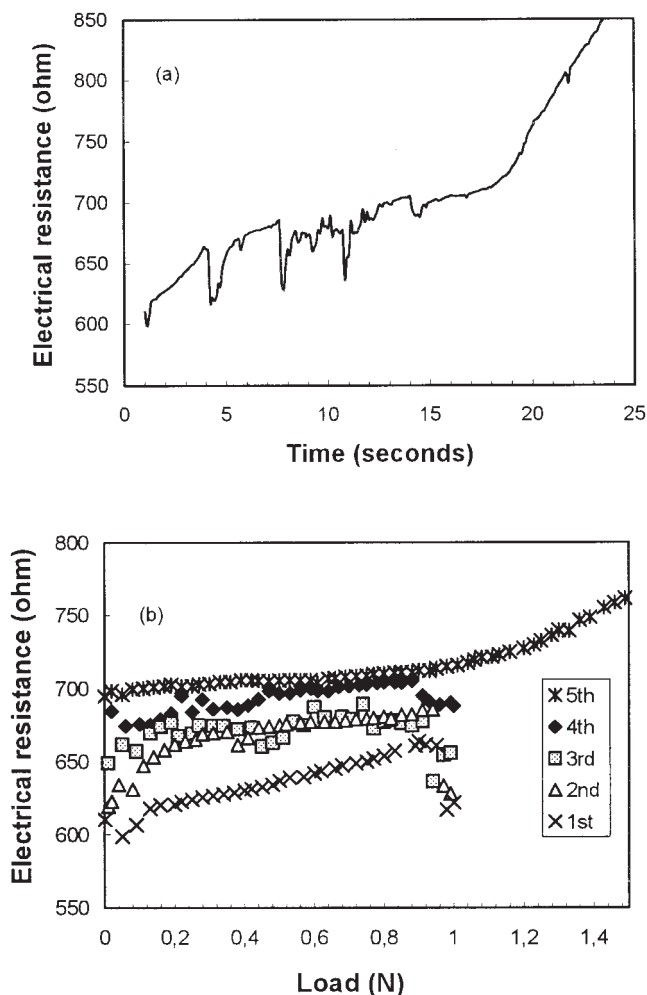
Figure 8. The four repeated cycles of stretch recovery tests for PANI-PET conductive yarn. (a) The electrical resistance as a function of time for total cycle and (b) the electrical resistance as a function of applied load for each cycles.

CONCLUSION AND DISCUSSION

PET conductive yarns have been prepared by coating process based on PANI. The electrical resistance of PANI-coated spun yarns decreases as the concentration of PANI solution increases. The concentration of PANI solution is important for achieving the homogenous coating on the yarn surface and we think the threshold of solution is between 6 and 9% of PANI concentration. PANI-coated PET conductive yarns show good environmental stability on the electrical properties, preserving their original strength and flexibility. The traction curve leads to the conclusion that the PANI coating improves their mechanical properties consequently. The electro-mechanical properties of PANI-PET conductive yarns indicate that many applications such as fibrous sensors, connection devices in smart clothing, or for electromagnetic shield-ing applications are possible. Morphological or thermal properties of PET conductive yarns are also interesting and we are going to study about these characterizations in the future.

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