Fibers and Polymers 2010, Vol.11, No.6, 813-818 DOI 10.1007/s12221-010-0813-2

Surface Characterization of Aromatic Thermotropic Liquid Crystalline Fiber Deposited by Nanostructured Silver

Xin Xia[1,2], Huifeng Wang[2], Fenglin Huang[2], Yibing Cai[2], and Qufu Wei[2]*

[1]*Xinjiang University, Xinjiang,Wulumuqi 830046, China*
[2]*Key Laboratory of Eco-textiles, Jiangnan University, Wuxi 214122, China*
(Received September 19, 2009; Revised April 4, 2010; Accepted May 14, 2010)

Abstract: Nanostructured silver thin films were sputtered onto the aromatic thermotropic liquid crystalline fibers of Vectran by magnetron sputtering technology. Plasma treatment was used as pre-treatment in order to improve the deposition of the coating layer. Surface morphology of the coated fibers was examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). A full energy dispersive X-ray analysis (EDX) was used to detect the elemental composition of the material. Its conductivity and mechanical properties were measured and analyzed as well. The study revealed that a very thin conductive silver deposition exhibited high electrical conductivity as well as less influence on the mechanical properties of the pre-treated Vectran fiber. The plasma treatment could improved the deposition of the coating layer, but the surface roughness caused by plasma treatment also affected the surface conductivity. It was found that the surface resistivity could reach very low value of 1.66×10^{-3} Ω·cm after sputtering deposition for 30 min.

Keywords: Vectran fibers, Plasma treatment, Sputtering, Surface morphology, Conductivity

Introduction

Thermotropic liquid crystalline polymer (TLCP, Vectran) is a new family number of high-performance fibers compared to lyotropic liquid crystals polymer (aromatic polyamide, Kevlar), providing unique properties such as high strength and modulus, heat resistant, waterproof and flame retardance, which make them promising materials for reinforcements and safety applications [1-5]. Typically, an important potential application for TLCP is in the field of sensitive electronics packaging which needs electrostatic dissipative materials. However, due to the high degree of molecular order in the TLCP matrix and its anisotropy in the nanocomposite, Vectran fiber, an aromatic co-polyester, is difficult to conquer its low electrical conductivity. Consequently, graphite or carbon nanofibers have been conducted as fillers to improve electrostatic dissipative properties [6,7]. However whether the proportion of the fillers in the compounded materials has effects on the fibers' original mechanical properties still needs further investigation. Moreover, to what extent the electro-conductivity can be improved still deserves further study.

In this paper, surface functionalization of Vectran fibers was adopted to expand its applications using a conventional direct current magnetron reactive sputtering system. One of the key issues in the application of sputter coatings onto fibers is the interfacial adhesion between coated layer and substrate. Therefore, plasma treatment, a more economical and ecological pre-treatment process, was performed to enhance the interactions in the interphase by a combination of a plasma induced increase in bonding surface such as micropitting or mechanical interlocking. The primary objective of this study was to analysis the morphology of the silver (Ag) coated fibers before and after the substrates was treated by plasma, as well as their effects on the mechanical properties. In addition, the electrical conductivity and elemental compositions of the sputter coated fibers were investigated comprehensively.

*Corresponding author: qfwei@jiangnan.edu.cn

Experimental Details

Materials

The material used in this study was commercially available Vectran yarn which is a wholly aromatic liquid-crystalline polymer supplied by Korteks, Turkey. Yarn count was 110 tex and the number of filaments were 200.

Plasma Treatment

Plasma treatment was performed in a HD-1A vertical laboratory plasma treatment machine. The yarns were cut into about 10 cm in length and hang on a glass rod which was placed in the middle of the reactor chamber of the machine. Prior to plasma treatment, the chamber was purified for 3 times using oxygen at a power of 30 W. Then oxygen plasma treatment was carried out and controlled by means of varied values of pressure, power, and time. The treated conditions which lead to different surface topographies after sputter coating are presented in Table 1. Sputter coating was carried out shortly after plasma treatment was finished.

Sputter Coating

In the process of Ag sputter coating, a 99.99 % pure target was used on the cathode in a magnetron reactive sputtering system JZCK-420B (Shenyang, Juzhi Co., Ltd. China). Vectran yarns, pre-laid on a piece of insulating nonwoven material with one side facing the target, were fixed on the

Table 1. Plasma treatment and sputtering parameters

Material	Plasma treatment parameters (power, pressure, time)	Sputter coating parameters (time, power, pressure)
Raw sample	No	No
Raw sample-coated	No	30 min, 120 w, 0.5 Pa
Sample 1	30 w, 20 pa, 90 s	30 min, 120 w, 0.5 Pa
Sample 2	30 w, 20 pa, 180 s	30 min, 120 w, 0.5 Pa
Sample 3	40 w, 20 pa, 60 s	30 min, 120 w, 0.5 Pa
Sample 4	50 w, 30 pa, 60 s	30 min, 120 w, 0.5 Pa
Sample 5	50 w, 30 pa, 60 s	60 min, 120 w, 0.5 Pa

substrate board (the anode). So the sputter coating was enriched on one side of the yarns. The bombardment gas contained argon (99.999 %, gas flow 20 sccm) at a sputtering pressure of around 0.5 Pa. The direct current power used for Ag sputtering was adjusted to appropriate values (details compiled in Table 1). And the substrates were kept at room temperature by water-cooling.

Characterization

Structure and Morphology

Scanning electron microscopy (Hitachi S-4800, Japan) studies were carried out in order to analyze the surface morphology of the yarns. The raw and plasma treatment samples were coated with a thin layer of gold by sputtering before SEM imaging, while Ag coating yarns were examined without any further treatment. An AFM (CSPM4000, Benyuan, China) was also used to observe the surface morphology quantitatively. Tapping mode was chosen in this study. All images were obtained at ambient conditions and they were analyzed by the Imager 4.40 Software equipped with CSPM4000 AFM.

The surface chemical compositions were examined by energy dispersive X-ray (EDX). It allows analyzing of elemental compositions down to boron including the light elements such as carbon, nitrogen and oxygen. In the EDX analysis, an accelerating voltage of 20 kV with accounting time of 100 s was applied.

Electrical Property

Electrical property was characterized by resistivity measurement, which was measured using a collinear four-probe array at room temperature. The apparatus used was SX1934 produced by Baishen Technologies (China). In order to minimize the deviations brought by the single recognizable fiber of the yarn, the tests were operated on the substrate board directly. The resistivity of each sample was measured five times, and the average values were adopted.

Mechanical Strength

Strength and elongation at break of single fibers were measured at a gage length of 50 mm by an YG020 model electronic Yarn Strength Tester at ambient temperature. Monofilaments were randomly extracted from the yarns and the average values were calculated from the mean of five measurements.

Results and Discussion

Film Structures and Surface Morphology

Figure 1 contains the surfaces of untreated and plasma treated fibers in the presence of different treated conditions to reveal the surface features at less than 100 nm scale. The SEM micrograph shows a relatively smooth surface of untreated Vectran fiber, but some streak flaws and spots can be seen in the scope of the observation (Figure 1(a)). Whereas the oxygen plasma treated yarns creates the new features on the fiber surface as shown in Figures 1(b), 1(c), and 1(d). It can be clearly observed that some pitting aggregate structures form on the fiber surface. This is attributed to the etching effect of the plasma treatment, which roughens the surface of the fiber. It is also obvious that the aggregates appear to have different sizes, indicating the uneven effect of the surface etching by plasma treatment, which is mostly attributed to the preferential etching of the softer amorphous parts of the fiber in plasma treatment [8]. It is apparent to observe that the enhancement of surface roughness is in dependence on the plasma treatment conditions. Figure 3(b) displays a relatively large area of notches gathered together as a thin longitudinal strip at the plasma-treatment power of 50 w and a pressure of 30 Pa for 60 s.

Plasma treatment significantly alters the adhesion of Ag coating to Vectran fibers, as shown in Figure 2. It is revealed by SEM observation that the coating on the untreated Vectran fibers looks uneven with some impurities and deformation as presented in Figure 2(a), which may be caused by the poor adhesion of the deposited Ag film to the fibers. Contrarily, Ag coating shows affinity for the pre-treated substrate, as can be seen in Figure 2(b)-(d). Particularly, the sputtered Ag nanoparticles on the Vectran fibers appear to be smoother and more uniform on sample 1 than those on samples 2 and 3, due to its satisfied plasma process parameters which provide better improvement in the interfacial adhesion between the composite materials.

The details of the sputtered Ag nanoclusters on the vectran fibers can be seen from the high magnification AFM images obtained by 5.0×5.0 um^2 scan, as illustrated in Figure 3. The different morphologies of coated fibers are showed due to different nucleation and island formation stages on the fiber surface. The AFM images in Figure 3 clearly reveal the particle clusters on the fiber surface. Furthermore, Figure 4 reveals some larger and compacter clusters are built on the fiber surface of sample 4 after a longer treatment time 60 min as compared to the topography of 30 min-treated sample which is coated with insufficient Ag. The larger cluster size is formed because of the increasing collision of the sputtered Ag particles.

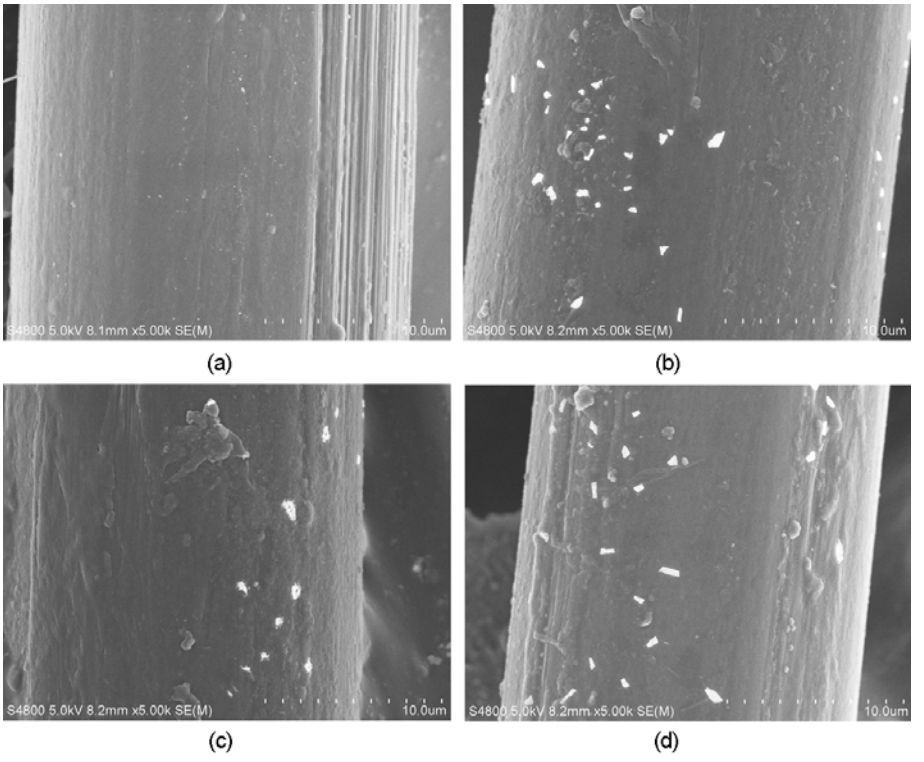

Figure 1. SEM images of plasma treated Vectran yarns (a) raw sample, (b) sample 1, (c) sample 2, and (d) sample 3.

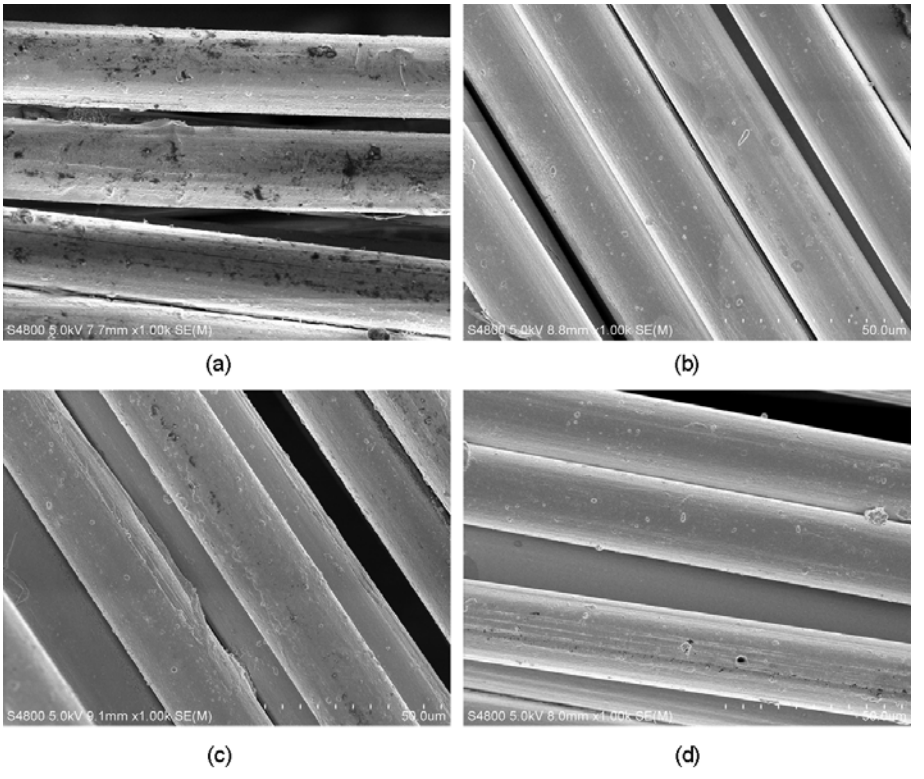

Figure 2. SEM images of sputtered Vectran yarns (a) raw sample : coated for 30 min, (b) sample 1: coated for 30 min, (c) sample 2: coated for 30 min, and (d) sample 3: coated for 30 min.

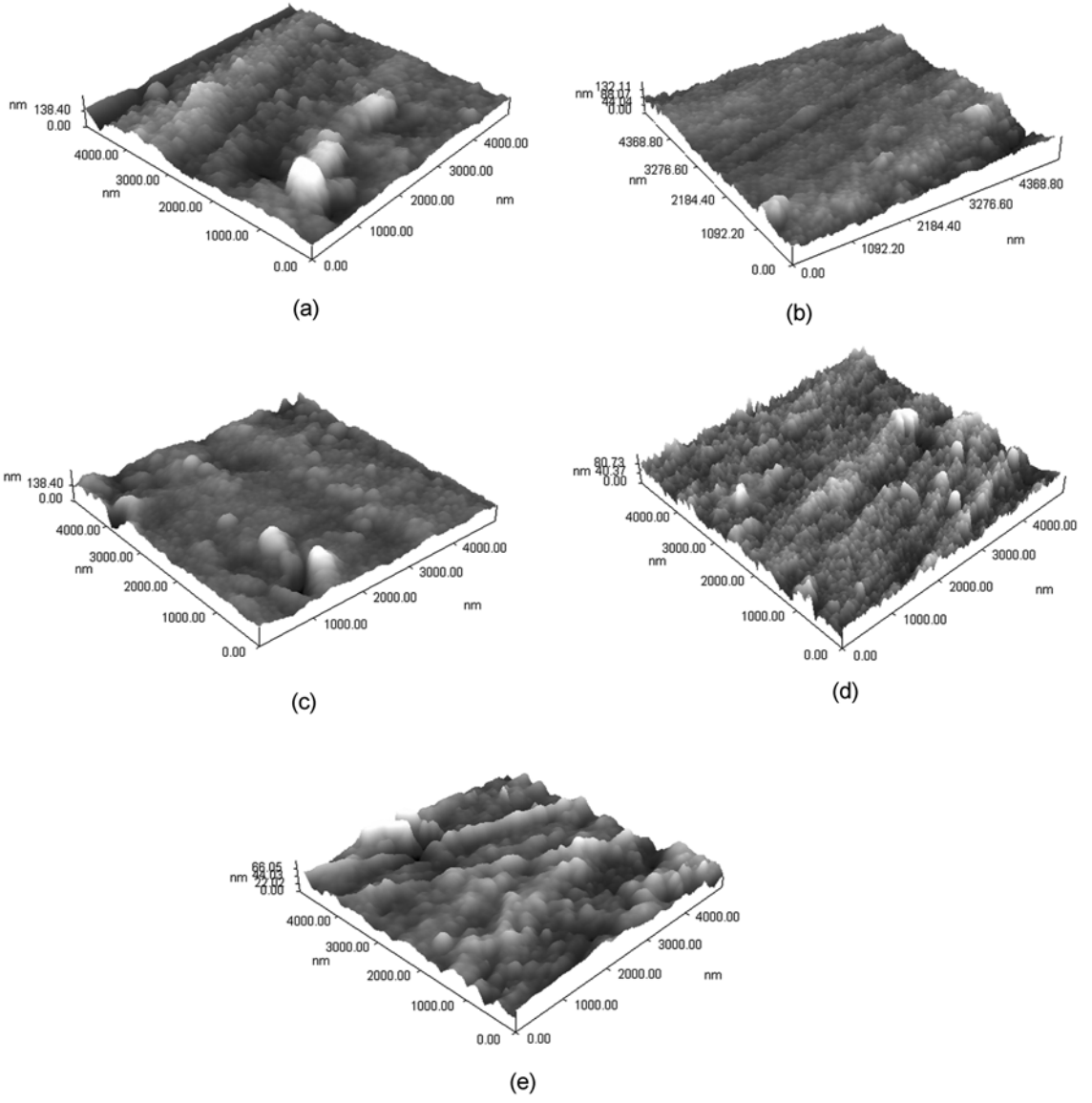

Figure 3. AFM images of sputtered Vectran yarns (a) raw sample: coated for 30 min, (b) sample 1: coated for 30 min, (c) sample 2: coated for 30 min, (d) sample 3: coated for 30 min, and (e) sample 4: coated for 30 min.

EDX Analysis

EDX survey spectra are used to determine elements existing on the fiber surface before and after sputtering coating. The results are displayed in Figure 5. It can be seen that only carbon (C) and oxygen (O) are detected as major elements before the sputter coating as illustrated in Figure 5(a). The composition of hydrogen (H) in the material is too light to be detected in this EDX analysis. After being pre-treated by plasma for 90 s and sputtered for about 30 min, a significant amount of Ag is detected on the fiber surface as displayed in Figure 5(b). At the same time the amount of C and O on the fiber surface is decreased compared to those in Figure 5(a), indicating the deposition of Ag on the Vectran fibers, which confirms the SEM observations as presented in Figures 2 and 4.

Electrical Conductivity

The Ag coatings lead to a significant decrease in the surface resistivity, as revealed in Table 2. All the samples before sputter coating is out of the range of the test apparatus (106 Ω·cm), indicating the electrical isolation behavior of the material. Nevertheless, several observations have to be pointed out. First, the pre-treated samples with Ag sputtered exhibit an increase in conductivity by an order of magnitude compared with that of the raw sample. It is believed that the surface resistivity is significantly affected by the continuity

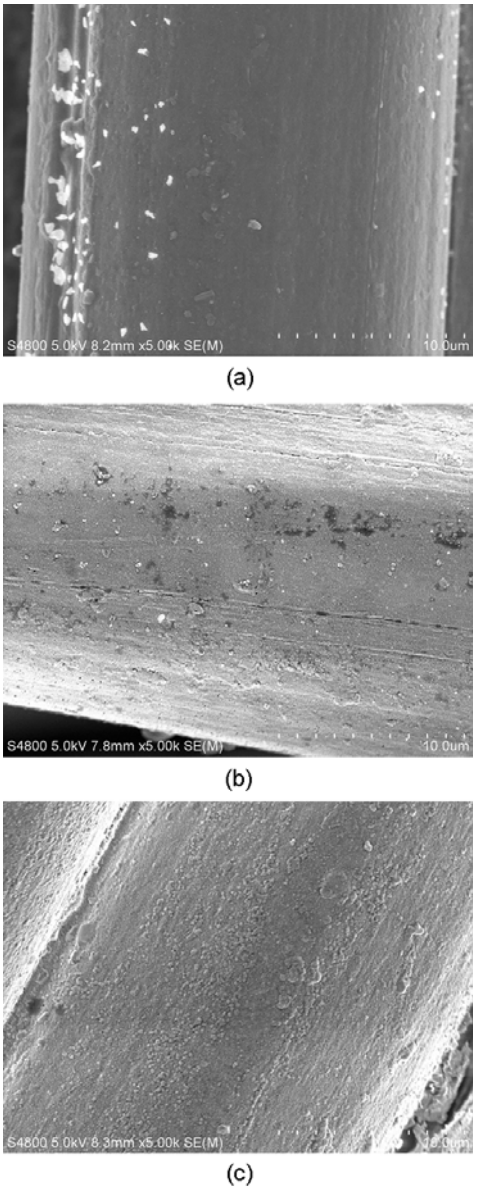

Figure 4. SEM images of sample 4 (a) plasma treatment, (b) Ag coated for 30 min, and (c) Ag coated for 60 min.

Table 2. Surface roughness and resistance values

Material	Surface roughness Root mean square (nm)	Average resistivity (Ω·cm)
Raw sample	71.7	out of range (>10^6)
Raw sample	71.7	2.9×10^{-2}
Sample 1	39.4	1.66×10^{-3}
Sample 2	50.5	1.92×10^{-3}
Sample 3	47.5	1.96×10^{-3}
Sample 4	79.2	5.20×10^{-3}
Sample 5	67.3	3.50×10^{-3}

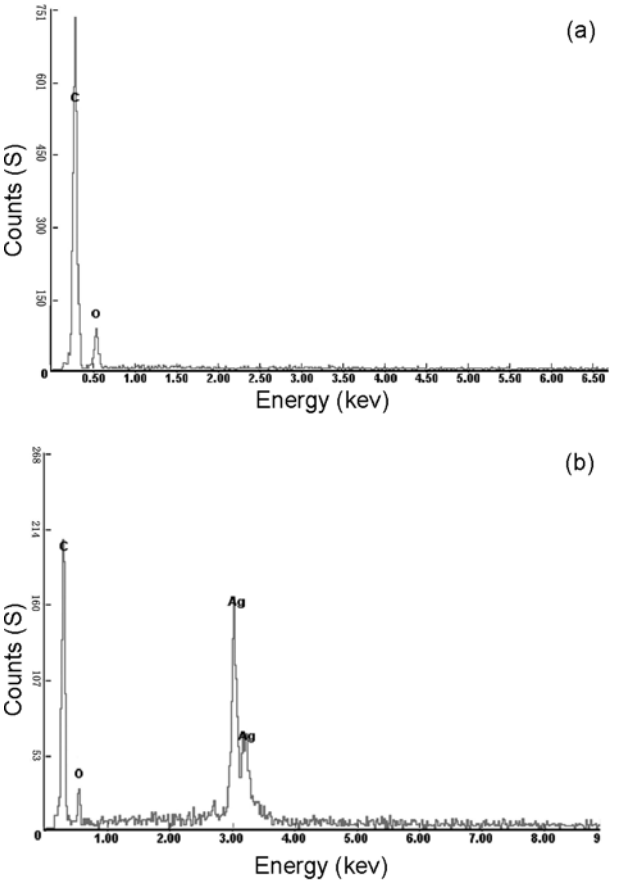

Figure 5. EDX spectra of samples (a) raw sample and (b) samper 1 coating 30 min.

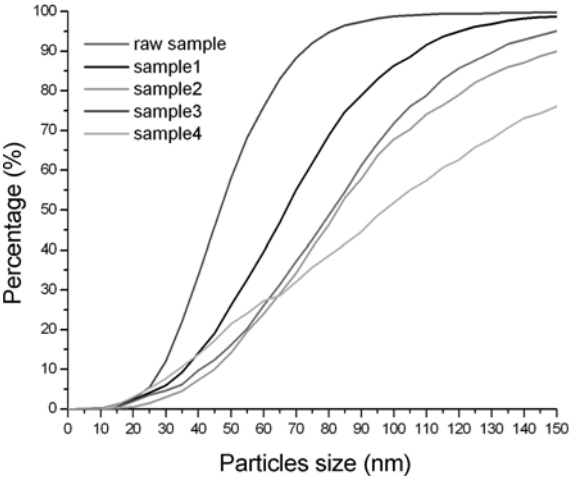

Figure 6. The distribution of nano-silver particles size.

and smooth of Ag coating, in which plasma treatment has some effect depending on the treatment conditions. The effect of the plasma treatment on the cluster structures can be seen in Figure 6 when the same sputtering conditions

Table 3. Tensile strength

Material	Strength (N)	Elongation at break (%)
Raw sample	119.6	3.23
Pre-treated sample 1	117.4	3.20
Coating sample 1	117.3	3.20

were used for the samples 1-4. The particles sizes vary depending on the preparation conditions as shown in Table 2. Combined with Figure 3, sample 3 shows the smallest nano-aggregates which form clearly independent clusters. While the particles size of sample 1 may be attributed to such independent secondary or tertiary nucleation. Therefore, the ditches among those clusters disappear and the continuum structure is born. At the same time, the situation of raw sample and sample 2 are between sample 1 and sample 3. Especially, the defect of raw sample contributes to the growing of islets. Conversely, the silver particle size of sample 4 is the largest among those sample as serious etch by plasma treatment which leads to form agglomerate peaks. Table 2 also indicates the relationship between surface roughness and electrical conductivity. The surface roughness analyzed by Imager Software with sample images scanning range 8.0×8.0 μm^2.

It is reasonable to assume that the mobility ratio of electron would be increased in a compact and even film, which explains why sample 1 shows the lowest value of 1.66×10^{-3} Ω·cm. Table 2 clearly indicates that the surface roughness could have a significant effect on the surface conductivity. The increase in surface roughness could lead to the decrease in surface conductivity as revealed in Table 2. It is also found from Table 2 that Sample 5 has the lower resistivity compared to Sample 4. This is because the increase in sputtering time lead to the formation of thicker and improved coverage of the Ag clusters on the fiber surface.

Tensile Testing

Owing to the best matching parameters of plasma and magnetron sputtering treatment, pre-treated sample 1 and sputtered sample 1 were chosen to do the tensile testing at room temperature. Raw sample also tested as prototype model comparison. If plasma treatment conditions are well chosen, the loss in fiber strength can be reduced to the minimal value 1-2 %. However, in some cases the fiber strength even increases [10]. As expected, the obtained values (see in Table 3) are quite similar with a slightly lower strength and elongation at break of the raw Vectran fiber. It clearly identifies that plasma treatment only modifies the fiber surface, though it acts as an etchant to improve interlaminar shear strength of composite materials as well as their resistance to fatigue, delamination and corrosion. And the reaction only occurs on the uppermost surface of fibers and will not change the bulk properties significantly. Sputter coating is a kind of surface processing technology as well as less destructive to the substrate.

Conclusion

Conductive thermotropic liquid crystalline fibers were developed by introducing nanostructured silver films via magnetron sputtering technique. The surface treatment of Vectran fibers was performed for improving the adhesion of the sputtered film to the fiber substrates. Analysis in morphology and strength testing indicated that the uniform deposition of Ag on the Vectran fibers could be achieved by plasma pre-treatment with less loss in mechanical properties. The work has exploited a new way to enhance or alter the surface properties of thermotropic liquid crystalline fibers using sputtering coatings for a wide range of applications.

Acknowledgements

The work was financially supported by the Program for New Century Excellent Talents in University (NCET-06-0485) and the Self-determined Research Program of Jiangnan University (No. JUSRP20903).

References

1. Campoy, M. A. Gómez and C. Marco, *Polymer*, **41**, 2295 (2000).
2. C. K. Saw, G. Collins, J. Menczel, and M. Jaffe, *J. Therm. Anal. Calorim.*, **1**, 175 (2008).
3. M. Tanaka and Y. Moritaka, *Adv. Space. Res.*, **34**, 1076 (2004).
4. G. Tovar, P. J. Carreau, and H. P. Schreiber, *Colloid. Surface. A.*, **161**, 213 (2000).
5. G. Wiberg and U. W. Gedde, *Thermochim. Acta*, **319**, 123 (1998).
6. V. R. Mehta and S. Kumar, *J. Mater. Sci.*, **29**, 3658 (1994).
7. S. Lee, M. S. Kim, A. K. Naskar, and A. A. Ogale, *Polymer*, **46**, 2663 (2005).
8. Q. F. Wei, Q. X. Xu, Y. B. Cai, W. D. Gao, and C. Z. Bo, *J. Mater. Process. Tech.*, **4**, 2028 (2009).
9. Q. F. Wei, H. Ye, D. Y. Hou, H. B. Wang, and W. D. Gao, *J. Appl. Polym. Sci.*, **99**, 2384 (2006).
10. A. Vesel, I. Junkar, U. Cvelbar, J. Kovac, and M. Mozetic, *Surf. Interface Anal.*, **40**, 1444 (2008).