THE STUDY OF PROPERTY-STRUCTURE RELATIONSHIPS IN CARBON FIBERS USING ELECTROCHEMICAL POLISHING

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Abstract
It has been shown that some polyacrylonitrile(PAN)-based carbon fibers exhibit skin-core microstructure with a higher preferred orientation of graphene layers in the skin region. In this investigation, variations of the fiber properties across the fiber diameter were studied by reducing the fiber diameter using electrochemical polishing refining. The diameter of carbon fibers can be reduced uniformly from ~7 μm to ~3 μm. Different variations of electrical resistivity as a function of fiber diameter were found for different types of fibers and for the same type of fibers with different heat treatment temperatures. Degradation of fiber strength was measured after electrochemical polishing due to the introduction of surface defects.

1. Introduction

Some polyacrylonitrile (PAN)-based carbon fibers (CFs) have been known to exhibit skin-core microstructure [1,2]. Transmission electron microscopy study indicated that the degree of preferred orientation angle of the graphitic basal planes decreases gradually from the skin region to the core region. With increasing heat treatment temperature, the basal planes tend to orient parallel to the fiber axis, first in the skin region and then in the core region, also resulting in the decrease of the diameter of the core region. The skin-core heterogeneity could cause the variation of the fiber properties across the fiber diameter, concentrating stresses in certain regions, the formation and growth of microvoids, and residual stresses [3] which could be as large as ~1 GPa. Therefore, it is desirable to study the relationships between the heterogeneous structure and the fiber properties. However, little work has been done in this area, presumably due to the difficulty to refine the fiber diameter uniformly and measure the corresponding fiber properties. Hao et al. [2] studied the structure-mechanical heterogeneity by plasma etching-assisted radius profiling. In this study, the diameter of PAN-based CFs were etched by electrochemical polishing refining, and the electrical resistivity and tensile strength were measured for the single fiber after electrochemical refining.

2. Experimental

2.1. Electrochemical polishing

The surface layers of the CFs were removed continuously by electrochemical polishing refining and Fig.1 shows the experimental setup. As shown, a single carbon fiber was attached to the anode and a platinum wire was used as the cathod. A dc voltage was applied to the system. The fiber diameter can be reduced uniformly using this technique and can be monitered by laser diffraction technique [4].

2.2. Characterizations

The electrical resistivity of CFs with and without electrochemical polishing was measured at room temperature using four point probe method on single fibers [5]. The electrical contacts were made by using silver paint. A Keithley model 580 micro-ohmmeter was used in the measurements. Single fiber tensile test was used to measure the fiber strength using a universal testing machine (Shimadzu) with a load cell of 1 N. The surface morphology was observed using SEM.

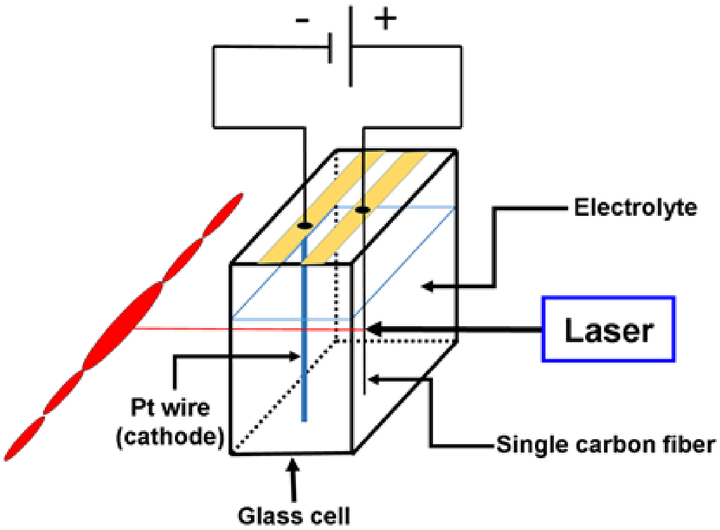

Figure 1. Experimental setup for the electrochemical polishing of single carbon fiber.

3. Results and Discussion

3.1. SEM observation

Electrical polishing was adopted to remove the surface materials of CFs layer by layer and Fig.2 presents the SEM surface morphology of T700 CFs before and after electrochemical polishing at three etching points (0.5, 1 and 2 μm) in depth using a voltage of 150 V. As shown in Fig.2(a)-2(d), the diameter of CFs can be reduced continuously to ~3 μm with a quite smooth surface morphology in the lower magnification (10 k). However, the SEM images (Fig.2(e)-2(h)) at the higher magnification (100 k) show surface defects due to electrochemical etching. The size of surface defects decreases as the etching proceeds from 0.5 to 2 μm.

3.2. Electrical resistivity

Fig.3 shows the variations of electrical resistivity in etched CFs for different types of CFs (Fig.3(a)) and for T700 CFs with different heat treatment temperatures (Fig.3(b)). Different trends were observed for different types of CFs. For T700 CFs, a larger increase of resistivity was measured when 2 μm of the diameter was etched. On the other hand, only a little increase of resistivity was found for TC33 CFs. When the diameter was further etched to 4 μm, a significant increase of resistivity for TC33 CFs was obtained, but the resistivity for T700 CFs shows an obvious decrease. T700 CFs have been shown to exhibit skin-core microstructure with a higher preferred orientation of graphene layers in the skin region [1,6]. Therefore, in the beginning of etching, a removal of surface layers with a higher preferred orientation resulted in an increase of resistivity. As the etching proceeded into the core region, the resistivity started to decrease due to the removal of more randomly arranged graphene layers. As the

CFs were heat treated to a higher temperature (2500℃), the basal planes tend to orient parallel to the fiber axis in the skin region and the diameter of the skin region increases. Consequently, decrease of resistivity was not observed for CFs heat treated at 2500℃.

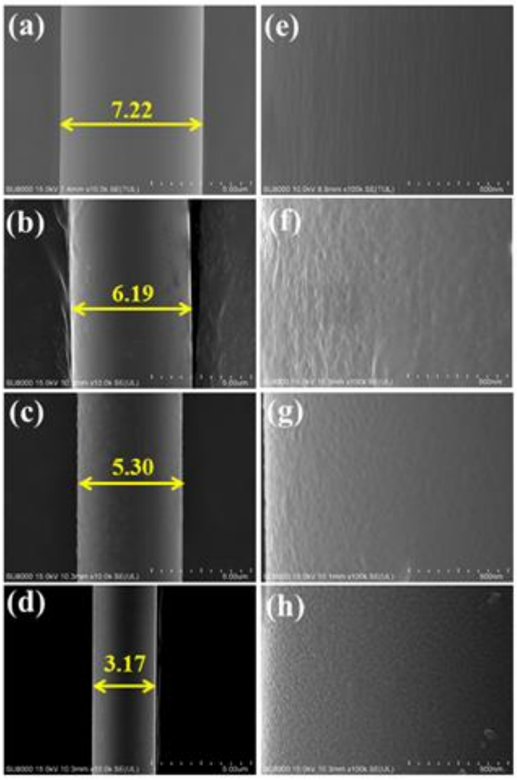

Figure 2. SEM surface morphology of T700 CFs after electrochemical polishing at different etching points in depth using a voltage of 150 V: (a)(e) original; (b)(f) 0.5 μm; (c)(g) 1 μm; (d)(h) 2 μm.

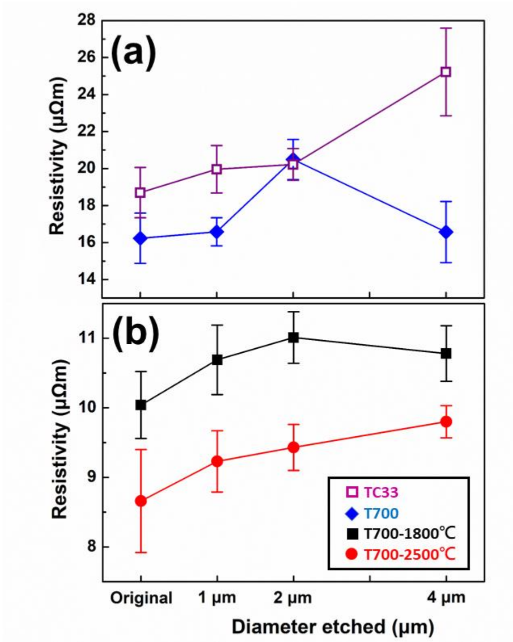

Figure 3. Variations of electrical resistivity in etched CFs: (a) different CFs; (b) CFs with different heat treatment temperatures.

3.3. Mechanical properties

Single fiber tensile strength was also measured for the etched fibers, and the results were presented in the Weibull plots in Fig. 4. As shown in Fig.4(a), degradation of fiber strength for T700 CFs was measured after electrochemical polishing. However, similar strength distributions were found for CFs with a diameter etched for 0.5, 1 and 1.5 μm. It is suggested that similar defects were introduced after electrochemical etching. On the other hand, although the strength distribution was also shifted to the left after electrochemical polishing for TC33 CFs (Fig.4(b)), more shift was found for CFs with a larger diameter etching.

4. Conclusions

Electrochemical polishing refining was used to reduce the diameter of two types of PAN-based CFs, T700SC from Toray and TC33 from Formosa Plastics Corporation in Taiwan. Then the electrical resistivity and tensile strength of single carbon fibers after electrochemical polishing were measured to study the effects of skin-core heterogeneity on the fiber properties. SEM observations indicated that the fiber diameter can be reduced uniformly from ~7 μm to ~3 μm. However, surface defects were also introduced after electrochemical etching, which leads to the decrease of fiber strength. Results of single fiber resistivity measurements after electrochemical etching show that different trend of resistivity-diameter relationship could be obtained for different types of fibers (T700SC v.s. TC33) and for the same type of fibers (T700SC) with different heat treatment temperatures.

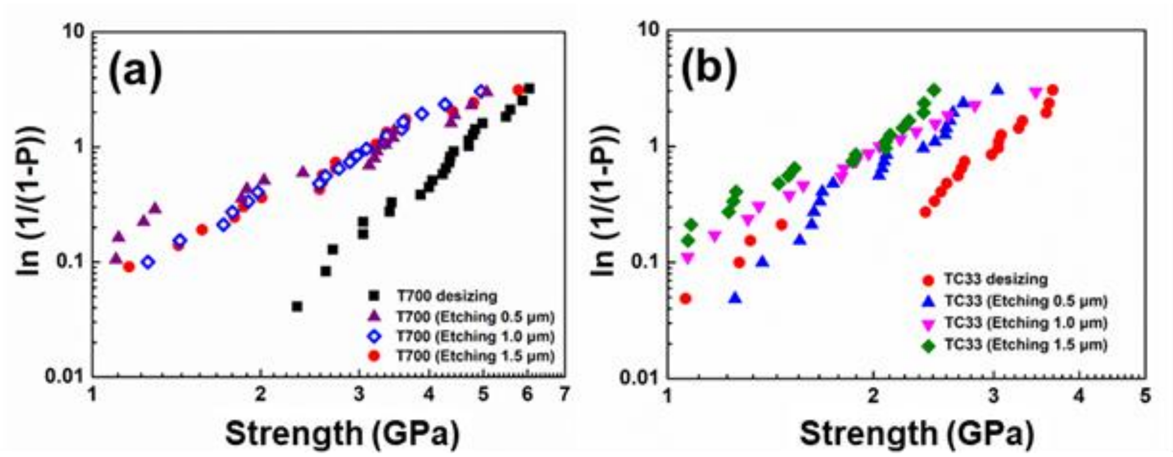

Figure 4. Weibull plots of CFs with a diameter etched for 0.5, 1 and 1.5 μm: (a) T700 CFs; (b) TC33 CFs.

Acknowledgments

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