Reinforcing effect of Single Wall Carbon Nanotubes on Acrylic Fibers

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Abstract

The reinforcing effect of single wall carbon nanotubes (SWNTs) on polyacrylonitrile (PAN) fiber were investigated. The tensile fracture images of the composite fibers demonstrate that SWNTs are well dispersed in PAN matrix as bundles (ropes) ca. 20nm in thickness. It was found that SWNTs play a role not only to reinforce but also to toughen the PAN fiber by increasing breaking strain as well as modulus and strength of the fiebrs. The composite fibers exhibited improved dimensional stability at elevated temperature compared to the neat PAN fiber.

Introduction

Recently, extensive studies have been performed to use carbon nanotubes because of their lightweight, unusual mechanical [1] and electronic properties [2,3] to improve the performance of a matrix or to achieve new properties. The nanotubes having large surface area can induce a better adhesion with the polymeric matrix as a reinforcement, which is an important factor for an effective enhancement of the composite properties. Particularly, SWNT-polymer composites have generated considerable interest because they may possess a novel combination of electrical, optical and mechanical properties [4, 5]. SWNT-polymer composites have a potential for large increases in strength and stiffness due to their lightweight, when compared to conventional carbon-fiber-reinforced polymer composites.

On the other hand, PAN fiber usually including a comonomer is the most important precursor for manufacturing carbon fibers.

In the present work, we have investigated the effects of SWNT on the properties and morphology of PAN fibers before and after thermal oxidation.

Experimental

As prepared (HiPCO 86) and purified (HiPCO 87) SWNT produced by the HiPCO process [6] were obtained from Rice University. Laser oven SWNT (grade CNI PO 42600) were supplied by Carbon Nanotube Inc. PAN was supplied by Sigma- Aldrich.

Dried SWNT was mixed with excess of solvent and sonicated for two hours using a bath sonicator. PAN was added to the mixture after boiling off the excess solvent to a required final volume. The solutions containing PAN and SWNT in the ratios 100:0, 95:5 and 90:10 were prepared.

The fiber spinning was carried out on a spinning machine supplied by Bradford University Research Ltd. using a singe hole spinneret of 500 μm diameter. All the fibers were drawn by passing a heating chamber to draw ratio of 4.3.

The drawn fibers were thermally oxidized in an oven at 250°C for 10 hours under continuous air flow. The length of fibers was maintained constant during oxidation by clamping both ends to a steel holder.

The mechanical properties of the neat and composite fibers determined using a RSA III instrument supplied by Rheometrics scientific. Fiber shrinkage was determined using TA instruments' thermo-mechanical analyzer (TMA 2940) at a heating rate of 5 °C/min. The stress and weight changes of the fibers generated during isothermal oxidation at 250°C were measured using the TMA.

SEM images of PAN and PAN-SWNTs composite fibers after oxidation were obtained by using Leo 1530 Scanning Electron Microscope.

Results

The tensile fracture images of the oxidized composite fibers in Figure 1 demonstrate that SWNTs are well dispersed in PAN matrix as bundles (ropes). Some SWNT ropes looks as wrapped by PAN to give the thickness ca. 50-70 nm. A molecular mechanics simulation suggested that helical polymer conformations in which chains can wrap around nanotubes might enhance non-bonded nanotube-polymer interactions [7]. As PAN molecules are known to form irregular helices due to the strong dipole-dipole interaction between adjacent nitrile groups, it is expected

that this composite system may have good dispersion and interfacial bonding to result significant reinforcing effect by nanotubes. Thus it is presumable that PAN molecules wrap SWNT ropes in the composite.

On the other hand, most of SWNT bundles are seen as broken after pulled-out in the fracture formed by tensile force. It is noted that the thickness of the pulled-out ropes is around 20nm (arrow in the figure) while the roots of the ropes are still anchored in the matrix (rectangles in the figure) implying good adhesion between SWNT ropes and oxidized PAN matrix. The pulled-out length of the ropes is mostly less than 500nm even though some has been pulled out by more than 1000nm.

It was clear that the PAN/SWNT composites offer improved tensile properties regardless of thermal oxidation. For the oxidized fibers, all the tensile values increased with increasing SWNT content, while the ultimate strength showed maximum value at 5 wt% and the fracture strain has tendency to reduce by the addition of the SWNT for the untreated fibers. It is notable that work of rupture, area under the stress-strain curve, of the PAN fiber increased significantly proportional to the addition of SWNT.

Thus, it can be concluded that SWNTs play a role not only to reinforce but also to toughen the PAN fiber. The load transfer from the matrix to the SWNTs was likely caused by a kind of micro-mechanical interlock, that is, wrapping SWNT by helical PAN molecules.

The lower thermal shrinkage of the composite fibers generated by heating implies that the SWNTs hinders entropic shrinking of the matrix molecules by favorable adhesion between SWNTs and PAN molecules. The enhanced thermal stability of PAN fiber by incorporation of SWNT was also notable.

Conclusions

It has been demonstrated that the SWNTs was dispersed in PAN fiber at the level of ropes in a diameter of ca. 20nm. It is concluded that a favorable adhesion between SWNTs and PAN molecules is sure to exist. These reinforcing effects of SWNTs on PAN fiber can play a favorable role in the process to make carbon fibers from acrylic precursor.

References

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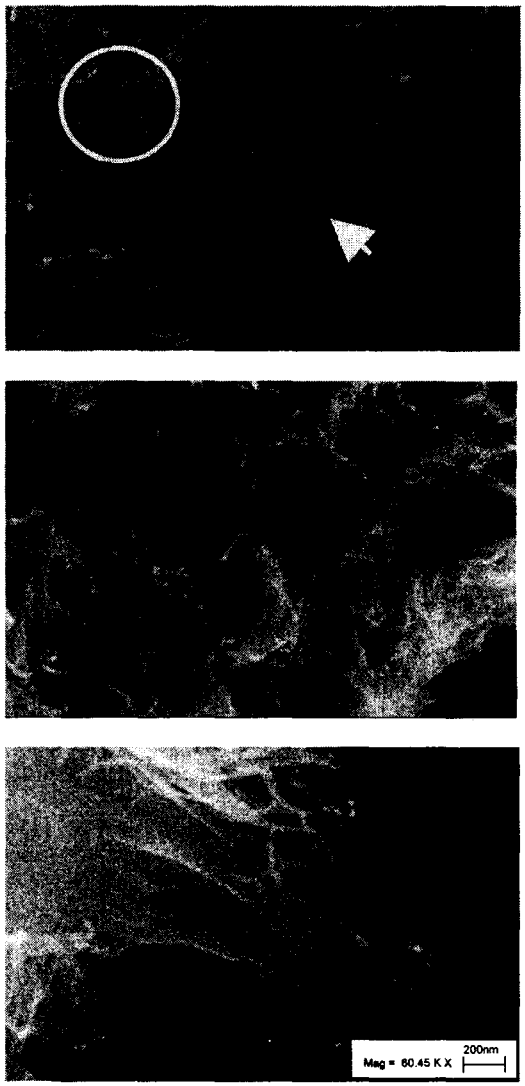

Fig. 1. The magnified tensile fracture images of tne PAN/SWNT composite fibers.