PROBING THE STRUCTURE OF CARBON NANOTUBE REINFORCED COMPOSITES BY RAMAN SPECTROSCOPY

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Abstract

Mini-composites were developed using multiwall carbon nanotubes (CNTs) in their as-received form as well as in a carpet form grown by the catalytic CVD technique. The CNT carpets were infiltrated with carbon generated by cracking of methane using CVD technique. Another series of composites were obtained using liquid routes (pitch and phenolic resin) for generation of the carbon matrix. These composites were heat treated at 1000°C and 2400°C, and the microstructure was studied using Micro-Raman spectroscopy and FE-SEM. When viewed under FE-SEM, the CNTs were found to be uniformly distributed in the matrix for pitch and phenolic resin-derived carbon matrices composites. As expected, in CVD based composites, the CNTs retained their orientation transverse to the plane. Further, the matrix was found to exhibit orientation at a nanoscale around the carbon nanotubes. However, the nature and extent of graphitic matrix in the two types of composites was found to be distinctly different.

Key Words: Carbon composites, carbon nanotubes, carbonization, FE-SEM, Raman spectroscopy

Introduction:

Carbon nanotubes have attracted attention from physicists, chemists, and engineer due to their unique physical, mechanical and electrical properties. Their potential applications include electronic devices such as flat panel displays, Li-ion batteries, capacitors, as probe tips for atomic force microscopy, and hydrogen storage (1). Due to successful application of carbon fibers as reinforcing materials, carbon nanotubes are regarded as futuristic reinforcing materials for composites as well.(2) However, a lot of basic studies need to be performed on surface properties of carbon nanotubes and their bonding with the matrix systems. The objective of this research project was to probe the structure and bonding of multiwall carbon nanotubes with thermosetting as well as thermoplastic matrix precursors.

Experimental

In one set of experiments, multiwall carbon nanotubes were grown by CVD technique using xylene as the source. These tubes were purified and then mixed with thermosetting phenolic resin and thermoplastic pitches. The mix was examined using FE-SEM. These were carbonized to 1000^{o}C and further examined by FE-SEM and Raman spectroscopy. In another set of experiments, carbon nanotube carpets were prepared through CVD technique wherein carbon nanotubes were aligned parallel to the thickness direction. Mini-composites were developed through infiltration of these carpets by methane cracking using CVD technique. These composites were heat treated at 1000^{o}C and 2400^{o}C. These mini-composites were also characterized by using FE- SEM and Raman spectroscopy (Renishaw InVia Raman microscope). An argon laser with a wavelength of 514 nm provided the monochromatic light source. The laser power was kept low for the composites sample to avoid any heating effect, which can lead to a shift in the Raman signal.

Results and Discussion

HRTEM micrographs of CNTs (fig. 1 and 2) (as-received and after purification) showed that unorganized carbon at the surface is removed through purification. The organized graphitic nature of latter type carbon nanotubes was confirmed by Raman spectroscopy. FE-SEM of purified CNT in pitch matrix, displayed in Fig. 3, clearly shows CNT pullout without any significant matrix adhesion. Fig. 4 shows

treated CNTs, Fig. 4 displays the pitch matrix adhered to the surface. This phenomenon is similar to the one normally observed for surface treated carbon fibers and liquid matrix systems.

Figure 5 shows Raman spectrum of mesophase pitch mixed with multiwall carbon nanotubes composites heat-treated at 1000°C and 2400°C. The typical Raman spectra show G-band at 1581cm^{-1}and D-band at 1361 cm^{-1}. The ratio of I_D/I_G is 0.52, which is nearly equal to I_D/I_G ratio of mesophase pitch heat treated at 1000^{0}C. In this spectrum, a shift in D band is due to thermal heating of sample during analysis.(3,4)

The composite heat-treated at 2400^{0}C shows (Fig. 6) a Raman spectrum in which the G band appears at 1584 cm^{-1} and D band appears at 1355 cm^{-1}. The weak D' band also appears at 1620 cm^{-1}. In this Raman spectra shift in peaks is very small as compared to that heat-treated at 1000^{0}C. The ratio of I_D/I_G was 0.60 that shows a presence of SP^3 carbon(3,4), which results from mixing of carbon nanotubes in mesophase pitch.

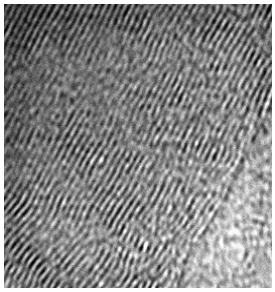

FIG. 1 shows image of HRTEM

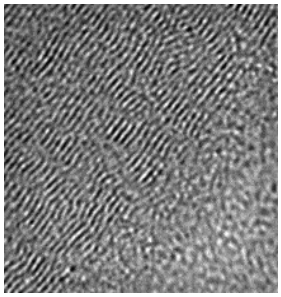

FIG. 2 shows image of HRTEM

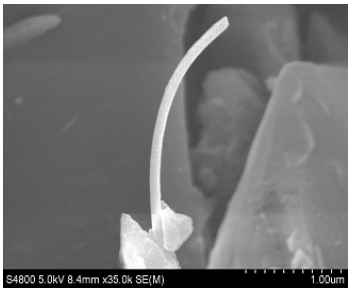

Fig. 3 shows FE-SEM of purified CNT in pitch matrix

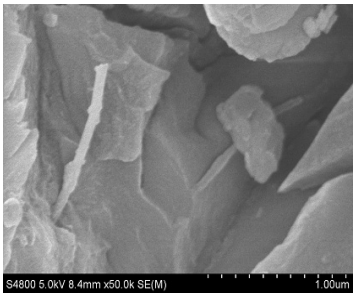

Fig. 4 shows FE-SEM for treated CNTs

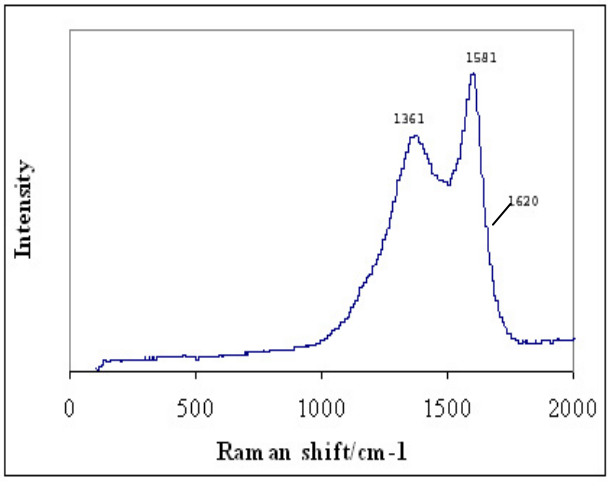

Fig. 5 Mesophase Pitch /CNT composites heat treated to 1000˚C

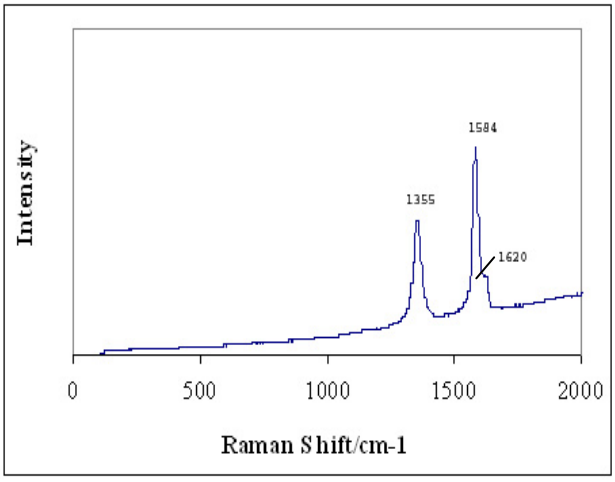

Fig. 6 Mesophase Pitch CNTs HTT 2400˚C

Conclusion

The carbon nanotubes as such exhibit unorganized carbons at the surface, which on cleaning get removed making the surface smooth. Such nanotubes, with carbon matrix exhibit pullout behaviour. On treating these nanotubes with chemicals, the fiber/matrix adhesion gets enhanced exhibit sticking of carbon matrix to the surface of carbon nanotubes.

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