Functionalization of Multi-walled Carbon Nanotubes Via UV/O$_3$ and Silane Treatments

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Abstract. This paper presents a method for chemical functionalization of CNTs through the combined process of UV/O$_3$ treatment and silanization process. FT-IR and TEM were employed to characterize the changes in surface functionalities and morphology. The results indicate improved dispersion and attachment of silane molecules on the surface of CNTs. Epoxy matrix nanocomposites containing functionalized CNTs showed much better dispersion with associated higher mechanical properties than those without functionalization. These findings confirmed the improved interfacial interactions due to covalent bonding between the functionalized CNTs and epoxy resin.

Introduction
With unique structural and transport properties, such as excellent strength, modulus, electrical and thermal conductivities along with low density, carbon nanotubes (CNTs) have attracted much interest as the reinforcement for polymer matrix composites. The CNT/polymer nanocomposites hold the promise of delivering exceptional mechanical properties and multi-functional characteristics. To ensure effective reinforcements for polymer composites, proper dispersion and good interfacial bonds between the CNTs and polymer matrix have to be guaranteed [1]. To achieve this, many surface treatment and functionalization techniques have been devised with varied successes. In the present work, improved dispersion and interfacial adhesion of multi-walled carbon nanotubes (MWCNTs) with an epoxy matrix is achieved through UV/O$_3$ treatment and functionalization using a silane coupling agent. The effects of functionalization are evaluated on the mechanical properties and dispersion of the CNT/epoxy nanocomposites.

Experimental
Materials. The epoxy matrix used in this work is diglycidyl ether of bisphenol A (DGEBA, Shell Epon 828) with amine hardener of m-phenylene-diamine (m-PDA). MWCNTs (Iljin Nanotech, Korea) used in this study were produced via chemical vapor deposition and are the same as those employed in our recent works [2,3]. 3-glycidoxypropyl-trimethoxysilane (GPTMS, Aldrich) with a 98% purity was used as the functionalization agent. The process steps used for CNTs functionalization and preparation of the MWCNT/epoxy nanocomposites are shown in the flow chart (Fig.1) [3]. Eight different nanocomposites containing different contents (0.05, 0.10, 0.25 and 0.50 wt%) of pristine MWCNTs (P-MWCNTs) and silane functionalized MWCNTs (Si-MWCNTs) were produced.
Characterization. FT-IR and TEM were used to characterize the changes in chemical structure and surface morphology of the MWCNTs. The mechanical properties of nanocomposites were measured on a universal testing machine according to ASTM standard D790-96. SEM was employed to examine the dispersion states of MWCNTs on the fracture surfaces. The electrical conductivity of nanocomposites was measured using a resistivity/hall measurement system.

Results and Discussion

Surface Functionalities of MWCNTs. Fig. 2 shows the FT-IR results of the MWCNTs before and after functionalization. For the P-MWCNT (Fig. 2A), the bands at 3419 and 1058 cm$^{-1}$ are attributed to the presence of hydroxyl groups (-OH), which probably arise from either ambient atmospheric moisture bound to the MWCNTs or oxidation during purification of the raw material [4]. Another band at 1626 cm$^{-1}$ is assigned to the C=O stretching of quinone groups. In the Si-MWCNTs (Fig. 2B), two new bands at 2914 and 2848 cm$^{-1}$ are associated with the stretching of the methylene groups of the silane used. The weak signal at 793 cm$^{-1}$ confirmed the presence of epoxy groups derived from the silane agent. The FT-IR spectral data also confirmed the attachment of silane molecules on the CNTs.
Dispersion and surface morphology of MWCNTs. Fig. 3 shows the typical TEM images of the MWCNTs. The P-MWCNTs were severely agglomerated (Fig. 3A). After the silane treatment (Fig. 3B), the agglomeration was significantly reduced. The individual MWCNTs were detached loosely without significant changes in their lengths. The high magnification TEM photograph (Fig. 3C) indicates a closed end tip of the P-MWCNT. After ball milling and silane functionalization (Fig. 3D) the end tip was opened up, and some amorphous materials were attached to the end tips of the Si-MWCNTs (spot A). The detection of silicon by the EDX (Fig. 3E) suggests the amorphous materials originating from the silane molecules. These findings further confirm the attachment of silane molecules on the surface of MWCNTs.

![TEM images of MWCNTs](image)

Flexural properties of the nanocomposites. Fig. 4 shows the flexural properties of the nanocomposites plotted as a function of MWCNT content. The nanocomposites containing Si-MWCNTs exhibited a higher modulus than those containing P-MWCNTs: the flexural modulus increased 22.3% and 8.7%, respectively, for the Si-MWCNT and P-MWCNTs nanocomposites with...
the same 0.25 wt% of CNTs. These results confirm the ameliorating effect of functionalization on the modulus of nanocomposites. The flexural strength of nanocomposites presented a similar trend: the strengths of the Si-MWCNT samples were in general higher than the untreated MWCNT counterparts when the reinforcement contents were below 0.25wt%. However, an abnormal result with a reversed trend was observed for the composites with 0.5wt%. It is suspected that the curing reaction between the DGEBA and m-PDA was adversely affected by the epoxy end-groups on the Si-MWCNTs at a high MWCNT content, which in turn reduced the composite flexural strength.

**Dispersion of MWCNTs in epoxy.** Fig. 5 shows the SEM images of nanocomposite fracture surface, providing some insight into the CNT dispersion. The P-MWCNTs were present mainly in the form of agglomerates, whereas the Si-MWCNTs were dispersed more uniformly, confirming much better dispersion of CNTs in polymer resin after functionalization with silane.

![SEM photographs of fracture surface of nanocomposites showing CNT dispersion states.](image)

**Conclusions**

In the present work, a novel method for chemical functionalization of MWCNTs through UV/O$_3$ and silane treatment is successfully developed. The effects of functionalization are investigated on the mechanical properties and CNT dispersion in the epoxy matrix. Silane-functionalized MWCNTs showed much better dispersion with improved flexural modulus and strength compared to those without functionalization. These findings confirmed the improved interfacial interaction due to covalent bonding between the silane-functionalized MWCNTs and epoxy resin.

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