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Characteristics of hydrogen plasma treated carbon nanotubes and their influence on the mechanical properties of polyetherimide-based nanocomposites

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ABSTRACT

The structural phase transformation and etching of the sidewalls of multi-walled carbon nanotubes (MWCNTs) by hydrogen plasma and the effect on the dispersion and mechanical properties of polyetherimide (PEI) composites was investigated. Surface-modified MWCNTs with various plasma treatment times were characterized using FESEM, HRTEM, Raman spectroscopy, FT-IR, and XPS. The results showed that plasma treatment facilitates the attachment of functional groups while damaging and detaching the sidewalls of the MWCNTs and modifying the crystallinity of the graphene layer. The mechanical properties of the PEI composites with the modified MWCNTs depended on the degree of damage to the surface and crystallinity modification of the MWCNTs. Hydrogen plasma treatment led to a significant improvement in the dispersion and mechanical properties of PEI/MWCNT composites due to the surface modification of the MWCNTs.

1. Introduction

Carbon nanotubes (CNTs) have attracted intensive attention as a reinforcement material in many engineering applications due to their high aspect ratio and good electrical, thermal and physical properties [1–3]. These properties make CNTs suitable for a broad range of applications. High-strength epoxy composite systems made of CNTs and polymer are important materials for vehicle, machine, and electrical parts as well as countless other industrial applications [4–6]. In particular, the excellent mechanical properties of CNTs make them a promising candidate for added fillers in polymer composites. Nevertheless, because of the strong intrinsic van der Waals forces, CNTs tend to aggregate, which leads to poor dispersion and chemically inert materials; thus, good adhesion with a polymer matrix is hard to achieve. Thus, an applied load cannot be efficiently transferred from the polymer matrix to the CNTs because of this weak adhesion. To solve the problem of poor CNT dispersions, many research efforts have been devote to developing a chemical or mechanical dispersion method, such as CNT dispersion by attrition milling, adding surfactant, polymeric passivation and chemically functionalizing the surface of the CNTs [7–9].

In a previous study on the chemical treatment of CNT surfaces, Ruan et al. [10] used magnetic stirring and sonication to disperse the nanotubes in xylene followed by reflux to mix the CNTs into a polymer. However, this method relies on the efficient dispersion of CNTs in the relevant solvent, while CNTs cannot be well dispersed in most solvents. In addition, treatment with a mixture of concentrated sulfuric and nitric acids [11] can introduce carboxyl groups onto the CNTs' surfaces to enhance interfacial bonding. However, this treatment was found to seriously damage the structure of the CNTs and reduces the length of the CNTs, which led to a degradation in the properties of the CNTs [12]. In the case of mechanically dispersed CNTs, Thostenson et al. [13] dispersed CNTs well into epoxy using shear mixing (roll to roll), and the results showed a 60% improvement in the thermal conductivity epoxy/CNT (5 wt%) composites. However, the experimental results showed weak interfacial bonding between the CNT surfaces and the polymer matrix.

Plasma treatment is an environmentally friendly and cost-effective method, and it provides a highly cross-linked polymer composite while not significantly affecting the original structure of CNTs. Shi and coworkers [14] used plasma to deposit polystyrene on the surface of CNTs, and their results show that these CNTs can be dispersed well into a polymer matrix. Surface modifying the CNT

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surfaces by plasma coating can significantly lower their surface energy. To take advantage of the high strength of carbon nanotubes in a polymer matrix, achieving both a good dispersion and sufficient CNT/polymer interfacial bonding is critical [15,16]. Some plasma treatments have been proposed to avoid agglomeration, including chemical treatments, controlled oxidation, etching, polymer wrapping/absorption and the adsorption of functional groups. Moreover, plasma treatment has been used to reduce agglomerations by modifying the surface of the CNTs [17,18]. Plasma treatment generally contains functional groups that can electrostatically prevent agglomeration and enhance interactions with the polymer matrix. Various plasma methods have been used for the surface modification and surface activation/grafting of CNTs [19]. Although the effect of plasma treatment on polymer composites has been studied experimentally, few details are known about the mechanism of the hydrogen plasma effect with various gases on polymer composites.

Chen et al. reported that compare to the untreated MWCNTs the MWCNTs after Ar/O_2 plasma treated had a very good dispersion in aqueous solution [20]. Lee et al. also showed that oxygen plasma exhibited excellent dispersibility [21]. Compared to oxygen plasma, hydrogen plasma was less effective for dispersion. Yang et al. reported that a novel method combining ultrasonication and hydrogen passivation to MWCNTs improved dispersion and mechanical properties [22]. Hydrogen plasma treatment could contribute dispersing of MWCNTs and mechanical properties of composites due to the hydrogen binding to MWCNTs and modified sp^3 bonding [23]. In spite of expectation, there are no reports on plasma treated MWCNTs for improvement of mechanical properties of MWCNTs reinforced polymer composites.

In this study, the effect of hydrogen plasma treatment on the surface properties of MWCNTs was investigated. The generation of nanocrystalline particles on the MWCNT sidewalls, the enhancement of the dispersion of MWCNTs in a polymer matrix and the interfacial bonding between the MWCNTs and the polymer matrix were also investigated using hydrogen plasma treatment on MWCNTs.

2. Experimental details

The MWCNTs (Applied carbon nano technology Co., Ltd. Republic of Korea) were used as a filler to fabricate a polymer composite in this study. First, a plasma treatment was performed on these MWCNT specimens using PECVD. The pressure within the vacuum chamber was maintained at 128 Pa, and the temperature was raised to 300 °C. As the temperature reached 300 °C, 10 standards cc/min (sccm) of hydrogen gas was injected into the chamber as a plasma generating source, and 450 W of radio frequency (RF) plasma power was applied to a 13.56 MHz RF generator to generate the hydrogen plasma, which irradiated the MWCNTs. The plasma exposure time was set to 30, 60, 90 and 120 min.

The microstructure of the MWCNTs was characterized by Raman spectroscopy (LabRam HR, Jobin-Yvon, France) equipped with an Ar ion laser ($\lambda = 532$ nm). The binding energy was analyzed via X-ray photoelectron spectroscopy (XPS, Ulvac PHI, Inc.) using a 15 kV/25 W monochromated Al Kα X-ray source and a take-off angle of 45°. The Raman and XPS spectra were deconvoluted into peaks using spectral analysis software (PeakFit v4.06) to calculate the intensity ratio. FT-IR spectra of the MWCNTs were recorded with KBr in the range of 4000–500 cm^{-1} using a FT-IR Spectrometer (LabRam ARAMIS IR2). High-resolution transmission electron microscopy (HRTEM) was performed using a Titan™ 80–300 microscope (FEI, USA). The cross-section of the polymer composite was observed using a field-emission scanning electron microscope (FESEM, Hitachi- S-4700).

Both untreated MWCNTs and plasma-treated MWCNTs were used to fabricate polymer composites at 260 °C using a Bench Kneader (PBV-01K, Irie shokai Co., Ltd. Japan). PEI (Ultem® 1000) was supplied by GE Plastics. The samples for the mechanical testing were fabricated using a hot-pressing method. For the mechanical property tests, Instron universal testing equipment (UTM 3367) was used. Test specimen dimensions were in accordance with the respective ASTM standards (D638). Each value obtained represented the average of six samples.

3. Results and discussion

Fig. 1 shows the FT-IR measurements of the plasma-treated MWCNTs as a function of the processing temperature. The sp^3 CH (2850 cm^{-1}) and a CH_2 asymmetric vibration mode (2920 cm^{-1}) appear in the spectra of MWCNTs treated at 300 °C. The sp^2 C–H related peaks (3031 cm^{-1}) are also observed in the spectrum of untreated MWCNTs. This sp^2 C-H peak was shifted toward the sp^3 C-H related peaks as the process temperature increased to 300 °C. The FT-IR spectrum of the MWCNTs plasma treated at 300 °C indicated the generation of C-H functional groups, the processing temperature was fixed at 300 °C.

The effect of the plasma treatment on the MWCNT sidewalls was further investigated by HRTEM. Fig. 2 shows HRTEM images of the untreated and plasma-treated MWCNTs. After a 30 min treatment, the surface of MWCNT becomes rougher, probably due to the local etching of carbon bonds compared to the untreated sample, as shown in Fig. 2(a). After a 60 min treatment, nanoparticles consisting of nanocrystalline diamond (NCD) particles appear on the exterior of the MWCNTs (Fig. 2 (c)). The NCD phase formed with a d-spacing of 0.206 nm (Fig. 2 (f)). Several groups have reported that hydrogen plasma plays an important role in the transformation from CNTs to NCD [23,24]. These NCD particles could be easily removed by prolonging the plasma treatment (Fig. 2 (d)). After longer treatments, the number of CNT layers tends to decrease, probably due to layer-by-layer etching, as shown in Fig. 2 (e).

The effect of the plasma exposure time on the surface of the MWCNTs was studied by Raman spectroscopy. The Raman spectra of the MWCNTs after various plasma exposure times are shown in Fig. 3. The conventional carbon peak shape was observed for all

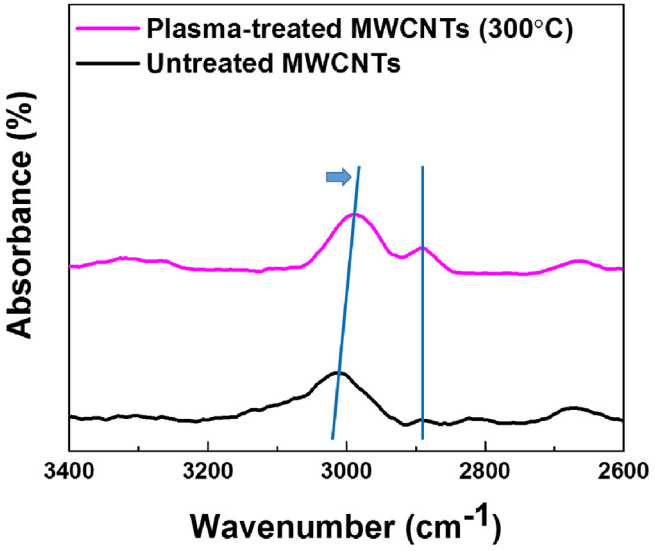

Fig. 1. Functionalization of the MWCNTs surface: FT-IR spectra of untreated MWCNTs and MWCNTs treated with hydrogen plasma at room temperature and 300 °C. (A colour version of this figure can be viewed online.)