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Radical scavenging efficiencies of silane-grafted carbon nanotubes and their effects on crosslinking reaction of vinyl ester/styrene resin

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ABSTRACT

Carbon nanotubes (CNTs) that were first grafted with vinyl trimethoxysilane (VTMS) and then with methacryloxypropyl trimethoxysilane (MATMS) could result in well dispersion in thermosetting vinyl ester/styrene resin and exhibit significant enhancement in storage modulus of the composite. If the VTMS-grafted CNTs were grafted with VTMS, rather than MATMS, in the second step of grafting, significant phase separation was found in the composite. The scavenging efficiencies of the silane-grafted CNTs for hydroxyl (OH·) radicals measured by electron paramagnetic resonance (EPR) were investigated as a function of the step and degree of grafting. The EPR data revealed that the radical scavenging efficiency of a given CNTs exhibited a significant decrease after the first step of grafting with VTMS but exhibited insignificantly further decrease after the second step of grafting with MATMS. The radical scavenging efficiency of a given silane-grafted CNTs was decreased with increasing degree of the silane grafting, an indication that the radical scavenging mechanism involved the reactions of radicals with the CNTs, rather than with the silane grafts. The radical-initiated crosslinking of the vinyl ester/styrene composite was significantly retarded by the silane-grafted CNTs; this should be taken into consideration when producing thermoset polymer/CNT composites having highly enhanced moduli.

1. Introduction

Carbon nanotubes (CNTs) used as effective reinforcements in polymer composites are hindered by their very strong aggregation tendency, and thus very poor dispersion in the composites. This aggregation problem can be solved by sidewall functionalization or modification. Silane-grafting modifications have been reported for solving the aggregation problem of CNTs [1–6]. The methodology adopted in these papers for the silane modifications of CNTs was all involving reactions of the OH groups of CNTs and the OH groups of the hydrolyzed alkoxy silane. The reactivities of both types of OH groups were, however, quite different and would result in ineffective condensation reactions between them. The OH groups of silane were much easier to react with the OH groups of another silane other than with the OH groups of CNTs, resulting in a very low degree of silane grafting of CNTs, as demonstrated by the very low Si content on the silane-modified CNTs [1,3]. Moreover, to adopt this methodology, CNTs have to be oxidized usually in strong acids to obtain the OH-functionalized CNTs; this would damage the structure of CNTs. The oxidations of CNTs would not only cause environmental pollutions because of the strong acids used but also be detrimental to reinforcing effect of CNTs in polymer because of damaged structure of CNTs. To overcome problems of the low degree of silane grafting and the structural damage of CNTs, vinyl silanes have been grafted directly onto the as-synthesized CNTs *via* radical-initiated reactions of C=C double bonds of CNTs with vinyl groups of the silane, without a prior OH-functionalization on CNTs [7,8]. To prepare CNTs with a high degree of silane grafting this way, however, the reaction was usually conducted at a high temperature for a long time. To shorten the reaction time, microwave-assisted reaction was carried out and the grafting of CNTs could be done in several minutes [9].

In this study, we used microwave-assisted heating to graft vinyl trimethoxysilane (VTMS) directly on pristine CNTs in a few minutes, followed by reaction with methacryloxypropyl trimethoxysilane (MATMS) *via* hydrolysis and condensation of methoxy groups in VTMS and in MATMS. MATMS was used to produce methacrylate-ended silane grafts on CNTs. The adoption of the two-step silane grafting is to produce silane-modified CNTs with methacrylate chain ends for enabling homogeneous dispersion in vinyl ester resin which has also methacrylate chain ends. This study found that if the VTMS-grafted CNTs were grafted with VTMS, rather than MATMS, in the second step of grafting, significant phase separation was found in the composite.

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CNTs have high electron affinity and can behave as radical scavengers and/or antioxidants [10–18]. In a recent study [19], the radical scavenging efficiencies of various modified MWCNTs featuring different contents of defects were investigated for hydroxyl (OH·) and 2,2-diphenyl-1-picrylhydrazyl (DPPH) radicals, as measured using electron paramagnetic resonance (EPR) and UV–vis spectrophotometry, respectively. The results revealed that the modified CNTs were effective scavengers for both types of radicals, with the scavenging efficiencies increasing upon increasing the content of defect sites on the modified CNTs. In this study, following preparations of the two-step silane-grafted CNTs, we also examine the effect of the silane grafting on radical scavenging efficiencies of these silane-grafted CNTs featuring different degrees of grafting. We then examine the retardation effects of the silane-grafted CNTs on the radical-initiated exothermic crosslinking reactions of vinyl ester/styrene resin as measured through differential scanning calorimetry (DSC).

2. Materials and methods

2.1. MWCNTs and silane-grafted CNTs

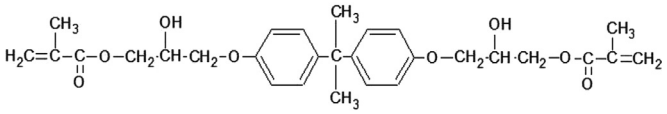
CNTs were synthesized through thermal chemical vapor deposition at 750 °C for 1 h in a quartz tube furnace in our laboratories [20]. The deposited product consisted of multiwalled carbon nanotubes (MWCNTs) which had diameters of approximately 20–30 nm and lengths of approximately 1 μm as examined using transmission electron microscopy (TEM, JEOL JEM-100CXII at 300 kV). The as-prepared MWCNTs were purified by mixing with a mixture of sulfuric acid and nitric acid in a composition of 3/2 by volume at room temperature for 6 h. The purified MWCNTs were pulverized by a ball mill for 2 min to obtain bmCNTs. The bmCNTs, without further purification, were then used for grafting reactions with vinyl trimethoxysilane (VTMS) using benzoyl peroxide (BPO) as an initiator—in a microwave oven, to obtain mwCNT-VTMS, or in a flask under reflux for 8 and 20 h to obtain r8CNT-VTMS and r20CNT-VTMS, respectively.

The mwCNT-VTMS was prepared by mixing bmCNTs (50 mg), BPO (30 mg), and VTMS (10 g) in a vial under sonication until the BPO had dissolved and the bmCNTs had dispersed. The vial containing the mixture was then placed in a microwave oven with power of 900 W, heated for 15 s, cooled in an ice bath for 2 min, and treated with BPO (30 mg). The cycle of heating in the microwave oven and cooling in the ice bath and adding BPO was repeated nine more times to give a total reaction time in the microwave oven of 150 s. The resulting dispersion of mwCNT-VTMS was filtered with a 0.2 μm pore-sized membrane and the solids washed with dry MeOH to remove BPO residue, unreacted silane monomer, and ungrafted silane polymer. The filtered and washed cake was then added into 95% EtOH (10 g) containing methacryloxypropyl trimethoxysilane (MATMS, 3 g) in a 250-mL-flask under sonication to give well-dispersed mixture, which was heated under a N_2 purge at 80 °C for 2 h to perform hydrolyses and condensations of the methoxy groups in VTMS and in MATMS. The reaction mixture was filtered and washed with dry MeOH to remove any ungrafted MATMS. The filtered and washed cake was dried in an oven at 60 °C to obtain mwCNT-VTMS-MATMS.

The preparations of r8CNT-VTMS and r20CNT-VTMS were similar to those of mwCNT-VTMS, except that the grafting reactions of bmCNT with VTMS were conducted in a flask under reflux at 90 °C for 8 and 20 h, respectively. To obtain r8CNT-VTMS-MATMS and r20CNT-VTMS-MATMS, the methoxy groups in r8CNT-VTMS and r20CNT-VTMS were condensed with the methoxy groups in MATMS using the same procedure as that described for the preparation of mwCNT-VTMS-MATMS.

2.2. VE/SM/BPO and its composite with silane-grafted CNTs

Vinyl ester (VE) resin, having molecular structure as below and containing 55 wt% of styrene monomer (SM), was supplied by Swancor Company (Taiwan) with grade code 901.



BPO (Alfa Aesar, 50 mg) was added to the VE/SM 45/55 resin (5 g) under sonication for 10 min, followed by magnetic stirring for 10 min, to obtain VE/SM/BPO 45/55/1. The amount of BPO added in this formulation was 1 phr (per hundred parts of resin). For 3 phr of BPO, as in VE/SM/BPO 45/55/3, 150 mg of BPO was added to the VE/SM 45/55 resin (5 g). For samples containing 1 phr of silane-grafted CNTs, the silane-grafted CNTs (50 mg) were added to the VE/SM/BPO to obtain VE/SM/BPO/silane-grafted CNT 45/55/1/1.

2.3. Characterization of silane-grafted CNTs and their composites

A thermogravimetric analyzer (SDT-Q600, TA Instruments) was used to determine the degree of grafting in the silane-grafted CNTs. Raman spectroscopy (NT-MDT, NTFGRA) was used to examine the D bands (*ca.* 1340 cm^{-1}) that characterize carbon atoms with sp^3 hybridization and defective carbon atoms with sp^2 hybridization and the G bands (*ca.* 1580 cm^{-1}) to characterize carbon atoms with graphitic sp^2 hybridization. The ratio of the intensities of the D and G bands (*i.e.*, I_D/I_G) was used as a measure of the content of defect structures on a CNT sample.

X-ray photoelectron spectroscopy (XPS), or electron spectroscopy for chemical analysis (ESCA, PHI 1600), was used to characterize the elemental compositions of the surfaces of the silane-grafted CNTs. Field emission scanning electron microscopy (FESEM; HITACHI, model S-4800, operated at 3 keV) was used to examine the appearance of the various silane-grafted CNTs and cross sections of the crosslinked composite samples. Samples for FESEM were fixed with conductive copper glue onto a support and coated with gold in a vacuum sputter system. A dynamic mechanical analyzer (DMA8000, PerkinElmer) operated at 5 °C/min from 25 to 230 °C was used to measure the storage modulus, loss modulus, and tanθ of the completely crosslinked composite samples which could be obtained by heating at 100 °C for 4 h followed by heating at 120 °C for 10 h.

2.4. Radical scavenging efficiencies of silane-grafted CNTs

An EPR spectrometer (Bruker, model EMX-10/12) operated at room temperature in the x-band frequency was used to measure the content of OH· radicals in the presence of the silane-grafted CNTs. All EPR spectra were obtained using the following settings: center field 3480 G, sweep width 100 G, microwave frequency 9.771 GHz, microwave power 10.100 mW, receiver gain 89,300, modulation frequency 100 kHz, modulation amplitude 1 G, and signal channel time constant 20.480 ms. The Fenton reaction [11] was used to produce OH· radicals, which were captured by 5,5-dimethyl-1-pyrroline N-oxide (DMPO) to form DMPO/OH· complexes, followed by reactions with the silane-grafted CNTs (1 mg) dispersed in Tween 20 (50 μL); the radical scavenging efficiency of the silane-grafted CNTs was measured in terms of the variation in intensity of the characteristic EPR peaks of the OH· radicals. In the Fenton reaction, OH· radicals were generated by adding 2 M H_2O_2 (40 μL) to an aqueous solution (795 μL) containing 1 M DMPO (75 μL) and 1 M $FeSO_4$ (40 μL).