Fracture Behavior of Covalently Re-Modified MWNT/ Epoxy Nanocomposites

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Summary: In this work, a surface re-modified multi-walled carbon nanotube (MWNT) was prepared by the chemical attachment of oligomeric unsaturated polyester on the MWNT surface. The re-modified MWNT was incorporated in two concentrations of 0.35 and 0.70 Wt.% into epoxy resin in order to investigate its effect on morphology and mechanical behavior of the MWNT/epoxy nanocomposite. The transmission electron microscopy showed that the re-modification of MWNT surface improves its dispersion state in the epoxy matrix. The tensile measurements for the nanocomposite having different amounts of surface re-modified/not-modified MWNT showed that the fracture mechanism changed from brittle to tough beyond a certain amount of surface re-modified MWNT. The scanning electron microscopy findings on the fracture surface morphology of the resulted nanocomposite substantiated the observed phenomena.

Keywords: carbon nano tubes (CNT); multiwalled carbon nanotubes (MWNT); morphology; mechanical properties; nanocomposites

Introduction

Since the discovery of carbon nanotubes (CNT) in 1991, one of challenges with respect to its application remains their surface modification. The appropriate surface assists the preparation of polymeric nanocomposites with the strong interface between the nanoparticles and the polymer matrix.[1–11] Such a modification can be performed chemically or physically. One of the major drawbacks of physical treatment is inability of physical bonds formed at the interface between nanoparticles and matrix due to the weakness of the van der Waals forces. In turn, in chemical modification due to the formation of covalent bonds at the interface, the interaction between nanoparticles and matrix is strong. Great attempts have been done to modify the surface of CNT.[12–14] Many researchers have studied the tethering of CNT surfaces through graft polymerization.[15–18]

The reaction between a carboxylic acid and an alcohol as well as the kinetics of this reaction has been well described in the classic organic chemistry.[19] Heating up to reflux an acid (usually, but not always, a carboxylic acid) and a primary or secondary alcohol in the presence of a catalyst (commonly sulfuric acid) forms ester, and water as by-product. Water can be removed to force the equilibrium to a desired direction. This method is called Fischer esterification. For example, esterification of acetic acid in excess ethanol (possibly as the solvent) in the presence of sulfuric acid results in an ester (ethyl acetate).[19]

This reaction can also be accelerated by the catalytic effect of alkaline hydroxyls such as potassium hydroxide. Figure 1 shows a schematic representation of Fischer esterification reaction.

Some research have been conducted to study the effect of carbon nanotubes on the mechanical properties of epoxy/CNT systems.[20–30] Through a physical route, Kyo

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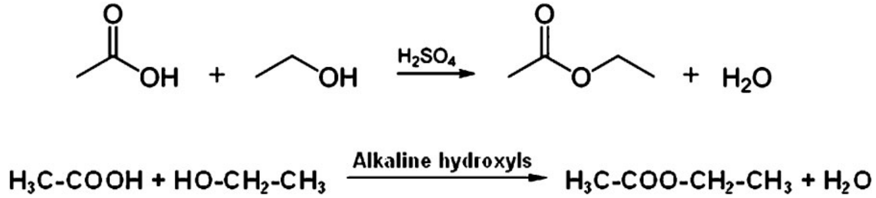

Figure 1.
Schematic representation of Fischer esterification reaction.

and co workers prepared a surface modified CNT using a non-ionic surfactant.[20] They reported that the surfactant having both hydrophilic and hydrophobic end groups acts as a bridge between the nanofiller and matrix, facilitating CNT dispersion within matrix. Chen and coworkers utilized an oxidation process to form carboxylic groups on the MWNT surface.[21] Then, the carboxylated CNT was reacted with amine ended polypropylene oxide. Finally, they reported that modified CNT having longer tethered chain showed a more improved mechanical response compared to the one having shorter tethered chain.[21] Dean and coworkers showed that fluorination of CNT improves epoxy matrix curing parameters and results in robust mechanical properties.[22] Youn and coworkers studied the effect of CNT surface carboxylation, thorough the acid and plasma treatment, on the mechanical and rheological properties of the epoxy based nanocomposite systems.[24,29] They observed that the incorporation of carboxylated CNT through plasma method within the epoxy matrix improves the above mentioned properties more significantly. Eitan and coworkers showed that epoxidized CNT enhances mechanical properties of the prepared nanocomposites.[28]

Since there is no report in the literature on the surface modification of CNT with oligomeric polyester resin, it is anticipated that such modification will result in an improvement in the morphology and mechanical properties of the epoxy based nanocomposites. Therefore, in this study, the surface re-modified multiwalled carbon nanotube (MWNT) is prepared by the chemical attachment of oligomeric unsaturated polyester on the MWNT surface. Then, this modified MWNT is incorporated in different amounts into the epoxy resin to investigate its effect on the morphology and mechanical behavior of MWNT/epoxy system.

Experimental Part

Materials

MWNT with purity of 99.9% and specific surface area of 200 ± 25 m^2/g was purchased from Carbon21™. Sulfuric and nitric acids were Merck grade. Hydroxyl terminated unsaturated polyester resin (RTM1000) was supplied by Resitan™. Epoxy resin (epon828) was purchased from Shell™ (The Netherlands) with EEW of 190. The curing agent was methaphenylene diamine (M-PDM) from Sigma-Aldrich™.

Preparation

The Carboxylation Process of MWNT

Primarily, MWNT were surface-modified with a mixture of two concentrated acids according to a procedure described in literature.[31] 0.1 g of MWNT was added to 400 cc of a mixture of sulfuric acid/nitric acid (3:1 v:v). The resultant mixture was agitated in an Ultrasonic bath powered to 60 W for 3 h at room temperature. The final mixture was diluted with distilled water (1:5 v:v) and then filtered.

The Re-Modification Process of Carboxylated MWNTs

In situ esterification of carboxylated-MWNT was performed as follows: Carboxylated-MWNT dispersed in styrene were shook in an ultrasonic bath for 1h. The Oligomeric unsaturated polyester dissolved in styrene was mixed with an initial mixer and the resultant mixture was shook for another 1h. Potassium hydroxide was added to this mixture, under vigorous stirring, as a catalyst for the esterification reaction to be accomplished within 5h at 80°C. After the completion of reaction the resultant product was washed with styrene and filtered.

Preparation of the Nanocomposites

Two different amounts 0.35 and 0.70 Wt.% of re-modified MWNT were added to the diluted epoxy resin. It was agitated in an ultrasonic bath for 15 min. to reach a higher degree of dispersion. Then, the curing agent was added to the mixture under vigorous stirring. The obtained homogeneous mixture was then poured into the standard molds at the ambient temperature and solidified. The sample codes for samples studied in this paper are presented in Table 1.

Characterization

FTIR analysis was performed using a Bruker Equinox55 model spectrometer (TENSOR 27, Germany). Samples for FTIR were casted in our made-in-house silicone rubber molds. Transmission electron microscopy (TEM) was performed using a CEM902A ZEISS instrument. Samples for TEM were microtomed in a way to prepare 50 nm thick specimens. To study the fracture surface of the nanocomposite samples, a 20 kV Philips Scanning Electron Microscope (SEM) was utilized. Nanocomposite samples in SEM were broken and gold coated to minimize the electron beam reflection.

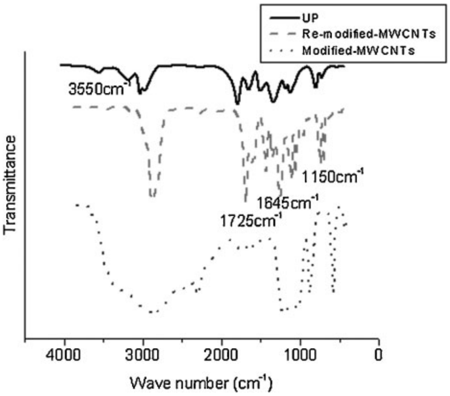

Figure 2.
FTIR spectra of oligomeric polyester resin, modified-MWNTs and re-modified MWNT.

Results and Discussion

FTIR Analysis

Figure 2 depicts the FTIR spectra of unsaturated polyester resin which are the modified- and re-modified-MWNT. The presence of a peak at 1720 cm^{-1} in the spectrum of modified-MWNT is related to carbonyl group of carboxyl tethered to the surface of MWNT. A peak at 1240 cm^{-1} may be associated with the C-O stretching in the same functionalities. A peak at 1580 cm^{-1} is for C=C stretching which originates from intrinsic MWNT structure.

A peak at 3550 cm^{-1} which corresponds to the terminal hydroxyl group of unsaturated oligomeric polyester chain disappears in the spectrum of re-modified MWNT. The 1725 cm^{-1} peak is related to the carbonyl group of carboxyl. Also, the peak appeared at 1150 cm^{-1} is attributed to stretching C-O-C(O)- bond. The peak at 1645 cm^{-1} is attributed to the olefin -C=C- bond. The peaks appeared in the range of 2800 to 3100 cm^{-1} is related to the stretching of

Table 1.
Composition of the studied samples.

Sample code	Epoxy (Wt.%)	Re-modified MWNT (Wt.%)
neat epoxy	100	0
Epoxy/re-modified MWNT (0.35 Wt.%)	99.65	0.35
Epoxy/re-modified MWNT (0.70 Wt.%)	99.30	0.70

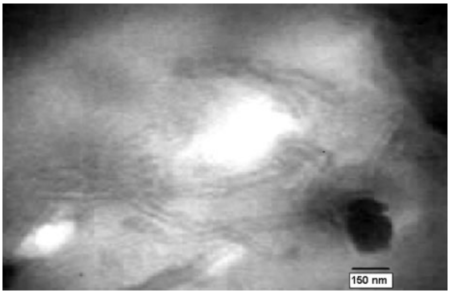

Figure 3.
TEM image of epoxy resin and 0.70 Wt.% of re-modified MWNT.

methylene groups. It is observed that these characteristic peaks of unsaturated polyester resin are appeared in the re-modified MWNT spectrum. It is observed that these characteristic peaks of unsaturated polyester resin are appeared in the re-modified MWNT spectrum.

TEM Analysis

Figure 3 shows TEM image of epoxy/re-modified MWNT nanocomposite. Generally, a nanometric scale of re-modified MWNT dispersion is observed in epoxy matrix. The MWNT bundles thickness is ca. 100nm. This desired dispersion state is attributed to the presence of interaction between unsaturated polyester oligomers tethered to the MWNT surface and also the cured epoxy network blocking agglomeration phenomenon.

Mechanical Properties

Figure 4 depicts the stress-strain behavior of the samples. As observed, the incorporation of 0.35 Wt.% of the re-modified MWNT to the epoxy matrix shows an increase of 8.6% in Young's modulus with respect to that of neat epoxy system. This rise in these values is 19.5% for the concentration of 0.7 Wt.% of the re-modified MWNT. Also, it is observed that this incorporation increases the elongation at break ca. 11% for the sample containing 0.35 Wt.%; and 16.6% for the sample containing 0.7 Wt.% of MWNT. We note that for 0.70 Wt.% of the re-modified MWNT incorporation, at the same time as an increase in Young's modulus, the nanocomposite system shows stress yielding behavior. This behavior is attributed to the interaction between tethered surface of re-modified MWNT and epoxy network. However, at the lower MWNT inclusion, the stress yielding behavior is not observed. By the way, an increase in both Young's modulus and elongation at break parameters indicate that higher amounts of energy is required to be absorbed in order to reach the state of failure. Table 2 presents the tensile test results of the studied samples.

SEM Analysis

Figure 5a and 5b show the SEM images taken from the fracture surface of the re-modified MWNT/epoxy system including

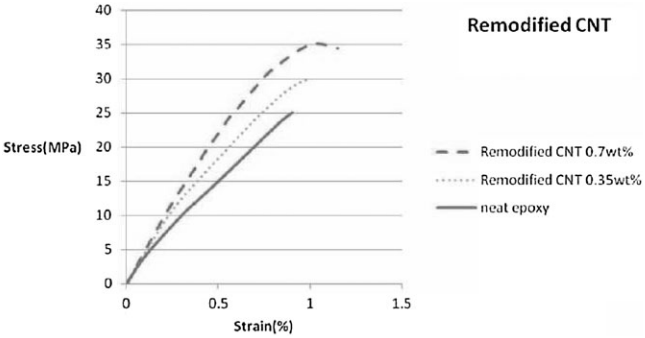

Figure 4.
Stress-strain behavior of the studied samples.

Table 2.
Tensile parameters of the studied samples.

Sample	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Tensile strength at yield (MPa)	Elongation at yield (%)
Neat epoxy	4000	25	0.9	–	–
Epoxy/Re-modified CNT0.35%	4340	30	1.0	–	–
Epoxy/Re-modified CNT0.70%	4780	34.5	1.2	35	1.0

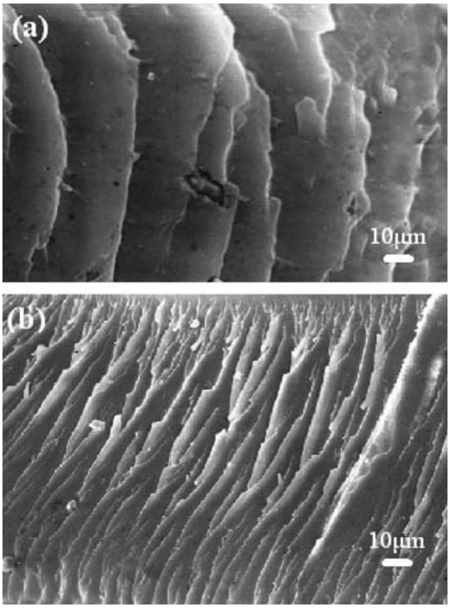

Figure 5.
SEM images obtained from the fracture surface of the studied nanocomposite samples: (a) Epoxy/0.30 Wt.% re-modified MWNT and (b) Epoxy/0.70 Wt.% re-modified MWNT.

0.35 and 0.70 Wt.% MWNT, respectively. It is noticeable that MWNT pull-out phenomenon is not observed in the fracture surface of these nanocomposites. This is attributed to a strong interaction between oligomeric unsaturated polyester resin tethered to the surface of MWNT and epoxy network.[32] On one hand, this level of interaction stems from the polar nature of the unsaturated polyester oligomeric chains having ester and hydroxyl groups as well as the unsaturated carbon-carbon double bonds to the epoxy group. On the other hand, the polyester chains on the MWNT surface act as an interface layer blocking the MWCT re-zipping.[33] It is observed that fracture surface is in the form of an ordered striation.[34] It is noteworthy that this kind of fracture surface has been reported in the case of toughened polymer blends including a rubbery counterpart.[35]

Fracture Surface Behavior

According to the previous studies on the fracture mechanism of carbon nanotube filled polymer systems, the main fracture mechanism is conducted through bridging phenomenon.[36,37] However, in the studied case, presence of tethered polyester chains on MWNT surface causes stress yielding during tensile loading as discussed in the mechanical properties section. Hence, before de-bundling or wall cracking of multiwalled carbon nanotubes, the polyester chains elongate till stress yielding occurs. This interface region acts as an efficient stress transfer agent to the carbon nanotubes. Stress yielding phenomenon is approved by the observation of stress whitened zones nearby the fracture surface as observed in the SEM micrograph of the samples. Although, these phenomena occurs if the amount of re-modified MWNT loading is beyond a certain value as stress yielding/stress whitening is not observed clearly in the epoxy matrix incorporated with 0.35 Wt.% of the re-modified-MWNT.

Conclusion

The carboxylated-MWNT was reacted with the unsaturated oligomeric hydroxyl terminated polyester (the re-modified MWNT). The FTIR showed the state of the reaction and also the reaction occurrence confirmation. The transmission electron microscopy showed a desired re-modified MWNTs dispersion state within the epoxy matrix. The tensile parameters of the nanocomposite samples having different amounts of the surface re-modified/not-modified MWNT demonstrated that the fracture mechanism was changed from the brittle mode to a tough mode beyond a certain amount of the surface re-modified MWNT i.e. 0.75 Wt.%. The presence of tethered polyester chains on the MWNT surface causes stress yielding behavior during tensile loading at a certain amount of MWNT.

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