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ORIGINAL PAPER

Improving rheological properties of covalently MWCNT/epoxy nanocomposites via surface re-modification

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Abstract This article describes the application of the chemical surface re-modification of carboxylated multi-walled carbon nanotubes (MWCNTs) through in-situ esterification of oligomeric unsaturated aliphatic hydroxyl terminated polyesters. The Fourier transform infrared spectroscopy and the thermogravimetric analysis proved covalent treatment of MWCNTs. Consequently, the acid–base titration method was employed to determine the population of the re-modified sites within the polyester chains. The dispersion state of the re-modified MWCNTs was investigated by the transmission electron microscopy relevant to the cured nanocomposite sample along with the Ultraviolet–Visible spectroscopy while using various solvents. The degree of dispersion was correlated to the Hansen solubility parameters. In summary, our study shows an appropriate dispersion of the re-modified MWCNTs into the solvents with a high dispersive fashion. In addition, the rheological properties of the re-modified MWCNTs/epoxy resin having various nanoinclusions were considerably studied and discussed. Also, an improved rheological response was observed in the case of the re-modified MWCNT nanocomposite samples.

Keywords Rheological properties · MWCNT/epoxy nanocomposites · Surface re-modification

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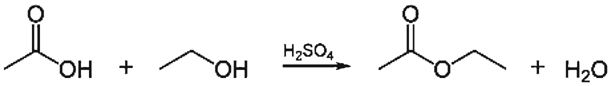
Introduction

Since the discovery of carbon nanotubes (CNT) in 1991, one of the primary challenges regarding its application was assigned to its surface modification. In fact, the appropriate surface assists the preparation of polymeric nanocomposites with strong interface between the nanoparticles and the polymer matrix [1–11]. Such a modification procedure 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 the matrix due to the weakness of the van der Waals forces. For chemical modification, in turn, the interaction between nanoparticles and the matrix is strong due to the formation of covalent bonds at the interface. Thus, huge attempts have been made to modify chemically the surface of a CNT [12–14]. To date, some researchers have decided to recast the CNT surfaces through the graft polymerization [15–18]. The reaction between carboxylic acid and alcohol as well as its kinetics has been well described in the classic organic chemistry [19]. Heating to reflux with an acid (usually, but not always, a carboxylic acid) along with a primary or secondary alcohol in the presence of a catalyst (commonly H_2SO_4) leads to form an ester, with water as a by-product which can be removed to force the equilibrium in the desired direction. This method is called the Fischer esterification. Esterification of acetic acid in excess ethanol (possibly as the solvent) in the presence of sulfuric acid results in an ester (ethyl acetate), for instance.

This reaction can be accelerated by the catalytic nature of an alkaline hydroxyl such as potassium hydroxide. Scheme 1 shows a schematic representation of Fischer esterification.

Regardless of the recent papers on dealing with the surface treatments of CNT, it would be of interest if one could measure the degree of modification toward CNT/nanocomposites. In this study, we were anxious to know how the re-modification treatment affects the rheological properties, thus, carboxylated multi-walled CNTs (MWCNT) were re-modified via in-situ esterification of oligomeric unsaturated aliphatic hydroxyl terminated polyesters. Afterward, the Fourier transform infrared spectroscopy (FTIR), along with, thermogravimetric analysis (TGA) confirmed that this reaction was carried out successfully. Consequently, a quantitative analysis was performed to determine the degree of re-modification. In addition, the ultraviolet (UV)–Visible spectroscopy was employed to investigate the state of dispersion. In this attempt, either the modified MWCNT or the re-modified MWCNT are adequately studied and discussed, from the rheological point of view. Finally, it is observed that some viscoelastic behavior changes are obviously accomplished after re-modification through the MWCNT/epoxy nanocomposites.



H_3C-COOH + HO-CH_2-CH_3 → H_3C-COO-CH_2-CH_3 + H_2O (alkaline hydroxyls)

Scheme 1 Schematic representation of Fischer esterification method

Experimental

Materials

MWCNT with purity of 99.9% and specific surface area of 200 ± 25 $m^2\ g^{-1}$ was purchased from Carbon21 Co. and sulfuric and nitric acids from Merck. Hydroxylated unsaturated polyester resin (RTM1000) was supplied by Resitan Co. (I. R. Iran). Epoxy resin (epon828) was purchased from Shell Co. (The Netherlands) with the EEW of 190. It should be mentioned that the selected curing agent was metaphenylene diamine (M-PDM) produced by Sigma-Aldrich Co.

Surface modification of the MWCNTs

Primarily, CNT were surface-modified with a mixture of concentrated acids. 0.1 g of CNT was added to 400 cc of a mixture of sulfuric acid/nitric acid (3:1 volume ratio). The resultant mixture was sonicated for 3 h at room temperature in an ultrasonic mixer with 60 W power. The final mixture was consequently diluted with distilled water (1:5 volume ratios) and then filtered [20].

Re-modification of carboxylated MWCNTs

In-situ esterification of carboxylated MWCNTs was performed as follows: the dispersed mixture of carboxylated MWCNT with styrene was stirred in an ultrasonic bath for 1 h. The oligomeric unsaturated polyester dissolved in styrene was mixed up with the produced dispersion and the resultant mixture was stirred for another 1 h. Afterward, potassium hydroxide, as a catalyst for the esterification reaction, was added to this mixture under vigorous mixing conditions which continued for 5 h at 80 °C. When the reaction was completed, the resultant product was washed with styrene and then filtered.

Characterization

FTIR analysis was carried out using a Bruker Equinox55 model spectrometer (TENSOR 27, Germany). The UV spectrometer was an ULTROSPECT instrument. TGA was also performed using Q50V603TA TGA Instruments under nitrogen atmosphere with a heating rate of 10 °C min^{-1}, wherein, the temperature range was 25–600 °C. The quantitative determination of carboxylic groups tethered to the surface of MWCNT along with the oligomeric polyester chains was fulfilled using the acid–base titration method. The procedure was as follows: first, the carboxylated-CNT dispersion was stirred in distilled water for 1 h. Afterward, a 0.01 N solution of NaOH was added to the dispersion and the mixture was stirred for 8 h, filtered and washed with water. Lastly, the filtered solution was titrated with a 0.01 N solution of HCl to calculate the amount of un-reacted NaOH. By abstracting the amount of un-reacted NaOH from the total amount of NaOH, the population of carboxyl groups adhered to the surface of MWCNT was measured. A similar method was employed to obtain the number density of adhered oligomeric polyester chains.

Ultimately, the transmission electron microscopy (TEM) was carried out using a CEM902A ZEISS instrument on the microtomed 50-nm thick specimens. As well, the rheological investigation was conducted using a cone and plate rheometer (MCR300; Anton Paar Physica, Stuttgart). A frequency sweep test in the range of 0.1–100 rad s^{-1} under shear stress of 0.1 Pa at 25 °C was also performed.

Results and discussion

FTIR analysis

Figures 1 and 2 delineate the FTIR spectra of as received-MWCNT, oligomeric polyester resin, carboxylated MWCNT and the re-modified MWCNT. The presence of a peak at 1,720 cm^{-1} in the spectrum of carboxylated MWCNT with respect to the spectrum of as received-MWCNT is the evidence of a carbonyl group of carboxyl adhered to the surface of CNT. Another peak at 1,240 cm^{-1} may be associated with C–O stretching in the same functionalities; somewhere, a peak at 1,580 cm^{-1} can be considered for C=C stretching which inherently originates from the CNT structure. Furthermore, the peak at 3,550 cm^{-1} which corresponds to the terminal hydroxyl group of the unsaturated oligomeric polyester chain disappears in the spectrum of the re-modified MWCNT. Undoubtedly, at 1,725 cm^{-1} the observed peak is related to the carbonyl group of carboxyl; wherein, the peak appeared at 1,150 cm^{-1} is attributed to C–O–C(O)– bond stretching. By analyzing through the transmittance peaks, it is also recognized that the oleic peaks of –C=C– bond, both at 1,645 cm^{-1} and in the range of 2,800–3,100 cm^{-1} are appeared, in which, the latter is due to the methylene groups stretching. In summary, it is observed that these characteristic

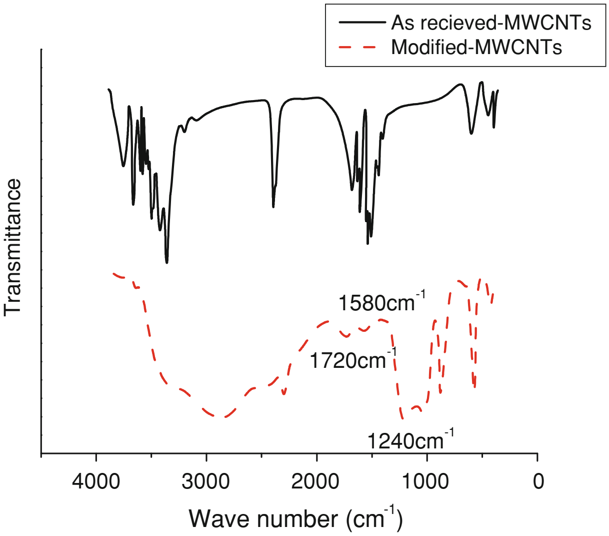


Fig. 1 FTIR spectra related to as received-MWCNT and modified MWCNT

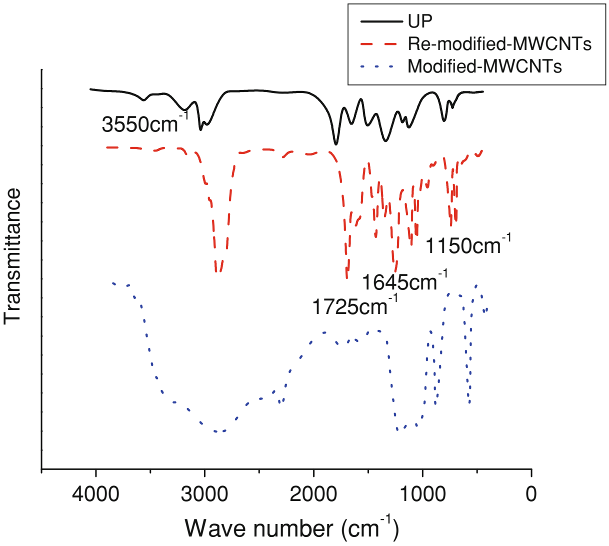


Fig. 2 FTIR spectra related to oligomeric polyester resin, modified MWCNT, and re-modified MWCNT

Table 1 The acid–base titration result

Samples	Weight (mg)	Added NAOH (mol)	Added HCl (mol)	Relative carboxyl groups concentration attached on MWCNT (mol COOH g^{-1} MWCNTs)
Modified-MWCNTs	100	5×10^{-4}	3.7×10^{-4}	1.3×10^{-3}
Re-modified-MWCNTs	200	5×10^{-4}	4.0×10^{-4}	0.5×10^{-3} ($\equiv 2.8 \times 10^{-2}$ g oligomeric polyester g^{-1} MWCNT

peaks of unsaturated polyester resin are basically appeared regarding the re-modified MWCNT transmittance spectrum. As a result, some reactions are evidently occurred throughout the final product. In addition, the distance between these spectra can be taken into account as the consequence of modification; somewhere, the re-modification treatment.

Acid–base titration

The results of acid–base titration are represented in Table 1. These results suggest that the concentration of functional acidic groups is dramatically decreased after the re-modification process, demonstrating the consumption of these groups through esterification process.

TGA

In terms of the results, Fig. 3 shows the TGA thermograms of the modified MWCNT, the re-modified MWCNT, and the oligomeric polyester resin. From the figure, the

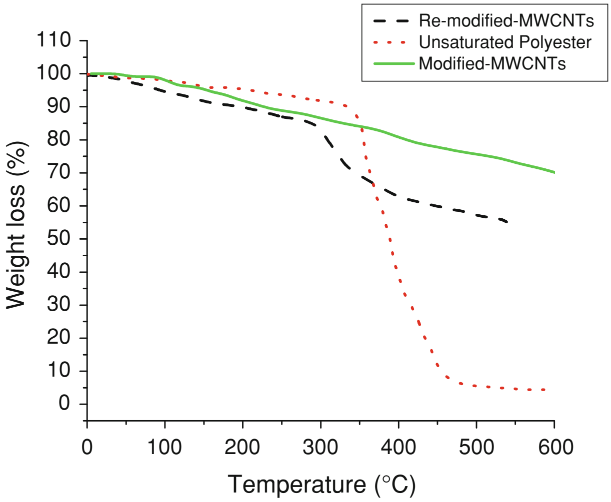


Fig. 3 TGA thermograms of modified-MWCNTs, re-modified-MWCNTs, and oligomeric polyester resin

temperature of degradation of polyester resin starts at ca. 330 °C, somehow the behavior of the re-modified MWCNT. Another consequence throughout TGA peaks is to compare the reduced weight of the re-modified MWCNT to those for polyester resins, so that the relative weight of the adhered oligomeric polyester chains in the re-modified MWCNT is estimated to be ca. 20 wt%. This decrease in the degradation temperature within the re-modified MWCNT is attributed to the promotion of degradation of polyester adhered to the surface of MWCNT, as previously reported in the literature [21].

UV spectroscopy

Figure 4 illustrates UV–Visible spectra of the modified and re-modified MWCNTs dispersed into H_2O, toluene, and dimethylformamide; representing polar, semi-polar and non-polar solvents, respectively, which provide a wide range of solubility parameters. Furthermore, Table 2 summarizes the dispersion state of the re-modified MWCNT in all the above mentioned solvents with different Hansen solubility parameters. It is observed that the re-modified MWCNT is dispersed well in non-polar solvents due to the polar contribution of the Hansen solubility parameters.

TEM analysis

Figure 5 shows the TEM image of epoxy/re-modified MWCNT nanocomposite. This figure signifies that a nanometric scale of the re-modified MWCNT dispersion is partially observed within the epoxy matrix. The MWCNT bundles thickness is assumed to be ca. 100 nm. This desired dispersion state is attributed to the presence of the oligomeric polyester chains on the MWCNT surface hindering agglomeration phenomenon.

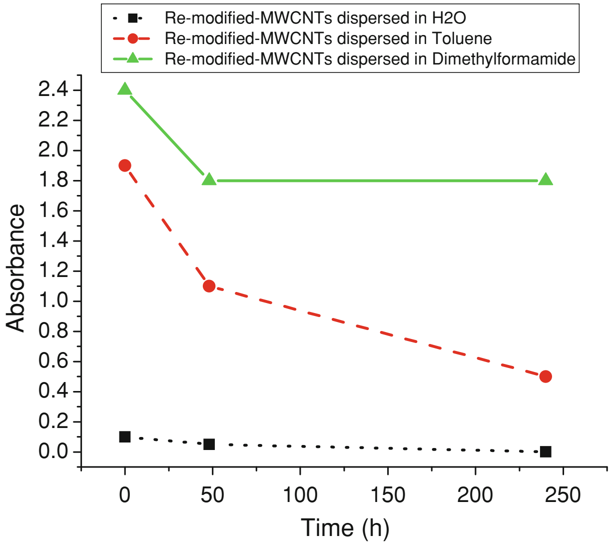


Fig. 4 UV–Visible spectra of carboxylated- and re-modified-MWCNT dispersed into H_2O, toluene, and Dimethylformamide

Table 2 Dispersion state of re-modified-MWCNTs in solvents with different Hansen solubility parameters

Solvent	$\delta_d{}^a$ (MPa$^{1/2}$)	$\delta_p{}^a$ (MPa$^{1/2}$)	$\delta_h{}^a$ (MPa$^{1/2}$)	$\delta_t{}^a$ (MPa$^{1/2}$)	Dispersion state
H_2O[a]	15.6	16.0	42.3	47.8	Sedimentation
Toluene[b]	18.0	1.4	2.0	18.2	Swelling
Dimethylformamide[c]	17.4	13.7	11.3	24.8	Dispersion

[a, b, c] Data obtained from [22]

Rheological properties

Figure 6 shows either storage or loss modulus behavior, simultaneously, versus angular frequency for neat epoxy and modified-MWCNT/epoxy nanocomposites containing 0.35 and 0.70 wt% modified-MWCNTs. Accordingly, in all cases, the loss modulus is higher than the corresponding value of storage one for each sample; thus, the shape of alteration throughout angular frequency window indicates a viscous-like behavior. Although, the storage modulus is more sensitive with respect to the MWCNT dispersion state, compared to the loss modulus. For the neat epoxy resin, the storage modulus is very small; however, it is increased by introducing CNT within the epoxy matrix, up to 0.35 wt%. In contrast, further increase in the modified-MWCNT content, up to 0.70 wt%, caused diminishing storage modulus, especially at higher angular frequencies. Thus, one can find that; the degree of improvement depends on the state of CNT modification. Actually, the dependency of the storage modulus on the angular frequency is more pronounced at higher contents of CNTs. In fact, when the slope of the storage modulus against frequency

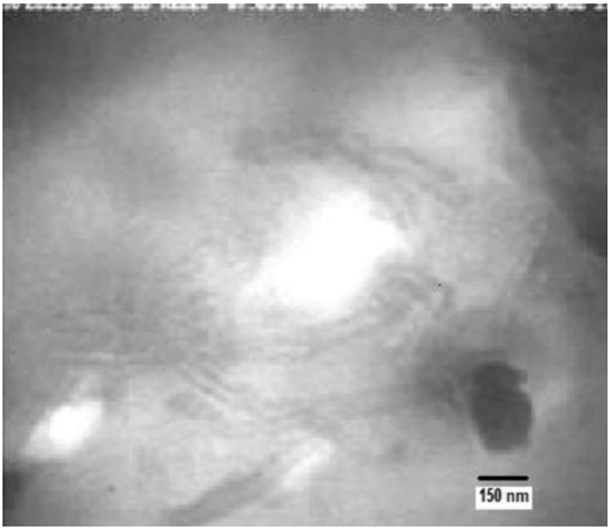


Fig. 5 TEM image of epoxy/re-modified-MWCNT nanocomposite sample

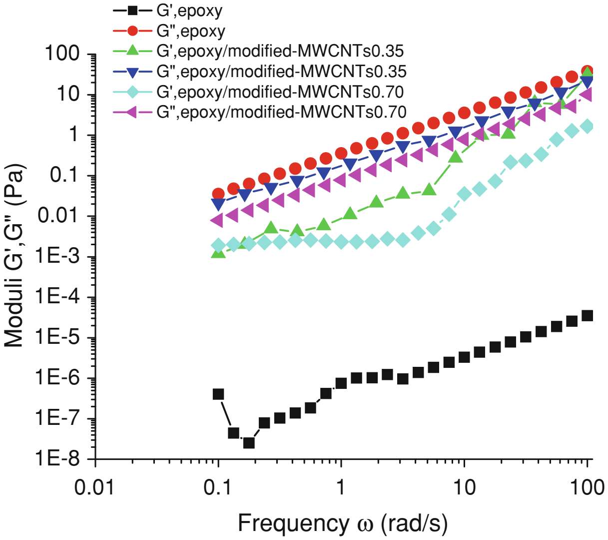


Fig. 6 Storage and loss moduli for neat epoxy and Modified-MWCNTs/epoxy nanocomposites containing 0.35 and 0.7 wt% modified-MWCNTs

approaches zero, a 3D network structure is assumed [23]. In this attempt, the same behavior is observed in the case of modified-MWCNT/epoxy samples. Upon further increase in the modified-MWCNT concentration, the slope of storage modulus curve became zero at low frequencies, ca. 0.2 rad s^{-1}. By further increment in the

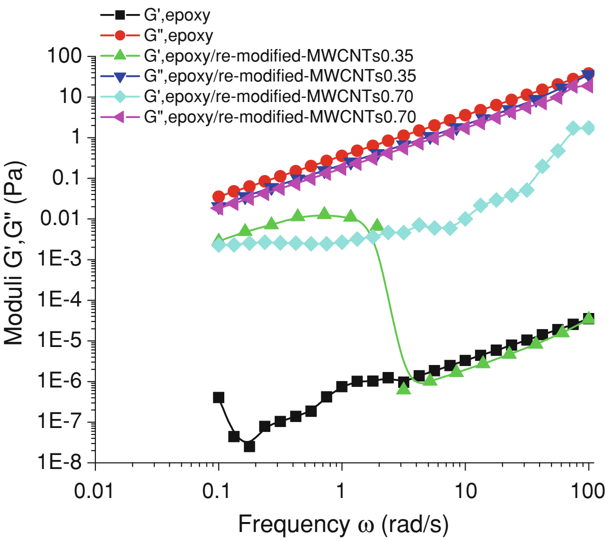


Fig. 7 Storage and loss moduli for neat epoxy and re-modified-MWCNTs/epoxy nanocomposites containing 0.35 and 0.7 wt% of re-modified-MWCNTs

modified-MWCNT content, this valley is shifted to 5.5 rad s^{-1}, indicating a more reinforced network-like structure.

In order to investigate the impact of the surface re-modification toward the rheological properties for the CNT nanocomposites, both the storage and loss moduli are measured for the neat epoxy and the re-modified-MWCNT/epoxy nanocomposites containing 0.35 and 0.7 wt% of the re-modified-MWCNT, respectively, as drawn in Fig. 7. Then, it is observed that with 0.35 wt% of the re-modified MWCNT inclusion, the storage modulus is nearly plateau at the angular frequency of 2 rad s^{-1} while with increasing MWCNT to 0.7 wt%, this plateau continues to 11 rad s^{-1}. This observation can be attributed to a better dispersion and a gel-like structure of the re-modified MWCNT in the epoxy matrix. It should be mentioned that, this behavior is already supported by the TEM image which was evident due to a good dispersion state of the re-modified MWCNT. In particular, this research signifies that, the rheological properties can be considered as the effective tools to study the role of surface re-modification of MWCNT toward the epoxy matrix. However, the surface re-modification has serious impacts on the storage modulus, especially at 0.35 wt% of CNT.

Conclusion

Carboxylated MWCNTs are efficiently reacted with the unsaturated oligomeric hydroxyl terminated polyester chains. The FTIR spectrums declared the reacted functional groups and confirmed the completion of the reaction. Besides, a quantitative analysis is performed to determine the population of the re-modified sites of MWCNT. In addition, the TGA analysis confirmed the weight density of oligomeric polyester chains adhered to the surface of CNT. In part, the UV–Visible spectroscopy showed that the interfacial interaction of the re-modified MWCNT differs from that of carboxylated- or as received-MWCNT. Finally, the enhanced rheological response of the re-modified MWCNT dispersed in the epoxy matrix boosted the stress transfer at the interface of nanocomposite counterparts. Also, two distinct plateaus are observed through the storage modulus of 0.35 wt% concentration of the re-modified sample, at low and high angular frequencies, indicating the role of surface re-modification on the rheological properties.

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