Mechanical and Electrical Properties of Multiwalled Carbon Nanotube Nanocomposites with Different Resin Matrices

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Abstract—Researchers have investigated the effects of different nanoenhancers on the physical properties of polymer-based nanocomposites. However, the effect of resin type on the properties of nanocomposites reinforced by multiwalled carbon nanotube (MWCNT) has not been studied very well. This study aims to understand the link between the nature of polymer as the base material for nanocomposite and the reinforcement role of MWCNT. Three common polymers, with high industrial applications, namely vinyl ester, polyester and epoxy were chosen. The standard tensile specimens were prepared for both neat and reinforced resins using 0.5 wt % of MWCNTs. The results indicated that while for the vinyl ester and polyester resins there was no improvement in the elastic modulus, for the epoxy resin the elastic modulus increases by 5.6% with addition of MWCNT. On the other hand, the electrical test results showed that electrical conductivity was greatly increased in the presence of MWCNT, for both vinyl ester and epoxy resins. But for the polyester resin, little improvement was observed with the addition of MWCNT. The mechanisms causing this trend were investigated. Moreover, several optical microscopy and scanning electron microscopy images were taken from the fracture surfaces to evaluate the surface features and fracture mechanisms.

Keywords: multiwalled carbon nanotubes, polymer-based nanocomposites, mechanical properties, electrical properties

1. INTRODUCTION

Many different types of polymers have been produced during the last century for various purposes. Even in each specific class of polymers, such as epoxy, there are many subsets with different properties and applications. The main reasons for such a wide range of applications of polymers are their relatively low costs and density, and ease of their processing. However, polymers exhibit high electrical and thermal resistivity, poor damage tolerance, low mechanical strength and stiffness relative to other engineering materials such as metals. Therefore, reinforcing the polymers using nanofillers seems to be a promising way to extend the range of application of these materials.

In this respect, carbon nanotubes (CNTs) [1] have received a great deal of attention due to their high aspect ratio, low density [2], high strength and stiffness [3–6] and very high specific surface area (up to 1315 m^2/g) [7], which makes them potential candidates to augment mechanical, and even thermal and electrical properties of polymers [8, 9]. That is because of the graphitic structure of these nanoparticles, which results in high thermal [10] and electrical [11, 12] conductivity. During the last decade, many researchers have investigated the effect of CNTs on different properties of polymers [13–18], but little attention has been paid to the effect of matrix type on the enhancement properties of nanocomposites.

Epoxy is a thermosetting polymer, formed from reaction of an epoxy or epoxide resin with a suitable hardener. Epoxy resins are characterized by two or more oxirane rings or epoxy groups, which is a triangle ring made of two carbon atoms and an oxygen atom. Number of these groups in the molecule can be used to classify different types of epoxy resins. The

most common type which is used in most of the composite applications (as in here) is difunctional epoxy known as DGBEA (diglycidyl ether of bisphenol A) [19]. The epoxy groups normally locate at the two ends of epoxy molecule and are the most reactive sites of it. The curing of the epoxy groups takes place either between epoxide molecules themselves or by the reaction between the epoxy group and other reactive molecules introduced into the resin as hardener, forming a crosslinking network [20]. Epoxy resins are widely used in structural adhesives, surface coatings, engineering composites, electrical laminates, etc. [21].

Unsaturated polyester (UPE) resins are the most commonly used matrix in the marine and composite industry, especially glass fiber reinforced polymer composites, mostly because of their good cost/property relation [22]. Vinyl ester (VE) also is a common resin in the marine industry due to its corrosion resistance and ability to withstand water absorption. The unsaturated polyester and vinyl ester resins are used in combination with a suitable comonomer, normally styrene, which serves as a reactive diluent. The objectives of adding styrene are to reduce viscosity, to adjust cure schedule and to improve the mechanical properties of the resulting networks. Unlike UPE resins and similar to epoxy, unsaturation occurs only at the end of VE backbone resulting in fewer crosslinks compared with UPE resin networks. Curing of both UPE and VE resins takes place through the free radical polymerization of unsaturated resins and monomer. Free radicals are generated by addition of a suitable initiator [19].

As mentioned above, numerous researchers have attempted to investigate different properties of polymer/CNT nanocomposites. The development of polymer/CNT nanocomposites, firstly reported by Ajayan [23], has encountered many challenges in different ways [24–26]. The main issues that have always affected opportune exploitation of extraordinary potential of CNTs are their dispersion in the resin, besides establishing strong interfacial bonding between the polymer and the nanotube surface [27]. Therefore, several techniques have been developed, in order to eliminate these difficulties. Since CNTs have strong tendency to form aggregates due to their large specific surface area, it is necessary to implement high energy to break them into single nanotubes. This energy is implemented as shear forces or ultrasonic waves. Ultrasonication and calendaring are common techniques in dispersion of CNTs, but both may damage CNTs and shorten their lengths, and hence reduce their high aspect ratio [28, 29]. Some other researchers have used

nano- or mesoscale simulations to obtain equivalent material properties in polymer nanocomposites [30, 31].

More recently, a wider range of polymer matrices have been used to produce polymer-based nanocomposites with improved physical properties [32, 33]. For instance, Li et al. [32] investigated the foaming behavior of poly(methyl methacrylate) (PMMA)/MWCNT nanocomposites and their associated thermal insulation and mechanical properties. PMMA/MWCNT nanocomposites containing various amounts of multi-walled carbon nanotubes (MWCNTs) were first prepared by combining solution and melt blending methods, and then foamed using CO_2. The aim was to optimize environmental-friendly thermal insulation nanocomposite foams with enhanced thermal-insulation and compressive mechanical properties. Kim et al. [33] grafted poly(vinyl alcohol) (PVA) onto the MWCNT using ultrasound in water and prepared a modified MWCNT/PVA nanocomposite which had good attraction with PVA matrix with better dispersion state and improved mechanical and electrical properties.

Considering that mesomechanics develops an interaction between the materials sciences and the solid mechanics disciplines, it attempts to apply mechanics principles to the micro/nanostructural elements of multiphase materials. This paper deals with the physical mesomechanics of polymer-based nanocomposites in terms of their mechanical and electrical properties. To this end, three different industrial thermosetting polymers namely, polyester, vinyl ester and epoxy are used as base materials and the effect of MWCNT, as a single nanoparticle, on their mechanical and electrical properties are investigated and compared. The aim is to find appropriate choice for adding MWCNT to a polymer matrix for achieving better properties in the nanocomposites. It is shown that the epoxy resin is the best choice among these three thermosetting polymers, as it provides enhancement in both mechanical and electrical properties when mixed by MWCNT nanoparticles.

2. EXPERIMENTAL

2.1. Preparation of Specimens

The vinyl ester resin, SWANCOR-901, with 45 wt % styrene monomer content, and the isophthalic polyester resin SWANCOR-9307, were purchased from SWANCOR Co. Cobalt Naphtanate (CoNAP), DMA and methyl ethyl kethone peroxide (MEKP) were introduced into the vinyl ester resin at a ratio of 0.35, 0.04 and 1.05 wt %, respectively, as accelerator, promoter and initiator to polymerize the resin. For the

polyester resin, only CoNAP and MEKP were used at a ratio of 0.27 and 1.7 wt %. The epoxy resin, EPOLAM 2002 and the hardener EPOLAM 2002, were purchased from AXSON Co. The hardener was mixed with the resin at a ratio of 12 wt %.

Multiwalled carbon nanotubes were used here as reinforcement for all types of resins. They have the diameter between 10 and 20 nm, and the length of 10–30 μm.

In order to prepare the pure polymer specimens, all resins were mixed with desired amount of additives by a mechanical stirrer at speed of 250 rpm for about 15 min for vinyl ester and polyester and 20 min for epoxy. In case of nanocomposites, each resin blended with 0.5 wt % MWCNTs by the stirrer at the speed of 2000 rpm for 10 min, followed by 40 min of sonication for vinyl ester and polyester, and 60 min for epoxy. During sonication, the temperature of the mixture was measured several times and kept from rising too much by putting the mixture container in an ice/water mixture. After sonication, the additives were added and blended thoroughly with resins at the speed of 250 rpm for 10 min for vinyl ester and polyester resins and 20 min for epoxy. Subsequently, all specimens were allowed to cure at room temperature for 24 hours, followed by postcuring at 105° for 2 h, for vinyl ester/MWCNT and 80° for 3 h for polyester/MWCNT specimens.

2.2. Testing

Mechanical performance of the pure and reinforced resins was evaluated through uniaxial tensile testing. Standard dog-bone specimens, casted for uniaxial tensile test were prepared to be tested at the speed of 1 mm/min, in order to obtain elastic modulus and ultimate strength. After testing, optical microscopy pictures were taken from the fracture surfaces in order to better understand the fracture mechanisms.

Electrical conductivity of specimens was tested by MERTEL MI 3201 high resistance tester, using high voltage DC current. The voltage used in the test was 2150 kV which was enough to establish a stable electrical current through specimens.

3. RESULTS

3.1. Tensile Properties

Figure 1 represents the elastic modulus E of the neat resins and nanocomposites. It was found that while addition of MWCNTs does not have any significant effect on the elastic modulus of the vinyl ester and polyester-based nanocomposites, the elastic modulus of epoxy/MWCNT nanocomposite increases by
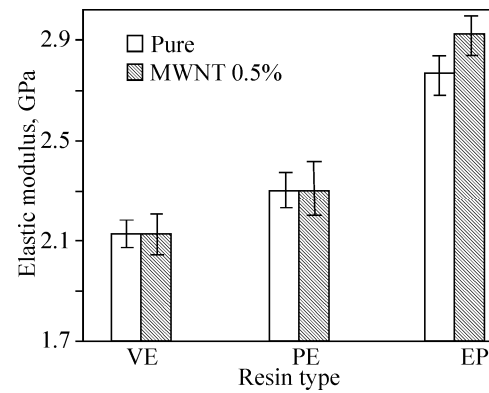
Fig. 1. Elastic moduli of neat resins and nanocomposites.

about 6%. Meanwhile, the addition of MWCNTs leads to remarkable decrease in tensile strength of all three nanocomposites (Fig. 2).

This might be because epoxy systems have different ways of polymerization from vinyl ester and polyester resins. As mentioned earlier, the polymerization process in the latter ones, initiates with the decomposition of curing agent (MEKP), generating free radicals that leads to chain reactions of cross linking process. It is reported in some studies [34], that free radicals could be easily entrapped in the galleries of CNTs, especially single-walled CNTs with high specific surface area. This fact results in heterogeneous polymerization across the specimen, with the final material having variant cross-linking density distribution.

Furthermore, it has been observed in a number of researches (e.g. [35]) that CNTs have a better interaction with a soft matrix than with a brittle matrix. AsMWCNT can be treated as a flexible reinforcement, its reinforcing efficiency is likely to be better in tough thermosets, such as epoxy (Fig. 3), rather than in brittle ones. As a result, the reinforcing role of CNTs seems to be low in brittle matrices. Therefore,
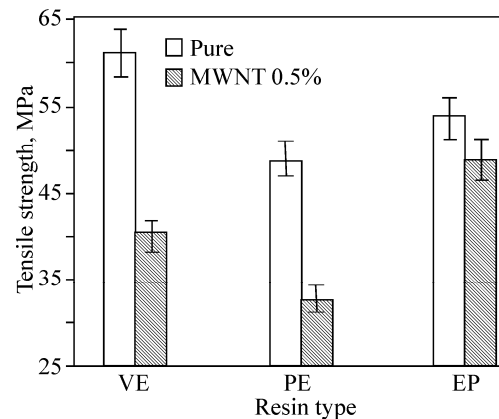
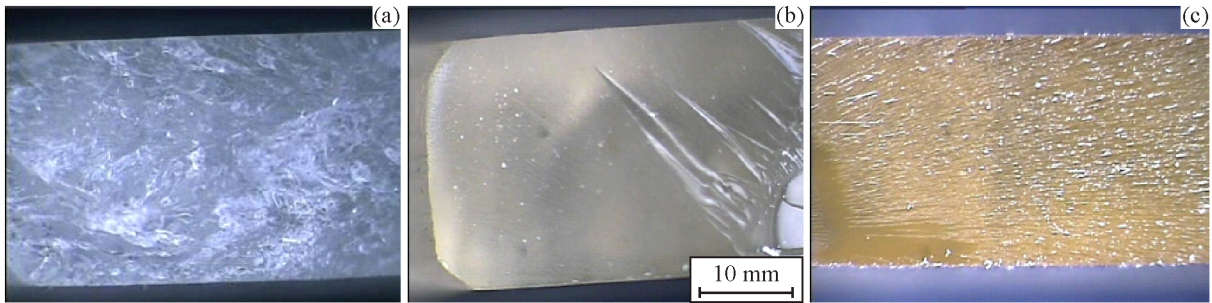**Fig. 2.** Tensile strengths of neat resins and nanocomposites.

Fig. 3. Fracture surfaces of pure polymers: epoxy (a), polyester (b), vinyl ester (c) (color online).
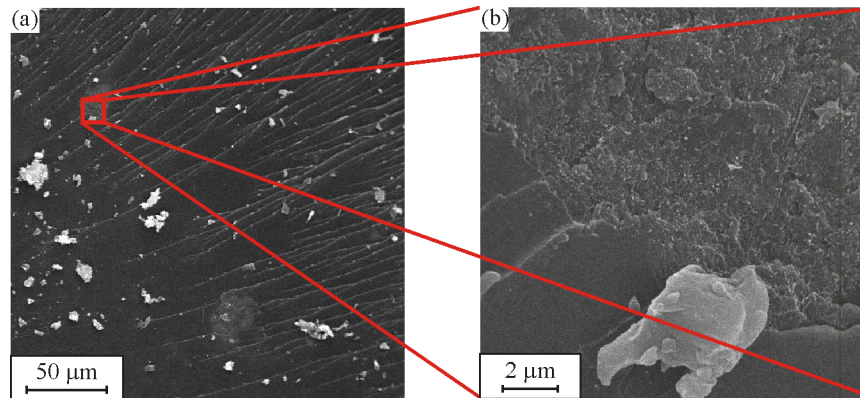

Fig. 4. Agglomerations formed in epoxy resin.

due to the brittle behavior of both polyester and vinyl ester resins, as also shown by their smooth fracture surfaces in Fig. 3, the improvement in mechanical properties such as tensile strength and elastic modulus, is expected to be negligible.

Above all, the most important factor which can dramatically affect the nanocomposite mechanical properties is the dispersion state of MWCNTs in the resins. Interactions of CNTs with surrounding matrix are highly critical for the mechanical strength of the resulting nanocomposites. Since our study was concentrated only on nonfunctionalized MWCNTs, a po-

or dispersion was observed. Therefore, CNTs could not exhibit their expected effects on enhancing the mechanical properties of nanocomposite. The scanning electron microscopy images taken from the fracture surfaces show agglomerations formed in epoxy resin (Fig. 4) and vinyl ester and polyester resins (Fig. 5). Therefore, with MWCNTs not well dispersed, agglomerations formed within the resin (which act like defects), reduced the tensile strength of nanocomposites. Meanwhile, the decrease in the tensile strength of epoxy specimens is less than those of the other two polymers. This can be due to relatively
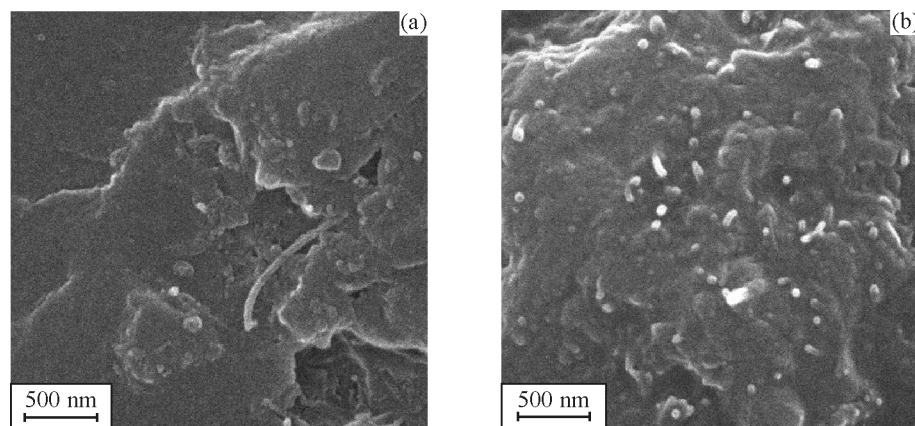

Fig. 5. Dispersion state of MWCNTs in vinyl ester (a) and polyester resins (b).

Table 1. Results of electrical conductivity test (1×10^{-12} s m^{-1})

	UPE	VE	EP
Neat resin	2.23 ± 0.101	3.17 ± 0.23	4.28 ± 0.29
Nanocomposite	3.56 ± 0.15	$1.49 \times 10^8 \pm 1.04 \times 10^7$	$1.33 \times 10^5 \pm 1.01 \times 10^4$

better interactions between the epoxy matrix and MWCNTs.

3.2. Electrical Properties

Table 1 shows the measured values of electrical conductivity of neat and reinforced polymers. It is seen that the electrical conductivities of both vinyl ester and epoxy resins are improved by several orders of magnitude. All three resins are almost resistant to electrical current in the absence of MWCNTs. However, as it appears, the introduction of MWCNT into these resins has great influences on the electrical conductivity of vinyl ester and epoxy resins, while its effect on polyester is negligible. Although the dispersion of nanotubes in the resins was not good enough, but this cannot be the only reason for electrical behavior of MWCNT/polyester nanocomposite, as the electrical conductivities of the two other resins are greatly increased. One may attribute these findings to the degree of polymerization in the resins. As mentioned earlier, the active sites of both vinyl ester and epoxy resins locate at the two ends of polymer backbone, and cross linking process occurs at these active spots. Polyester, on the other hand, form crosslink networks through several locations within the backbone, where there are unsaturated carbon atoms. This behavior, results in more dense networks. In two other resins used here, network density is such that it allows the distinct agglomerates to build up a conductive network and reach the percolation threshold. But in the case of polyester, very dense crosslinking network seems not to let the agglomerates establish effective connections to each other and pass the electrical current, at this level of dispersion. Other amounts of MWCNTs can be used to determine the percolation threshold of these resins, which should be absolutely above 0.5% for polyester. The results reported in the literature show that less amounts of percolation threshold can be reached with better dispersion of MWCNTs in polyester resin [36, 37].

4. CONCLUSIONS

It was found that the addition of 0.5 wt % of MWCNTs into two thermosetting resins of vinyl ester and unsaturated isophthalic polyester has no positive influence on their mechanical properties, including the elastic modulus and the tensile strength but improves the elastic modulus of epoxy resin. This could be mainly because of the poor dispersion of MWCNTs in the resins and consequently the formation of agglomerates that leads to the nucleation of defects and microcracks. These flaws drastically affect the tensile properties, especially tensile strength, of the nanocomposites. The electrical conductivity of vinyl ester and epoxy resins increased in the presence of MWCNTs significantly, but remained nearly unchanged for the polyester-based nanocomposite. This may be because of the compact crosslinking network in the polyester resin which limits the interconnections between MWCNTs and hinders the formation of a spatial structure of agglomerates that passes electrical current.

In conclusion, the addition of MWCNT to unsaturated isophthalic polyester provides no enhancement in terms of electrical and mechanical properties. But epoxy resin can be considered as the best matrix, among the three investigated polymers, to produce a polymer-based nanocomposite because not only its mechanical properties but also its electrical properties are improved in the presence of appropriate contents of MWCNT.

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