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Tensile mechanical behavior and fracture toughness of MWCNT and DWCNT modified vinyl-ester/polyester hybrid nanocomposites produced by 3-roll milling

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ABSTRACT

This study aims to investigate the tensile mechanical behavior and fracture toughness of vinyl-ester/polyester hybrid nanocomposites containing various types of nanofillers, including multi- and double-walled carbon nanotubes with and without amine functional groups (MWCNTs, DWCNTs, MWCNT-NH_2 and DWCNT-NH_2). To prepare the resin suspensions, very low contents (0.05, 0.1 and 0.3 wt.%) of carbon nanotubes (CNTs) were dispersed within a specially synthesized styrene-free polyester resin, conducting 3-roll milling technique. The collected resin stuff was subsequently blended with vinyl-ester via mechanical stirring to achieve final suspensions prior to polymerization. Nanocomposites containing MWCNTs and MWCNT-NH_2 were found to exhibit higher tensile strength and modulus as well as larger fracture toughness and fracture energy compared to neat hybrid polymer. However, incorporation of similar contents of DWCNTs and DWCNT-NH_2 into the hybrid resin did not reflect the same improvement in the corresponding mechanical properties. Furthermore, experimentally measured elastic moduli of the nanocomposites containing DWCNTs, DWCNT-NH_2, MWCNTs and MWCNT-NH_2 were fitted to Halphin–Tsai model. Regardless of amine functional groups or content of carbon nanotubes, MWCNT modified nanocomposites exhibited better agreement between the predicted and the measured elastic moduli values compared to nanocomposites with DWCNTs. Furthermore, Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) were used to reveal dispersion state of the carbon nanotubes within the hybrid polymer and to examine the CNT induced failure modes that occurred under mechanical loading, respectively. Based on the experimental findings obtained, it was emphasized that the types of CNTs and presence of amine functional groups on the surface of CNTs affects substantially the chemical interactions at the interface, thus tuning the ultimate mechanical performance of the resulting nanocomposites.

1. Introduction

Nano-particles have recently gained great interest in science and industry due to their highly considerable promises in enabling the future nano-structured materials with novel properties [1,6]. In this respect, carbon nanotubes (CNTs) with their huge aspect ratio in combination with high strength and stiffness have become potential reinforcing constituents to get common engineering polymers into multi-functional composites with superior properties such as conductive polymers with improved mechanical performance [1,5]. Despite many reported studies in the literature, the achievement of the desired improvement via CNTs in final properties of their polymer based composites has not been successfully realized so far [2,7]. This compromise arises primarily from the weak interfacial bonding of CNTs with the surrounding polymer matrices because of their very inert surfaces as well as their non-homogeneous dispersion within polymers due to their huge surface area [5,8]. To promote the compatibility at the interface between CNTs and the surrounding polymer matrix, some chemical functional groups are applied over the surfaces of CNTs [4,8]. Kim et al. [7] found that addition of untreated, acid and NH_2 treated multi-walled carbon nanotubes (MWCNTs) into epoxy resin resulted in 61, 69 and 73% increase, respectively, in tensile strength of the resulting nanocomposites as compared to neat epoxy resin, without significantly reducing the elastic modulus of the nanocomposites. Yaping et al. [8] investigated the effect of MWCNT-NH_2 on the mechanical properties of the epoxy resin. They stated that flexural bending stress and modulus of the nanocomposites were significantly improved as compared to those of neat epoxy resin. Moreover, in the same study, impact strength of the corresponding nanocomposites was measured to

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be two times higher than that of neat epoxy resin. Grujicic et al. [9] studied the atomic level mechanical properties of three-walled carbon nanotubes (3 WCNTs) reinforced vinyl-ester resin with epoxy group, using molecular mechanics to interpret the effect of covalent functionalization. They revealed that covalent functionalization has a profound effect on the nanocomposites as the load is applied in a direction orthogonal to nanotube axis. Homogeneous dispersion of CNTs within polymers is another crucial issue to observe the desired final properties in the resultant nanocomposites [5,8]. Strong Van der Waals forces and interactions between relatively small diameter nanotubes lead to aggregates of nanotube ropes to exist [1,9]. Therefore, length of the tubes, their degree of entanglement and volume fraction as well as the viscosity of the surrounding matrix resin are critical to dispersion state of CNTs within the matrix resin. A number of different techniques including high speed mechanical stirring and sonication are commonly used for proper dispersion of CNTs within polymers [3,5–9,10,13,16]. Of all, sonication has been the most widely utilized technique for CNT/thermosetting resin systems such as epoxy and vinyl-ester. In this technique, a pulsed ultrasound with certain amplitude is intended for uniform dispersion of CNTs by dividing their agglomerates into individuals or smaller ones. However, the magnitude of vibration energy applied is limited to distance from the sonicator tip. Therefore, it is not scalable from laboratory to industrial manufacturing settings and not cost effective any more. Gojny et al. [2,4] alternatively utilized the 3-roll milling to accomplish relatively good dispersion of nanotubes with and without NH_2 functional group within epoxy resins. They revealed based upon TEM investigations that double-walled carbon nanotubes (DWCNTs) have moderately fine dispersion in epoxy resins via 3-roll milling. In the same study, they also showed that blending of very low content (0.1 wt.%) of DWCNTs with epoxy resin via 3-roll milling improved the mechanical properties, such as elastic modulus and fracture toughness of the polymers. Thostenson and Chou [16] investigated recently the influence of processing parameters on the final dispersion state of CNTs during 3-roll milling. In this manner, they produced epoxy/CNT suspensions at various gap settings ranging from subsequently 5 to 50 μm through 3-roll milling by means of Teflon guides which help keep the blend centered on the rollers. They observed that nanocomposites processed at gap settings of 5 and 10 μm have relatively high fracture toughness values.

In the present study, 3-roll milling was used to prepare vinyl-ester–polyester hybrid resin based nanocomposites containing various contents of MWCNT, MWCNT-NH_2, DWCNT and DWCNT-NH_2. To produce the nanocomposites, the CNTs were first dispersed within specially synthesized styrene-free polyester resin followed by blending the collected resin stuff with vinyl-ester resin via mechanical stirring. The dispersion state of the CNTs within the resulting nanocomposites was revealed via Transmission Electron Microscopy (TEM) studies. The influence of CNTs upon the tensile mechanical response and fracture toughness of the nanocomposites were comprehensively evaluated in association with the fracture modes obtained via SEM examination.

2. Experimental

2.1. Materials

Thin MWCNTs and DWCNTs with and without NH_2 functional groups were purchased from Nanocyl (Namur Belgium) and utilized as reinforcing constituents for the corresponding hybrid resin. Table 1 gives the physical properties of the corresponding CNTs used in this study. Styrene-free polyester resin POLIYA 420 and vinyl-ester-epoxy resin (bisphenol A epoxy based) POLIPOL 701 with 35 wt.% of styrene were provided from POLIYA Polyester, Turkey.

Table 1
Physical property of carbon nanotubes.

Nanotube types	P_{CNT}	L	d_{in}	d_{out}
DWCNT	0.98 g/cm^3	10 μm	2.1 nm	2.8 nm
DWCNT-NH_2	0.98 g/cm^3	5 μm	2.1 nm	2.8 nm
MWCNT	2.09 g/cm^3	50 μm	4 nm	15 nm
MWCNT-NH_2	2.09 g/cm^3	10 μm	4 nm	15 nm

Styrene emission agent BKY 740, purchased from Alton Chemie, Germany, was utilized to prevent evaporation of styrene during polymerization reaction. To polymerize the resin suspensions, cobalt naphtanate (CoNAP) and methyl ethyl kethone peroxide (MEKP) were then used as accelerator and initiator, respectively.

2.2. Principles of 3-roll milling

3-Roll milling is highly capable of dispersing CNTs homogeneously within thermosetting polymers without leading to a rupture and damage of CNTs that reduce their aspect ratio, unlike other solvent based techniques or treatments do [2,4]. Fig. 1 shows the photo of resin suspension on the rolls at 30 s after it was fed. 3-Roll milling differs principally from other types of mills in that it applies almost pure shear rather than compressive load. The first and third rolls labeled in Fig. 1 are usually called feed and apron rolls, respectively. They rotate in the same direction, while the center roll (2) rotates in the opposite direction. In order to create high shear rates, angular velocity of the center roll must be higher than that of feed roll (w2 > w1) [2,14]. As the resin suspension is fed into the narrow gap between feed and center rolls, the liquid stuff flows down covering the adjacent rolls through its surface tension under intensive shear forces. At the end of each subsequent intended dwell time, the processed resin suspension is collected by using a scraper blade in contact with the apron roll.

2.3. Preparation of nanocomposites

Various amounts of MWCNTs, MWCNT-NH_2 DWCNTs, DWCNT-NH_2 (0.05, 0.1 and 0.3 wt.%) were first mixed manually with styrene-free polyester resin prior to 3-roll milling processing for 10 min. A 3-roll mill (Exakt 120 S Exakt Gmbh) with alumina ceramic rolls was used to disperse the CNTs within styrene-free

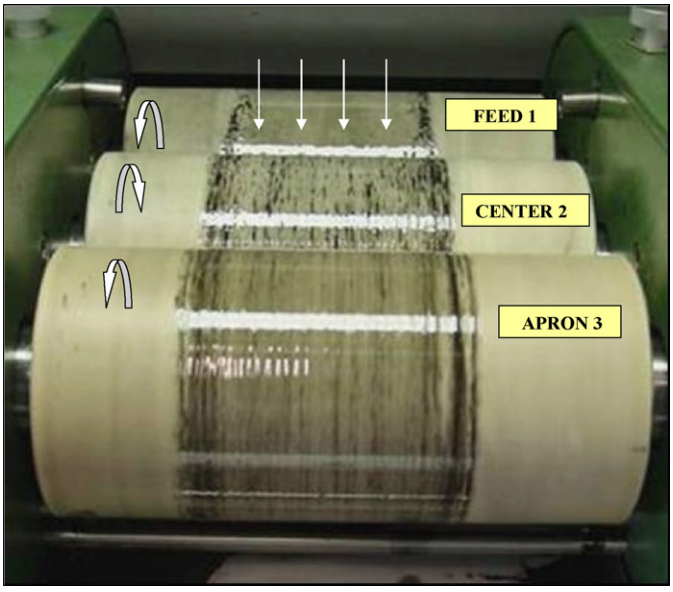

Fig. 1. Nanotube hybrid resin suspension on the rolls at time t =30 s after it was fed.