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Multiscale reinforcement and interfacial strengthening on epoxy-based composites by silica nanoparticle-multiwalled carbon nanotube complex

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ABSTRACT

The multiscale reinforcement and interfacial strengthening on epoxy-based composites by nanoscale complex composed of zero-dimensional silica nanoparticles (SiO_2) and one-dimensional multiwalled carbon nanotubes (MWCNTs) was examined. The SiO_2–MWCNT complex was successfully prepared by multi-step functionalization, which was characterized with FTIR, XPS and TEM. Mechanical properties of epoxy (EP) composites were significantly enhanced by SiO_2–MWCNTs rather than other functionalized MWCNTs, due to synergy reinforcing effect of MWCNTs and SiO_2 as well as enlarged interfacial areas by SiO_2. The chemically bonded nanoscale interfacial area between glass fiber and matrix was generated and bridged by SiO_2–MWCNTs, making glass fiber like a branched reinforcement, resulting in strong interfacial adhesion and effective stress transfer. Mechanical properties of SiO_2–MWCNT/EP composites and GF/SiO_2–MWCNT/EP composites were even higher than those predicted by Halpin–Tsai model and rule of mixtures, resulting from strengthened interfacial adhesion in the composites, high chemical reactivity of SiO_2–MWCNTs and additional reinforcing effect of SiO_2.

1. Introduction

Epoxy-based composites such as glass fiber reinforced epoxy (GF/EP) have been increasingly used in a variety of fields like civil engineering and public transportation, due to their advantages of high mechanical strength and low cost, [1,2]. With the rapid development of the energy industries in this century, GF/EP composites were widely considered as the prospective materials to produce high-voltage cables in electricity transmission industry and turbine blades in the wind power industry, which urgently called for the further enhancement of the mechanical properties and interfacial adhesion of such composites and their related epoxy matrix. Generally, the addition of nanofillers such as nanotubes and nanoparticles was the most efficient path to achieve this aim, since the combination of conventional fiber and nanofillers in the polymer matrices had led to a new generation of multiscale, multifunctional materials with high performance [2–4], as the resulting composites were synchronously reinforced and functionalized with both of micron diameter fibers and nanoscale fillers. It is necessary to investigate the reinforcing mechanism of these microfibers and nanofillers, which provided theoretical foundation to design and fabricate high performance composites. Thus, a great deal of theoretical models such as Halpin–Tsai equation [5], rule of mixtures [6], Mori–Tanaka equation [7] and Cox equation [8] have been carried out to predict mechanical properties of multiscale composites. Among them, Halpin–Tsai equation and rule of mixtures were two of most effective theoretical models and commonly used [5,6]. With these theoretical predictions, the multiscale reinforcing mechanisms of microfibers and nanofillers could be fundamentally elucidated by analyzing the discrepancies between experimental and predicted results.

Among various nanofillers, carbon nanotubes (CNTs) have served as an ideal filler for high performance composites due to their unique physical properties like high strength and aspect ratio [6,9–11]. However, the disadvantages of the atomically smooth nonreactive surfaces, the distinctively poor interfacial adhesion and the spontaneously entangled aggregation have limited the reinforcing effectiveness of CNTs and even deteriorated mechanical properties of the composites [10–12]. Therefore, the vital issue of preparing high performance composites was to ensure the strong interfacial adhesion between CNTs and matrix and the homogeneous dispersion of CNTs in the matrix. Chemical functionalization of CNT surface has been proposed as an effective way to strengthen the interfacial adhesion and positively affect the dispersibility of CNTs [6,11,13].

In this contribution, we suppose to prepare a novel nanostructural complex composed of zero-dimensional silica nanoparticles (SiO_2) and one-dimensional MWCNTs, whose microstructure and chemical reactivity are suggested in detail in Fig. 1. In the complex,

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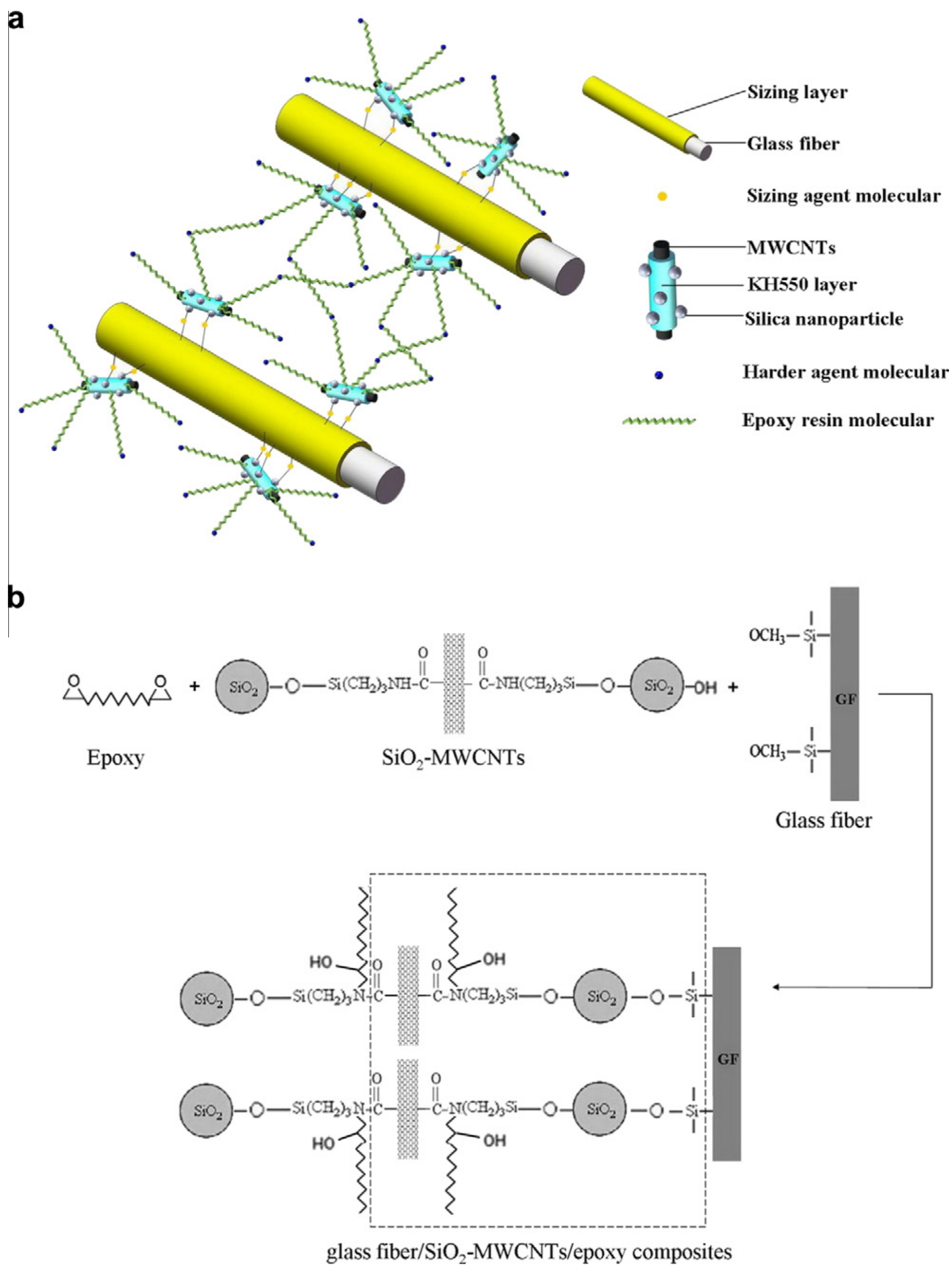

Fig. 1. Schematic of (a) microstructure and (b) interfacial chemical reaction of GF/EP composites with silica nanoparticle-multiwalled carbon nanotube (SiO_2–MWCNT) complex. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

MWCNTs were covalently coated with coupling agent and silica nanoparticles were anchored on the coupling layer, as shown in Fig. 1a. Compared with other carbon nanotube–silica hybrids [14,15], the coupling layer introduced onto the surface of MWCNTs supplied substantial reaction sites to covalently link MWCNTs with silica nanoparticles and epoxy matrix, as illustrated in Fig. 1b. Furthermore, silica nanoparticle based functionalization was known as a favorable method for CNT reinforcement on polymer composites [16,17], since silica nanoparticles had the characteristics of high interfacial chemical reactivity with sizing agent of glass fiber and fine compatibility with polymer chains of the matrix as presented in Fig. 1, which was beneficial to strengthen interfacial adhesion of glass fiber with the matrix and dispersion degree of CNTs. Besides, zero-dimensional silica nanoparticles showed isotropic nanoscale reinforcing ability on the matrix and naturally offset the shortage that the reinforcing effect of CNTs was only generated along their axis direction. All these advantages gave this unique complex promising application-potential in the new generation of GF/EP composites. In our experiments, the SiO_2–MWCNT complex were supposed to be obtained by multi-step functionalization of oxidation with mixed acid, grafting with a silane coupling agent and subsequent adhesion of silica nanoparticles on the coupling layer, which were characterized with Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The reinforcing effect of the complex on epoxy was compared with as-received functionalized MWCNTs, and mechanical properties of epoxy and GF/EP composites with various loadings of SiO_2–MWCNTs were evaluated and compared with predicted values by Halpin–Tsai model and rule of mixtures, while the interfacial adhesion in GF/SiO_2–