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New generation of hybrid filler for producing epoxy nanocomposites with improved mechanical properties

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ABSTRACT

This paper presents a multi-scale hybridization of carbon nanotube (CNT) with clay in polymers, which offers improvement in the mechanical properties of the composites. In this study, hybrid filler, comprised of CNT grown directly on muscovite particles by chemical vapour deposition using methane as the carbon precursor, is prepared. This CNT–Muscovite Hybrid compound is incorporated into the epoxy matrix at various filler loadings (1–5 wt.%) and compared with physically mixed CNT–Muscovite. The tensile strength, tensile modulus, and micro-hardness of Epoxy/CNT–MUS HYB nanocomposites are determine to exhibit an improvement of up to 86.58%, 134.59% and 14%, respectively, compared to neat epoxy. These improvements are mainly attributed to by the good dispersion of CNT–Muscovite Hybrid in the epoxy composites.

1. Introduction

Epoxy, which is one of the interesting thermosetting classes of polymer, is commonly used as it has better properties, such as high tensile strength, stiffness and hardness, low shrinkage during the curing process, good chemical and heat resistances, and high adhesive strength. Due to its unique characteristics, epoxy is widely used to fabricate composite structures with a variety of applications, such as anticorrosive coatings, adhesives, electronic encapsulates and aerospace. [1–4]. However, most epoxies show low fracture resistance and undesirable brittle properties; thus leading researchers to create significant epoxy composite improvements, such as modified epoxy resin structures by incorporating long hydrocarbon chains into the polymer or incorporating different filler particles into the epoxy matrices [5,6]. Ridzuan et al. reported that the modification of epoxy resin structures by introducing the pendant phenyl group into aromatic based epoxy resin could enhance the hardness and chemical properties of the final product [7]. However, considering previous works that incorporated various fillers, such as rubber [8,9], thermoplastic [10,11], organic [12,13] and inorganic [14,15] particles, in epoxy, reported in recent decades to improve the fracture toughness of the epoxy matrix. Particularly, the demand of advanced nanotechnology in recent years has attracted the attention of researchers to modify epoxy resin with nanoparticles, such as carbon nanotubes [16,17] or nanofibers [18–21] to form superior properties of nanocomposites. It has been verified that many CNT based epoxy nanocomposite studies have been explored [22–24].

Carbon nanotubes (CNTs) were expected to be an ideal reinforcement candidate, based on different matrices [25–28] for composites due to their high strength, good electrical conductivity, and chemical and thermal stability. This led to the production of polymer nanocomposites based carbon nanotubes, with a full set of desired properties for advanced electronic and engineering applications. However, the dispersion of CNT in the polymer matrix always became a crucial factor in CNT filled polymer composite fabrication, as the CNT tended to form a bundle due to high Van der Waals interaction, high aspect ratio and high surface area. Many works have been performed to solve this dispersion problem [29–31]. Nevertheless, conventional methods, involving physical mixing via a milling process [32] of two or more fillers, could damage the carbon nanotube (CNT) structure, due to a high compression force present during the process. Furthermore, this method could not promise homogeneous dispersion for the entangled CNT. In order to achieve a high dispersion of CNT in the polymer matrix, some researchers carried out the functionalization process on the CNT to improve dispersibility by introducing covalent linkages between the CNT and the functional group [33–35]. Unfortunately, the yields of the functionalized CNT decreased and the CNT structure was damaged due to the highly corrosive inorganic acids used [36]. To date, organic–inorganic hybrid composites have received much interest by researchers [37–39], due to their improved thermal [40], optical [41], and mechanical properties [42]. The hybridization of CNT with inorganic particle methods, which include chemical vapour deposition (CVD) [43–49] has proved to

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be the most successful way of producing homogenous CNT. The hybridization of CNT with inorganic particles by CVD leads to a uniform dispersion of CNT; without changing or damaging the CNT's structure.

This paper addresses the development and characterization of both the filler and the resulting composite of Epoxy/Muscovite–CNT Hybrid nanocomposites endowed with improved performance and good dispersion of CNT. CNT–Muscovite was synthesized by CVD to produce a hybrid compound, which was then incorporated into the epoxy matrix at various filler loadings. The effect of fillers on the composites was analysed in light of the resultant composite's morphology and mechanical properties.

2. Experimental

2.1. Production of CNT–Muscovite Hybrid

CNT–Muscovite Hybrid (CNT–MUS HYB) compound was synthesized using chemical vapour deposition (CVD). The CNT was grown on the muscovite particle as a support material using nickel as the catalyst. The catalyst was prepared by precipitating Ni $(NO_3)_2 \cdot 6H_2O$ (0.01 mol) on muscovite (0.03 mol) powder in NaOH (0.02 mol) solution. After 24 h, the precipitated catalyst was dried and calcined at 900 °C for 10 h. Then, the catalyst underwent a reduction process under hydrogen gas at 400 °C for 2 h followed by methane decomposition in a horizontal tube furnace in the presence of a methane and nitrogen atmosphere at a ratio of 1:7 at 800 °C for 30 min. Physically mixed CNT–Muscovite (CNT–MUS MIX) was prepared by a physical mixing method for comparison with the CNT–Muscovite Hybrid. Pure CNT and muscovite were mixed using a ball milling machine for 48 h at 20 rpm at a ratio of 30:70 according to the quantitatively measured weight percentage of CNT–Muscovite Hybrid using Energy Dispersive X-ray (EDX). Muscovite powder was supplied by Bidor Mineral Sdn. Bhd with average size 100–120 μm and the pure CNT supplied by SkySpring Nanomaterials Inc. was multiwalled carbon nanotubes with 98% purity and 10–30 nm size. Table 1 shows the description of the filler.

2.2. Characterization of hybrid CNT–Muscovite filler

The morphologies of CNT–MUS HYB and CNT–MUS MIX were analysed using a Leo Supra-35VP Field Emission Scanning Electron Microscope (FESEM) and High Resolution Transmission Electron Microscopy (HRTEM — Model Philip TECNAI 20 (200 kV)). The composition of carbon (C) and muscovite ($KAl_2(AlSi_3O_{10})$) was analysed using Energy Dispersive X-ray (EDX).

2.3. Preparation of CNT–Muscovite epoxy nanocomposites

CNT–MUS HYB and CNT–MUS MIX were dispersed in epoxy resin Diglycidyl Ether of Bisphenol A (DGEBA) using a QSonica sonicator machine at a frequency of 25 kHz for 30 min at different filler loadings of 1.0 wt.%, 3.0 wt.% and 5.0 wt.%. Subsequently, the curing agent trimethylhexane–thylenediamine (TMD) was added to the mixture with a mass ratio of 6:10 to the epoxy resin. The mixture obtained was degassed in a vacuum for 30 min to remove air bubbles formed during mixing. After degassing, the mixture was poured into a silicon mould and cured at 120 °C for 1 h. Table 2 shows the description of the composites samples.

Table 1
Description of the filler.

Samples	Descriptions
MUS	Muscovite filler
CNT–MUS HYB	CNT–Muscovite filler prepared by chemical vapour deposition
CNT–MUS MIX	CNT–Muscovite filler by physically mix

Table 2
Description of the composite samples.

Samples	Descriptions
Epoxy/MUS 1	Epoxy filled with 1 wt.% muscovite filler
Epoxy/MUS 3	Epoxy filled with 3 wt.% muscovite filler
Epoxy/MUS 5	Epoxy filled with 5 wt.% muscovite filler
Epoxy/CNT–MUS HYB 1	Epoxy filled with 1 wt.% CNT–Muscovite hybrid compound
Epoxy/CNT–MUS HYB 3	Epoxy filled with 3 wt.% CNT–Muscovite hybrid compound
Epoxy/CNT–MUS HYB 5	Epoxy filled with 5 wt.% CNT–Muscovite hybrid compound
Epoxy/CNT–MUS MIX 1	Epoxy filled with 1 wt.% CNT–Muscovite physically mix
Epoxy/CNT–MUS MIX 3	Epoxy filled with 3 wt.% CNT–Muscovite physically mix
Epoxy/CNT–MUS MIX 5	Epoxy filled with 5 wt.% CNT–Muscovite physically mix

2.4. Characterization of epoxy nanocomposites

Tensile tests of the Epoxy/MUS, Epoxy/CNT–MUS MIX and Epoxy/CNT–MUS HYB were conducted using a Universal Testing Machine (Instron, Model 5982). The samples were dumbbell shaped with 60 mm long, 10 mm wide and 3 mm thick; according to ASTM D638. The tensile tests were carried out at a rate of 1 mm/min. At least five specimens were tested to ensure the reliability of the test's results. The dispersion states of Epoxy/MUS 5, Epoxy/CNT–MUS MIX 5 and Epoxy/CNT–MUS HYB 5 were observed under FESEM. Micro-hardness tests of Epoxy/CNT–MUS MIX and Epoxy/CNT–MUS HYB were performed using a Shimadzu micro-hardness tester Type-M. The dimensions of the samples for micro-hardness were 2 mm thickness and 30 mm diameter. The test load for the micro-hardness indentation was 300 g with an indentation time of 10 s on the surface of the sample.

3. Results and discussion

The elements identified in the CNT–MUS HYB were obtained using EDX analysis. From Fig. 1, the horizontal axis shows the elements present in the CNT–MUS HYB and the vertical axis represents weight percentage (wt.%) of the elements present. Based on the EDX analysis, the carbon element showed the most intense peak at 30.49 wt.%. The presence of the carbon element referred to the existence of carbon nanotubes in CNT–MUS HYB. However, relatively intense peaks, which were assigned to oxygen, alumina, and silica, represent the parts of the muscovite elements. Note: the Ni peak observed indicates the elements from the metal catalyst (Ni $(NO_3) \cdot H_2O$).

The comparison of FESEM morphologies between CNT–MUS MIX and CNT–MUS HYB are shown in Fig. 2. From Fig. 2a, b and c, CNT–MUS MIX shows poor distribution between CNT and muscovite particles. The separation between CNT and muscovite particles can be seen clearly at a higher magnification. In addition, the CNT tended to agglomerate and form a bundle due to van der Waals interactions [50]. Fig. 2d–f shows the morphologies of CNT–MUS HYB. The observation reveals that the CNT was successfully grown on the flake-shaped

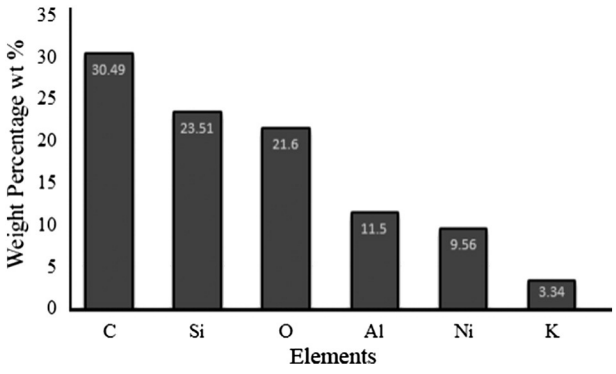

Fig. 1. Elemental analysis of CNT–MUS HYB by EDX.