Izod impact performance of hybrid carbon nanotube-alumina filled epoxy nanocomposites

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Abstract. In this paper, multi-walled carbon nanotube (CNT) was hybridized with alumina (Al₂O₃) particles via chemical vapour deposition using nickel as a metal catalyst. The purpose of hybridization between CNT and Al₂O₃ particles is to prevent the agglomeration of the CNT due to van der Walls forces as well as to improve the impact performance of the epoxy nanocomposites. The Al₂O₃ particles work as “transport” for the CNT to homogenously disperse within the epoxy matrix. As a comparative study, the CNT-Al₂O₃ was also prepared through a physical mixing method. The assessment showed that the CNT–Al₂O₃ hybrid filler produced more homogeneous dispersion in the epoxy matrix with a higher Izod impact strength than the physically mixed CNT–Al₂O₃ filler. The izod impact strength of epoxy nanocomposites at 5 % wt of CNT–Al₂O₃ hybrid has increased up to 32 % compared to the neat epoxy.

1. Introduction

Epoxies are a major class of engineering polymeric materials, because of their outstanding mechanical strength, thermal stability, long pot life, low curing shrinkage and excellent adhesive strength [1]. The impressive performance characteristics of epoxy resin, together with their good processability and reasonable cost, are considered useful for intensively used diverse field applications [2]. To further improve their functionalities and expand their applications, epoxy resin has often been incorporated with various types of fillers; especially particulate filler, to produce composite materials [3].

Over the last decade, several research groups have focused their efforts on using carbon nanotube (CNT) as particulate fillers, due to their remarkable mechanical, thermal and electrical properties, as quoted by previous experimental and theoretical studies [4, 5]. However, CNT needs to be dispersed uniformly within the epoxy matrix, in order to reveal its extraordinary properties. The small size of CNT tends to aggregate or entangle with itself due to the van der Waals interaction [6, 7]. To overcome this dispersibility issue, the hybridization of CNT with inorganic filler, such as alumina (Al₂O₃), magnesium oxide (MgO), silicon dioxide (SiO₂), calcium oxide (CaO) and muscovite, has become a popular technique via several approaches [8-12]. The conventional hybridization method uses a ball milling approach to mix CNT and alumina. However, this method results in breakage and
damage of the CNT into smaller lengths, and is considered to be a major disadvantage. Therefore, the idea of the hybridization of CNT and Al$_2$O$_3$ via a chemical vapour deposition (CVD) method has been proposed by depositing the CNT onto the Al$_2$O$_3$ particles [13, 14]. In this concept, the Al$_2$O$_3$ particles work as a transport to help the CNT disperse homogenously into the epoxy matrix; as the dispersion of CNT is dependent on the dispersion of the Al$_2$O$_3$ particles.

In this paper, a CNT-Al$_2$O$_3$ hybrid compound was synthesised by growing the CNT on the Al$_2$O$_3$ particles under a methane atmosphere using nickel as the catalyst. The characteristics of the CNT-Al$_2$O$_3$ hybrid compound were examined using Field Emission Scanning Electron Microscopy (FESEM) and High Resolution Transmission Electron Microscopy (HRTEM) to observe the morphology of the CNT structure forming on the alumina particle. The aim of this study was to investigate the Izod impact performance of the CNT in the epoxy nanocomposite, which is relatively poor when CNT alone is added due to poor dispersion. The dispersion state of the CNT in the epoxy nanocomposites was also examined using FESEM. The possible explanations for the difference between the CNT-Al$_2$O$_3$ hybrid compound filled epoxy and the CNT-Al$_2$O$_3$ physically mixed filled epoxy are discussed.

2. Experimental

2.1. Production of CNT–Al$_2$O$_3$ Hybrid

A CNT–Al$_2$O$_3$ hybrid compound was synthesized using a chemical vapour deposition (CVD) method. The catalyst was prepared by precipitating Ni(NO$_3$)$_2$.6H$_2$O on aluminium powder in a NaOH solution. The catalyst was then dried at 110°C for 2 h and calcined at 900°C to form a NiO-Al$_2$O$_3$ complex. The NiO-Al$_2$O$_3$ complex underwent a reduction process under hydrogen gas at 400°C for 2 h, followed by growth of CNT onto the Al$_2$O$_3$ under a methane and nitrogen gas atmosphere, at a gas flow ratio of 1:7 at 800°C for 30 min in a horizontal tube furnace. Physically-mixed CNT–Al$_2$O$_3$ was produced using a ball milling machine for 48 h at 20 rpm for comparison with the CNT–Al$_2$O$_3$ hybrid compound. Pure CNT (supplied by SkySpring Nanomaterials Inc.) and Al$_2$O$_3$ were mixed at a weight percentage ratio of 12:100, based on the energy dispersive X-ray (EDX) analysis reported in our previous paper [12].

2.2. Characterization of Hybrid CNT– Al$_2$O$_3$ Filler

The morphologies of CNT–Al$_2$O$_3$ hybrid compound and CNT–Al$_2$O$_3$ physically mixed were analysed using a Leo Supra-35VP Field Emission Scanning Electron Microscope and a High Resolution Transmission Electron Microscope (Model Philip TECNAI 20 (200 kV)).
2.3. Preparation of CNT–Al₂O₃ Epoxy Nanocomposites

1.0, 3.0, and 5.0 wt% of CNT–Al₂O₃ hybrid compound and CNT–Al₂O₃ physically mixed were dispersed in epoxy resin Diglycidyl Ether of Bisphenol A (DGEBA) using a QSonics sonicator machine at a frequency of 25 kHz for 30 min. A curing agent, trimethylhexamethylenediamine (TMD) with mass ratio of 6:10 epoxy resin was then added to the mixture. The mixture was placed into a vacuum at 76 cm Hg pressure for 30 min to remove any trapped air and then poured into a silicon mould. Finally, the epoxy composites were cured at 120°C for 1 h. Table 1 shows the descriptions of the samples.

| Samples       | Descriptions                                      |
|---------------|---------------------------------------------------|
| HYB           | CNT–Al₂O₃ hybrid compound                         |
| MIX           | CNT–Al₂O₃ physically mix                           |
| Epoxy/HYB     | Epoxy filled with CNT–Al₂O₃ hybrid compound         |
| Epoxy/HYB1    | Epoxy filled with 1 % wt CNT–Al₂O₃ hybrid compound  |
| Epoxy/HYB3    | Epoxy filled with 3 % wt CNT–Al₂O₃ hybrid compound  |
| Epoxy/HYB5    | Epoxy filled with 5 % wt CNT–Al₂O₃ hybrid compound  |
| Epoxy/MIX     | Epoxy filled with CNT–Al₂O₃ physically mix         |
| Epoxy/MIX1    | Epoxy filled with 1 % wt CNT–Al₂O₃ physically mix   |
| Epoxy/MIX3    | Epoxy filled with 3 % wt CNT–Al₂O₃ physically mix   |
| Epoxy/MIX5    | Epoxy filled with 5 % wt CNT–Al₂O₃ physically mix   |

2.4. Characterization of the Epoxy Nanocomposites

Izod impact tests of Epoxy/HYB and Epoxy/MIX were performed with a pendulum apparatus (Zwick Impact Testing Machine) using conventional V–notched specimens. Specimens were made in accordance with ASTM standard D256. At least five specimens were tested for each case to ensure reliability of the test results. The fracture surfaces of the Epoxy/HYB and Epoxy/MIX samples were examined by FESEM after coating with a 5–10 nm Au–Pd layer by sputtering.

3. Results and Discussion

Figure 1a-b show the SEM images of the HYB. From the observation, it can be seen that CNT was successfully grown on the alumina particles. The CNT was attached to the Al₂O₃ particles with a diameter of approximately 10 - 30 nm. The CNT was distributed homogenously on the Al₂O₃ particles and wrapped around the Al₂O₃ particles. The Al₂O₃ surface was fully covered by CNT due to the large amount of the CNT deposited. The dispersion of the CNT was dependent on the dispersion of the Al₂O₃ particles. Meanwhile, Figure 1c-d show the SEM images of the MIX, which illustrates that the CNT was poorly distributed and independent of the dispersion of the Al₂O₃ particles. In addition, CNT
did not physically attach to the Al₂O₃ particles and tended to agglomerate due to the van der Waals interactions.

**Figure 1**: SEM Images of HYB with magnification of (a) 80,000X and (b) 200,000X and MIX with magnification of (c) 80,000X and (d) 200,000X.

Figure 2 shows the HRTEM images of the HYB. From the HRTEM images, the CNT was confirmed as multiwalled carbon nanotube (MWCNT) by the existence of hollow structures and multi-layered walls. The MWCNT contained several layers of graphene sheets along the longitudinal direction of the nanotube, approximately 15 - 25 walls, and an inner hollow with a diameter of 4 - 8 nm. The nickel catalyst can be seen clearly at the end of the MWCNT tip, which indicates the MWCNT grown by the tip growth mode. The size of the MWCNT is dependent on the size of the nickel catalyst as shown in Figure 2b.

**Figure 2**: HRTEM Images of HYB.

Figure 3 shows the Izod impact strength of the Epoxy/HYB and Epoxy/MIX at various filler loadings. As shown in the figure, the Epoxy/HYB and Epoxy/MIX nanocomposites exhibited an improvement
in Izod impact strength compared to the neat epoxy. The Izod impact strength increased gradually after the addition of the CNT-Al$_2$O$_3$ hybrid filler into the epoxy matrix. The enhancement of the Izod impact strength was due to the extraordinary properties of the CNT fillers in the epoxy matrix. From the graph, it can be seen that the Epoxy/HYB showed a higher Izod impact strength than the Epoxy/MIX. The highest Izod impact strength of the Epoxy/HYB was achieved at 5 wt% with 375 J/m, and exhibited an enhancement of up to 32% compared to the neat epoxy. Meanwhile, the Izod impact strength of the Epoxy/MIX3 was 335 J/m, which presented the highest Izod impact strength with an enhancement of up to 18% compared to the neat epoxy. The higher Izod impact strength of the Epoxy/HYB may be explained by the dispersion of CNT and alumina within the epoxy matrix being better than the Epoxy/MIX. The good dispersion of CNT in the Epoxy/HYB was due to the Al$_2$O$_3$ particles acting as a vehicle for the CNT to disperse within the epoxy matrix. As a result, this provided a uniform stress distribution and reduced the stress concentration in the epoxy composite. In the Epoxy/MIX, several agglomerations of CNT formed large particles, which consequently reduced the surface area of the CNT. Thus, the agglomeration of CNT led to a lower Izod impact strength.

![Izod Impact Strength](image)

**Figure 3.** Izod Impact Strength of Neat Epoxy and the Epoxy Composites with 1%, 3% and 5% Weight Percentage of HYB and MIX.

In order to investigate the failure mechanism of epoxy nanocomposites, the fracture surfaces of the Epoxy/HYB and Epoxy/MIX specimens were comparatively examined using FESEM. Figs. 4a-b show the surface of the Epoxy/HYB; which demonstrates that the HYB is distributed homogeneously in the epoxy matrix. This HYB structure prevents the CNT from agglomerating with each other and ensures a large contact area between the CNT and the epoxy matrix. The bridging network, which is easily formed by HYB, enables it to transfer load from the matrix to the filler. Thus, enabling increased impact strength of the epoxy nanocomposites. Figure 4c–e show the surface of the Epoxy/MIX; which demonstrates that the MIX is not distributed homogeneously in the epoxy matrix. As seen on the
surface of the Epoxy/MIX, the CNT and Al₂O₃ particles were found to be dispersed separately and some CNT were detached from the alumina Al₂O₃ particle all together. This was probably caused by a weak interaction bonding between the CNT and the Al₂O₃ particles, as a result of the high frequency vibration sonication process. The agglomeration of the CNT and the Al₂O₃ particles in the epoxy matrix can be clearly observed from the close-up views shown in Fig. 4d and Fig. 4e, respectively. This agglomeration induces stress concentration and thus reduces the impact strength of the epoxy nanocomposites.

**Figure 4.** SEM images of the Epoxy/HYB at magnification of (a) 1,000X, (b) 20,000X and Epoxy/MIX at magnification of (c) 1,000X, (d) 10,000X and (e) 5,000X.

4. Conclusions
This study investigated the izod impact strength of CNT–Al₂O₃ filled epoxy composites. The CNT–Al₂O₃ hybrid compound was successfully synthesized via CVD to improve the dispersion of CNT in the epoxy matrix. The Epoxy/HYB composites showed higher izod impact strength than Epoxy/MIX. The izod impact strength of Epoxy/HYB was enhanced by approximately 32% at 5 % wt, whereas the izod impact strength of Epoxy/MIX was enhanced by approximately 18% at 5 % wt. In the Epoxy/HYB system, Al₂O₃ particles worked vehicles to disperse the CNT homogenously within the
epoxy matrix. Homogenous dispersion of CNT–Al₂O₃ in Epoxy/HYB and some agglomeration of CNT–Al₂O₃ in Epoxy/MIX were observed using FESEM.

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