Dielectric performance of Hybrid Carbon Nanotube-Alumina Filled Epoxy Nanocomposites

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ABSTRACT

The multi-scale hybridisation of alumina (Al_2O_3) and carbon nanotubes (CNTs) was synthesised with the use of chemical vapour deposition (CVD). The CNTs were grown directly on the Al_2O_3 particle by utilising a nickel catalyst while being under an atmosphere of methane. When incorporated into the epoxy matrix, the CNT-Al_2O_3 hybrid filler provided new opportunity for the development of high performance multifunctional composites. The goal of hybridizing CNTs and Al_2O_3 particles is to avoid CNT agglomeration as a result of van der Waals attractions. The particles of Al_2O_3 serve as "vehicles" for CNTs so that they can homogenously disperse in the epoxy matrix. As a comparative study, preparation of CNT-Al_2O_3 was also done through a physical mixing method. The result revealed that compared to the CNT–Al_2O_3 filler that was physically mixed, the CNT–Al_2O_3 hybrid filler exhibited a more homogeneous dispersion within the epoxy matrix and it had a higher dielectric constant. Furthermore, compared to the neat epoxy, the dielectric constant of the CNT–Al_2O_3 hybrid epoxy nanocomposites was enhanced by up to 22%.

Keywords: *Carbon Nanotubes (CNT), Epoxy Nanocomposites, Chemical Vapor Deposition (CVD)*

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Introduction

Epoxy resin possesses unique properties like excellent heat and chemical resistance, relatively high modulus and strength, and low shrinkage during curing. These properties also make them well-suited for many important industrial applications [1]. Integrating nanoparticles in an epoxy resin has become a more appealing option since they considerably enhance the epoxy nanocomposites performance. These days, carbon nanotubes (CNT) have attracted a considerable amount of attention from the engineering and scientific communities because of their potential to be utilised as a particulate filler for epoxy nanocomposites [2]. The CNT have also turned into candidates for a broad range of applications that include sensors, nanoprobes and nanobearings, field emission displays, and energy conversion and energy storage devices [3]. However, CNT in epoxy nanocomposites often offer limited potential benefits because of the extremely gradual viscosity increases of epoxy resin even when CNT addition is on a low volume percentage. The CNT has a tendency to agglomerate because of the inherent van der Waals force attraction, high aspect ratio, and high surface area [4]. However, there are some techniques that can be used to improve CNT dispersion in epoxy nanocomposites such as physical blending (high shear mixing or ultrasonication), hybridisation [6, 7], and chemical functionalization [5]. Recently, CNT hybridisation using inorganic filler has gained the attention of researchers because it has shown the capacity to improve CNT dispersion without causing damage to its structure. The most popular approach for the production of CNT hybrid particles is to use chemical vapour deposition (CVD) to directly grow the CNT on the inorganic substrate. This method has been used for a broad range of inorganic substrate like silica [9],alumina [8], muscovite [10], and dolomite [11].

In this study, synthesis of the CNT-Al_2O_3 hybrid compound was done by growing the CNT on the particles of Al_2O_3 under a methane atmosphere. Nickel was used as the catalyst. The CNT-Al_2O_3 hybrid compound's characteristics were studied using a Field Emission Scanning Electron Microscope (FESEM). Furthermore, a High Resolution Transmission Electron Microscope (HRTEM) was also used to examine the morphology of the CNT structure that was formed on the alumina particle. This study aims to study the epoxy nanocomposites dielectric properties. The CNT's dispersion state in the epoxy nanocomposites was studied using HRTEM. It then discusses the possible explanations for the variations between the CNT-Al_2O_3 physically mixed filled epoxy and the CNT-Al_2O_3 hybrid compound filled epoxy.

Experimental

Production of CNT–Al_2O_3 hybrid

Synthesis of a CNT-Al_2O_3 hybrid compound was done using the chemical vapour deposition (CVD) method. Preparation of the catalyst was done by the precipitation of the $Ni(NO_3)_2.6H_2O$ on aluminium powder. This reaction was done in a NaOH solution. Afterwards, the catalyst was dried for 2 h at 110°C before being calcined at 900°C so that it could form a NiO-Al_2O_3 complex. The NiO-Al_2O_3 complex was then made to undergo a reduction process for 2 h under hydrogen gas at a temperature of 400°C. This was followed by CNT growth onto the Al_2O_3 under an atmosphere of methane and nitrogen gas. This was performed at a ratio of 1:7 for 30 min at 800°C inside a horizontal tube furnace. Production of a physically-mixed CNT-Al_2O_3 was performed for 48 h using a ball milling machine at 20 rpm. The purpose of this is for making comparisons with the CNT-Al_2O_3 hybrid compound. Pure CNT (obtained from SkySpring Nanomaterials Inc.) and Al_2O_3 were combined at a ratio of 12:100. This combination has its basis in the energy dispersive X-ray (EDX) analysis that was discussed in our previous paper [12].

Characterization of hybrid CNT– Al_2O_3 filler.

The morphologies of the physically mixed CNT-Al_2O_3 and the CNT-Al_2O_3 hybrid compound were analysed using a High Resolution Transmission Electron Microscope (Model Philip TECNAI 20 (200 kV)) and a Leo Supra-35VP Field Emission Scanning Electron Microscope.

Preparation of CNT– Al_2O_3 epoxy nanocomposites.

1.0 wt%, 3.0 wt% and 5.0 wt% of the CNT-Al_2O_3 hybrid compound and the physically mixed CNT-Al_2O_3 were dispersed within an epoxy resin of Diglycidyl Ether of Bisphenol A (DGEBA) for 30 min using a QSonica sonicator machine at a frequency of 25 kHz. Trimethylhexamethylenediamine (TMD), a curing agent with a mass ratio of 6:10 epoxy resin, was then combined with the mixture. The resulting mixture was put in a vacuum for 30 min at 76 cm Hg pressure to eliminate any trapped air. The mixture was then poured into a mould made out of silicon. Finally, curing of the epoxy composites was done at 120°C for 1 h. Table 1 contains the samples’ descriptions.

Table 1. Descriptions of the samples.

Samples	Decriptions
HYBRID	CNT–Al_2O_3 hybrid compound
MIXED	CNT–Al_2O_3 physically mixed
Epoxy/HYBRID	Epoxy filled with CNT–Al_2O_3 hybrid compound
Epoxy/HYBRID1	Epoxy filled with 1 % wt CNT–Al_2O_3 hybrid compound
Epoxy/HYBRID3	Epoxy filled with 3 % wt CNT–Al_2O_3 hybrid compound
Epoxy/HYBRID5	Epoxy filled with 5 % wt CNT–Al_2O_3 hybrid compound
Epoxy/MIXED	Epoxy filled with CNT–Al_2O_3 physically mixed
Epoxy/MIXED1	Epoxy filled with 1 % wt CNT–Al_2O_3 physically mixed
Epoxy/MIXED3	Epoxy filled with 3 % wt CNT–Al_2O_3 physically mixed
Epoxy/MIXED5	Epoxy filled with 5 % wt CNT–Al_2O_3 physically mixed

Characterization of the epoxy nanocomposites

The epoxy nanocomposites' dielectric constant was measured at room temperature using an Agilent 4284A LCR meter over a frequency range of 1 kHz to 1 MHz. The samples' dimensions were 30 mm diameter and 2 mm thickness. The nano-scale morphology of the MIXED and HYBRID through the epoxy matrix was subjected to analysis using HRTEM. Samples that were 50 nm thick were prepared at −85 °C by cryo-ultramicrotomy using a Leica microtome (model Reichert-Jung Ultracut E).

Results and Discussion

The morphologincal characteristics of HYBRID and MIXED were studied under varying magnifications that ranged from 10,000X to 100,000X using FESEM. Figure 1a-b shows the HYBRID's SEM images and Figure 1c-d shows the MIXED SEM images. From observations made on the HYBRID, one can see how the CNT was deposited and wrapped around the particles of the Al_2O_3. Furthermore, the CNT was homogenously distributed and attached on the Al_2O_3 particle's surface. The growth of CNT on the alumina particle had a diameter that ranged from 10 to 30 nm. From the MIXED observation, one can note poor distribution of the CNT and Al_2O_3 particles. The particles of CNT and Al_2O_3 seemed to have separately dispersed. Moreover, the particles of CNT and Al_2O_3 have a tendency to agglomerate. CNT agglomeration is typically a result of the van der Waals interactions [13].

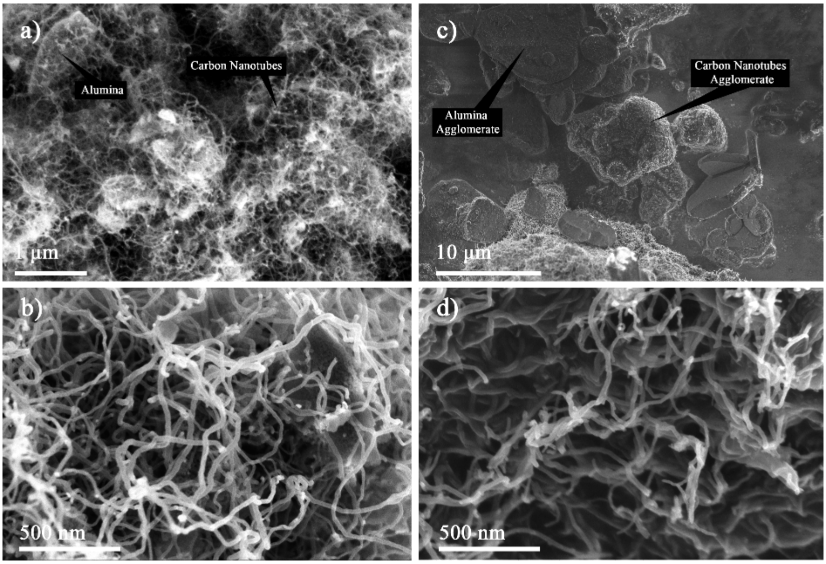

Figure 1: SEM images of HYBRID with magnification of (a) 35,000X (b) 100,000X and MIXED with magnification of (c) 10,000X and (d) 100,000X.

HRTEM was used to study the HYBRID morphology at nanoscale and in close-up view under magnifications of 15,000X and 400,000X. Figure 2a shows that the HRTEM images for the HYBRID revealed its wire-like structure. This wire-like structure was also seen for observations under SEM. Figure 2b shows the multi-layered wall and hollow structure of CNT, which reveals that this CNT is a multi-walled carbon nanotube (MWCNT). This CNT is made up of numerous layers of graphene sheets along the nanotube‘s longitudinal direction with about 15–30 walls. Furthermore, the black dot found at the tip of the CNT is an indication of the presence of the nickel particle. This nickel particle served as the catalyst to CNT growth on the Al_2O_3 particle. It should also be noted that this CNT grew via the tips growth mode as a result of the presence of the nickel particle at the CNT tips. Therefore, the CNT wall’s size depends on the nickel particle.

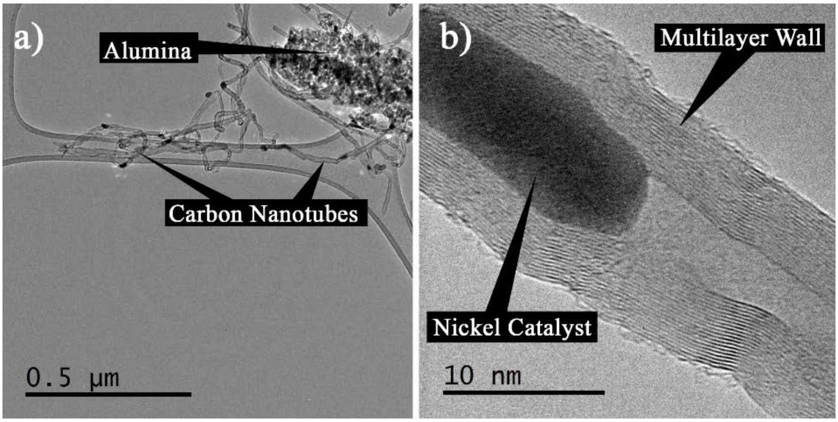

Figure 2: HRTEM images of HYBRID with magnification of (a) 15,000X and (b) 400,000X.

The dielectric constant is important to engineers and researchers as this parameter offers insights into the filler and its applicability in electronic applications [14]. The dielectric constant's variations as a function of frequency for Epoxy/MIXED and Epoxy/HYBRID at various filler loadings are demonstrated in Fig. 3. The figure reveals that the dielectric constant of Epoxy/MIXED and Epoxy/HYBRID decreases when the frequency increases. The decrease in the dielectric constant under high frequency is a result of the reduced polarisation when the frequency is higher. At lower frequency, the changes in the electric field are slower and the surface charges' polarisation would therefore be high. When the frequency is higher, the changes in the electric field take place very quickly and this means that the surface charges have lesser time to polarise. Thus, the surface charges' polarisation would decrease. The decrease in polarisation will also lead to a decrease in dielectric constant. As seen on the graph, Epoxy/HYBRID exhibited a dielectric constant that is higher compared to the Epoxy/MIXED. The Epoxy/HYBRID5 achieved the highest dielectric constant with an increment that is up to 201.7. This increment corresponds to a 22% increase compared to the neat epoxy used at 1 MHz. Meanwhile, for Epoxy/MIXED, the highest dielectric constant was obtained at 5 wt% with 190.4. This was equivalent to a 15% increment in comparison to the neat epoxy at 1 MHz. The Epoxy/HYBRID high dielectric constant is a result of the good CNT dispersion, which gives the epoxy nanocomposite some polarity and generates significant amounts of micro-capacitors. The vast number of micro-capacitors therefore results in higher dielectric constant for the epoxy nanocomposites.

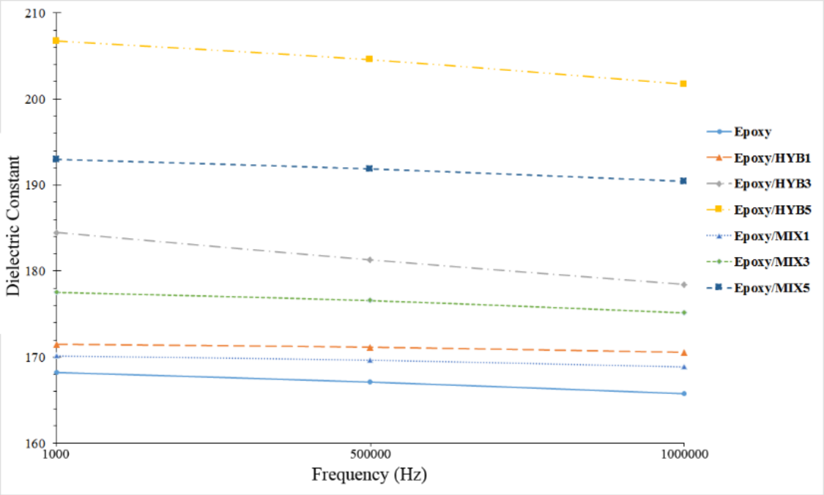

Figure 3: Frequency dependent dielectric constant of neat epoxy and epoxy filled with HYBRID and MIXED at various different filler loadings.

The HRTEM was used on the Epoxy/MIXED and Epoxy/HYBRID and to examine their dispersion state within the epoxy nanocomposites. Analysis of their morphologies was done under magnification ranging from 9,900X and 15,000X. Figure 4a shows the Epoxy/HYBRID HRTEM image, which reveals good dispersion within the epoxy matrix. The Al_2O_3 and CNT particles appear to be homogenously distributed and dispersed together. This is because CNT was able to attach itself onto the surface of the Al_2O_3 particle. For this system, Al_2O_3 particles served as a medium for CNT to homogenously disperse. The particles also prevented the CNT from forming agglomerates. Figure 4b shows the Epoxy/MIXED HRTEM image, which shows the poor dispersion of MIXED within the epoxy matrix. It shows how the Al_2O_3 particles dispersed on their own instead of helping the CNT to homogenously disperse within the epoxy matrix. Thus, CNT will have a tendency to agglomerate due to the van de Waal force. This means that MWCNT dispersion in the Epoxy/HYBRID depended on the Al_2O_3 particles while the MWCNT dispersion in the Epoxy/MIXED did not depend on Al_2O_3 particles.

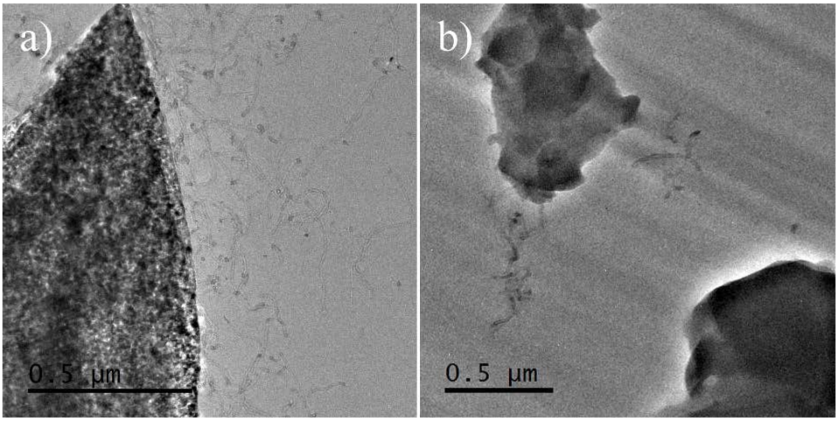

Figure 4: HRTEM images of the Epoxy/HYBRID at magnification of (a) 15,000X, and Epoxy/MIXED at magnification of (b) 9,900X

Conclusion

The effect of MIXED and HYBRID on the epoxy composites dielectric properties was studied. In terms of dielectric constant for a specific filler loading, the Epoxy/HYBRID had better performance compared to the Epoxy/MIXED. This is attributed to the good HYBRID dispersion in the epoxy matrix, where Al_2O_3 also serves as the medium for the CNTs to homogenously disperse. This led to the improvement in the dielectric constant of the epoxy nanocomposites.

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