EFFECT OF FILLER LOADING CONCENTRATION, CURING TEMPERATURE AND MOLDING PRESSURE ON THE ELECTRICAL CONDUCTIVITY OF CNTS/GRAPHITE/ EPOXY NANOCOMPOSITES AT HIGH LOADING OF CONDUCTIVE FILLERS

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ABSTRACT

Effect of filler loading concentration, curing temperature and molding pressure on the electrical conductivity of Carbon Nanotubes (CNTs)/Graphite/Epoxy nanocomposites at high loading of conductive fillers were investigated. Dispersion and incorporation mechanism between two conductive fillers with different sizes (CNTs and Graphite) in the polymer matrix are the key factors in the fabrication of high electrical conductivity plate. Different loading concentration of CNTs (0~5 wt. %) and graphite (40 ~ 80 wt. %) were dispersed in epoxy resin by a high speed mechanical mixer. Plates were than formed by compression molding. The electrical conductivity of the molded plates were measured by the four point probe method. The electrical conductivity measured the significance of variation in loading concentration, curing temperature and molding pressure. Additional of 5 wt.% of CNTs to graphite/epoxy matrix showed tremendous increase of the electrical conductivity of nanocomposites, approximately 200% higher than the graphite/epoxy composite at the same amount of conducting filler loading concentration. The dispersion quality of single filler composite (graphite/epoxy) and hybrid fillers nanocomposites (CNTs/graphite/epoxy) was observed on the fractured surface by scanning electron microscopic.

Keywords: Electrical conductivity, carbon nanotubes, graphite, high conductive plate

1. INTRODUCTION

Polymer nano-composites have attracted the attention of many researchers and have been the focus of study for application in various fields. In particular, conductive polymeric composites have been extensively studied in recent years because of their potential applications in electromagnetic shielding, batteries, light emitting devices, antistatic, corrosion resistance coating and other functional application (Ray & Biswas, 2000). The conventional material for producing high electrical conductive plates is from compressed graphite or graphite-polymer composites, and metal. Graphite plates are preferred over the metal plates because of their high corrosion resistance and low density. On the other hand,

the disadvantages of graphite are difficulties in machining and its brittleness. Metal plates which offer good electrical conductivity, can be made very thin, have excellent mechanical properties, and are relatively easy to fabricate, but in general have low corrosion resistance (Tian & Wang, 2006). Graphite-based polymer composite bipolar plates have the potential to replace graphite plates, because they offer the advantage of greater ease of manufacturing than graphite plates (Dhakate *et al.,* 2007). However, polymer composites are associated with poor electrical conductivity of polymer that still remains to be solved. Thus excessive amount graphite fillers have to be incorporated in the polymer matrix to meet the minimum requirement of electrical conductivity. Graphite-based polymer composite have been fabricated from the combination of high concentration of graphite and carbon black to enhance electrical conductivity (Cunningham & Baird, 2007; Yen *et al.,* 2006; Dweiri & Sahari, 2008; Dweiri & Sahari, 2007). The reinforcing and/or electrically conducting fillers commonly used, including graphite, carbon fiber, and carbon black, have been reported to enhance the overall performance of composite plates formed by the conventional polymer processing technique (Yen *et al.,* 2006; Dweiri & Sahari, 2008; Dweiri & Sahari, 2007; Kuo & Chen, 2006; Scholta *et al.,* 1999). Since the discovery of single-walled carbon nanotubes (SWCNT) and subsequently of multi-walled carbon nanotubes (MWCNT) and their exceptional mechanical properties, the idea of using them as reinforcing fibers in composite materials has been the driving force for composite design (Scholta *et al.,* 1999; Lourie *et al.,* 1998; Treacy *et al.,* 1996; Yu *et al.,* 2000). Theoretical and experimental results show superior electrical properties of the CNTs. Due to their one dimensional nature, as produced CNTs are extremely conductive because charge carriers can pass through CNTs without scattering and resulting in ballistic transport. The absence of scattering means that Joule heating is minimized, so that it can carry very large current densities of up to 100 MA/cm^2. Thus, the CNTs can produce electric current carrying a capacity which is 1000 times higher than that by copper wires (Collins & Avouris, 2000). MWCNTs are reported to be always electrically conductive, and to have an electrical conductivity approximately 1.85 x 10^3 S/cm (Ando *et al.,* 1999). Graphite-based polymer composite for bipolar plate have been fabricated from the combination of high

concentration of graphite, carbon black and CNTs (Lee *et al.,* 2009), where the electrical conductivity increased by more than 100%. To the best our knowledge, there has been no study on the effect of curing temperature and curing pressure for high filler loading concentration on the electrical conductivity of CNTs/Graphite/Epoxy nanocomposites. Therefore this will be the objective of the study reported in this paper.

2. EXPERIMENTAL SET-UP

Synthetic Graphite powder (G) used in this study has electrical resistivity of 0.03 Ω-cm, surface ratio of 1.5 m^2/g and an average particle size of 44 μm. It was purchased from a local agent of Asbury Carbons, New Jersey. Multi walled carbon nanotubes (MWCNTs) NC 7000 type was purchased from Nanocyl, Belgium. The diameter is 9.5 nm, and length is 1.5 μm, with purity $\geq$90%, as reported by manufacturer.
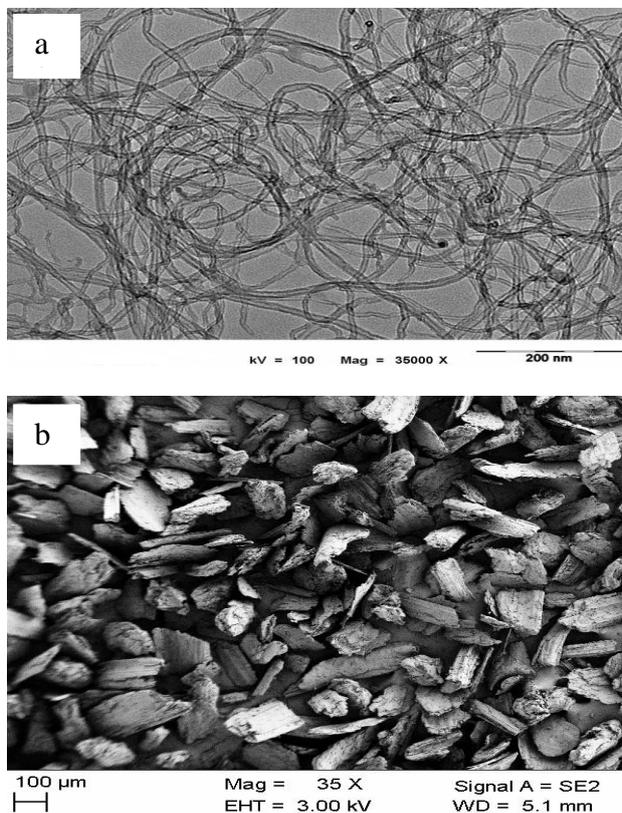

Figure 1 (a) TEM image of as received CNTs, and (b) SEM image of as received graphite

Figure 1 shows (a) TEM image of as received CNTs, and (b) SEM image of as received graphite. The epoxy resin is a bisphenol-A based epoxy resin (635 types), with viscosity 6 Poise, purchased from US Composites. The curing agent 4-Aminophenylsulphone was purchased from Fisher Scientific (M) Sdn Bhd, Malaysia. The curing agent is the diamine type (tetra functional) to facilitate rapid and dense cross-linking of epoxy resin. A lower viscosity of epoxy matrix was selected for better wetting conditions with conductive fillers. The epoxy and

curing agent were mixed at ratio 3:1 in wt.%. The mixture was mixed using a high speed mechanical mixer (RW 20-KIKA-WERK) at 1200 rpm for 40 s. Graphite with different loading concentrations were added into epoxy and curing agent mixture, then the suspension was mixed again at 1200 rpm for 3 min. CNTs/graphite/epoxy nanocomposites were prepared by adding CNTs with different mixture concentration into graphite/epoxy mixture. The mixture was mechanically stirred at 1200 rpm for 3 min, in order for the epoxy resin to intercalate inside the conductive fillers, especially into the graphite inter layers and pores. The composites mixture were poured into a steel mould for compression molding at different curing temperatures (80,100,120 °C) and curing pressures (5, 7, 8, 10 MPa) for 1.5 hours.

3. CHARACTERIZATION

3.1 Electrical Conductivity Measurement

The electrical conductivity of the nanocomposites were measured using a Jandel Multi Height Four-Point Probe combined with a RM3 Test Unit. It has a constant-current source and digital voltmeter. This equipment is able to measure sheet resistance in the range from 1mΩ/cm up to 5×10^8 Ω/cm and volume resistivity range from 10^{-3} to 10^6 Ω-cm.

3.2 Fracture Surface Morphology

Fractured surfaces of nanocomposites were observed by SEM to study dispersion and intercalation mechanism of conductive fillers in polymer matrix. Prior to SEM measurement, nanocomposites plates were cyro-fractured in liquid nitrogen to initiate brittle fracture and minimize fibers pull out mechanism.

4. RESULTS AND DISCUSSION

4.1 Electrical Conductivity of Graphite/Epoxy Composites

The variation of electrical conductivity of single filler epoxy composite as a function of the graphite loading concentration is shown in figure 2. The electrical conductivity of graphite/epoxy composite at 80 wt.% graphite loading concentration increased nearly 56% compared to 50 wt.% loading concentration. These data support the theoretical and experimental result reported by Lee *et al.* (2009) and Dweri & Sahari (2007), where the electrical conductivity of graphite/polymer composite is increase gradually with increasing graphite filler. This phenomenon shows that the graphite acts as the transfer medium for electrons hence the electrical conductivity of the composite would be increased. However, the electrical conductivity of the graphite composite is still low, reaching only 7 S/cm at loading concentration of 80 wt.%. Higher loading concentration of graphite is required to create a conductive path throughout the entire composite. This suggests that composites filled with graphite only are not suitable for the achievement of high electrical conductivity.
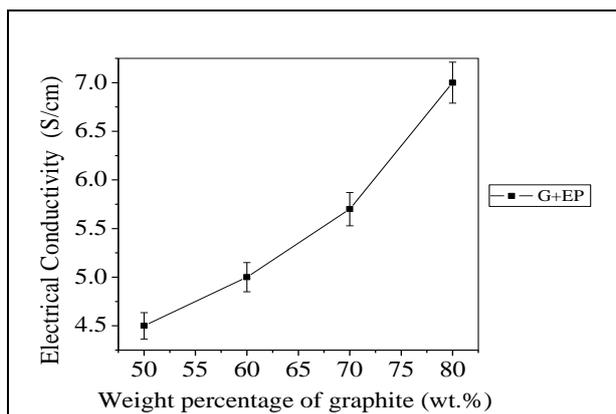
Figure 2 Electrical conductivity of composite in variation graphite/epoxy composition

4.2 Electrical Conductivity of CNTs/Graphite/Epoxy Nanocomposites

Clingerman *et al.* (2002) reported through a statistical analysis that the combination of multiple carbon based conductive fillers provided a synergistic effect, resulting in a significantly higher electrical conductivity than single filler polymer composite. Therefore, in this study CNTs was chosen as second filler to incorporate with graphite due to their excellent electrical conductivity (Ando *et al.,* 1999). The electrical conductivity of nanocomposites at fixed composition of epoxy (55 wt.%) and different loading concentration of graphite (40, 41, 42, 43 wt.%) and CNTs (2, 3, 4, 5 wt.%) is shown in figure 3. The electrical conductivity of the nanocomposites at 5 wt.% CNTs is 132% higher than that for 2 wt.% CNTs loading concentration. Furthermore, the electrical conductivity of the nanocomposites is 19 S/cm at 5 wt.% CNTs, which is approximately 200% higher than that of the graphite/epoxy composite (single filler). Results from figure 3 showed that the addition of the CNTs for hybrid nanocomposite from 2 to 5 wt.% enhanced the electrical conductivity compared to single filler nanocomposite. The gaps between graphite particles due to its flake liked geometry to be effectively filled with CNTs, which have smaller diameter and tube geometry. Thus, conducting networks are formed between CNTs, graphite and epoxy matrix. Synergistic effects of CNTs and other conducting fillers such as carbon black has been reported in reduction of the percolation threshold of hybrid filler polymer composites (Ma *et al.,* 2009 and Le *at al.,* 2008). The results of their study reported that there are still benefits that can be obtained by incorporating hybrid fillers way above the percolation threshold, even though the improvement in the electrical conductivity may not be in the order of magnitude scale. Results from Figure 3 confirmed that the incorporation hybrid conducting fillers with have different geometry and size capable introduce synergistic effects on the electrical conductivity of nanocomposites.
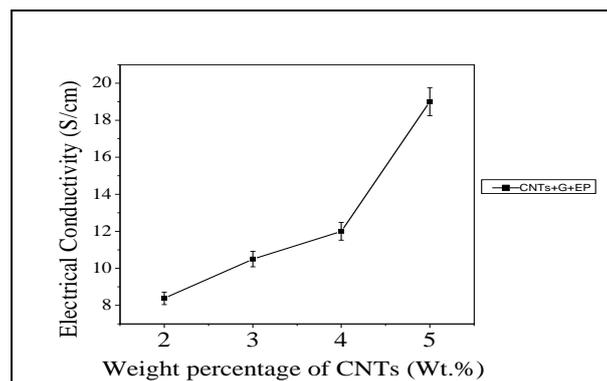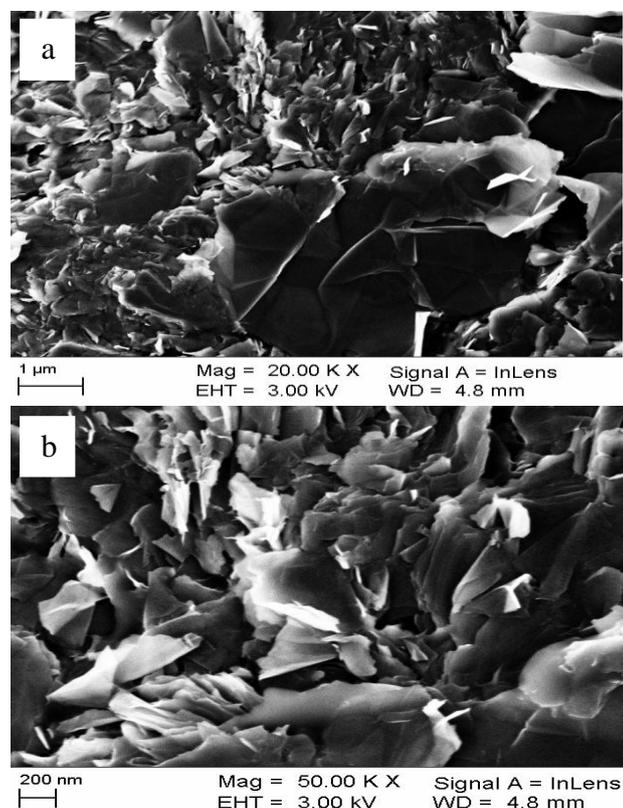

Figure 3 Electrical conductivity nanocomposites with variation composition of CNTs/G concentration

SEM images of graphite/epoxy composite and CNTs/graphite/epoxy nanocomposites are shown in figure 4. For single filler composite indicates that electrical conducting networks are well dispersed (figure 4a and 4b). For the composite with hybride fillers of CNTs and graphite, both well dispersed graphite and CNTs agglomeration can be observed (figure 4c and 4d) on the fracture surface (every bright spot depicts a CNT agglomerate). The CNTs used in this study is as produced MWNTs which easily entangle to form agglomerates due to the high aspect ratio of the individual CNTs. Once the filler loading concentration exceeds the percolation threshold, agglomerates can better improve the electrical conductivity than well dispersed CNTs (Xu *et al.,* 2002).
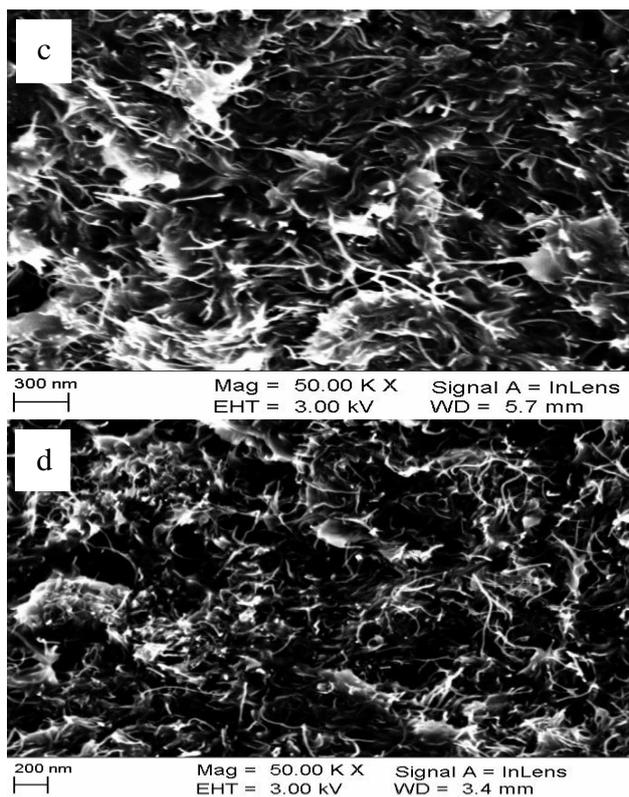
Figure 4 SEM images of fracture surface graphite/epoxy composite at (a) lower, and (b) higher magnification, and epoxy nanocomposites at (in wt.%) (c) 3/42/55 and (d) 5/40/55, respectively

4.3 Effect of Curing Temperature on Electrical Conductivity of Nanocomposites

High temperatures during the curing process are required to reduce the viscosity of epoxy resin in order to increase mobility of CNTs and graphite in the polymer matrix. This will increase the tendency of CNTs and graphite to interact with each other and form conductive filler networks. Composites with hybrid filler compositions of CNTs/G/EP respectively of 5/40/55 wt.%, 4/41/55 wt.%, 3/42/55 wt.% and 2/43/55 wt.% were fabricated. Three different curing temperatures namely 80^0C, 100^0C, and 120^0C was applied to each of the four compositions above. Figure 5 shows the results of this experiments where the electrical conductivity of the composites increased with increasing CNTs loading as expected. The highest electrical conductivity was achieved for the specimen cured at 120 ^{0}C where the electrical conductivity increased by 134% with an addition 5 wt.% of CNTs. The recommended cure temperature of the epoxy is 80^0C as suggested by the manufacturer. However, the high loading of the filler caused dissipation of epoxy to filler. Therefore, a higher curing temperature is required for epoxy to start cross linking with the curing agent. The curing temperature dependence of the network formation can be explained by considering the curing behaviour of the epoxy. The electrical conductivity at 120 ^{0}C curing temperature is increased by 45% compared to that cure at 80^0C. The higher the curing temperature, the lower the initial viscosity. Particle movement in the

dispersion is progressively enhanced in the curing temperature from 80^0C to 120^0C. It was reported by Martin *et al.* (2004) and Hu *et al.* (2008), the convection contributes to the formation of a macroscopic conductive network.
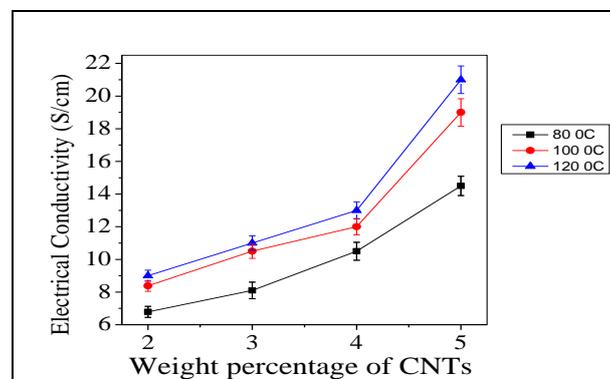

Figure 5 Electrical conductivities of CNTs/G/EP nanocomposites with contents (in wt.%) of (5/40/55), (4/41/55), (3/42/55) and (2/43/55), respectively for various temperature

4.4 Effect of Curing Pressure on Electrical Conductivity

High loading concentration of conductive fillers is required to obtain high electrical conductivity. However, high viscosity of the mixture of resin and fillers contribute to difficulties in processing and cause formation of voids (or air bubbles) in the final solid nanocomposites, especially if the filler loading concentration is higher than a critical volume concentration, known as the critical pigment volume concentration (Mehta & Copper, 2003). In theory, increasing the curing pressure of the mixture would cause more dense compact of mixture which would than contribute to an increase of electrical conductivity. Therefore, increased compression pressure was applied to eliminate these voids. The electrical conductivity of CNTs/G/EP at composition (1/59/40) and (2/68/30) nanocomposites at different curing pressure is given in figure 6. It revealed that the electrical conductivity sharply increase (400%) at curing pressure of 8 MPa compared to that fabricated at 5 MPa. The electrical conductivity of the nanocomposites slightly increase (1.8%) when the curing pressure increased above 8 MPa for the (2/68/30) composition. Similar to the (2/68/30) and (1/59/20) composition, the electrical conductivity sharply increased (420%) at curing pressure of 7 MPa but only slightly increased (3.8%) when the curing pressure was increased above 7 MPa. The electrical conductivity increased with increasing curing pressure due to the reduction of the contact distance between CNTs and graphite. At higher viscosity (70 wt.% filler concentration), higher curing pressure is needed to reduce distance between conductive filler, where it can be seen that the optimum curing pressure for the (2/68/30 wt.%) composition is higher than for (1/59/40 wt.%).
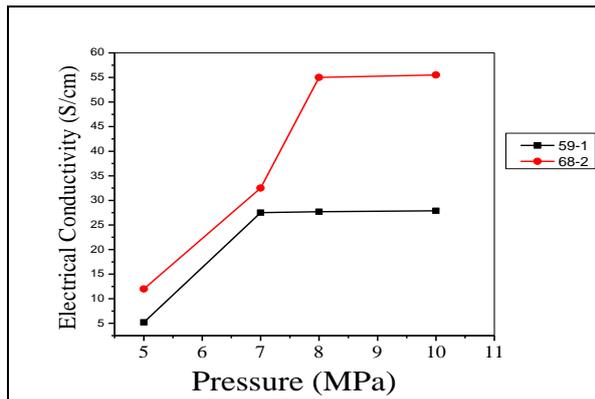
Figure 6 Electrical conductivity of CNTs/G/EP nanocomposites with contents (in wt.%) of 1/59/40 and 2/68/30, respectively

For comparison between 70 wt.% and 60 wt.% filler concentration, the 70 wt.% produced higher contact and higher curing pressure than 60 wt.% due to their shear force regime in order to minimize distance between conductive fillers. Voids or air burbles will were produced during the fabrication process and it will be increase with higher nano particles contents (Choi *et al.,* 2005). Low viscosity allowed epoxy resins and the curing agent to penetrate into the graphite and fill the micro pores of the graphite particles. In addition, the large pressure applied during the curing process led to the reduction of these voids. Boey & Lye (1992) utilised a compressive pressure in order to reduce the voids content. Increasing the curing pressure applied during fabrication resulted in lower voids content within the composite specimens (Olivier *et al.,* 1995; Boey & Lye,1992, Sudarisman & Davis, 2008), and this could be the reason why the optimum curing pressure on 70 wt.% conducting filler is higher than 60 wt.%. When the concentration of the filler is large (above the percolation threshold), conducting network of contacting particles appear and electrical conductivity of the nanocomposites are controlled by conductivity of the filler and contacts between them.

5. CONCLUSIONS

Effects of filler loading concentration, curing temperature and curing pressure on the electrical conductivity on CNTs/G/EP were investigated. Based on the results, the following conclusions are reached:
1. Incorporation of CNTs and graphite in hybrid nanocomposites give synergetic effect on the enhancement of the electrical conductivity compared to single filler composites.
2. Curing temperature contribute to reduction of resin viscosity, where enhanced mobility of multi-fillers in order increase possibility of electrical conductive pathway network. Thus, the electrical conductivity of nanocomposites are increased with increasing curing temperature.
3.   High Curing pressure during compression molding cause reduction and/or elimination of voids and

reduce contact resistance between multi-filler with polymer matrix. Thus the electrical conductivity of nanocomposites are increased with increasing curing pressure.

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