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# COMPARISON OF PROPERTIES OF MWCNT/CARBON FIBRE/ EPOXY LAMINATED COMPOSITES PREPARED BY SOLVENT SPRAYING METHOD

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## ABSTRACT

The incorporation of multi-walled carbon nanotubes (MWCNT) in laminated composites is believed to improve the mechanical and thermal properties of the composites. However, the nature of the MWCNT, which tend to agglomerate and form into ropes, restricts their dispersion in the composites. MWCNT-filled carbon fibre laminated composite was fabricated via hand lay-up followed by the vacuum bagging technique. MWCNT at different loadings of 0.5 to 1.0 vol% was dispersed by a solvent spraying method with two different dispersing agents, namely ethanol and Triton X-100. The flexural and thermal properties of the hybrid laminated composites were investigated. The CF laminated composites filled with 1.0 vol% of MWCNT dispersed in ethanol possessed better mechanical properties than other hybrid CF composites.

***Keywords***: Carbon fiber; multi-walled carbon nanotubes; flexural properties; thermogravimetry analysis

## INTRODUCTION

Owing to their remarkable mechanical properties as well as low densities, carbon fibre reinforced epoxy composites are extensively chosen for use in engineering applications [1-4]. On the other hand, very active research on CNT over the last decades has revealed the remarkable flexibility of CNTs, their low mass density and large aspect ratio (typically > 1000) [5, 6]. The success of carbon nanotubes (CNT) in improving the toughness properties of polymer has attracted increasing interest in their use as an additional reinforcement material in laminated composites [7].Though incorporation of CNTs has been reported to improve the toughness of composites, the fabrication of these laminated composites is constrained by the agglomeration of CNTs [8]. CNTs have a high tendency to form into bundles and ropes in the matrix due to their strong inter tube van der Waals forces [8, 9]. The CNTs agglomeration limits the load transfer process from the matrix to the CNTs; therefore the effective dispersion of CNTs in the matrix is vital [8]. In order to improve CNTs dispersion on the reinforcement, a solvent spraying method [2] was chosen, by which the CNTs were sprayed onto the fabric prior to hand lay-up. This study intends to fabricate hybrid laminated composites of carbon fibre (CF)/ epoxy incorporated with multi-walled carbon nanotubes (MWCNT) in the composite system by using the hand lay-up technique, followed by the vacuum bagging technique. The effects of the type of dispersing agents and filler loadings on the flexural and thermal properties of laminated composites were investigated.

## EXPERIMENTAL

### Materials

Carbon fabric type 5-harness satin weave with identical warp and fills yarns of 6000 multi-filament continuous tow was used as reinforcement. The fabric with a linear density of 369.58 g/m$^2$ was supplied by Fibre Glast Corporation. The D.E.N. 431 epoxy novolac resin and Polyetheramine D230 (supplied by Penchem Industries Sdn. Bhd.) were used as a matrix and curing agent, respectively. A resin and a curing agent, with a ratio of 100 to 32, were used in the study[10]. The MWCNTs used in this study were synthesized by a group of researchers from the Universiti Sains Malaysia. The highly pure MWCNTs (99.8%), with nearly uniform diameter average of 6.2 nm ± 0.5 nm (mean ± standard deviation), were synthesized over magnesia-supported Co-Mo bimetallic catalysts through catalytic chemical vapour deposition [11]. Ethanol and octyl phenol ethoxylate or Triton X – 100 (TX-100) at a concentration of 1% were used as dispersing agents.

### Methodology

A control sample of 4-ply CF/epoxy (4CF) was prepared using 4 pieces of CF with similar dimensions. The fabric was first weighed to determine the amount of epoxy matrix needed. The amount of epoxy matrix was fixed at 40 vol%. The predetermined epoxy resin was mixed with curing agent at a ratio of 100:32. The fabrics were then stacked together by applying the hand lay-up technique followed by the vacuum bagging method. The laminated composite was consolidated for 1 hour, then left overnight to cure before being subjected to a curing and post-curing process at 100 °C (1 hr) and 125 °C (3 hrs), respectively. The same procedures were repeated in preparing 5-ply CF/epoxy laminated composite (5CF). MWCNT-filled laminated composites were prepared by first incorporating MWCNT into the composites by the spraying method prior to the hand lay-up and vacuum bagging technique. The predetermined mass of MWCNT (0.5 vol%) was first ultrasonicated in 30 ml of ethanol in a cold bath for about 30 minutes. The prepared mixture was then sprayed onto 4 pieces of CF with the same dimensions. The fabrics were then left to dry at room temperature for about 4 hours to allow evaporation of ethanol. The dried fabrics were stacked up together with 40 vol% of epoxy matrix. The vacuum bagging, curing and post-curing process were carried out as mentioned previously. Samples with 1.0 and 1.5 vol % of MWCNT were dispersed in 60 and 90 ml of ethanol respectively. The same procedure was applied to prepare samples which used TX-100 as dispersing agent. The sample designations are shown in Table 1.

Table 1.Sample designations.

| No. | Sample | No. of CF layers | Epoxy (vol %) | CF (vol %) | CNTs (vol %) |
|---|---|---|---|---|---|
| 1. | Epoxy | - | 100 | - | - |
| 2. | 4CF | 4 | 40 | 60 | - |
| 3. | 5CF | 5 | 40 | 60 | - |
| 4. | 4CNT E0.5 | 4 | 40 | 59.5 | 0.5 |
| 5. | 4CNT E1.0 | 4 | 40 | 59.0 | 1.0 |
| 6. | 4CNT E1.5 | 4 | 40 | 58.5 | 1.5 |
| 7. | 4CNT T0.5 | 4 | 40 | 59.5 | 0.5 |
| 8. | 4CNT T1.0 | 4 | 40 | 59.0 | 1.0 |
| 9. | 4CNT T1.5 | 4 | 40 | 58.5 | 1.5 |

### Characterization

The flexural properties of 5 composites samples were tested according to ASTM D-790 using an INSTRON 5982. The specimens with dimensions 80 mm long × 17 mm wide × 2 mm thick with a 40 mm support span were loaded under three-point bending at a cross-head rate of 2 mm/min until failure [10].The density of 6 composite samples with dimensions of 10 mm × 10 mm was measured using a gravity balance, Precisa 8000, based on Archimedes' Principle. The average density was calculated[10]. Raw fabric samples sprayed with MWCNT were observed under a scanning electron microscope (SEM), FESEM/Zeiss Supra 35 VP. The thermal stability of the samples was measured through thermogravimetry analysis (TGA) using a Mettler Toledo, TGA/DSC Star$^{e}$ System Analyzer. A small piece of the selected sample was weighed and heated in a nitrogen environment from ambient temperature to 600 °C at a heating rate of 10 °C per min.

## RESULTS AND DISCUSSION

### Flexural Properties

Figure 1 demonstrates the flexural strength and modulus of the unfilled epoxy, the laminated CF composites and MWCNT-filled CF laminated composites. As expected, the flexural strength of 4CF was 25% lower than 5CF. This is due to the reduction of the fibre reinforcement that is present in the composite system. It is observed that composites prepared by solvent spraying with TX-100 possessed lower flexural strength than either 4CF or 5CF. The drop in the flexural strength might be due to the nature of the Triton X, which caused the surface between the carbon fabrics to become slippery [12-14]. Conversely, composites prepared by spraying with ethanol show improvements in flexural strength compared to 4CF. In comparison with 5CF, composites incorporated with 0.5 vol% MWCNT exhibit a flexural strength 5% higher than 4CF but 22% lower than 5CF. This observation shows that incorporation of 0.5 vol% MWCNT increases the flexural strength of 4-ply CF. However, the amount of MWCNT used was insufficient to increase the flexural strength compared to that of 5-ply CF. Incorporation of 1.0 vol% of MWCNT recorded the most significant improvement in flexural strength compared to both 4CF and 5CF. These hybrid composites exhibit flexural strength that is 135% and 75% higher than 4CF and 5CF, respectively. On the other hand, addition of a higher filler loading of MWCNT (1.5 vol%) caused a drop in the flexural strength compared to samples incorporated with 1.0 vol% MWCNT. This drop in flexural strength might be due to agglomeration of the MWCNT, which is observed in the SEM micrographs in Figure 2. Figure 2 shows micrographs of CF sprayed with 1.0 and 1.5 vol% of MWCNT dispersed by ethanol and TX-100 respectively. From Figure 2(a) – (d), it is proven that the higher filler loading caused MWCNT to agglomerate and thus reduced the flexural modulus. On the other hand, it is found that MWCNT dispersed in TX-100 also shows agglomeration at the higher filler loading.

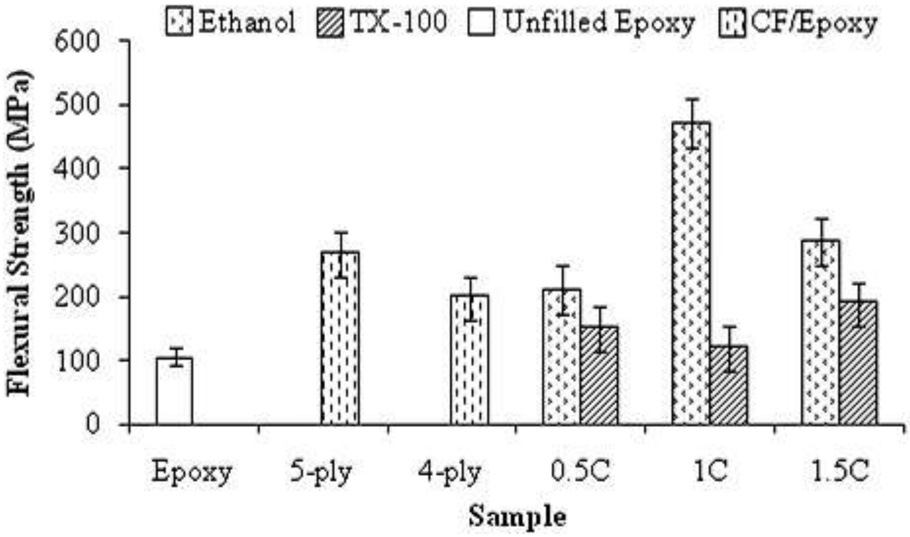

Figure 1. Flexural strength of the unfilled epoxy, the laminated CF composites and MWCNT-filled CF laminated composites.

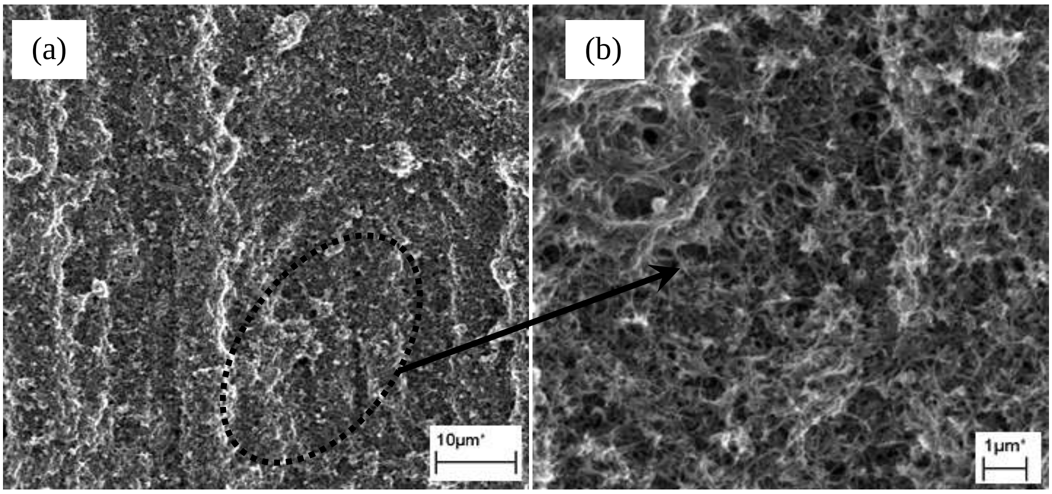

Figure 2. SEM micrographs of CF sprayed with MWCNT at different loadings using different dispersing agents: (a) and (b): 4CNT E1.0; (c) and (d): 4CNT E1.5; (e) and (f): 4CNT T1.0; (g) and (h): 4CNT T1.5.

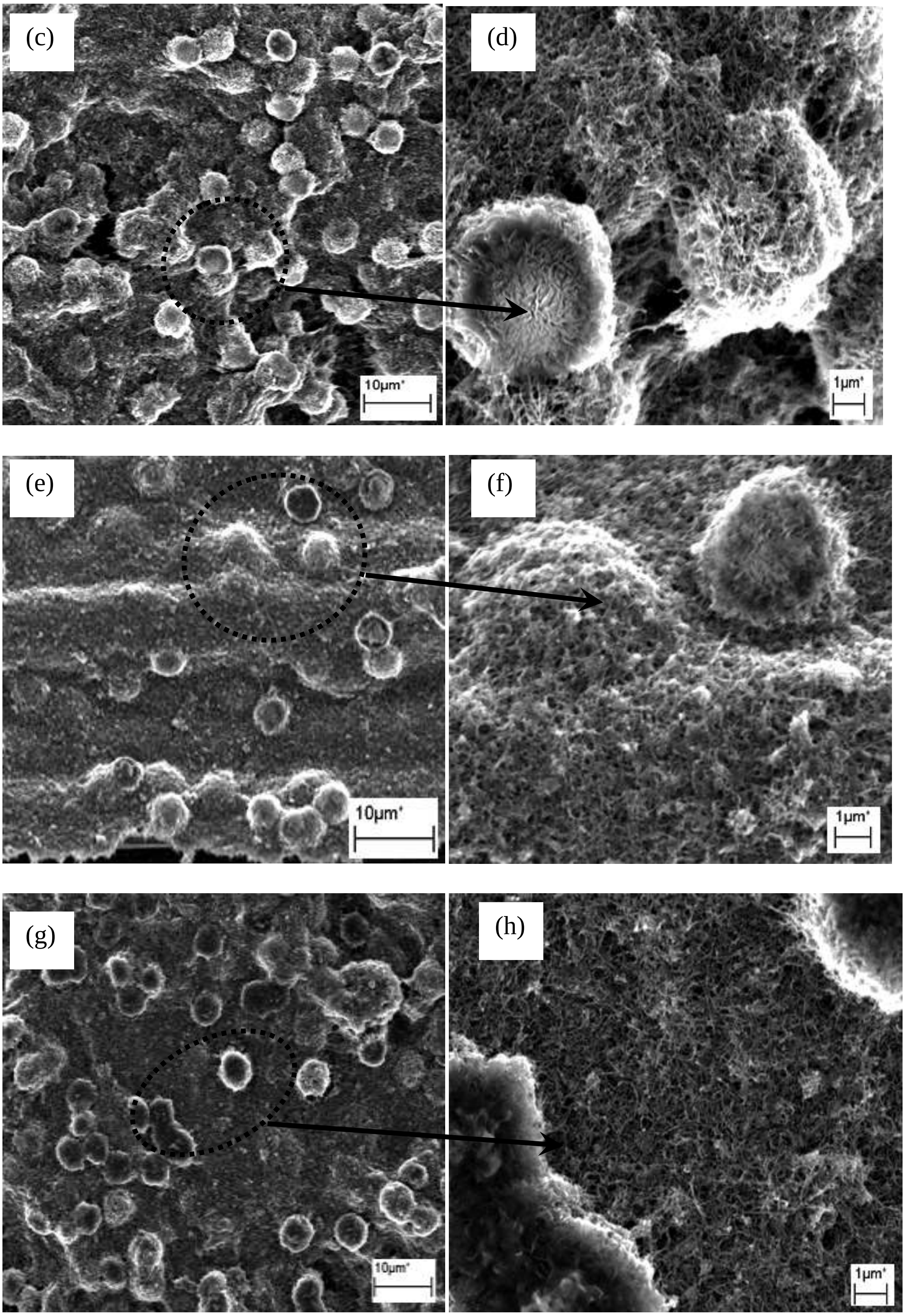

Figure 2.Continued.

Figure 3 demonstrates the flexural strength and modulus of the unfilled epoxy, the laminated CF composites and MWCNT-filled CF laminated composites. Reducing the number of CF from 5-ply to 4-ply caused a 19% reduction of flexural modulus.

Regardless of the vol% of the filler loading, composites incorporated with MWCNT dispersed by ethanol exhibit higher flexural modulus compared to 4CF. However, in comparison with 5CF, all the hybrid composite samples possessed lower flexural modulus except for composite laminates incorporated with 1.0vol% dispersed by ethanol. Comparing the hybrid samples dispersed by ethanol, it seems that the flexural modulus shows a similar trend to that for flexural strength. The flexural modulus dropped at higher filler loading (1.5 vol%). This observation is supported by the micrographs in Figure 2(a) – (d). The higher filler loading leads to agglomeration of the MWCNT and thus reduces the flexural modulus.

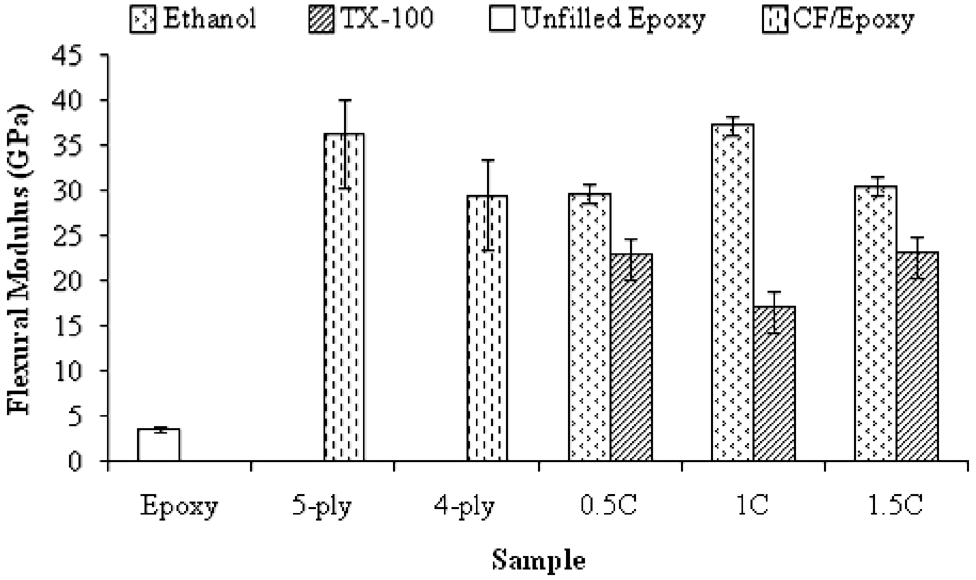

Figure 3. Flexural modulus of the unfilled epoxy, the laminated CF composites and MWCNT-filled CF laminated composites.

**Density**

Figure 4 shows the densities of the unfilled epoxy, CF/epoxy laminated composite samples and MWCNT-filled CF/epoxy laminated composites samples. As predicted, the density of 4CF and 4-ply MWCNT-filled CF laminated composites is lower than that of the 5CF samples. Samples incorporated with the same filler loading exhibit almost identical density regardless of the type of dispersing agent. Incorporation of MWCNT into 4-ply CF laminated composites caused the density to increase from4 to 7 % compared to 4CF. Gajendran and Saraswathy, (2008) also reported that the density of polyaniline-carbon nanotubes composites increased when CNT loading was added in the PANI-CNT system through the solution mixing method [15]. Ogasawara, Moon [16] also reported the same trend when aligned MWCNT was incorporated into epoxy [16]. However, the densities of these laminated composites are 3 to 7 % lower in comparison with the 5-ply CF. This observation indicates that a weight reduction can be achieved in the 4CF system.

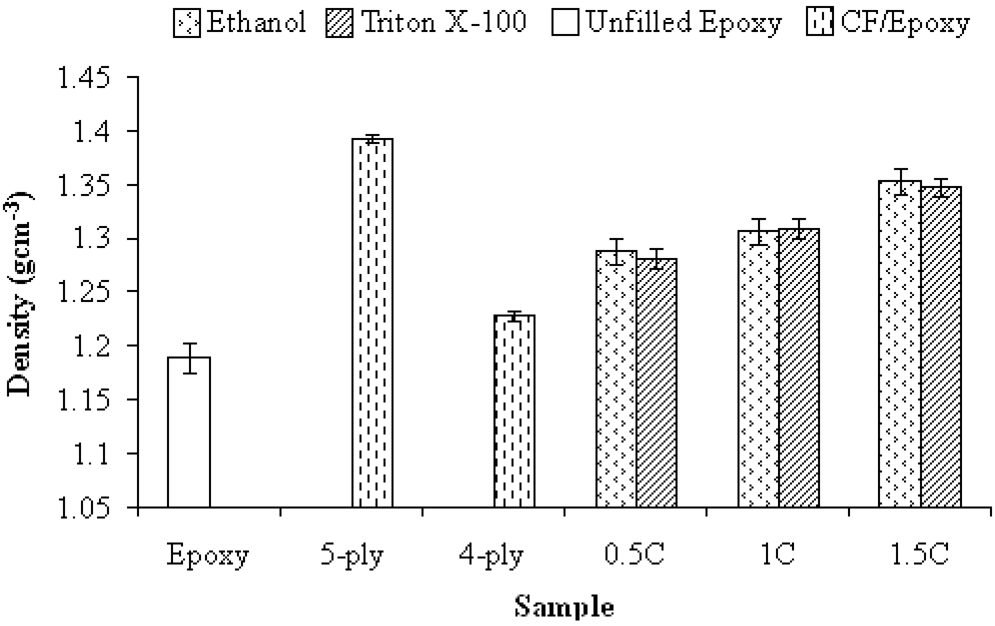

Figure 4. Density of the unfilled epoxy, CF/epoxy laminated composite samples and MWCNT-filled CF/epoxy laminated composites samples.

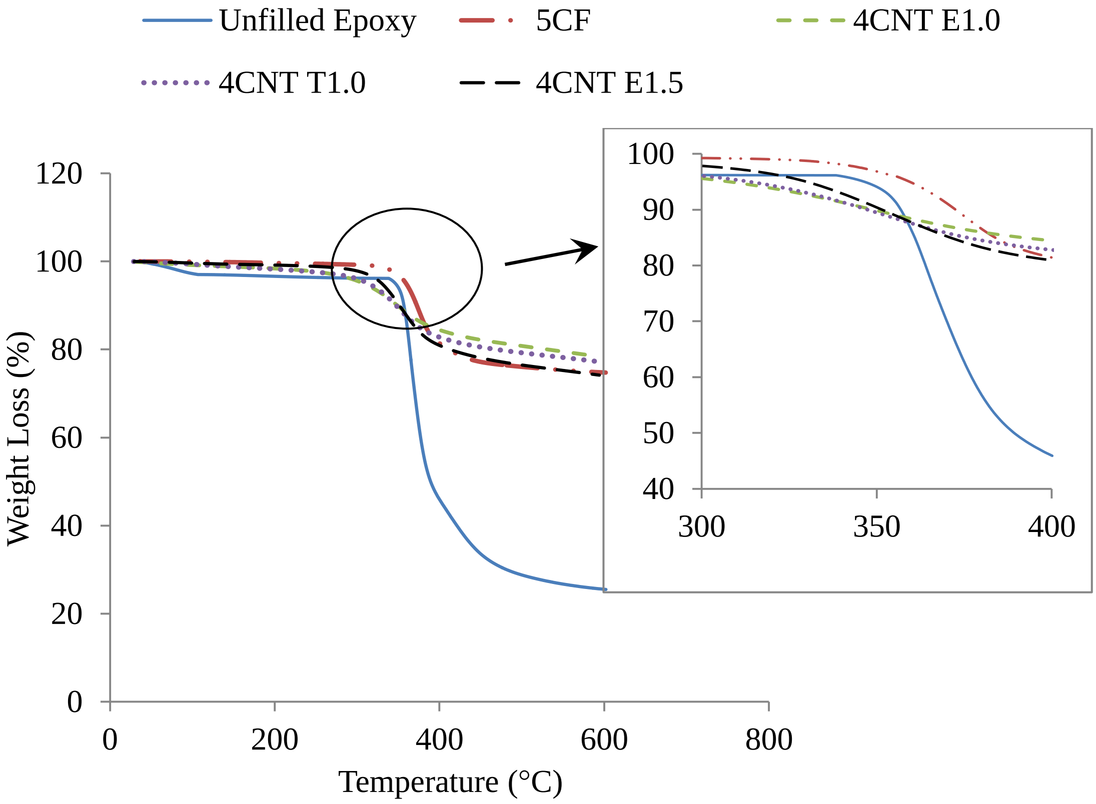

Figure 5. TGA curves of the unfilled epoxy, 5 CF and hybrid composites samples incorporated with 1.0vol% of MWCNT dispersed by ethanol and TX-100.

## Thermogravimetry Analysis

Figure 5 shows the TGA curves of the unfilled epoxy, 5 CF and hybrid composites samples incorporated with 1.0vol% of MWCNT dispersed by ethanol and TX-100. The TGA curves demonstrate single-step degradation. At 330 °C, the epoxy starts to decompose. 5CF exhibits thermal stability which is slightly higher than the samples incorporated with 1 vol% of MWCNT. On the other hand, it is observed that the thermal stability of composites incorporated with 1.0 vol% MWCNT dispersed by ethanol is almost identical to the composites filled with 1.0vol% MWCNT dispersed by TX-100. Comparing composites CF with MWCNT dispersed with ethanol, it is found that the thermal stability increases with the increasing filler loading. This observation is also in agreement with the observation reported by [16]. The presence of MWCNT produces a structured network layer which acts as a shield that re-emits much of the incident radiation back into the gas phase, thereby decreasing the degradation rate [17].

## CONCLUSIONS

Different types of dispersing agent affect the dispersion of MWCNT differently and thus affect the flexural and thermal properties of the laminated composites incorporated with MWCNT. On the other hand, the amount of filler loading also affects the flexural and thermal properties in different ways. A higher filler loading may lead to agglomeration of the MWCNT and thus have a negative impact on the mechanical properties, whereas the thermal properties of the composites increase with increasing filler loading. From the study, it can be concluded that 4-ply CF laminated composites incorporated with 1.0 vol% of MWCNT dispersed in ethanol exhibit better flexural properties compared to 5-ply CF. Judging from the discussion, we can conclude that the fabrication of light-weight hybrid composites with better mechanical properties is possible.

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