Thermal properties of nano-copper oxide reinforced epoxy composites

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Abstract - *The use of metal oxide fillers into polymer composite has been increasingly popular because of its ability to improve material properties. In this study, nano-copper oxide (nCuO) filler will be reinforced into epoxy matrix to form composites and then tested for its thermal properties. The aim of this study is to study the thermal stability of the composites so that it can withstand high operating temperature when used in electronic devices. The specimens are prepared using solvent casting method by mixing epoxy resin and hardener, then incorporating different filler contents of nCuO particles into the mixture. Thermogravimetric analysis and differential scanning calorimetry were conducted on three different specimens for thermal characterization of the materials. The addition of small amount of nCuO particles into the epoxy matrix has lowered the decomposition temperature and glass transition temperature of composites, hence decreasing its thermal stability making it less effective to incorporate into the epoxy for the use of electronic applications.*

Key Words: **Epoxy composite, nano-copper oxide, thermal analysis, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC)**

1. INTRODUCTION

Composites are material made from two or more constituent materials with significantly different physical or chemical properties, that when combined, create a material with characteristics distinctive from its individual components. Nanocomposites have a growing interest in the research and industrial sectors because of their attractive behavior in improving mechanical properties, increasing flammability resistant, and enhancing thermal properties. Polymer nanocomposites can be fabricated by hybridization of polymeric materials and nanofillers [1]. Nanoparticles have many significant properties due to their small size and high specific surface area [2].

Epoxy resin is one of the most used polymers in the manufacturing industry. Epoxy contains glycidyl groups that can be cured to form usable materials. It provides good chemical, moisture, and solvent resistance as well as good stability in mechanical and thermal properties [3]. Epoxy resins are increasingly used as matrices for a widespread application, for example, aircraft parts, printed circuit boards, surface coatings, structural adhesives, and engineering composites [4]. Epoxy is also extensively applied in electronic packaging. One of the many forms of epoxy employed in electronic packaging is as conducting adhesives. Here, metal fillers are incorporated into the epoxy.

The incorporation of nano-copper oxide reinforced into the epoxy is a potential alternative for the improvement of the thermal stability of epoxy composites. Metal or metal oxide nanoparticles have large specific surface area and high activity in most catalytic processes. It is noted that nanoparticles are not only effective in the catalytic processes such as gas-solid, gas-liquid or liquid–solid, where the nanoparticles as the catalyst are the solid phase, but also effective in the solid-solid catalytic processes [5]. Transition metal oxide nanoparticles exhibit a broad class of materials that have been investigated extensively due to their interesting catalytic properties and wide scope of their potential applications [6].

2. MATERIALS AND METHODS

Overview of the research methodology and materials is presented in this section. In this part, the standard experimental apparatus and procedures that were applied throughout the research work is described. Relevant information for certain scopes of experimental techniques, apparatus used and procedures will be shown when necessary.

2.1 Preparation and fabrication of nCuO reinforced epoxy composites

Epoxy resin (A) with hardener (B) type Bondite–8950 was purchased from AZ Usaha Dagang Enterprise, Malaysia and nano-copper oxide particles size 40-60 nm were used for the sample preparation. To prepare the composite, epoxy resin and its corresponding hardener are mixed at a ratio of 60:40 parts by weight. The measurement of the composite parts were employed using digital weight measurement and held as accurately as possible. The more exact the proportion, the more accurate the results. Table 1 depicts the theoretical mixing ratio for combination of epoxy resin and hardener with nCuO particle fillers with samples labeled as Ep, EnCuO-4, and EnCuO-8. The samples are casted into three different moulds using solvent casting method. Once the products are

dispensed into the mixing container, it is stirred manually and thoroughly for about a minute to disperse the resin and the hardener in the matrix. Thorough, careful and complete stirring of the mixture is important for proper curing. Finally, samples are left to cure under room temperature to stabilize the mixture and reduce air bubbles trapped on its surfaces. It is left in room temperature for 24 hours to let it cure completely. After samples are ready, it is cut into smaller pieces with equal sizes for thermal testing. Uniformity and homogeneity of composites are ensured when cutting samples.

Table 1: Theoretical mixing ratio for combination of epoxy resin and hardener with nCuO particles.

| Composite | Epoxy | | | | nCuO | |
| | Resin | | Hardener | | | |
Type of sample	Weight (wt%)	Weight (gram)	Weight(wt%)	Weight (gram)	Weight (wt%)	Weight (gram)
EP	60.0	14.40	40.0	9.60	0	0
EnCuO-4	58.0	13.92	38.0	9.12	4.0	0.96
EnCuO-8	56.0	13.44	36.0	8.64	8.0	1.92

2.2 Thermal analysis

TGA Q500, from TA Instruments, USA was used for performing thermogravimetric analysis (TGA) under nitrogen air flow. It measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. Measurements are used mainly to determine the characterization of materials and to predict their thermal stability. Materials that exhibit weight loss or gain due to decomposition, oxidation or dehydration is to be characterized. In this study, the nano-copper oxide reinforced epoxy composite is heated from room temperature up until 900°C with a heating rate of 50°C/min.

DSC Q200, from TA Instruments, USA was used for performing differential scanning calorimetry (DSC) under nitrogen atmosphere. Samples about 5–10 mg crimp are to be sealed in aluminum pans and heated from room temperature to 250°C at a heating rate of 20°C/min. Glass transition temperature, T_g can be determined by observing the graph of heat flow (w/g) against temperature (°C). Meanwhile, melting temperature, T_m, crystallization temperature, T_c, and degradation temperature, T_d, can be determined by observing the exothermic peaks and endothermic peaks of the graph. Thermal stability can be determined by measuring the degradation temperature of the reinforced composite.

3. RESULTS AND DISCUSSIONS

This segment explains about the results obtained from the thermal analysis conducted, which is TGA and DSC on nCuO reinforced epoxy composites samples. The results from the thermal analyses are discussed in detailed in this section.

3.1 Thermogravimetric analysis (TGA)

Figure 1 and 2 shows the TGA and DTG curves of epoxy with various compositions respectively as obtained from the TGA runs. The data from both curves were extracted and presented in Table 1. From Figure 1, it can be seen that the EnCuO-4 composite starts to lose weight earlier than other samples. This may be attributed to the higher in moisture content of EnCuO-4. Based on Monteiro et al., the initial drop in the TGA graph is usually disregarded by most researchers [7].

The peaks of the DTG curves correspond to the decomposition temperature of the samples. It was found that EP has the highest decomposition temperature at 340.31°C while the addition of nCuO fillers has shifted the curves to lower temperatures. For all the samples, there are two obvious slopes observed from the DTG curve. The first slope indicates the loss of moisture content while the higher peaks indicates the decomposition temperature of materials.
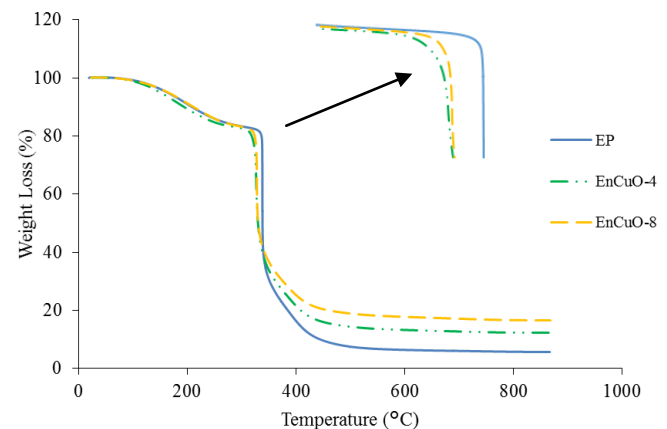

Figure 1: TGA curves of EP, EnCuO-4 and EnCuO-8.

The percentage of weight at 800°C reflects the amount of residues left after the samples were completely degraded. Epoxy has lowest residue due to the absence of char [7]. The amount of residue left after complete decomposition of samples increases with the incorporation of filler contents into epoxy. The higher the filler content, the higher the amount of residue that is left. This can be observed by the shift in graph in Figure 1. It can be highlighted that thermal stability of composites did not improved with addition of nCuO fillers, which is based on the drop in degradation temperature
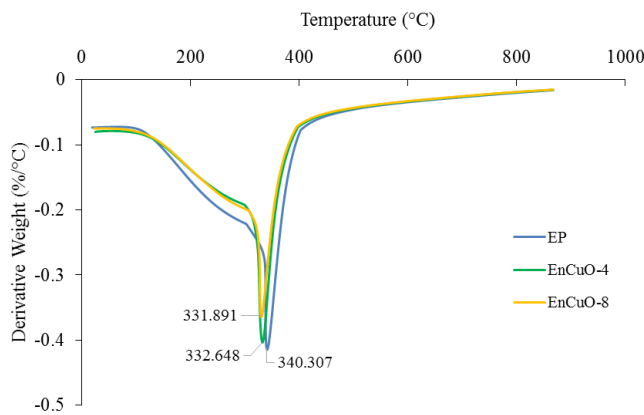
Figure 2: DTG curves of EP, EnCuO-4 and EnCuO-8.

3.2 Weight loss of samples at different temperatures

First of all, the first degradation curve of TGA graph in Figure 1 is analyzed. At the first degradation point, pure epoxy and nCuO-epoxy composites exhibited mass losses. This is due to the evaporation of moisture at around 70°C to 100°C. Moisture is removed through evaporation at 100°C. At this temperature, EP exhibited a weight loss of 3.79%, while EnCuO-4 and EnCuO-8 had 5.03% and 3.78% weight reduction respectively. Although weight loss due to moisture evaporation is small, voids caused by evaporated moisture might have an impact on thermal stability of composites.

Table 2: Summary data of thermal properties of EP, EnCuO-4 and EnCuO-8.

Samples	Decomposition temperature range (°C)	DTGmax (°C)	Tg (°C)	Maximum decomposition	
				Residue (%)	Weight loss (%)
EP	330 – 350	340.307	144.55	5.79	94.21
EnCuO-4	320 – 340	332.648	139.40	12.39	87.61
EnCuO-8	320 – 340	331.891	124.73	16.62	83.38

As observed on the TGA curve, there are still significant weight losses after 100°C found on the first degradation pattern. There may have been a lag of reduction of weight by moisture content, which is attributed by a thermal lag of sample temperature and oven temperature. Such lag is caused by the high heating rate of TGA apparatus when conducting experiment, as higher heating rates, in a study was said to have attributed to the increase of thermal lag on experimental temperature measurements [8]. This is known to be one of the sources of errors in TGA runs that can be reduced by lowering the heating rate of TGA apparatus when conducting the experiment to obtain more accurate results.

EnCuO-4 experienced higher weight loss than EP and EnCuO-8 at 100°C. This may be caused by a higher moisture content present in EnCuO-4 compared to the other samples. Poor interfacial adhesion between nano-copper oxide filler and epoxy causes void spaces in the composites which may also lead to higher water uptake [7]. This behavior can further be investigated using scanning electron microscopy.

Then, the decomposition temperatures of the samples is analyzed. This decomposition temperature is chosen based on the sample's major degradation that is when the samples begin to degrade most rapidly. From the graph plotted in Figure 1, it can be observed that the curve begins to drop rapidly between 320°C to 350°C. The decomposition temperature of EP is the highest at 338.22°C, while the decomposition temperatures of EnCuO-4 and EnCuO-8 are at 324.37°C and 327.08°C respectively. When added 4 wt% of nCuO into the epoxy, it was found that the decomposition temperature dropped to 324.37°C. However, when the filler content is increased to 8 wt%, the decomposition slightly increased back to 327.08°C but it is still found to be lower than neat epoxy. The decomposition temperatures of each samples are tabulated in the chart in Figure 3.
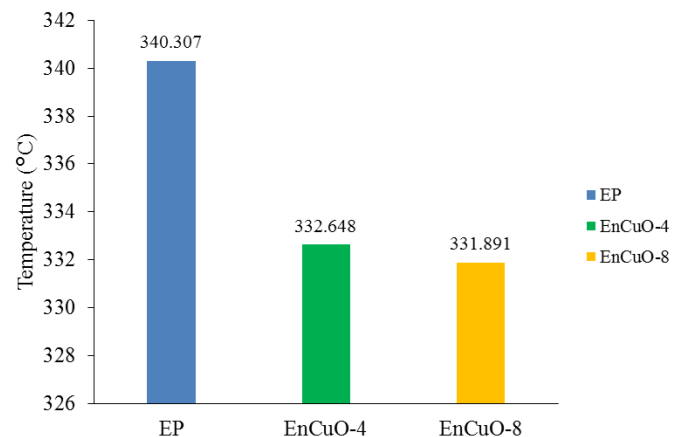

Figure 3: Decomposition temperatures (°C) of EP, EnCuO-4 and EnCuO-8.

The drop in thermal stability demonstrates poor interaction between matrix and the fillers. Besides that, it has been found in several studies that nCuO has acted as catalyst in composites, such as in a study conducted by Mostafa et al. where the decomposition temperature of ammonium perchlorate decreased with the addition of nCuO particles [9]. Thus, it is probable that nCuO filler have acted as catalyst in reducing decomposition temperature of the epoxy composites. However, when observing the derivative weight, the peak of EP is higher than its composites. This indicated that epoxy composites has higher residue compared to pure epoxy.

The higher amount of residues found in composites is due to the formation of precursor char similar to a previous study [10]. It was explained that the formation of char at earlier degradation stage delayed the further decomposition of epoxy at higher temperatures. It was discussed that char had retarded the transfer of heat and prevented the underlying

materials from further thermal destruction. The increase in residue of nano-copper oxide reinforced epoxy composites was due to the filler particles that constrained the motion of epoxy polymer chains which led to more residue formation. Besides that, nCuO particles acted as an insulator and mass transport barrier to volatile products generated during heating process at higher temperature ranges.

3.3 Differential scanning calorimetry (DSC) analysis

From the DSC test, a shift in heat flow can be observed on the samples. This indicates the glass transition temperature, Tg of the samples, where the material turns into its glassy state. The glass transition phase took place over a temperature range. The middle of the incline was roughly taken as the Tg.
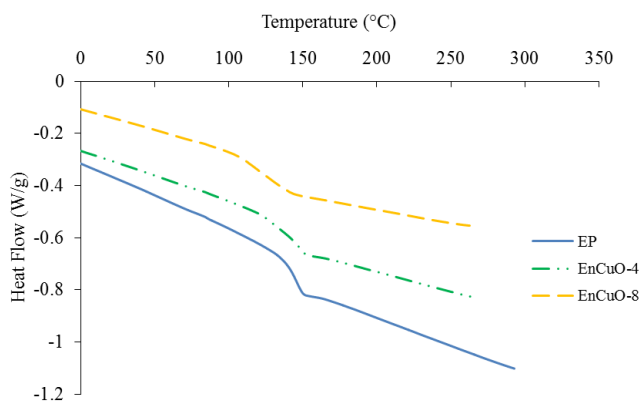

Figure 4: DSC thermograms of EP, EnCuO-4 and EnCuO-8.
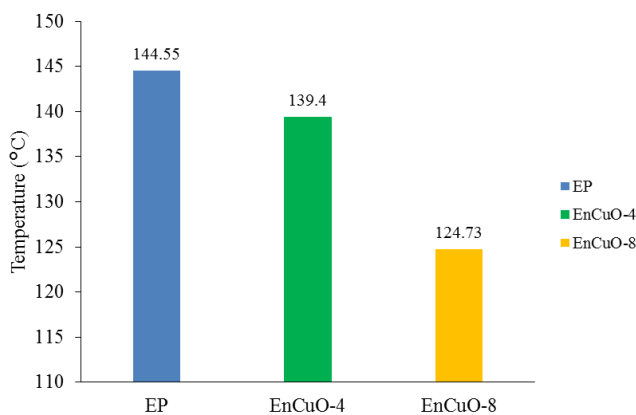

Figure 5: Glass transition temperatures, Tg (°C) of EP, EnCuO-4 and EnCuO-8.

As can be seen in the DSC thermograms in Figure 4, the Tg of the composites shifted to lower temperatures as it is added with nCuO fillers. The Tg of the samples are obtained by taking midpoint of the step transition and values are tabulated in the chart in Figure 5. Pure epoxy has the highest Tg at 144.55°C, followed by EnCuO-4 with Tg of 139.40°C and

finally, sample with the lowest Tg is EnCuO-8 that is at 124.73°C. The results from the DSC run correlates with the result from TGA, where the drop in Tg has caused the composites to have a drop in decomposition temperature. The lower Tg has made the epoxy composites to become less stable as it will undergo its glassy state faster when heated, making it less effective for nCuO to be employed into epoxy composites for the use of electronic applications.

As found in a studies by Chang-Hoon et al., a drop in the glass transition temperature of epoxy composites was due to the lower cross-link densities between filler and matrix [10]. It was explained that unhardened reactive matrices were found existed for higher filler contents. The mobility increased and the interface is weakened due to the cohesion of particles. Homogeneous dispersion of nanoparticles were also insufficient in large scales. However, after Chang-Hoon et al. introduced silane into its composites, the Tg of the composites improved considerably. This is due to the strengthening of coupling force between the nanoparticles and polymers with the addition of silane that in turn disrupted mobility and constrained the chains of polymer resins [10]. Hence, the addition of silane into nCuO-epoxy composites can be done in further research to identify if it improves the thermal stability of the composites.

4. CONCLUSION

Nano-copper oxide reinforced epoxy composites were successfully prepared by solvent casting method. The investigation conveyed on the thermal properties of nano-copper oxide reinforced epoxy composites such as decomposition temperatures and glass transition temperatures. EP, EnCuO-4 and EnCuO-8 were subjected to thermal degradation by means of TGA. Meanwhile, DSC runs were used to analyze the Tg. From this study, it can be concluded that the decomposition temperature and Tg of epoxy was found to decrease with the addition of nano-copper oxide fillers. The earlier Tg has caused the composites to decompose at an earlier temperature. The lower Tg of composite has made it less effective for epoxy to be employed in electronic applications as it will undergo its glassy state faster. The thermal stability of the composites did not improve by the addition of nCuO fillers. In fact, the thermal stability dropped further with the increase in filler content of nCuO into epoxy composites. This may be due to the catalytic action of nCuO, as found in previous studies. The final residue of the samples was lowest in pure epoxy in comparison to the nano-copper oxide epoxy composites. This is due formation of char in epoxy composites that has retarded the decomposition of the materials at higher temperature. The residue increased with the increased in filler contents.

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