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Thermal Properties of Epoxy Resin Reinforced Nano-Calcium Carbonate

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ABSTRACT

Polymer itself is a brittle materials and low of thermal properties. It cannot stand at high value of temperature and easy to soft or melt. Therefore, it is essential to improve the thermal properties of polymer. In this study, epoxy resin was reinforced with nano-calcium carbonate ($CaCO_3$) with different weight percentage (wt%) namely 0%, 2% ,5% ,7% and 10% respectively. Dispersion of nano $CaCO_3$ into the epoxy resin was observed from the scanning electron microscopy (SEM) micrographs. The thermal properties such as glass transition T_g, storage modulus E', and loss modulus E'', were investigated by using Dynamic Mechanical Thermal Analysis (DMTA) test. The integral procedure by using single cantilever beam mode of DMTA test with a constant frequency of 1 Hz and the temperature was ramped up at a constant rate of 2^0C/min from 25^0C to 100^0C. From the results obtained, it shows that epoxy resin with 7% content of nano $CaCO_3$ gives the best performance on the thermal properties. Both storage modulus and tan δ increased with increasing fillers from 0 wt% until 7 wt% and slightly decreased with 10 wt% of nano-calcium carbonate content.

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INTRODUCTION

Epoxy resins have been widely used as adhesives and coatings, as well as in structural applications. The unique properties of epoxy resin such as heat resistance, low shrinkage, high modulus and relatively high strength has made it one of the most important matrices used for such applications (Alamri *et al*. 2012; Jin *et al*. 2009). Despite the advantages, epoxy resin has weaknesses such as brittle at room temperature in the unmodified form (Long Jin *et al*. 2009).

In overcoming the weaknesses of epoxy resin, extensive studies done by scientists and researchers to improve the mechanical and thermal properties especially in making the resin tougher (Righetti *et al*. 2012). Improving the toughness of epoxy resins without affecting its important characteristics properties of the original epoxy resin is a major goal in developing these materials.

Introducing nanoparticles into epoxy resins is one of the methods used to improve their properties and expand applications in various areas especially in laboratory research and industry (Mohammad *et al*. 2012). There are several types of nanoparticles commercially available and regularly used for developing epoxy-nanocomposites for example, montmorillonite organoclay, nanosilica, carbon nanotubes and nanofibers (Jumahat *et al*. 2010). It has been well established that the addition of well dispersed nanoparticles in brittle epoxies can instantaneously increase their modulus of elasticity, yielding or tensile strength, ductility as well as plane strain fracture toughness (Tang *et al*. 2013).

Many researches have been reported on the incorporation of nanoparticles into epoxy. Hsieh *et al*. (2010) investigated the effect of adding silica nanoparticles to anhydride-cured epoxy polymer in bulk and found that the fracture energy of the bulk epoxy polymer was increased from 77 to 212 J/m^2 with the addition of 20 wt% of silica nanoparticles. Ferreira *et al*. (2013) analysed the influence of nanoclay reinforcement and water presence on the fatigue behavior of epoxy matrices, and reported that the fatigue strength of epoxy matrices decreased with the nanoclay incorporation into it.

In the study of resins and their applications, it is crucial to understand the concept of the glass transition temperature, T_g. The resin becomes more rubber-like as the temperature rises above the T_g, and the polymer becomes soft. Therefore, knowledge of T_g is important in the selection of materials for various applications. The use of thermal characterization studies in resin assists to determine

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the processing properties of the resin (Ahmad *et al*. 2010). According to the research done by Rodgers *et al*. (2005), 1 wt% content of silicon carbide nanoparticles derives the maximum improvement in both thermal and mechanical properties of epoxy resin. On the other hand, the study on the thermal properties of epoxy resin reinforced with $CaCO_3$ nanoparticles is still limited. Thus, this study investigated the thermal properties, as well as to evaluate the optimum glass transition T_g of epoxy resin reinforced with $CaCO_3$ nanoparticles with different percentages.

Experimental:

A. Materials

The main materials used in this study are epoxy resin and nano calcium carbonates. The resin comes in two parts which are the base resin, Asasin 8505 and the hardener, Asahard 8505. The resin was supplied by ASACHEM (M) SDN. BHD, Malaysia. R&M Chemicals supplied the calcium carbonates nanoparticles of size 20 nm. There were 5 percentages of nanoparticles used; 0%, 2%, 5%, 7% and 10%.

B. Resin preparation:

The resin was prepared in accordance with the manufacturers' instructions. Epoxy was added with nano $CaCO_3$ and stirred well using Daihan Scientific Ez HTS05 for approximately 10 minutes. This was done slowly and thoroughly to prevent bubbles. Then, hardener with ratio 2:1 (epoxy: hardener) was added and stirred again for another 5 minutes until the components were well blended.

Fig. 1: Perspex mould used in manufacturing the epoxy resin.

C. Preparation of resin specimens:

The resin that was prepared as in B was poured into a Perspex mould of size 80 mm x 20 mm x 3 mm (Fig. 1). Release agent, Freekote 700-Nc was applied onto the mould before pouring the resin to prevent the specimen from sticking onto the mould as well as to ease the process of demoulding the specimens. After pouring the resin into the mould, another glass plate was placed on top of the mould in order to achieve a flat surface. The resin was then left for 24 hours to cure. When cured, the specimens were cut into plates of 20 mm length, 5 mm wide and 3 mm thick according to BS ISO 6721- 11: 2012. Three (3) replicates were manufactured for every percentage of $CaCO_3$ nanoparticles. The prepared specimens are shown in Fig. 2.

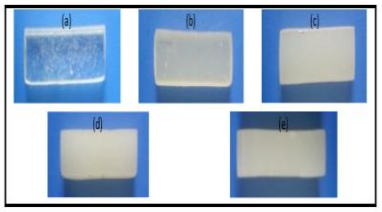

Fig. 2: Prepared specimens with different percentages of $CaCO_3$ nanoparticles; (a) control, (b) 2%, (c) 5%, (d) 7 %, (e) 10%.

D. Bulk density test:

The bulk density, ρ of the specimens were determined using electronic balance for every weight percentages of nano $CaCO_3$ using SHIMADZU UX4205 Electronic Balance.

E. Thermal analysis of epoxy resin:

The thermal properties analysis of epoxy resin were done using Mettler Toledo DMTA Analyzer. Dynamic mechanical thermal analysis (DMTA) was used to determine the thermal properties of epoxy resin specimens. The DMTA test will impose a small oscillatory deformation which generates viscoelastic properties to the resin such as the storage modulus, E', loss modulus, E'' and the mechanical loss, tan δ. From the loss modulus obtained from DMTA test, a quantitative method was used for the identification of mechanical relaxation temperatures of glass transition, T_g was determined.

The sample of size mentioned in C was gripped between two clamps as a cantilever beam in the DMTA system. Single cantilever bending mode was used (Fig. 3).

Fig. 3: The single cantilever mode for DMTA test.

A sinusoidally alternating force was applied to the end of the cantilever beam. A single thermal scan method was used with a constant frequency of 1 Hz and the temperature was ramped up at a constant rate of 2°C/ min from 25°C to 100°C.

F. Scanning Electron Microscopy:

Scanning electron microscopy was employed to observe the dispersion of $CaCO_3$ nanoparticles in the epoxy resin. The equipment used was NETZSCH Scanning Electron Microscope.

RESULTS AND DISCUSSION

G. Bulk density of epoxy resin:

The average density were calculated and listed in Table I. From the result, it can be seen that the density of filled resin was slightly increasing. This is because the $CaCO_3$ added was in nano-sized thus it is very light in weight. However, the addition of nanoparticles assisted in filling the pores so that the resin is more compacted.

Table 1: Bulk density of epoxy resin.

Percentage of Calcium Carbonates Nanoparticles	Density, ρ (g/cm^3)			
	Test 1	*Test 2*	*Test 3*	*Average*
0 (control)	1.0963	1.1133	1.1311	1.1136
2	1.2318	1.0990	1.2142	1.1817
5	1.2064	1.2105	1.2234	1.2134
7	1.2238	1.2385	1.2355	1.2326
10	1.2224	1.2230	1.2440	1.2298

H. Surface morphology of epoxy resin:

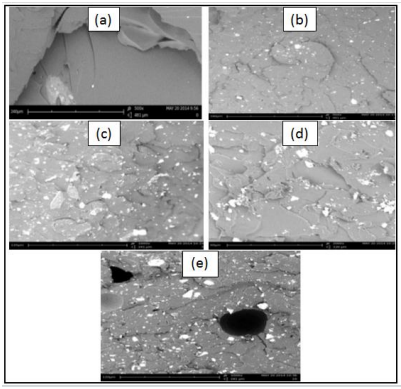

Fig. 4: The dispersion of nano $CaCO_3$ in epoxy resin with different weight percentages; (a) control, (b) 2%, (c) 5%, (d) 7 %, (e) 10%.

Figure 4 shows the general surface morphology of epoxy resin with different weight percentage of nano $CaCO_3$. The surface of the resin appeared to be coarser as the weight percentage of nano $CaCO_3$ increased. The voids seen in these micrographs were associated with air bubbles.

I. Thermal properties of epoxy resin:

On the first trial, one of the sample was tested within a temperature range from 25^{o}C to 180^{o}C, but at 80^{o}C the graph of storage modulus E', has dropped significantly to almost 0 MPa. Thus, the test was run only at temperature range from 25^{o}C to 100^{o}C.

The storage modulus E' represents the elastic component of stiffness and values are not constant in the glassy region but slightly decrease with temperature. As pointed out by Lewis and Nielsen (1970), the residual stress field due to different thermal expansion coefficients of the matrix and filler may induce relaxations in the polymeric phase which account for the negative slope of E' versus temperature in the glassy region. According to Mohd Ishak and Berry (1994), relaxation is assigned to the breakage of hydrogen bonds between the polymer chains which induces long range segmental motion in the amorphous area.

It can be observed that, in Fig. 5, generally the dynamic mechanical behaviors of the five resins are similar. The whole curve of the dynamic storage modulus versus temperature consists of three stages. The stages are; glassy (0 – 44^{o}C), viscoelastic (44 – 58^{o}C) and rubbery (58 – 100^{o}C). In the first stage, the resin had high range of stiffness while in the second stage, the molecular chains started to move freely, and the dynamic modulus decreases rapidly to 100 MPa. In the third stage, molecular deformation is dominated by viscous flow and the dynamic modulus fell to a value close to zero.

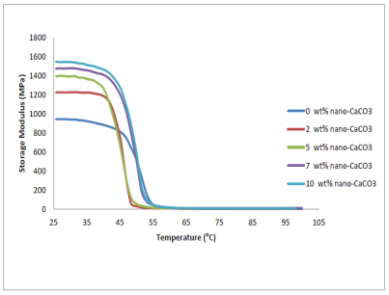

Fig. 5: Storage modulus for epoxy resin at different weight percentages of nano $CaCO_3$ as a function of temperature.

It is seen that, on the whole, the dynamic mechanical behavior of the five resins is similar. The differences are in the low temperature modulus and the temperature of the main transition from elastic to viscoelastic behavior, which are related to the types of nano-calcium carbonate addition.

From the storage modulus (E') versus temperature curve, T_g is defined here as the onset value. T_g is the temperature of the material just before it became viscoelastic property and loosing into elasticity hence losing its strength. Therefore, it is important to determine the T_g. A summary of the T_g values based on the onset E' value from the curves was shown in Table II and Table III.

Table 2: Storage Modulus Of Epoxy Resin.

Percentage of nano calcium carbonate (%)	Storage modulus E' (MPa)			
	Test 1	*Test 2*	*Test 3*	*Average*
0 (control)	944	853	928	908
2	1225	1500	1172	1299
5	1393	1319	1940	1550
7	1528	1475	1619	1540
10	1576	1547	1341	1488

Table 3: Glass Transition of Epoxy Resin.

Percentage of nano calcium carbonate (%)	Glass transition, T_g (^{O}C)			
	Test 1	*Test 2*	*Test 3*	*Average*
0 (control)	48.593	48.262	48.178	48.342
2	52.286	51.649	52.563	52.166
5	52.718	51.807	52.465	52.330
7	54.964	55.902	55.871	55.579
10	54.979	56.170	55.321	55.490

The T_g were increased from 48.34^{o}C to 55.58^{o}C and drop slightly to 55.49 ^{o}C with 10 wt % of nano-calcium carbonate. However, its T_g value was higher than neat epoxy resin. The addition filler to the epoxy resin can decrease the free space between the macromolecules which effects in decreasing of rotation or movement in the composites (Poletto *et al*. 2013). Therefore, the study show epoxy resin contains with 7 wt% nano-calcium carbonate has the optimum value of T_g. According Long Jin *et al* (2009), the thermal properties increased by increasing the fillers but if the thermal properties were not significantly varied they may due to the uncompleted dispersion at high content of fillers.

From the table II and III, both results of storage modulus, E' and glass transition T_g, had the same pattern with the result of bulk density (Table I). All the values increased up to 7% of nano $CaCO_3$ content, and dropped at 10% of nano $CaCO_3$. The thermal properties increase with the increment of bulk density.

The highest temperature for Malaysia's climate was about 40.1^{0}C, but the optimum T_g from this study is 55.579^{0}C with 7 wt % of nano-calcium carbonate. Therefore, the using epoxy resin reinforced with nano-calcium carbonate is suitable for Malaysia's climate.

Conclusion:

The following conclusions can be drawn from this study:

- The epoxy resin obtained the highest density with 7% nano $CaCO_3$.
- SEM test shows that the higher contents of nano $CaCO_3$ in the epoxy resin, the coarser the morphology surface.
- The result for thermal properties showed that the value of storage modulus E', increased with increasing weight percentage of nano $CaCO_3$.
- The glass transition T_g of epoxy resin is the highest with 7% nano $CaCO_3$ with 55.579^{o}C.

From the study, it showed that 7% content of nano $CaCO_3$ is the best percent value to improve the thermal properties of epoxy resin.

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