



Development and characterization of epoxy nanocomposites based on nano-structured oil palm ash



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ABSTRACT

The aim of this study is to utilize the bio-agricultural waste as filler material for composite production which are abundantly available and low cost compared to the silica, alumina etc. The lacks of sufficient scientific information about the utilization of the oil palm ash (OPA) on composites production were the driving force for the choice of this work. Furthermore, the effect of filler loading percentage on physical, mechanical, thermal and morphology properties of the epoxy nanocomposites were studied. It was concluded that the size of the OPA had been successfully reduced from macromolecular to the nano-size range by high energy ball milling and was confirmed by TEM analysis. The density of the nano-structured OPA filled epoxy composites revealed that increasing filler loading will eventually increase the density. The tensile and flexural strength attained maximum value when the filler loading was 3%. Also, increase in the thermal stability was observed in case of 3% filler loading and was attributed to the increase in cross-linking of the epoxy resin in the presence of nano-structured OPA and having minimum particle to particle interaction and well dispersed nanoparticles.

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1. Introduction

Towards the sustainable economic growth and higher human development, affordable products with advances properties are essential. Thus, the utilization of waste materials which are abundant and cheap, especially from clean resources, has become more pressing than ever especially oil palm biomass. It is estimated that the total potential oil palm biomass from 4.69 million hectares of oil palm planted area in Malaysia in 2009 is 77.24 million tonnes per year comprising 13.97 million tonnes of Oil Palm Trunks (OPT), 44.84 million tonnes of Oil Palm Fronds (OPF), 6.93 million tonnes of Empty Fruit Bunches (EFB), 4.21 million tonnes of Palm Kernel Shell (PKS) and 7.29 million tonnes of Mesocarp Fiber (MF) (all dry weight) [1]. Currently, oil palm biomass is mostly used for the purpose of compost and fertilizer, mulching mats, plywood and veneer from OPT, oil palm fiber-filled automotive upholstery parts, dampening sheets for automotive industry using oil palm fibres, molded particleboard, pulp and paper from EFB, molded pulp products for food packaging, containers from EFB, medium density boards, furniture, oil palm lumber, activated carbon, and compostable plastic film. But these biomasses are still often used as boiler fuel by palm oil mill plants to produce steam for electricity generation [2] and after combustion in the steam boiler,

there is approx. 5% of ash being produce [3] and generate another solid waste.

Oil Palm Ash (OPA) is an abundant agricultural solid waste in Malaysia. This bio agricultural waste ash which the source of siliceous material is produced after the combustion of oil palm fiber, shell, EFB and mesocarp as boiler fuel to produce steam for palm oil mill consumption. Although there are some studies on the utilization of OPA such as a cement replacement material [4], as an adsorbent for the removal of zinc from aqueous solution [5] and flue gas desulphurization [6], most of the ash is still disposed off in landfill that requires a lot of land area and will causing environmental problems. Also oil palm ash was developed as a nano-structured material to be used as a universal filler [7] Thus, creating, manipulating and exploring OPA in nanotechnological research as nano structured material will create an advance bio agricultural waste material.

In the last decade, nanocomposite materials consisting of a polymeric matrix materials and nanomaterial/nanofillers have attracted scientific and industrial interest ranging from high barrier packaging for food and electronics [8] to automotive and aerospace applications [9] due to their improved properties. At low filler contents as compared with the conventional micro and macro or neat counterparts, they exhibit superior property enhancements (improved mechanical and thermal properties, gas permeability resistance and fire retardancy).

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The potential of OPA as a new filler in composites had been studied by several researcher; [10–13]. The utilization of this solid waste as filler in polymer composites is very important, firstly as wastes are available abundantly at no cost; secondly, as the disposal of this waste poses an environmental problem. In most cases, the mechanical, thermal, physical and morphological properties of the composites varies upon the incorporation of OPA into the composites system, such as filler loading [11,12], effect of compatibilizer with OPA, and structural size of OPA [13]. However, there is no report available on the utilization of OPA as nanofiller in the epoxy matrix system.

2. Materials and methods

The epoxy resin D.E.R 311 used in this study is a general purpose liquid resin, clear epoxy resin which is based on diglycidyl ether of bisphenol A (DGEBA) was obtained from GT Instruments Sdn. Bhd., Malaysia.

The curing agent, epoxy hardener (A 062) was also supplied by Zarm Scientific & Supplies Sdn., Malaysia. Epoxy hardener (A 062) is a reactive polyamide of low molecular weight. A non reactive diluent (benzyl alcohol) was supplied by Aldrich Company.

OPA was provided from an incinerator at palm oil mill at Ulu Keratong, Segamat, Johor, Malaysia.

2.1. Composite density determination

Composite density was measured by using ASTM D1895 standard. The density of the samples was calculated by using Eq. (1) below.

$$\text{Density (gcm}^{-3}\text{)} = \frac{m}{v} \quad (1)$$

Where, m is the mass of the composites (g), v is the volume of composites (m^3). Five samples of each different types of composite were used and the average value was reported.

Mass determination was carried out by weighing the composites to four decimal places on an analytical balance (Mettler 5000). For volume determination the samples were measured by using a digital veneer calliper (Mitutoyo). All samples were oven dried at 50 °C for 24 h. After oven drying the samples were cooled in desiccators over granulated silica gel before mass and volume determination was conducted.

2.2. Void content of composites

For determination of voids content in composites, ASTM D2734 method was used. The void content was determined from the theoretical and experimental density of the composites through Eq. (2)

$$\text{Void Contents (\%)} = \frac{\rho_{\text{theoretical}} - \rho_{\text{experimental}}}{\rho_{\text{theoretical}}} \quad (2)$$

where $\rho_{\text{theoretical}}$ is the $\frac{1}{\left[\frac{W_f}{\rho_f} + \frac{W_m}{\rho_m}\right]}$, W_f is filler weight fraction, W_m is matrix weight fraction, ρ_f is filler density, and ρ_m is the matrix density.

2.3. Water absorption test

The composite samples were immersed in distilled water at room temperature. The water absorption was determined from Eq. (3) for various periods of times. Samples were weighed and weight of the samples was determined before and after removing from water at various time intervals. After the samples were removed, they were gently blotted with filter paper to remove excess water on the surface, and the weight of the samples was recorded. The water absorption test was continued for several days until the

constant weight of the samples was obtained. The percentage equilibrium water absorption was calculated as an average value of several measurements. The percentage of water absorption was calculated from Eq. (3) using ASTM D570.

$$\text{Water absorption (\%)} = \frac{W_n - W_d}{W_d} \times 100 \quad (3)$$

where W_n is the weight of composites samples after immersion, and W_d is the weight of the composite samples before immersion.

2.4. Tensile test

In the present work, the tensile strength, modulus and elongation at break of nano-structured OPA filled epoxy composites were measured by using Gotech Universal Testing Machine (GT-A1-7000I). This test was conducted as per the ASTM D 3039 specifications.

2.5. Flexural test

Flexural analysis was carried out at room temperature through three-point bend testing as specified in ASTM D790, using Gotech Universal Testing Machine (GT-A1-7000I).

2.6. Scanning electron microscopy (SEM)

Morphology of nano-structured OPA and the composites was investigated by using scanning electron microscope (Carl Zeiss EVO MA-10, U.K). The fracture surfaces of composites obtained from impact testing were sputter with gold prior to their morphological observation.

2.7. Thermogravimetric analysis (TGA)

A Perkin Elmer thermal gravimetric analyzer (TGA-6) was used to investigate the thermal stability of the composites. The powder of composites, and neat epoxy (about 4–5 mg) were heated from 30 to 800 °C under nitrogen at a heating rate of 20 °C/min.

2.8. Transmission electron microscopy

Transmission electron microscopy (TEM) was carried out with a Philips CM12 instrument. The transverse sections of thickness 1 μm were cut using Sorvall Ultra microtome (MT 500) with a glass and diamond knife.

3. Preparation of nano-structured OPA filled epoxy composites

Nano-structured OPA filled epoxy composites were prepared by loading 0%, 1%, 2%, 3%, 4%, and 5% of nano-structured OPA (based on wt% of resin) into epoxy resin.

Prior to nanocomposite development process, the nano-structured OPA was dried at 90 °C for 8 h and let cooled in the desiccator containing silica gel to prevent moisture absorption. For the development of composite material, a stainless steel mould with dimensions of 160 mm \times 160 mm \times 3 mm was used. The epoxy resin was mixed with 10% diluents (benzyl alcohol) to decrease the viscosity, and was then loaded with the desired amount (0%, 1%, 2%, 3%, 4% and 5%) of nano-structured OPA at room temperature for 30 min using a mechanical stirrer. Then, a stoichiometric ratio (60 parts curing agent: 100 parts epoxy by weight) of the polyamide curing agent was maintained, the mixture was once again mechanically stirred for 10 min. The mixture was outgassed in vacuum chamber to remove bubbles. The blend was then casted into a mould and the nanocomposite materials were left to cure at

105 °C for 1 h in a hot press (Gotech Hot Press-Gt-7014) at a pressure of 200 Psi as per supplier specification. Once the composite was cured, the composite sample was removed from the mould and followed by post curing in an oven (Gotech Drying Oven-Gt-7024) at 105 °C for 30 min.

4. Results and discussion

4.1. Physical properties

To evaluate physical properties of the nanocomposites developed in this study, density, void content, and water absorption measurement were performed. The physical properties of nano-structured OPA filled epoxy composites were investigated to determine the effects of nano-structured OPA as filler and the effect of filler loading.

4.1.1. Density

Table 1 shows the theoretical and measured densities of nano-structured OPA filled epoxy composites with different filler loading along with the void content percentage. From Table 1, it is clear that epoxy had an average theoretical and measured density of 1.14 g/cm³ and 1.118 g/cm³ respectively. After incorporating nano-structured OPA, an increase in the density of the composites was observed. This increase in density of the composites is attributed to the incorporation of high density nano-structured OPA (2.33 g/cm³) in low density epoxy matrix. The density values of the composites increases with increase in filler loading and it lies in the range of 1.118–1.145 g/cm³. Density of a composite depends on the relative proportion of matrix and reinforcing materials and this is one of the most important factors determining the properties of the composites.

4.1.2. Void content

The result from Table 1 also showed the composite density values calculated theoretically from weight fractions using Eq. (2) are not equal to the experimentally measured values. This difference is a measure of voids present in the composites. The void content of the composites lies in the range of 1.383–2.126%. As the filler loading increases from 1% to 5%, the percentage of voids is found to be increasing. It is clearly seen that with the addition of filler, more voids are found in the composites. The void content is the cause for the difference between the values of true density and the theoretically calculated one. Void formation in polymer composites attributed to the processing effect which arise from several sources such as air bubble entrapped within epoxy matrix, residual solvent and volatile arises during curing of the resin [14]. The voids significantly affect some of the mechanical properties and even the performance of composites in the workplace. Higher void contents usually mean lower fatigue resistance, greater susceptibility to water penetration and weathering resistance.

Nanoparticles/nanofiller tend to act as fillers in the voids, which in turn reduces the void content of the composites and thus translates into enhanced mechanical properties [15]. From the result,

incorporating nanofiller from 1%, 2%, 3%, and 4% filler loading reduce the void content by 28%, 20%, 16% and 7% respectively to the neat epoxy composites. While when incorporating 5% filler loading, the void content of the composites (2.126%) is much higher than void content of neat epoxy composites (1.930%). Thus, there is limitation for nanofiller to act as filler in the voids and filler agglomerations might have taken place during mixing, which could possibly lead to extra voids in the texture in the case of 5% filler loading [16]. The knowledge of void content is desirable for estimation of the quality of the composites. It is understandable that a good composite should have fewer voids.

4.1.3. Water absorption

Water absorption behavior of nano-structured OPA filled epoxy composites are shown in Fig. 1. The water absorption activities of polymer-filled composites at a particular environmental condition is determined by many factors, such as processing techniques, matrix filler characteristics, composition of the composites, and duration of immersion in water [17]. As it is clearly seen, generally water absorption increases with immersion time, reaching a certain value at saturation point at 240 h where no more water was absorbed and the composites water content remained constant. It can be seen that incorporating the nano-structured OPA as filler did not alter the water absorption behavior of the polymer matrix; moreover it increases the water absorption % with increase in filler loading %. From Fig. 1, it was observed that the water absorption for 5% filler loading was found to be 2.81% which is highest among the different filler loading % and the neat epoxy. This indicated that high porosity or high presence of void on the composites which can be seen in Table 1 where 5% filler loading has the highest void content percentage (2.126%). With the presence of void in the composites, the weight of composites will increase by trapping the water inside the void.

Furthermore, the hydrophilic nature causes the water uptake due to the formation of hydrogen bonds between filler and water molecules. Thus, increased filler loading will increase the formation of hydrogen bond between filler and water molecules.

Other researchers reported that, water absorption also take place in the epoxy resins itself. It occur by two modes (1) sorption by free volume of the polymer, depending on the cross link density and (2) hydrogen bonding of water molecules into hydrophilic sites present in the polymer network [18].

4.2. Mechanical properties

To evaluate mechanical properties of the nanocomposites developed in this study, tensile, flexural, and impact tests were performed. The mechanical properties of nano-structured OPA filled epoxy composites were investigated to determine the effects of nano-structured OPA as filler and the effect of filler loading.

4.2.1. Tensile strength

Fig. 2 shows the effect of filler loading on the tensile strength of nano-structured OPA filled epoxy composites. It is clear from the graph that the tensile strength initially increased and then decreased with increasing of filler loading. From 0% to 5% filler loading, the tensile strength reached the maximum value when the filler loading was about 3% which is 28.76 MPa. Therefore, 3% filler loading composites content was stiffer and tougher than the composites with higher filler loading and also, neat epoxy. As reported by several authors; tensile strength of a particulate composites generally decrease with filler content and it follows a power law in the case of poor filler matrix bonding [19,20]. In theory, tensile strength of the composite is likely to be lower than that of the unfilled polymer because the particles are unable to transfer the load during tensile loading [21]. But, the opposite result obtained as

Table 1
Density and void content % of composites with different filler loading.

Filler loading (wt%)	Theoretical density (g/cm ³)	Measured density (g/cm ³)	Void content (%)
0	1.140	1.118	1.930
1	1.146	1.130	1.383
2	1.152	1.134	1.542
3	1.158	1.139	1.619
4	1.164	1.143	1.785
5	1.170	1.145	2.126

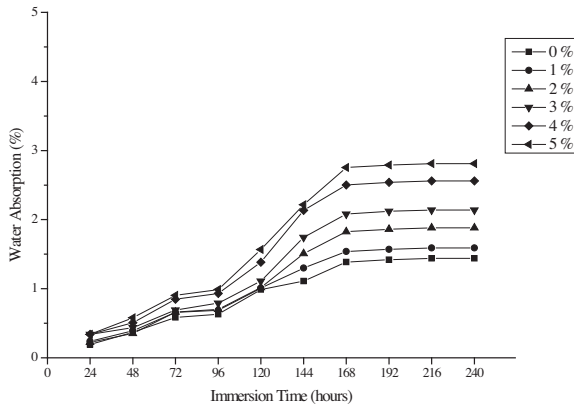


Fig. 1. Water absorption of nano-structured OPA filled epoxy with different filler loading.

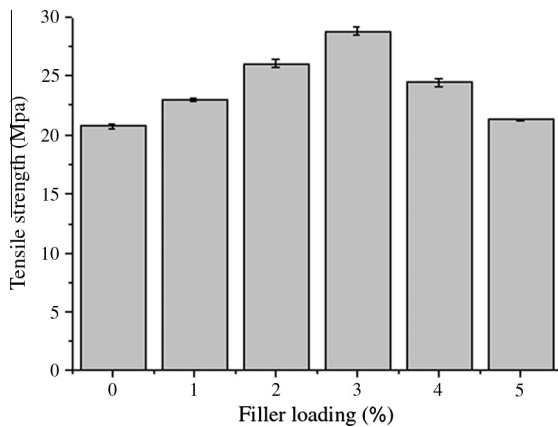


Fig. 2. Effect of filler loading on tensile strength of nano-structured OPA filled epoxy composites.

shown in Fig. 2. This is due to the increase in the tensile strength with the addition of filler up to 3% filler loading corresponding to the interaction between the filler and the matrix. Hence, this interaction resulted in better stress transfer between the filler particles and the matrix and consequently, enhanced the tensile strength of the composite. When bonding between matrix and filler is strong enough, the tensile strength of a particulate composite can be higher than the neat matrix polymer alone [22]. Even though these studies were developed based on the case of microsized particulate composites, but it still valid for the explanation of the composites filled with nanoparticles [23].

Beyond 3% filler loading, the tensile strength decreased. This was probably because of the decline in the filler–matrix interaction, weak interfacial bond, and the effect of the agglomeration of filler particles and caused premature failure. With those properties, the ability of the strong bond to transfer load from the weak matrix to the rigid filler is crucial. If such a bond does not exist or is weak, the load is borne primarily by the weak matrix causing the material to fail prematurely [24].

4.2.2. Tensile modulus

Fig. 3 shows the effect of filler loading on the tensile modulus of nano-structured OPA filled epoxy composites. From the graph, it is clear that the tensile modulus result shows identical trend with the tensile strength which is initially increased and then decreased with increasing of filler loading. From 0% to 5% filler loading, the tensile modulus reached the maximum value when the filler

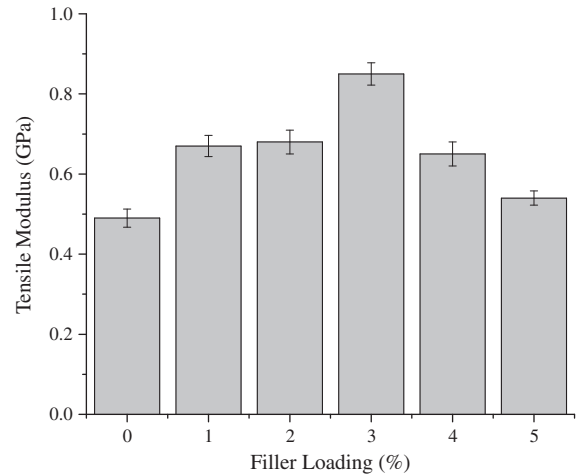


Fig. 3. Effect of filler loading on tensile modulus of nano-structured OPA filled epoxy composites.

loading was about 3% which is 0.85 GPa. Therefore, nano-structured OPA is able to stiffen the matrix, as reflected by relationship between tensile modulus and the filler loading up to 3% filler loading. The mechanical properties are dependent on the strength of interface. It occurs when a strong and fully bonded interface forms between the fillers and matrix, the matrix stresses can be easily transferred to the nano-fillers. As a result, the nanocomposites can bear more loads and exhibit higher values of tensile modulus. It is believed that the composite with 3% filler loading possess an optimum level of dispersion, and, hence, interparticle distance contributes to increase in tensile modulus [24]. The uniform dispersion of nano filler in the matrix will decrease the interparticle distance or free space between the particles which lead to the reduction in the flexibility of polymer chain, thus increases the tensile modulus [25].

Further increase in filler loading beyond 3% leads to a drop in modulus. This was probably because of the decline in the filler–matrix interaction and weak interfacial bond, and due to the effect of the agglomeration of filler particles. Nano-structured OPA is suggested to form some aggregates and the amount of the aggregation grows for higher filler loadings. Reported by other authors [26], due to the fact that nano-particles have a strong tendency to join each other and minimize their surface area via aggregation, it is difficult to achieve a uniform dispersion which leads to a strong interfacial adhesion between the nano-particles and the matrix. This agglomeration of filler particles will reduce the interfacial adhesion between nano-particles and matrix, thus decline the filler–matrix interaction.

4.2.3. Flexural strength

Fig. 4 shows the effect of filler loading on the flexural strength of nano-structured OPA filled epoxy composites. It is clear from the graph that the flexural strength initially increased and then decreased with increasing of filler loading. From 0% to 5% filler loading, the flexural strength reached the maximum value when the filler loading was about 3% which is 30.71 MPa. As reported by several authors; [27], the flexural strength of microparticle filled composites is known to be reduced with rising filler content. In this study of nanocomposites, the result showed an obvious difference with previous work. Some important characteristic of composites need to be considered in order to explain this phenomenon. The quality of the interface in composites, i.e. the static adhesion strength as well as the interfacial stiffness, usually plays a very important role in the materials' capability to transfer stresses

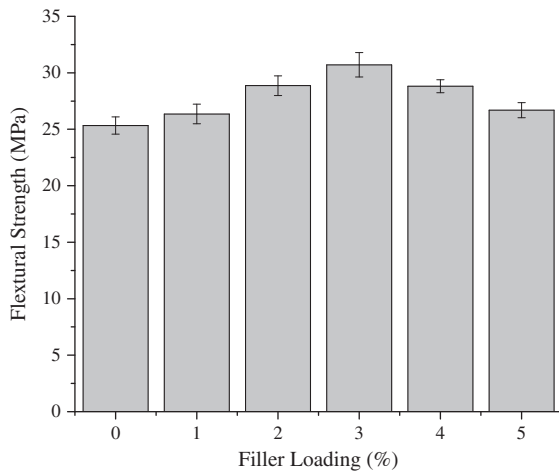


Fig. 4. Effect of filler loading on flexural strength of nano-structured OPA filled epoxy composites.

and elastic deformation from the matrix to the fillers. This is especially true for nanocomposites, because they impart a high portion of interface compare to microcomposites. If the filler matrix interaction is poor, the particles are unable to carry any part of the external load. In that case, the strength of the composite cannot be higher than that of the neat polymer matrix. If the bonding between the fillers and matrix is instead strong enough, the yield strength of a particulate composite can be higher than that of the matrix polymer [21]. In the same way corresponds a high interfacial stiffness and to a high composite modulus. Hence, the gradual increase in stiffness and flexural strength, as observed for the nanocomposites, reveals the stresses are efficiently transferred via interface.

Further increase in filler loading beyond 3% leads to a drop in flexural strength. This was probably because of the decline in the filler–matrix interaction and weak interfacial bond due to the effect of the agglomeration of filler particles. Filler agglomerations at high filler loading composites results in non-homogeneous dispersion and hence decline the interfacial interaction between the filler and the matrix [28]. This means that agglomerates resulting as a weak point and act as stress concentrator that initiate the initial failure under applied load which in turn lower the flexural strength. On the other hand, filler–filler interaction is much more dominant than filler–matrix interaction. This filler–filler interaction will result in filler agglomeration and subsequently reduces the flexural strength of the composites system [29].

4.2.4. Flexural modulus

Fig. 5 shows the effect of filler loading on the flexural modulus of nano-structured OPA filled epoxy composites. From the graph, it is clear that the flexural modulus result shows identical trend with the flexural strength which initially increases and then decreases - with increasing of filler loading. From 0 to 5% filler loading, the flexural modulus reached the maximum value when the filler loading was about 3% which is 1.19 GPa. The addition of nanoparticles, which are usually stiffer than the matrix will increase the stiffness of the matrix, generally led to an increased flexural modulus due to the contribution of hard particles [30]. Other than that, the improvements in flexural modulus from neat epoxy/0% filler loading up to 3% filler loading are attributed to the dispersion of nanoparticle and the interfacial adhesion between the epoxy matrix and the nanoparticle so that the mobility of chain matrix is restricted under loading [31].

Further increase in filler loading beyond 3% leads to a drop in flexural modulus. As reported by several author; the direct

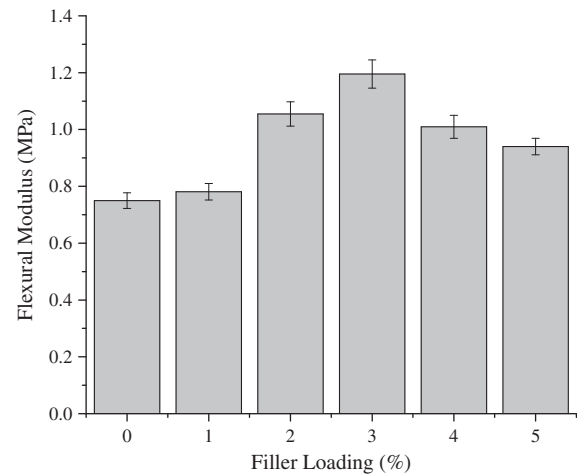


Fig. 5. Effect of filler loading on flexural modulus of nano-structured OPA filled epoxy composites.

relationship of the flexural modulus with filler loading obey the rule of mixtures [28,32]. The rule of mixtures suggests that theoretically, the moduli of composite materials increases with increased filler loading. But, from Fig. 5, beyond 3% filler loading, the flexural modulus decreases. This is probably because of the effect of the poor interface bonding or adhesion between the filler and the epoxy resin matrix, or the presence of a large agglomerate phase in the matrix. Agglomeration can enhance flow characteristics of ultrafine powders, which leads to poor packing and porous composites. The presence of agglomeration in the composites obviously deteriorates their mechanical properties.

4.3. Thermogravimetric analysis (TGA)

TGA was carried out to analyze the effect of filler loading on thermal stability and thermal degradation of the nano-structured OPA filled epoxy composites. Fig. 6 shows the TGA curve on the effect of filler loading of nano-structured OPA filled epoxy composites. In this study, the decomposition temperature (T_{max}) is considered as the temperature of the maximum rate of degradation determined from DTG curve from TGA analysis (not shown), which is summarized in Table 2. In addition, initial decomposition temperature (T_i) and final decomposition temperature (T_f) are determined from the intersection of the two tangents of the inflection point, while degradation at 50% weight loss ($T_{50\%}$) determined from

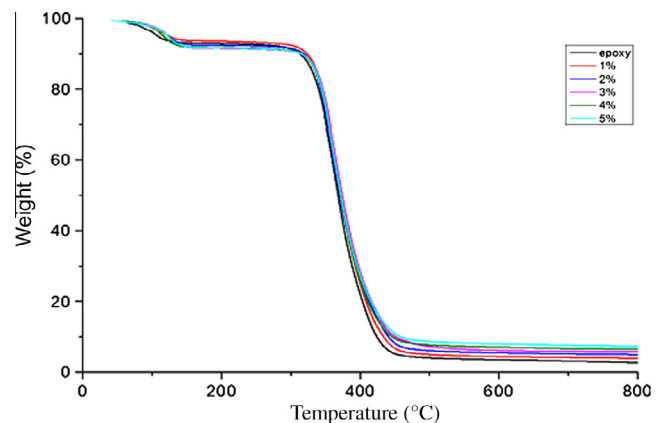


Fig. 6. TGA curve on the effect of filler loading of nano-structured OPA filled epoxy composites.

Table 2

Thermal properties of nano-structured OPA filled epoxy composites.

Composites (%)	Degradation temperature (°C)			Char residue (%)	DTG peak temperatures (°C)
	T_i	T_f	$T_{50\%}$		
0/epoxy	336	408	368	2.63	365
1	341	404	370	3.96	364
2	341	407	371	4.97	362
3	344	412	374	5.74	366
4	342	405	372	6.46	365
5	341	409	371	7.29	364

the mid-point of the degradation process at 50 wt% weight loss. Other than that, the fraction of non-volatile which remains at 800 °C denoted as char residue are also shown in Table 2.

Thermal degradation of the neat epoxy and nano-structured OPA filled epoxy composites gave an initial weight loss below 100 °C due to loss of moisture and evaporation of excess benzyl alcohol. Neat epoxy/0% and 1–5% filler loading of nano-structured OPA composites started to decompose at around 336 °C. As reported by several authors; 50% of weight percentage of the total weight loss ($T_{50\%}$) is considered as the structural destabilization point of the system or an indicator for structural destabilization [33–35]. As tabulated in Table 2, the neat epoxy composite is stable up to 368 °C. $T_{50\%}$ of 1–3% filler loading composites is higher than that of the neat epoxy, and shows an increasing trend with filler loading. The increase in the thermal stability is due to the increase in cross-linking of the epoxy resin in the presence of nano-structured OPA and having minimum particle to particle interaction. Other than that, improvement of thermal stability of the epoxy nanocomposites at high temperatures may be due to the well dispersed nanoparticles, which have a much higher thermal stability than the neat epoxy matrix and can shield and consume much heat for the matrix [35].

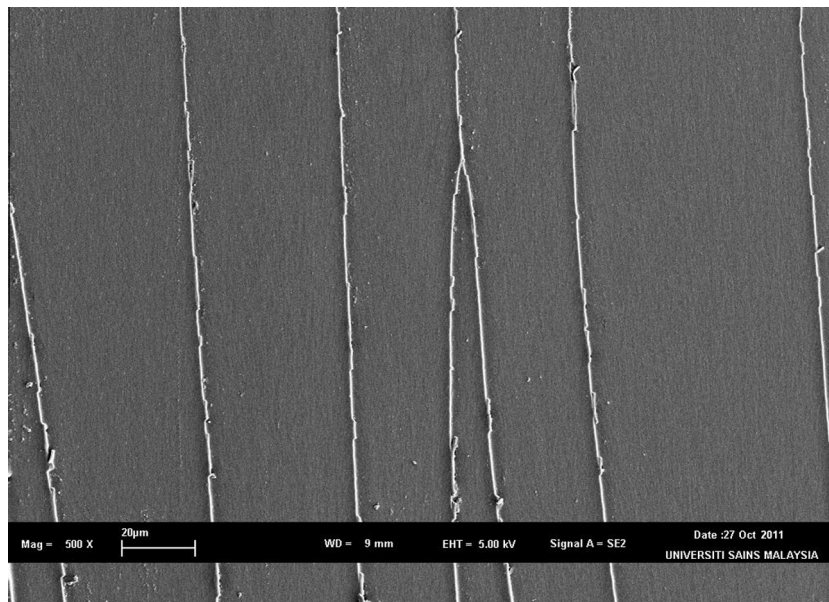
Beyond 3% filler loading, decrease in structural destabilization was observed. This can be attributed to the agglomeration of nano-structured OPA and weak compatibility between epoxy and nano-structured OPA particles. Once nanoparticles agglomerate, the interaction between particles and particles are stronger than particles and epoxy resin, which cannot impose any restriction on molecular mobility, and thereby leading to a decrease in

decomposition temperature. Similar trend was also observed in case of T_i , T_f and T_{max} . The results also show that the residual weight percent at 800 °C of the nano-structured OPA filled epoxy composites increases upon addition of filler loading due to inorganic residue.

4.4. Scanning electron microscopy

The izod impact fracture surface of nano-structured OPA filled epoxy composites were examined using SEM and typical micrograph are presented in Figs. 7a–7f. Crack propagation is from bottom to top in all figures. Fig. 7a shows the SEM micrographs of neat epoxy after impact testing at high (500×) magnification. From these figures, it was observed that the fracture surface of neat epoxy/0% filler loading composites is rather smooth with thin river line parallel to the crack propagation direction, which indicates that the crack propagates rapidly and little energy is absorbed during tensile fracture [36]. Hence, the resistance to crack propagation is less and leads to brittle failure. Also, there are no micro voids present which it could act as crack propagation sites.

Figs. 7b and 7c shows the fracture surface of 1% and 2% of fillers loading, respectively. Depth river line markings and sharp surfaces are observed as compared to the neat epoxy fracture surface, which act as evidence for the brittle fracture of nanocomposite as filler loading increase. As compared to 1% and 2% fillers loading composites fracture surface, the 2% filler loading fracture surface are more brittle. This is to be true because matrix breakage was observed in Fig. 7c indicated by white arrows. On both fracture surfaces in the micrographs, there is no obvious agglomerates were

**Fig. 7a.** SEM micrograph of neat epoxy, at 500×.

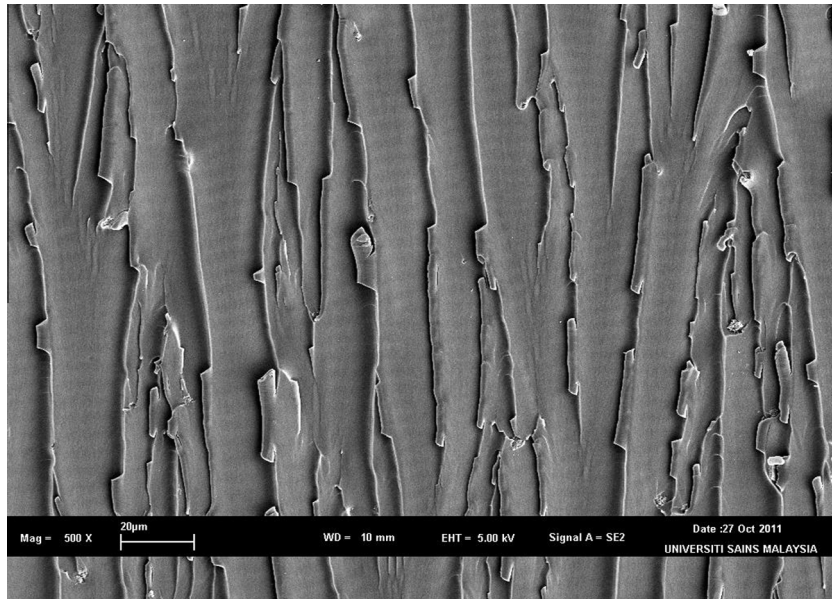


Fig. 7b. SEM micrograph of 1% filler loading of nano-structured OPA filled epoxy composites; at 500 \times .

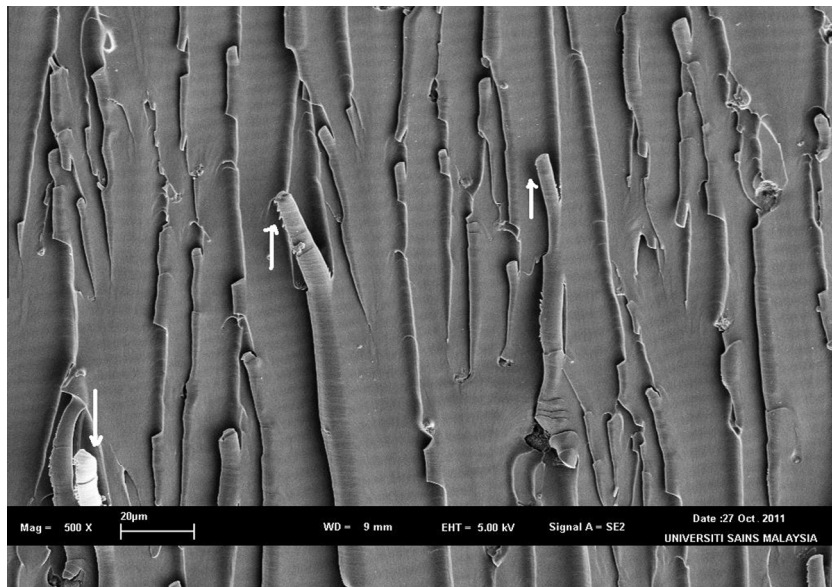


Fig. 7c. SEM micrograph of 2% filler loading of nano-structured OPA filled epoxy composites; at 500 \times , white arrow indicate matrix breakage.

observed. This can be attributed to good dispersion of nano-structured OPA without aggregation of nanoparticles. Fig. 7d shows the fracture surface of 3%, where crack propagation was rapid, and an indication that the cracks took more tortuous paths on well dispersed fillers on the composites. Thus no river line marking observed and the surface become rougher.

Generally, as filler loading increased, the fracture surface became rougher, as seen in Figs. 7b–7d. The presence of nano-structured OPA as filler may cause deflection along the crack, thus altering the path of the propagating crack from the straight unperturbed growth seen in the neat epoxy/0% filler loading. Consequently, crack deflection occurs by adding nanoparticles into the rougher regions surrounding them. Other than that, due to the nanoparticle size and an apparently lower interparticle distance, deflected crack paths intersecting with each other generate a severely rough textured surface morphology as the % of filler loading

increase, as shown in Figs. 7a–7d. Clearly, the crack deflection observed is responsible for the increase of impact strength. From Figs. 7b–7d, no indication of interfacial debonding between the epoxy matrix and the nano-structured OPA structures was noticeable, suggesting excellent interfacial interaction.

But, further adding % of filler loading beyond 3%, aggregation of filler occurs. Figs. 7e and 7f shows the fracture surface of 4% and 5% of fillers loading, respectively. No river line marking was observed and the surface are rougher with presence of filler agglomerations (indicated with white arrow). The presences of agglomeration are probably because the nanoparticles are poorly dispersed at higher % of filler loading. The agglomerated structure of nano-structured OPA would act as stress concentration site when applied stress and not the individual nanoparticles. Thus, made the cracks penetrated through them resulting as a weak point and initiate the initial failure, hence, exposed the aggregates on the surface.

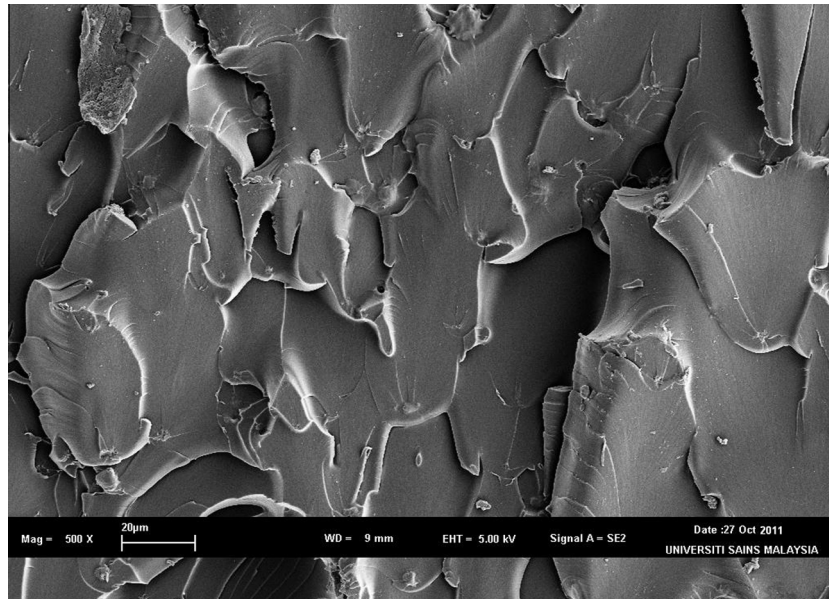


Fig. 7d. SEM micrograph of 3% filler loading of nano-structured OPA filled epoxy composites; at 500 \times .

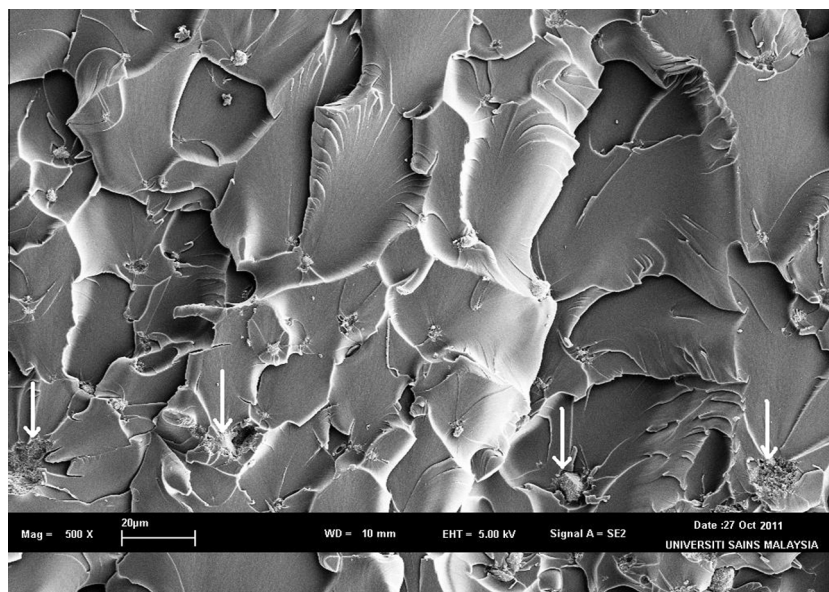


Fig. 7e. SEM micrograph of 4% filler loading of nano-structured OPA filled epoxy composites; at 500 \times , white arrow indicate filler agglomeration.

4.5. Transmission electron microscopy (TEM)

TEM has been proved to be good characterizing tools for nanocomposites, especially for the study of particle distribution in the nanocomposites. The dispersion of nanometer-sized particles in the polymer matrix is reported to have a significant impact on the mechanical properties of nanocomposites [37]. Fig. 8a–c shows the TEM micrograph on dispersion of 1%, 3% and 5% filler loading of nano-structured OPA filled epoxy composites, respectively. It can be seen that the particle dispersion of the 1% filler loading of nano-structured OPA in epoxy composites (Fig. 8a) illustrate poor distribution but good dispersion. However, the dispersion of 3% filler loading of nano-structured OPA (Fig. 8b) showed good distribution and good dispersion. Next, the dispersion of 5% filler loading of nano-structured OPA (Fig. 8c) showed very poor distribution and poor dispersion.

The TEM micrograph proved that incorporating 3% filler loading in the matrix resin give good dispersion result. Hence, 3% filler loading is an optimum weight % of filler loading to achieve uniform dispersion. This finding supported and could be the contribution to achievement of maximum value in mechanical properties of nanocomposites. This is to be true, given a uniform dispersion; the large specific surface area of nanofillers will produce a large interfacial area per unit volume, which increases the filler–matrix interaction between the nanofiller and the matrix. Thus, this interaction resulted in better stress transfer between the filler particles and the matrix and consequently, enhanced the mechanical properties.

As the nanoparticles have a strong tendency to agglomerate, incorporating high % of filler loading will give poor distribution and dispersion. Fig. 8c showed the poor distribution and poor dispersion of nano-structured OPA. This might be due to processing

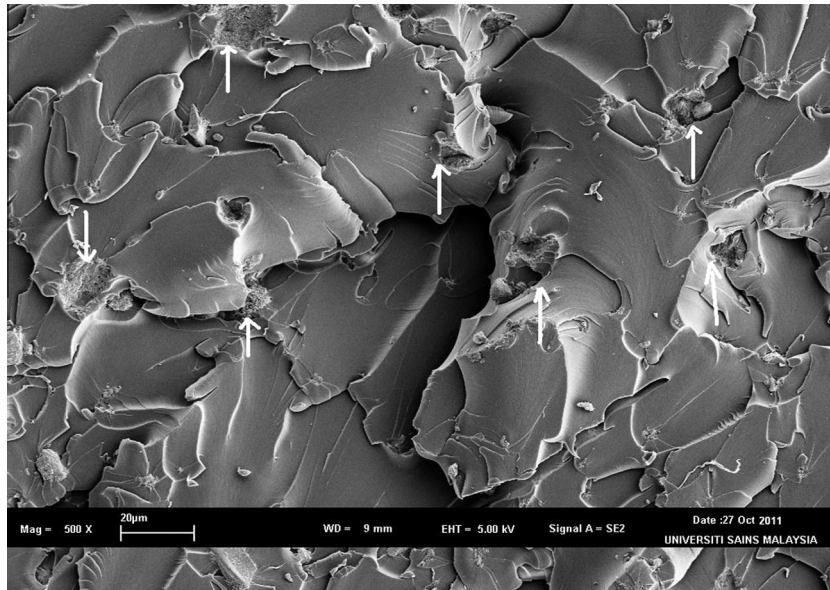


Fig. 7f. SEM micrograph of 5% filler loading of nano-structured OPA filled epoxy composites; at 500 \times , white arrow indicate filler agglomeration.

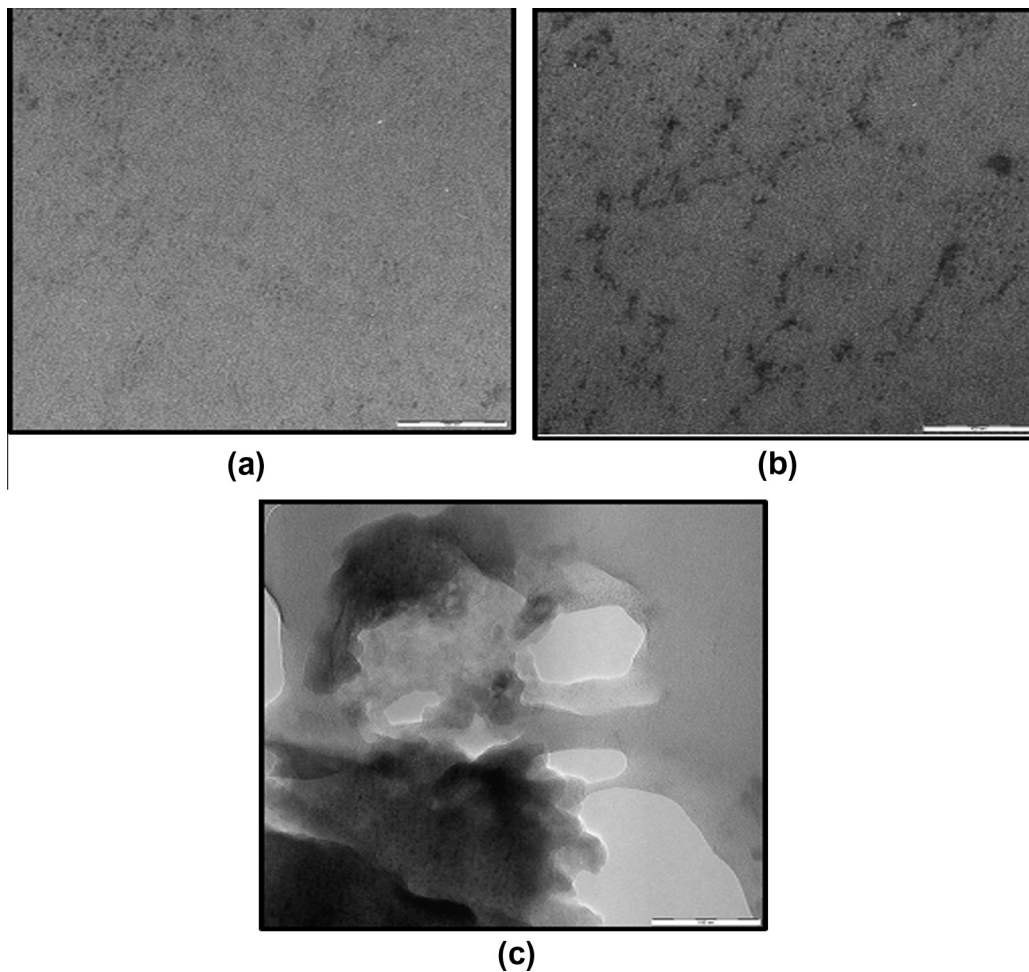


Fig. 8. TEM micrograph of nano-structured OPA filled epoxy composites with: (a) 1% (b) 3% and (c) 5% filler loading.

technique used during fabrication and the nanoparticles itself tend to agglomerate/bonded together via the surface functional groups on account of their high free energy [36]. From mechanical

properties results discussed earlier, the decrease in its mechanical properties is proved due to the poor distribution and dispersion of nano-structured OPA in filler loading beyond 3%.

5. Conclusions

The density of the nano-structured OPA filled epoxy composites revealed that increasing filler loading will eventually increase the density. As for the void content of the composites, as the filler loading increases from 1 to 5%, the percentage of voids is found to be increasing and lie in the range of 1.383–2.126%. The water absorption behavior of nano-structured OPA filled epoxy composites showed that the incorporation of nano-structured OPA as filler did not alter the water absorption behavior of the polymer matrix, and moreover it increases the water absorption capacity with filler loading percentage. Furthermore, 5% filler loading composites showed the highest value of water absorption among other samples due to high porosity or high presence of void on the composites.

The tensile strength and modulus showed same pattern of increase in strength and modulus initially and then decrease with increasing filler loading percentage. The tensile strength and modulus both reached the maximum value when the filler loading was about 3%, attributed to the interaction between the filler and the matrix.

The TGA analysis showed that the neat epoxy material is stable up to 368 °C. $T_{50\%}$ of 1–3% filler loading composites is higher than that of the neat epoxy, and shows an increasing trend with filler loading. Beyond 3% filler loading, decrease in structural destabilization was observed. Other than that, the residual weight percent at 800 °C of the nano-structured OPA filled epoxy composites increases upon addition of filler loading due to inorganic residue.

The TEM analysis depicts that the particle dispersion of the 1% filler loading of nano-structured OPA in epoxy composites illustrates poor distribution but good dispersion. While, 3% filler loading showed good distribution and good dispersion and 5% filler loading showed very poor distribution and poor dispersion. Overall, the 3% filler loading showed optimum properties by incorporating into epoxy matrix.

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