Preparation, Characterization, and Improvement of Hollow Epoxy Particle-Toughened Vinyl Ester Composites for High-End Applications

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ABSTRACT: Spherical hollow epoxy particles (HEPs) that can serve as advanced reinforcing fillers for vinyl ester thermosets were prepared using the water-based emulsion method. The HEP fillers were incorporated into the vinyl ester matrices at different loading amounts, ranging from 0 to 9 wt %, to reinforce and toughen the vinyl ester composite. The optimum mechanical properties of the HEP-toughened epoxy composite can be achieved by the addition of 5 wt % HEP filler into the vinyl ester matrices. The toughening and strengthening of the epoxy composites involved the interlocking of vinyl ester resins into the pore regions on the HEP fillers. The toughening and interlocking mechanisms of HEP-toughened vinyl ester composites were also proposed and discussed. The addition of HEP fillers into vinyl ester matrices increased the glass transition temperature (T_g) and thermal stability of the composites. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 3064–3071, 2012

Key words: hollow epoxy particles; thermoset; interlocking; polymer-filler interaction; emulsion

INTRODUCTION

Epoxy resins exhibit excellent mechanical properties, but their brittleness limits most of their end-use applications. Thus, much effort has been made to modify and improve the toughness of epoxy systems. For example, Thomas et al.[1] incorporated elastomers into an epoxy thermoset to toughen the system. Tan and Chow[2] added epoxidized palm oil (EPO) into petrochemical-based epoxy blends to increase the fracture toughness of the blends. Astruc et al.[3] introduced kaolin into an epoxy matrix to enhance the toughness of the epoxy composite and Johnsen et al.[4] found that the addition of a relatively small amount of silica nanoparticles into the epoxy system significantly increased the modulus and toughness of the epoxy thermosets. In recent years, spherical hollow particles have also been used as reinforcing fillers to improve the modulus, hardness, and toughness of the epoxy matrix.[5]

Among the various types of fillers, hollow spherical particles have recently attracted the interest of most researchers worldwide. Hollow particles not only show potential to toughen and reinforce the epoxy matrix, but also serve for the purpose in drug delivery, controlled release, membrane applications, and absorptive filters as well as confined reaction vessels.[6–8] In addition, Watanabe et al.[6] and Liang and Li[9] stated that the unique properties of hollow particles, such as their low density, low thermal conductivity coefficient, and surface permeability, make these hollow particles suitable for use in various applications. Zhao et al.[10] and Hwang et al.[7] also mentioned that hollow particles are appropriate low weight fillers for most materials because their specific structures can accommodate relatively large objects and give rise to the "micro-package" effect. Three types of hollow, spherical particles have been widely used as fillers: (1) hollow calcium carbonate, which can act as a paper filler, (2) hollow mesoporous silica spheres, to improve the water absorption properties of the membranes, and (3) hollow glass microspheres, to modify the dielectric properties of epoxy.[6,11–13]

Many techniques are used to synthesize hollow particles. According to Han et al.,[14] the organic-bead templating method, the emulsion templating method and the colloid-array templating method are several methods used to synthesize hollow particles. Chen et al.[11] mentioned that the porous structure on the surface of hollow microspheres can be easily formed using these templating methods. However,

the hollow spherical particles synthesized using these methods consist of only a few holes on their surfaces. Hence, in this present study, a novel, water-based emulsion technique was selected to synthesize hollow epoxy particles (HEPs) with many holes on their surfaces. Also, the HEP fillers produced using this technique possess small particle sizes, low density, and high surface area. Thus, it is hypothesized that these HEP fillers can be a new class of technologically advanced fillers for use in various applications.

Though much work has been done to investigate the applicability of hollow particles in various applications, to our knowledge there are only very limited research articles focused on HEP fillers prepared using the water-based emulsion technique for filler-reinforced applications. Thus, this research study has been conducted to characterize the HEP fillers produced by the water-based emulsion technique and to investigate the effect of HEP filler loading on the mechanical properties and thermal properties of the HEP-filled vinyl ester composite.

EXPERIMENTAL

Materials

Epoxy resin 331 [diglycidyl ether of bisphenol-A (DGEBA)] with an epoxy equivalent weight (EEW) of approximately 182 to 192 g/mol, vinyl ester Hetron 922, polyamide A026 hardener, and methyl ethyl ketone peroxide (MEKP) catalyst were supplied by Euro Chemo-Pharma Sdn Bhd, Malaysia. Calcium carbonate ($CaCO_3$) with a density of approximately 2.71 g/cm^3 was bought from Malaysian Calcium Corp. Sdn Bhd., Malaysia.

Preparation of hollow epoxy particles

Hollow epoxy particles (HEPs) were prepared using the water-based emulsion technique. The emulsion process was conducted at room temperature (approximately 30°C) with the relative humidity of 50%. Epoxy resin and $CaCO_3$ were combined in a predetermined ratio (weight ratio of epoxy resin: $CaCO_3$ was 2 : 3) and stirred with a mechanical stirrer at 300 rpm for 5 min. A polyamide hardener was then added to the epoxy mixture and stirred continuously for 2 min until a homogeneous mixture was produced. The mixture was then poured in water and the emulsion process was conducted using a homogenizer at a speed of 15,000 rpm for 9 min. Finally, the mixture was placed in an oven at 80°C for 24 h for thermal curing. A fine powder of HEP fillers with the particle size of about 22.65 μm was produced after the cured epoxy mixture was ground.

Preparation of hollow epoxy particle-filled composites

Vinyl ester composites were prepared using the casting method. HEP fillers were incorporated into the vinyl ester resin at different loading amounts, ranging from 0 to 9 wt %. The mixture was stirred mechanically until it was homogeneous before adding the MEKP catalyst. Next, the mixture was poured into a rubber mold and subjected to thermal curing in an oven at 80°C for 3 h.

Characterization

Hollow epoxy particles

The morphology (i.e., shape, size, and structure) of the hollow epoxy particles (HEP) was observed using a field-emission scanning electron microscope (FESEM) model Ziess Supra 35VP. The HEP fillers were coated with platinum/gold prior to FESEM characterization. Particle size analysis of the HEP fillers was conducted using a particle size analyzer (Cilas 1180). Approximately 1 g of HEP filler was subjected to this analysis. The lens range and beam length of the analysis were set at 100 mm and 2.4 mm, respectively. The particle size distribution (at 10%, 50%, and 90%) of the HEP fillers was determined. The surface area, pore volume, and pore size of HEP fillers were determined according to the Brunauer-Emmett-Teller (BET) method using NOVA 2200e surface area and pore size analyzer. The density of the HEP fillers was measured using a Micrometrics AccuPyc 1300-gas pycnometer.

HEP-filled composites

Three-point-bending fracture toughness testing was performed on single-edge notched bending (SENB) specimens according to the ISO13586: 2000 standard method using an Instron machine, model 3366. The dimension of the specimen was approximately 60 mm × 12 mm × 3 mm, with the crack length-to-width ratio (a/W ratio) of 0.5. The initial crack was made in the specimen using a razor blade before the fracture toughness test. The fracture toughness test was conducted at a crosshead speed of 10 mm/min. The fracture toughness values, K_{IC} of the vinyl ester composites with different HEP loadingwere determined using eqs. (1) and (2).[15]

$$y = 1.93 - 3.07\left(\frac{a}{W}\right) + 14.53\left(\frac{a}{W}\right)^2 - 25.11\left(\frac{a}{W}\right)^3$$
$$+ 25.8\left(\frac{a}{W}\right)^4 \tag{1}$$

$$K_{IC} = \frac{3PSa^{1/2}y}{2tw^2} \tag{2}$$

where y is a geometrical correction factor, a is the notch length (mm), W is the specimens width (mm),
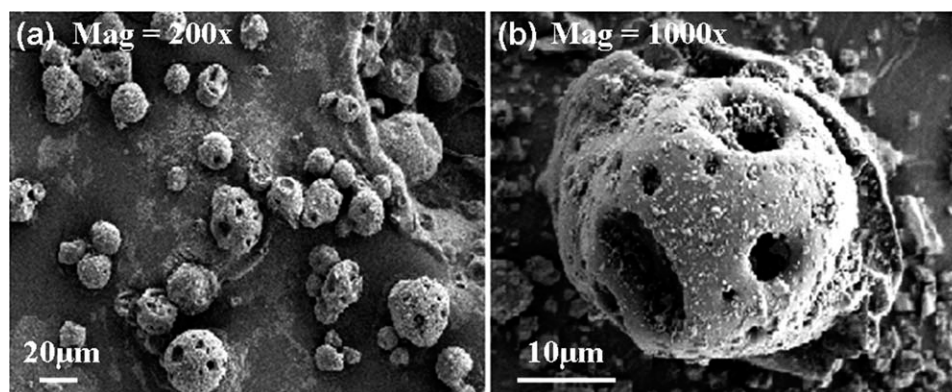
Figure 1 Surface morphology of HEP fillers.

S is the span length (mm), P is the load at peak (N), and t is the specimen thickness (mm).

The fractured surfaces of the HEP-reinforced epoxy composites after fracture toughness testing were observed by FESEM. The sample was coated with platinum/gold before FESEM testing.

Tensile testing on the HEP-reinforced epoxy composites were conducted using an Instron machine 3366 tensile tester equipped with a 10-kN load cell according to ASTM D 638. The Type-IV dumbbell tensile specimens with a 2-mm thickness were prepared using the casting method. Tensile testing was conducted at a cross-head speed of 5 mm/min on five tensile specimens. The tensile properties of the epoxy composites, such as tensile strength and tensile modulus, were determined.

Impact tests were conducted using an impact test instrument according to ASTM D 6110. The Charpy method was carried out on notched samples with the dimensions of 60 mm $\times$ 12 mm $\times$ 3 mm and a notch length of 2 mm. The impact strength is reported determined in units of kJ/m^2.

The flexural properties of the HEP-reinforced epoxy composite were determined according to ASTM D790 using an Instron machine, model 3366. The dimensions of the specimen were 120 mm $\times$ 12 mm $\times$ 3 mm. The specimen was placed on two supports with a span length of 100 mm. The test was conducted at a crosshead speed of 5 mm/min. The flexural strength of the vinyl ester composites was calculated using eq. (3).[16]

$$\sigma_f = \frac{3FL}{2bd^2} \qquad (3)$$

where σ_f is the stress at the sample midpoint (MPa), F is the load at a given point on the load-deflection curve (N), L is the span length (mm), b is the width of the test beam (mm), and d is the depth of the tested beam (mm).

The glass transition temperature (T_g) of the HEP-reinforced composite was determined using differential scanning calorimeter (DSC, Perkin–Elmer). Approximately 10 mg of the specimen (0, 5, and 9 wt % HEP loading) was placed into an aluminum pan and subjected to thermal scanning from 30 to 250°C at a heating rate of 10°C/min in a nitrogen atmosphere. The thermal stability of the composites were examined using thermogravimetric analyzer (TGA, Perkin–Elmer Pyris 6). Approximately 10 mg of the specimen (0, 5, and 9 wt % HEP loading) was heated from room temperature to 800°C at a heating rate of 10°C/min in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Characterization of hollow epoxy particles

The surface morphology of HEPs produced by the water-based emulsion method was observed by FESEM. Figure 1 shows the surface morphology of the HEP fillers. Based on these observations, microscale, spherical HEP fillers exhibiting many holes on the HEP filler surfaces can be manufactured using the emulsion technique. The particle size distribution of the HEP fillers was found to be in the range of 1.95 to 41.53 μm, whereas the surface area and pore volume of the fillers were 12.87 m^2/g and 11.36 nm, respectively. The density of the HEP fillers was approximately 1.15 g/cm^3. The HEP fillers possess a lower density, smaller particle size, and higher surface area compared to conventional fillers. In addition, an HEP filler with specific hollow structures on its surface can accommodate and interlock with other types of materials, especially polymers. Therefore, HEP fillers were incorporated into the vinyl ester resin in this present study to toughen and reinforce the composite as well as to produce a light weight composite.

Mechanical properties

Fracture toughness

Figure 2 shows the fracture toughness of the vinyl ester composites with different HEP loading. The
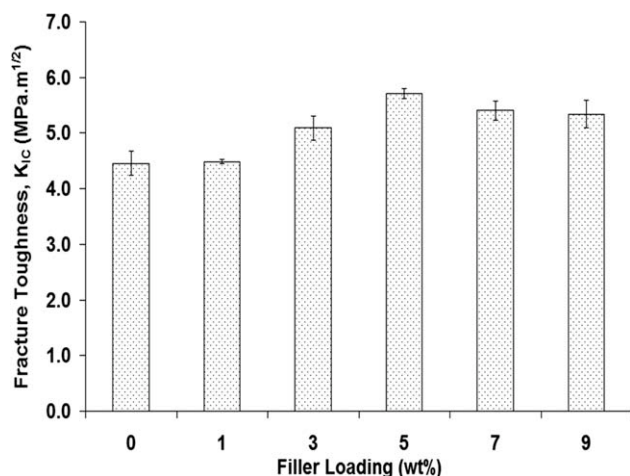
Figure 2 Fracture toughness of vinyl ester composites with different HEP filler loading.

fracture toughness of the HEP-reinforced composite increases with increasing HEP loading up to 5 wt %, after which there is a drop. The fracture toughness of the 5 wt % HEP-filled composites improves about 28.0% compared with that of the pristine vinyl ester thermoset. At relatively low HEP loading, the increase in fracture toughness with filler loading is mainly attributed to the ability of the HEP filler particles to resist crack propagation when an external force is applied. The HEP fillers act as an obstacle to the applied force, which increases the crack path length because the crack can only propagate by

bowing around the filler particles. This crack-pinning mechanism leads to an increase in the line energy and subsequently enhances the toughness of the vinyl ester composites. In addition, good adhesion between the polymer and filler as a result of the interlocking of the vinyl ester resin into the pore regions of the HEP filler [c.f. Fig. 3(b)] increases the ability of the HEP-filled composite to absorb more energy before fracture initiates. Therefore, the crack propagation rate will decrease, and the resistance to crack growth will improve. This effect will eventually lead to a higher fracture toughness as shown in Figure 2. However, the fracture toughness of the HEP-filled composites decreases as the HEP loading exceeds 5 wt %. This phenomenon is caused by filler-filler agglomeration in the vinyl ester composites. These undesirable weak regions that act as stress concentrators result in the reduction of the resistance of the composite to crack propagation and subsequently reduce the fracture toughness of the composites.

In addition, the fracture behavior of the HEP-filled composites can be further explained by the fracture morphology observed under FESEM. Figure 3 displays the fracture surfaces of the vinyl ester thermoset and HEP-filled epoxy composite after the fracture toughness test. As shown in Figure 3(a), a relatively smooth fracture surface is observed in the pristine vinyl ester thermoset. This smooth fracture surface of the pristine epoxy thermoset indicates a relatively low resistance of the thermoset to crack
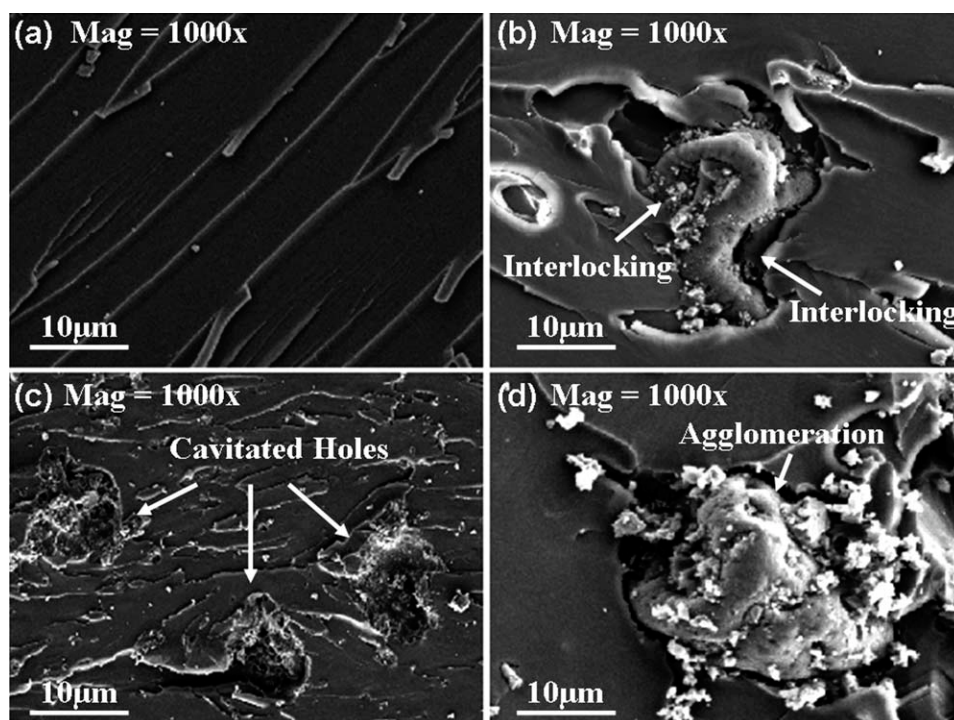

Figure 3 SEM micrographs of the fracture surface of (a) pristine vinyl ester thermoset; (b) 5 wt % HEP-filled epoxy composite (interlocking mechanism); (c) 5 wt % HEP-filled epoxy composite (cavitated holes); (d) 9 wt % HEP-filled epoxy composite.

deformation and propagation. This fracture surface shows catastrophic brittle fracture, and the vinyl ester thermoset tends to fail in a brittle manner. In contrast, the fracture surface of the 5 wt % HEP-filled epoxy composite is rougher, and many cavitated holes dispersed throughout the fracture surface are observed in Figure 3(c). These cavitated holes are believed to be occupied by the HEP fillers interlocking with the vinyl ester matrix and form when the HEP fillers are removed from the vinyl ester matrix. Thus, this phenomenon increases the resistance of the composites to deformation and subsequently slows the crack propagation throughout the vinyl ester matrix. This finding is in line with the findings shown in Figure 2. However, both agglomeration of the HEP filler and a small gap between the filler and the vinyl ester matrix were observed in the 9 wt % filled epoxy composite, as shown in Figure 3(d). The poor adhesion between the epoxy matrix and the HEP fillers and the filler-filler agglomeration tend to create stress concentrators. The production of stress concentrators will deteriorate the toughening properties of the composite. Hence, the lower fracture toughness values shown in Figure 2 can be justified.

Proposed toughening mechanism

Figure 4 shows the proposed toughening mechanisms in the HEP-toughened vinyl ester composites. Figure 4 illustrates that the HEP filler loading influences the fracture behavior of the HEP-filled composites. Without the HEP filler, the pre-existing crack (notch) tends to propagate through the vinyl ester matrix unhindered. Therefore, a smooth fracture surface is observed, and the crack fracture path is relatively straight and short, as shown in Figure 4(a). However, compared with pristine vinyl ester thermoset, a more tortuous and rougher surface was observed on the fracture surface of the 5 wt % toughened vinyl ester composite. The HEP filler is believed to play a role in toughening the vinyl ester resin, which is brittle in nature. Thus, in Figure 4(b), two mechanisms are proposed by which the HEP filler toughens the vinyl ester matrix. First, the HEP filler prolongs the fracture path by causing the pre-existing crack to propagate by bowing (crack pinning mechanism) if the external applied force is not sufficiently high to penetrate and break the HEP filler particles in the vinyl ester matrix. This crack-pinning mechanism will lead to an increase in the fracture resistance and toughness of the vinyl ester composite. Second, the pore regions in the HEP filler will act as a "crack holder" to halt the crack front and subsequently retard the crack growth through the vinyl ester matrix. This retardation of the crack growth is due to the fact that the "crack holders" reduce the outer applied force. Hence, a higher
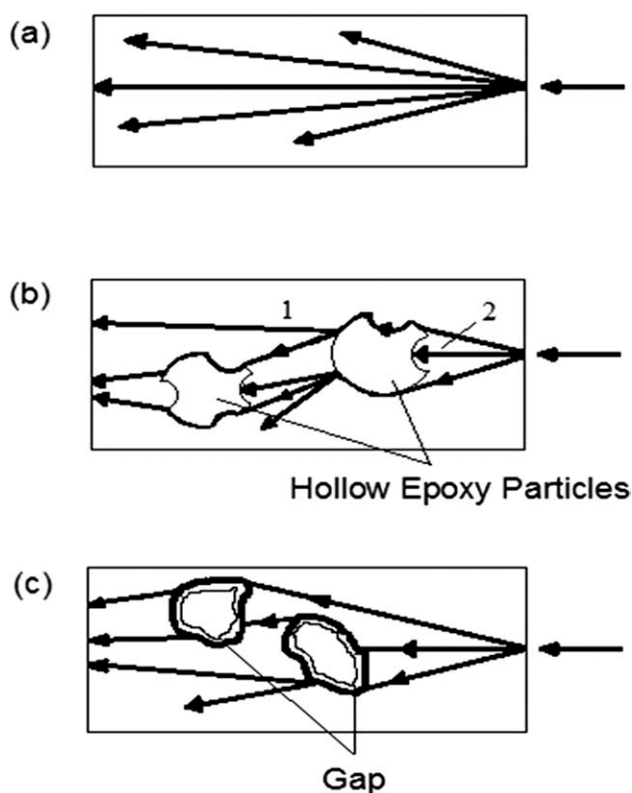

Figure 4 Proposed toughening mechanisms of HEP-filled vinyl ester composites.

external force or fracture energy is needed to re-initiate the crack fronts and to fracture the composite. At a relatively higher HEP filler loading (i.e., 9 wt %), filler-filler agglomeration and the presence of a small gap between the vinyl ester and the filler reduce the effectiveness of the crack-pinning mechanism. Wetzel et al.[17] also reported that the crack-pinning mechanism will be greatly influenced by the polymer-filler interaction. Thus, a less tortuous fracture surface is observed, and the crack path is mainly straight, as proposed in Figure 4(c).

Impact properties

The impact strength of the vinyl ester composites reinforced with different HEP loading is presented in Figure 5. The maximum impact strength of the epoxy composite is achieved with 5 wt % HEP filler. This result might be due to the good interaction between the filler and polymer matrix in the composite. Good polymer-filler interaction will enhance the resistance of the composite to crack propagation. Also, the increment in the crack length path due to the filler particles will increase the ability of composites to absorb the energy during the impact test. Thus, a higher impact strength in the epoxy composite reinforced with 5 wt % HEP filler is obtained, as shown in Figure 5. However, when there is greater than 5 wt % HEP filler, a reduction in impact
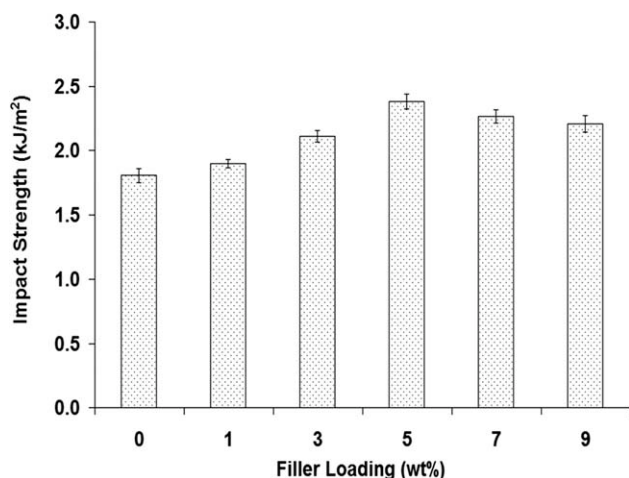
Figure 5 Impact strength of vinyl ester composites with different HEP filler loading.

strength is observed. This reduction is due to filler-filler agglomeration at relatively higher filler loading, which leads to poor interaction between the filler and polymer matrix and eventually results in a lower impact strength. Hence, the lower impact strength of the composite reinforced with 7 wt % and 9 wt % HEP filler, as shown in Figure 5, can be justified.

Tensile properties

Figure 6 displays the effect of HEP filler loading on the tensile properties (i.e., tensile strength and tensile modulus) of the HEP-filled epoxy composites. The tensile strength and tensile modulus of the epoxy composites increase with increasing HEP filler loading up to 5 wt %, after which there is a decrease. The tensile strength of the composite filled with 5 wt % HEP filler increases approximately double compared with the pristine epoxy thermoset. The continuous increase in the tensile strength up to 5 wt % HEP loading might be due to the good interaction between the vinyl ester matrix and the filler particles (interlocking of vinyl ester resin into the pores region of the HEP filler). The capability of the HEP filler to transfer external applied mechanical forces increases if good polymer-filler interaction takes place. As a result, an increase in the tensile strength of the epoxy composites is observed. However, the tensile strength drops gradually as HEP filler loading is further increased, exceeding the optimum filler loading of 5 wt %. At high filler loading, filler-filler interaction tends to cause agglomeration. This finding is in line with the finding reported by Mohamad et al.[18] who found that the incidence of agglomeration increases with the filler loading. This undesirable agglomeration as a result of the filler-filler interaction will act as a stress concentrator and subsequently deteriorate the tensile strength of the

composite. Hence, a lower tensile strength of the epoxy composites filled with 7 wt % and 9 wt % HEP filler, as shown in Figure 6, is obtained.

The tensile modulus of the epoxy composite is also affected by the filler loading. As shown in Figure 6, the tensile modulus of the epoxy composites increases with increasing filler loading from 0 wt % to 5 wt %. In other words, the toughness of the epoxy composite is enhanced. However, the tensile modulus of the vinyl ester composite decreases as the filler loading is further increased, exceeding 5 wt %. This decrease is due to the aforementioned filler-filler agglomeration. These undesirable weak agglomeration points will affect the stiffness and tensile modulus of the epoxy composites. Therefore, the tensile modulus of the vinyl ester composite decreases as the filler loading exceeds 5 wt %.

Flexural properties

Figure 7 shows the flexural strength of the epoxy composites with different HEP loading. The flexural strength is the highest in the 5 wt % HEP-filled vinyl ester composites. The flexural strength is the highest in the 5 wt% HEP vinyl ester composites is 17.7% higher than that of the pristine vinyl ester thermoset. This finding could be explained by taking into account good polymer-filler interaction and interlocking between the HEP fillers and the vinyl ester matrix. This interaction will enhance the load transfer capability of the epoxy composites and subsequently increase the resistance of the composites to deformation. However, the flexural strength of the composite decreases as excessive HEP (loading >5 wt %) is added to the composite. This phenomenon is believed to be caused by the agglomeration of the filler particles. The formation of a large cluster of filler agglomerate tends to reduce the ability of the
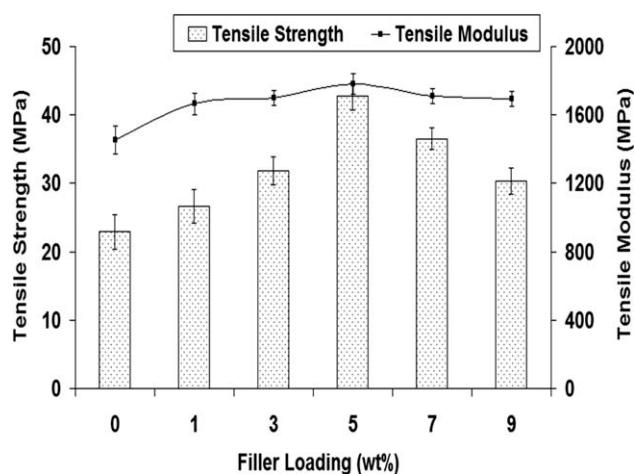

Figure 6 Tensile strength and tensile modulus of vinyl ester composites with different HEP filler loading.
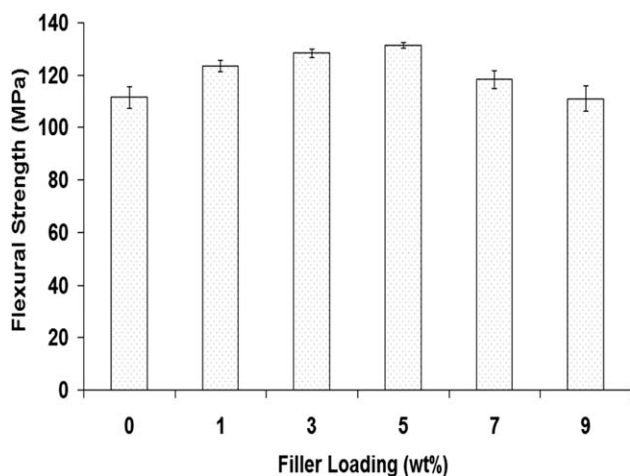
Figure 7 Flexural strength of vinyl ester composites with different HEP loading.
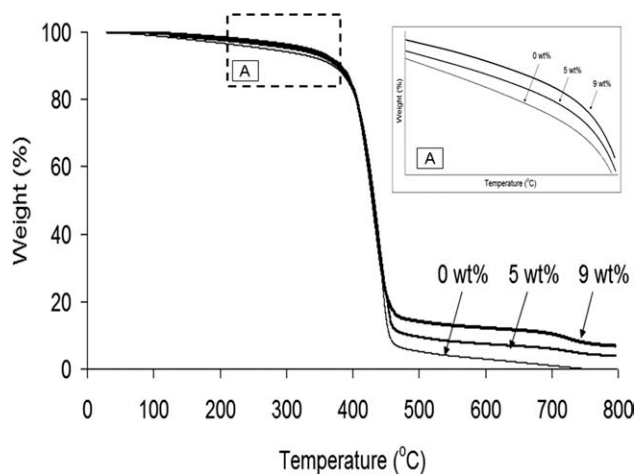

Figure 8 TGA curve of pristine vinyl ester thermoset and vinyl ester composite filled with 5 wt % and 9 wt % HEP filler, respectively.

composite to resist the external applied forces because the filler aggregates will act as stress concentrators. Therefore, as shown in Figure 7, the epoxy composite filled with relatively high HEP loading exhibits lower flexural strength.

Thermal properties

Differential scanning calorimetry

Table I shows the glass transition temperatures (T_g) of the pristine vinyl ester resin and epoxy composites with different HEP loading (i.e., 5 wt % and 9 wt %). An increase in the T_g was detected as the HEP fillers were incorporated into the vinyl ester resin, regardless of the amount of loading. The shift in the T_g to higher temperatures with the addition of HEP fillers might be attributed to the nature of the filler. HEP fillers were made of DGEBA resin, and the resin has a higher T_g compared with that of the vinyl ester resin. Therefore, the addition of HEP fillers into vinyl ester resin tends to increase the T_g value of the epoxy composites. In addition, the specific porous structures of the HEP fillers, which accommodate and interlock with the vinyl ester resin, act to increase the polymer-filler interaction. Good polymer-filler interaction tends to reduce the

mobility of the backbone of the polymeric chains and subsequently increase the rigidity of the epoxy composite. This reduction in chain mobility will eventually increase the T_g of the composite. Ash et al.[19] also found that interaction between fillers and the polymer matrix could alter the T_g of the polymer system.

Thermogravimetry analysis

Figure 8 displays the TGA curve of the vinyl ester resin and epoxy composites with 5 wt % and 9 wt % HEP filler. Figure 8 shows that the vinyl ester resin and composites experienced a one-stage thermal decomposition process when heated from room temperature to 800°C. However, the initial decomposition temperature ($T_{initial}$) shifts to higher temperature with the addition of HEP filler in the epoxy matrix. This phenomenon is mainly attributed to the good thermal stability of the HEP fillers, which originate from DGEBA resin. The bulky aromatic rings of the DGEBA resin make the HEP fillers thermally stable. Park et al.[20] also mentioned that the thermal stability of a polymer highly depends highly on its backbone structure. Thus, the addition of more thermally stable HEP fillers into the vinyl ester resin leads to the shift in $T_{initial}$ to higher temperature as shown in Figure 8.

An increase in the heating temperature exceeding 400°C leads to a major decomposition process in the vinyl ester resin and its composites, as shown in Figure 8. The weight loss of the neat epoxy thermoset as a result of thermal decomposition is much more rapid compared with that of the epoxy composites toughened with 5 wt % and 9 wt % HEP fillers. This finding is believed to be attributed to the better thermal stability and heat resistance of the HEP fillers. Therefore, the addition of these HEP fillers into

TABLE I
Thermal Properties of Vinyl Ester Thermoset and Vinyl Ester Composite with 5 wt % and 9 wt % HEP Filler

Thermal properties	Filler loading (wt %)		
	0	5	9
$T_g{}^a$(°C)	124	132	130
$T_{initial}{}^b$(°C)	380.2	386.2	393.1
$T_{decomposition}{}^b$(°C)	462.7	465.73	468.72

[a] Detected from DSC.
[b] Detected from TGA.

the vinyl ester matrix leads to an improvement in the thermal resistance of the composites. Liu et al.[21] also mentioned that the thermal resistance of a polymeric system can be enhanced by the incorporation of fillers with high thermal stability and heat resistance in that system. The thermal decomposition profiles of pure vinyl ester thermoset and HEP-filler composites are summarized in Table I.

Figure 8 shows that the epoxy thermoset completely decomposes at a temperature of approximately 800°C, though, some residue remains, even though the HEP-filled composites are thermally heated up to 800°C. The residue is believed to be the HEP fillers. These fillers tend to exhibit relatively good thermal stability because they are made up of DGEBA resin and $CaCO_3$, which possess excellent thermal resistance properties.

CONCLUSIONS

Advanced hollow epoxy particles (HEPs) were successfully prepared using the water-based emulsion technique. The mechanical properties (i.e., fracture toughness, impact strength, tensile strength, modulus, flexural strength) of vinyl ester composites could be improved by the addition of HEP filler up to 5 wt %. At relatively low HEP loading ($\leq$5 wt %), the improvement in the mechanical properties is mainly attributed to the good polymer-filler interaction and interlocking between the vinyl ester matrix and the HEP filler. However, the mechanical properties of HEP-filled composites will deteriorate as the filler loading exceeds the optimum loading (i.e., 5 wt %). The addition of HEP fillers into the vinyl ester thermoset increases the glass transition temperature (T_g) and improves the thermal stability of the vinyl ester composites. Generally, these HEP fillers could bring along unlimited future prospects which might not be able to gain from conventional filler, such as the ability to improve polymer-filler interaction, low weight, high surface area, and small particle size.

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