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Technical paper

Calcium Carbonate from Clam Shell as a Thermal Conductor in Particulate Filled Polymer Matrix Composites

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Abstract

The thermal conductivity of the raw and stearic acid treated calcium carbonate ($CaCO_3$) from clam (Polymesoda bengalensis) shell powder infused in unsaturated polyester matrix has been measured. Eight different mean diameter sizes of clam shell filler were infused into unsaturated polyester (UPE) matrix. Thermal conductivity of neat UPE sample and when embedded with raw and stearic acid treated $CaCO_3$ filler with different mean diameter sizes and filler loadings were measured according to ASTM E1225-99. The result showed that UPE matrix composites with untreated clam shell produced higher thermal conductivity than treated clam shell. At constant filler content, the thermal conductivity of UPE/$CaCO_3$ composites was increased gradually as the filler size was decreased. The higher the filler content, the higher the thermal conductivity of the composites. Therefore, the inclusion of higher filler loading with finer filler size of seafood waste from clam shell can improve the performance of polymer matrix composites as a heat conductor.

Keywords: *Calcium Carbonate; Clam Shell; Particulate-Filled Composites; Stearic Acid; Thermal*

1. Introduction

Metallic fillers such as silver, copper and nickel are among the most common fillers embedded in the polymer matrix composites (PMCs) to increase the thermal conductivity. However, due to some drawbacks of metallic filler such as high density, low corrosion resistance, and high manufacturing cost lead to the replacement of other materials which could overcome those problems. Polymers are generally good insulators and light weight. Adding sufficient amount of filler may improve thermal conductivity of polymer matrix. Traditional fillers and common polymers with their thermal conductivities as collected by Ebadi-Dehaghani and Nazempour [1] are listed in Table 1.

Previous studies showed that the thermal conductivity of the composite materials can be increased by increasing filler content [2-4], decreasing filler size [4-6] and increasing filler interconnectivity [7]. Adding 30 vol% micron size graphite filler into Bakelite resin can improve thermal conductivity to 4.84 W/mK compared to 1.4 W/mK for neat Bakelite. Then, adding the same filler up to 55 vol% might improve the thermal conductivity to 12.28 W/mK [2]. Another example of effect of increasing filler content is nano calcium carbonate ($CaCO_3$) and zinc oxide (ZnO) in polyprolyplene (PP). Increasing filler content up to 15wt% of nano $CaCO_3$ and ZnO in PP increased to 0.36 W/mK and 0.4 W/mK respectively compared to 0.22 W/mK for neat PP [8, 9]. Decreasing filler size also might increase the thermal conductivity. For example nano size of expanded graphite filler at constant filler loading (7 vol%) in high density polyethylene (HDPE) improved the thermal conductivity to 1.59 W/mK compared to only 0.78 W/mK at micon size [10]. Interconnectivity also affects the performance of heat conduction. It is defined as a relative measure to an ideally interconnected network of the high thermally conducting phase. Weidenfeller et al [7] claimed that thermal conductivity of low conductive filler in PMCs can be improved by improving the interconnectivity of filler. Better interconnectivity of talc powder in PP matrix results in twice as high as Cu/PP composites at similar filler loading even though thermal conductivity of copper is approximately 40 times higher than talc [7].

PMCs with high thermal conductivity might be very useful in many applications. The thermal conductivity required in applications for heat sinks in electric or electronic systems for example, is approximately from 1 to 30 W/mK [19]. However, to achieve the appropriate thermal conductivity, higher filler contents which is normally higher than 30 vol% was infused in the polymer matrix [19]. This quantity unfortunately leads to processing challenge such as possibility to be extruded and injection molded [19] and alters the polymer behaviour density.

This research uses $CaCO_3$ extracted from the local clam shell as a filler or reinforcement in the polymer composite. The clam was locally known as *lokan bakau* or in scientific name as *Polymesoda bengalensis*. $CaCO_3$ is not new filler for polymeric composites. In 2007, Europe used about 4.8 million tons of filler and carbon black and calcium carbonate were reported as the most widely used fillers [20]. However, most of $CaCO_3$ is determined from limestone. The usage of waste materials such as clam shell in this study may reduce the amount of waste disposed in the landfill

Table 1: Thermal conductivities of some thermally conductive fillers [11-15] and polymers [16-18]

Fillers		**Polymers**	
Material	**Thermal conductivity at 25 °C (W/mK)**	**Material**	**Thermal conductivity at 25 °C (W/mK)**
Graphite	100~400 (on plane)	Low density polyethylene (LDPE)	0.30

Carbon black	6~174	High density polyethylene (HDPE)	0.44
Carbon nanotubes	2000~6000	Polypropylene (PP)	0.11
Diamond	2000	Polystyrene (PS)	0.14
Copper	483	Polymethylmethacrylate (PMMA)	0.21
Silver	450	Nylon-6 (PA6)	0.25
Gold	345	Poly(ethylene terephthalate) (PET)	0.15
Aluminum	204	Poly(butylene terephthalate) (PBT)	0.29
Nickel	158	Polycarbonate (PC)	0.20
Boron Nitride	250~300	Polyvinyl chloride (PVC)	0.19
Aluminum oxide	20~29	Epoxy resin	0.19

2. Materials and Methods

2.1. Materials

Unsaturated polyester (UP) resin (pre-mix thixotripic) and its hardener (methyl ethyl ketone peroxide (MEKP)) were manufactured by Akzo Nobel Industrial Chemicals B.V. The clam shell of *Polymesoda bengalensis* was collected at Sungai Merdang, Kota Samarahan, Sarawak, Malaysia.

2.2. Preparation of Shell Powder

The shells of *Polymesoda bengalensis* were scrubbed, cleaned thoroughly with distilled water and dried in the oven at 85°C for 24 hours. The dried shells were crushed using a manual mortar and pestle, then followed by using a blender machine. The clam shell powder was then sieved through different aperture sizes, arranged from bigger size at the top and the finest at the bottom; 850 µm, 600 µm, 500 µm, 300 µm, 212 µm, 150 µm, 75 µm and 63 µm. The powder was then dried for 1 hour at 75°C. Finally, the dried powder was kept in sealed polyethylene plastic bag.

2.3. Determination Powder Mean Size

5 g of clam shell powder was stirred in the 100 ml of distilled water. The mixture was then mounted in the Malvern mastersizer 2000 particle size analyzer. The particle size was analysed and mean size of the powder was taken at 50% distribution width.

2.4. Stearic Acid Treatment

The modification procedure applied in this study was published by Rezaei Gomari et al [21] and also applied by Mihajlović et al [22]. 1 wt% of stearic acid was dissolved in the chloroform. 10 ml of the solution was poured into 100 ml of warmed distilled water at 50 °C which was already mixed with 10 g $CaCO_3$. The dispersion was then stirred at 500 rpm for 15 minutes at constant temperature at 50 °C. The powder was then filtered and washed with distilled water, and finally dried at 50 °C for 4 hours.

2.5. Sample Fabrication

To produce neat UPE specimen, UPE was mechanically stirred with 1 wt% of MEKP for 5 minutes. The mixture was then poured into the non-stick mould and degassed for 30 minutes to remove the air bubble. The curing process was finally done at room temperature for 24 hours. To produce UPE/$CaCO_3$ composites samples, certain amount of clam shell powder was mixed with UPE to produce 2, 4, 6 and 8 wt% $CaCO_3$ filler. The mixture was mechanically stirred for 5 minutes, then was soaked in the ultrasonic bath for 15 minutes. Next, 1 wt% of MEKP was added into the mixture for rapid curing. The mixture was poured into the mould and degassed for 30 minutes. The curing was done at room temperature for 24 hours. For surface morphology study, the sample was sputtered with gold coating before mounted on SEM (model Hitachi S3400N). For thermal conductivity measurement, the UPE/$CaCO_3$ composites were cut into cylindrical shape with 25 mm diameter. The thermal conductivity of the UPE/$CaCO_3$ composites was measured according to ASTM E1225-99. The sample was placed between two brass terminals of thermal conduction unit (Model P.A. Hilton) as shown in Figure 1. The heat flux was set at constant value of 10 W at hot terminal. The cooling end terminal was connected with water circulation system. The water was circulated at constant rate of 4 L/min. The temperature reading were taken every 30 minutes, up to 3 hours at six points at hot terminal (T1, T2 and T3) and cold terminal (T4, T5 and T6). As the sample reach the steady state condition, the temperature readings were taken every 15 minutes for 1 hour. Steady-state is defined when the temperature change is not more than ±1 ^{o}C/min [2]. The temperatures at the interfaces of hot (Th) and cold (Tc) ends of the specimen were calculated by extrapolating the values of T1-T6. The effective thermal conductivity of the composite sample (W/mK), Kc can be calculated by the following steps.

Heat flow in hot zone, q_h:

$$q_h = K_{brass} A \frac{[T_1 - T_3]}{[Z_1 - Z_3]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Heat flow in cold zone, q_c:

$$q_c = K_{brass} A \frac{[T_4 - T_6]}{[Z_4 - Z_6]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The average of heat input, Q_{avg}::

$$Q_{av} = \frac{q_h + q_c}{2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Therefore, thermal conductivity:

$$K_C = \frac{Q_{avg} \Delta Z_C}{A \cdot \Delta T_C} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where

$\Delta Z_c =$ the length (m) of composite sample
$\Delta T_c = T_h - T_c =$
temperature(K) difference across composite sample
Area, $A = 4.91x10^{-4} m^2$

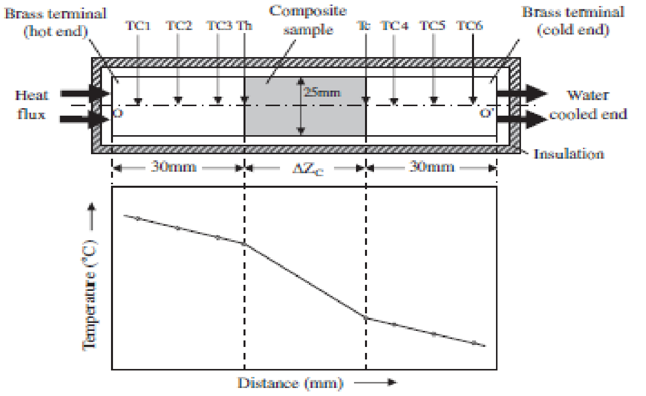

Fig. 1: Experimental setup and temperature measurement [2]

3. Results and Discussion

Figure 2 shows the effective thermal conductivity of UPE/$CaCO_3$ composites at different filler sizes and filler contents (2, 4, 6 and 8 wt%). The thermal conductivities of the composites are higher than the pure UPE matrix. The infusion of aragonite $CaCO_3$ from clam shell powder increases the composites' thermal conductivity and a significant enhancement is achieved by untreated filler at the highest filler content with the finest filler size.

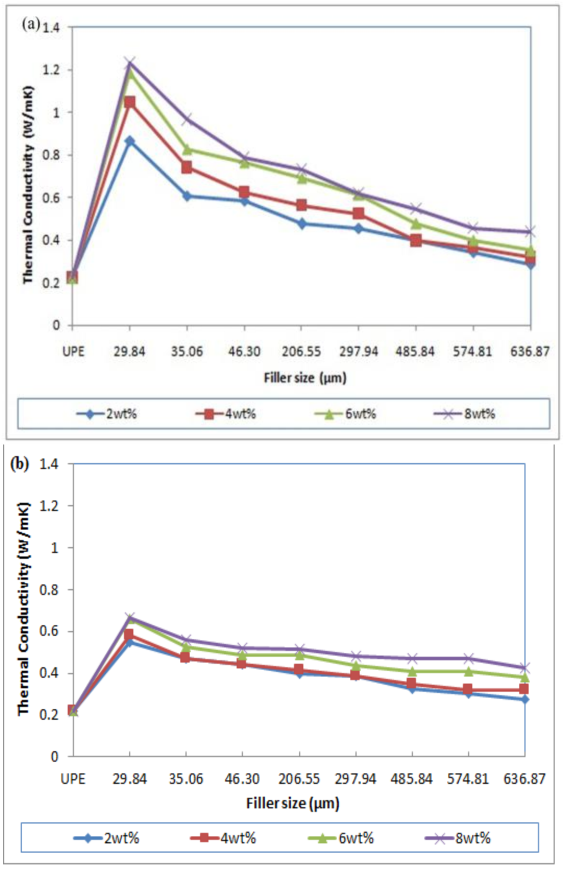

Fig. 2: Effective thermal conductivity of (a) untreated, and (b) stearic acid-treated aragonite $CaCO_3$/UPE composites of different sizes and filler contents

Initially, the thermal conductivity of neat UPE resin was 0.222 W/m·K. Introducing 2 wt% coarse filler with size of 636.87 µm increased the thermal conductivity of the composite to 0.2856 W/m·K. Replacing the same weight fraction with finer filler increased the thermal conductivity, for example to 0.3980 W/m·K, 0.4570 W/m·K and 0.4747 W/m·K as the filler size reduced to 485.84 µm, 297.94 µm and 206.55 µm, respectively. The finest filler with a size of 29.84 µm improved the thermal conductivity 3 times more than coarser filler with a size of 636.87 µm and almost 4 times more than unfilled UPE matrix. The improvement was tremendous at higher filler loading. At 8 wt% filler contents, the thermal conductivity achieved by 29.84 µm particulate-filled composites was 1.23 W/mK, or 5.5 times better than the pure UPE matrix compared to only 2 times higher for the coarser filler size of 636.87 µm.

The finer the filler, the better the efficiency of heat conduction occur in the UPE/$CaCO_3$ This may due to the tendency of the fine filler which has larger interfacial areas to be attached with the resin molecules. With the same filler content, finer filler tends to be well-dispersed and it fulfills the free volume in the matrix phase, providing small distances among the filler, hence improving the filler "bridges" at very low loadings. Better filler dispersion with low average inter-particle distance was observed in finer filler specimens, as shown in Figure 3.

The effective thermal conductivity of stearic acid-treated aragonite $CaCO_3$/UPE composites, however, is found to be lower than untreated $CaCO_3$, as it is expected that the treated filler is well-dispersed in the polymer matrix. This result is quite similar to what Deshmukh et al. [23] reported. Including $CaCO_3$ filler in the polymer increases the degree of crystallinity more than neat UPE. Filler such as $CaCO_3$ acts as a nucleating agent during the crystallization of the composites, thus increase the %crystallinity. Modifying the $CaCO_3$ with stearic acid however, reduce the surface energy, hence reducing the performance as a nucleating agent [23, 24]. As a result, the effective thermal conductivity of stearic acid-treated aragonite $CaCO_3$ filler is lower than untreated $CaCO_3$/UPE composites.

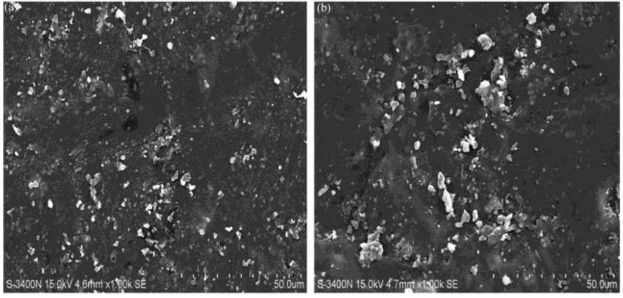

Fig. 3: Surface morphology by FESEM displaying better filler dispersion by finer filler in UPE polymer composites with (a) 29.84 µm and (b) 35.06 µm particle size distribution

This result is somewhat interesting for untreated aragonite $CaCO_3$ because as Ebadi-Dehaghani and Nazempour [1] found that inclusion of 15 wt% nano-sized $CaCO_3$ into polypropylene (PP) matrix may improves the thermal conductivity from 0.22 W/mK for neat PP to 0.36 W/mK for PP/$CaCO_3$ composites. This represents the improvement about 64%. The improvement is however, very low compared to 540% in this study. According to King et al.[19], composites with thermal conductivity ranging from 1 to 30 W/mK can be applied as heat sinks in electrical or electronic systems. Hence, to obtain the required level of thermal conductivity, more than 30 vol% of filler was infused in the polymer matrix composites. Rather than using high filler content to achieve the required level, only 8 wt% filler content of micron-sized $CaCO_3$ was infused into the UPE polymer matrix in this study. The results from this study may be valuable because infusing high filler content could increase the heat conductivity. However, to some extent, higher filler content may create the problem especially during processing such as injection molding and the possibility of extrusion. Besides, too much filler in polymer composites also can alter the mechanical behaviour and density of the composites [19].

The thermal conductivity of particulate-filled polymer composites is also influenced by the particulate shape [25, 26]. Basically, the higher the aspect ratio of the filler, the better the polymer composites can conduct heat. This is because higher aspect ratio filler can easily build filler "bridges" in the polymer matrix. Good filler interconnection then produces better thermal conductivity. Figure 4 illustrates that at low filler loading better filler interconnections are produced by higher aspect ratio particles. This may be the reason why UPE composites filled with untreated $CaCO_3$ filler yields higher thermal conductivity than stearic acid-treated $CaCO_3$. Figure 5 shows that the morphologic changes occurred as the powder was treated with 1 wt% stearic acid. The untreated powder is originally in rod-like form. Treating the powder with 1 wt% stearic acid shortens the powder length, thus reducing the aspect ratio. Table 2 represents the average effective thermal conductivity values of untreated and 1 wt% stearic acid-treated $CaCO_3$/UPE composites with different filler sizes and filler loadings.

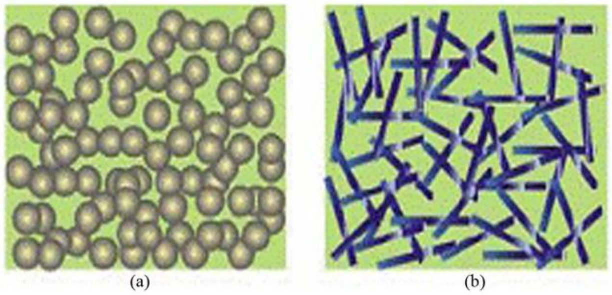

Fig. 4: Schematic illustrations of better filler interconnections produced by higher aspect ratio particles (fiber/wire) than spherical fillers [25]

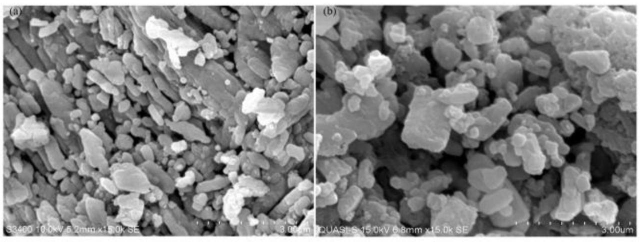

Fig 5: SEM images of (a) untreated and (b) stearic acid-treated $CaCO_3$ powder from *Polymesoda bengalensis* clam shell

Table 2: Effective thermal conductivity of untreated and stearic acid-treated $CaCO_3$-filled unsaturated polyester (UPE) with different sizes and filler loadings

	Weight fraction wt%)	2 wt%		4 wt%		6 wt%		8 wt%	
	Size (µm)	Raw	Treated	Raw	Treated	Raw	Treated	Raw	Treated
Effective thermal conductivity of untreated $CaCO_3$/UPE (W/mK) ± Standard error	29.84	0.8673 ±0.0007	0.5468 ±0.0001	1.0470 ±0.0002	0.5838 ±0.0003	1.1845 ±0.0003	0.6595 ±0.0002	1.2300 ±0.0004	0.6651 ±0.0004
	35.06	0.6062 ±0.0003	0.4695 ±0.0001	0.7400 ±0.0005	0.4695 ±0.0002	0.8277 ±0.0003	0.5246 ±0.0001	0.9656 ±0.0003	0.5593 ±0.0001
	46.30	0.5854 ±0.0002	0.4402 ±0.0002	0.6240 ±0.0003	0.4403 ±0.0002	0.7658 ±0.0004	0.4893 ±0.0001	0.7850 ±0.0003	0.5185 ±0.0001
	206.55	0.4747 ±0.0004	0.3974 ±0.0002	0.5623 ±0.0004	0.4118 ±0.0001	0.6930 ±0.0003	0.4880 ±0.0002	0.7280 ±0.0005	0.5150 ±0.0002
	297.94	0.4570 ±0.0006	0.3852 ±0.0001	0.5245 ±0.0003	0.3867 ±0.0002	0.6130 ±0.0006	0.4351 ±0.0001	0.6182 ±0.0001	0.4809 ±0.0005
	485.84	0.3980 ±0.0005	0.3275 ±0.0001	0.3960 ±0.0003	0.3481 ±0.0002	0.4767 ±0.0003	0.4099 ±0.0001	0.5450 ±0.0001	0.4711 ±0.0001
	574.81	0.3410 ±0.0001	0.3029 ±0.0001	0.3636 ±0.0002	0.3216 ±0.0001	0.3987 ±0.0003	0.4095 ±0.0002	0.4561 ±0.0004	0.4689 ±0.0001
	636.87	0.3410 ±0.0001	0.3029 ±0.0001	0.3180 ±0.0006	0.3198 ±0.0002	0.3987 ±0.0003	0.4095 ±0.0002	0.4386 ±0.0002	0.4279 ±0.0001
	Neat UPE (0 wt%)	0.2220±0.0001							

4. Conclusion

Adding $CaCO_3$ filler to unsaturated polyester matrix improved the thermal conductivity of the composites. The filler size and filler content had substantial influence on the efficient thermal conductivity of the composites. The thermal conductivity increased as the filler size decreased and filler content increased. Treating the filler with stearic acid was not helpful to increase the thermal conductivity of the aragonite $CaCO_3$/UPE composites. At similar filler content and filler size, the treated $CaCO_3$ filler exhibited lower thermal conductivity than untreated $CaCO_3$/UPE composites. Higher thermal conductivity was gained by untreated $CaCO_3$ filler because higher aspect ratio particles produces better filler interconnection than treated $CaCO_3$ filler.

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