Effects of Stearic Acid on Tensile, Morphological and Thermal Analysis of Polypropylene (PP)/Dolomite (Dol) Composites

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The effects of stearic acid treated dolomite (Sa-Dol) on the mechanical, morphological and thermal properties of polypropylene (PP) composite were studied. Prior treatment, raw dolomite was ground in planetary mill using different grinding time to obtain the submicron size (under 10μm). Particle size and specific surface area of dolomite was analyzed and validated using particle size analyzer (Malvern Mastersizer) and Brunauer-Emmett-Teller (BET) method respectively. Dolomite with five filler loadings (5, 10, 15, 20 & 25%) were mixed with PP thermoplastic and were compounded using hot melt blending method. Fourier Transform Infrared (FTIR) spectroscopy confirms the successful of filler treatment using stearic acid according to the new peak at 2917 cm^{-1} attributed to the alkyl group that represented the addition of C-H bond. Tensile properties indicated that tensile strength of PP/Dol decreased with the increasing of filler loading for both systems. The elongation at break decreased with filler loading and showed better and improved result after treatment with stearic acid. The incorporation of stearic acid coated filler into PP matrix enhanced the break elongation of the composites that makes the composites more ductile. Morphological analysis using Scanning Electron Microscopy (SEM) proved better interfacial adhesion and less agglomeration of dolomite filler after treatment with stearic acid at low filler loading (5 wt.%).

Keywords: Dolomite; Polypropylene; Stearic Acid Treated Filler; Submicron Particles

Nowadays, petroleum based thermoplastic materials are being used increasingly in various applications. A lot of researches have been conducted regarding the shortage of current oil resources worldwide since the production of petroleum crises are getting worse and frightened [1]. The use of petroleum based polymer also may lead to environmental pollution, thus the addition of mineral filler is to reduce the petroleum based material usage and also one of the effort in saving the environment. Furthermore, there is abundance of inorganic mineral filler (dolomite) in Perlis, which has not been fully utilized as at the time being the dolomite has only been used widely in cement and concrete industries.

One of the major key challenges of producing an inorganic/organic composite with excellent properties is to overcome unwanted agglomeration of mineral filler particles in the polypropylene matrix [2]. The homogenous dispersion of inorganic particles in organic polymer is difficult to achieve due to the strong tendency of the particles to agglomerate and generate high viscosity during composite processing. Since the inorganic mineral filler is hydrophilic and the organic polymer is hydrophobic, there is an issue regarding the interfacial adhesion between the particles and polymer matrix [3]. In order to improve the compatibility and dispersability of inorganic fillers in polymer media (organic material), the surface of inorganic filler is often convert into organophilic by modifying the surface of the filler by using varieties of modifier such as silanes, titanates, phosphates and etc [4]. For carbonate mineral surface coating such as calcite and dolomite, the most widely used surface coating is fatty acids, usually stearic acid where a layer of hydrophobic organic molecules is attached to the mineral surface [5]. When fatty acids are adsorbed onto carbonate surface, they initially form a monolayered array of alkyl chains oriented, thus the carboxylic groups are adjacent to the mineral surface. If the amount of fatty acid used in the practical application is low, the desired effect will not be achieved, while if excessive amount of acid is used, additional acid molecules might be physisorbed in a second layer that will reduce the properties of the composites [6]. Many studies are known with focus on mechanical and morphological properties of composites [7-11].

In this study we are focusing on the mechanical, morphological and thermal properties of PP/Dol composites before and after treatment using stearic acid ($CH_3(CH_2)_{16}COOH$). This study is only the preliminary study on the use of 0.5 wt.% of stearic acid just to observe the effects of stearic acid on the PP/Dol composites properties, so we expected that not all the result will enhance the composites properties.

Experimental

Materials

Polypropylene (PP) with density of 0.9 g/cm^3 and MFR of 1.7 g/10 min at 230°C was supplied by Titan Petchem

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Grinding Time (Hour)	0.5	1	**2**	5	10	20
Particle Size (μm)	40.085	15.451	**8.183**	7.714	7.762	7.553

Table 1
GRINDING TIME (HOUR) VERSUS PARTICLE SIZE OF DOLOMITE (μM)

	Specific Surface Area (m^2/g)	Particle Size (μm)
Raw Dolomite	2.211	318
Ground Dolomite	2.328	8.183

Table 2
SPECIFIC SURFACE AREA AND PARTICLE SIZE OF DOLOMITE BEFORE AND AFTER GRINDING

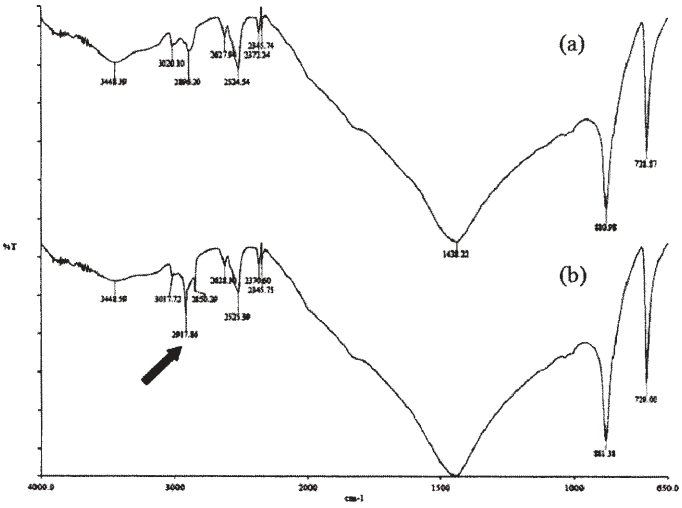

Fig. 1. FTIR spectra of dolomite (a) before treatment with stearic acid and (b) after treatment with stearic acid

(M) Sdn. Bhd. Dolomite powder with average particle size of 318μm was supplied by Perlis Dolomite Sdn. Bhd. The dolomite was first grind using planetary mill (Fritsch Pulverisette 100) for 0.5, 1, 2, 5, 10 and 20 h with speed 200 rpm to find the optimum grinding time for particle size less than 10 μm. The dolomite was then sieved using 63μm siever. Stearic acid and 2-propanol was purchased from Fischer Scientific UK and HmbG Chemicals respectively.

Surface treatment of dolomite

10g of dolomite was added into 100mL of distilled water and the suspension was stirred for 30 min at the temperature 50°C. 0.1g of stearic acid was dissolved into 10mL of 2-Propanol and the solution was poured into dolomite suspension, continuously stirred for 3 h at maintained temperature. The modified dolomite was centrifuged and dried in an oven at 80°C for 24 h to remove the excessive solution. The success of modification was confirmed by Fourier Transform Infrared (FTIR) analysis.

Preparation of the composites

The composites were prepared with different composition, consisting of filler loading between 5 wt% to 25 wt%. Polypropylene/dolomite were mixed using Brabender Plastograph® EC Plus fitted with mixer W 30 EHT at 180°C with rotors speed 60 rpm and the processing duration is 10 mi9n . Polypropylene was first added into mixing chamber until constant torque is obtained then the dolomite powder was added into the chamber.

Compression moulding

One millimeter thickness dumbbell shape samples were prepared by molding process using electrically heated hydraulic press model GT 7014 A. Hot press procedures involved pre-heating at 180°C for 8 min, followed by compressing for 2 min at the same temperature.

Fourier Transform Infrared (FTIR) analysis

The spectrums of untreated and treated dolomite were collected in the 400 cm^{-1} to 4000 cm^{-1} region, 32 scans using Perkin Elmer Spectrum 100.

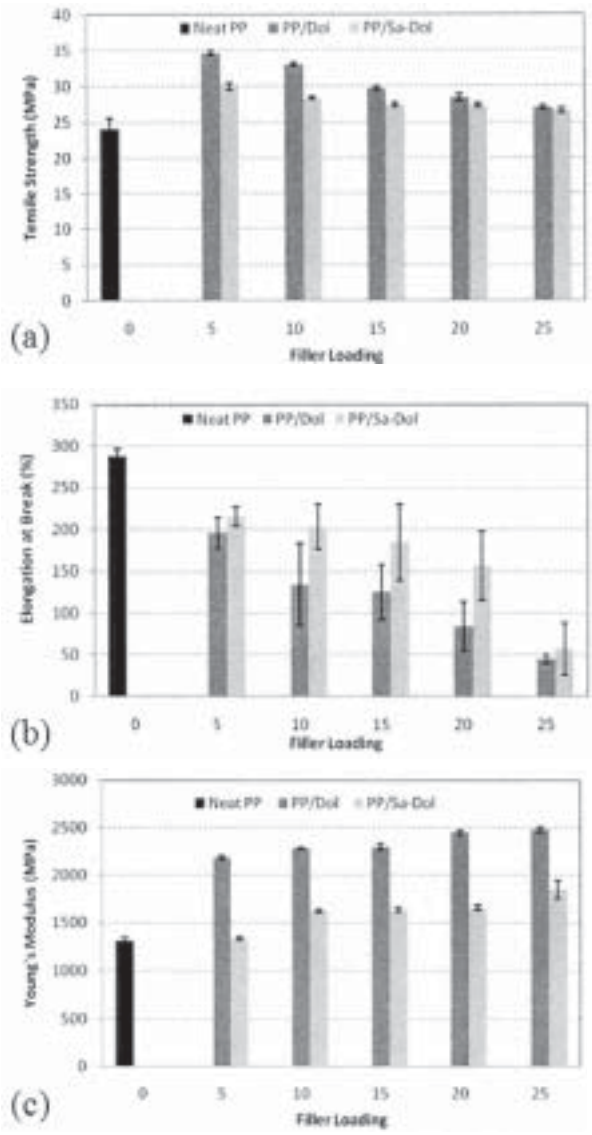

Fig. 2. Effect of stearic acid on (a) tensile strength of PP/Dol composite (b) elongation at break of PP/Dol composites and (c) Young's modulus of PP/Dol composites

Tensile test

Tensile tests were carried out on dumbbell specimens using Instron 5569 tensile testing machine. The test was done according to ASTM-D638 with crosshead speed 20 mm/min. Five specimens were used in each case, and the average value was selected. Prior testing, the thicknesses of the specimens were measured by using thickness gauge. Readings of tensile strength, elongation at break (Eb) and Young's modulus were recorded directly from the digital displays at the end of each test.

Scanning Electron Microscopy (SEM) of fractured surface study

A direct examination of the surface morphology for both ungrind and grind samples were observed using Scanning Electron Microscope (SEM - Jeol JSM-6460LA). The fracture ends of specimens were mounted on aluminium stubs

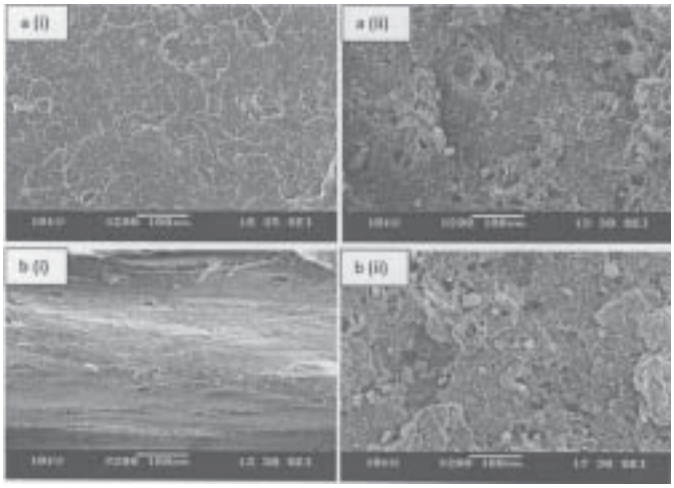

Fig. 3. The fracture surface of PP/Dol composites (a) before treatment (i) 5 wt.%, (ii) 25 wt.% and (b) after treatment (i) 5 wt.%, (ii) 25 wt.%

and sputter coated with a thin layer of palladium to avoid electrostatic charging during examination.

Thermogravimetric Analysis (TGA)

Thermo gravimetric analysis (TGA) of the samples of treated and untreated dolomite filled composites were carried out in a Q-250 thermal analyzer in nitrogen atmosphere at a heating rate of 10°C/min as per ASTM standard. This analysis was performed using Model Pyris Diamond TG/DTA.

Results and discussions

Particle size analysis

According to table 1, six different grinding time 0.5h, 1h, 2h, 5h, 10h and 20h have been used to study the effect of grinding time on the production of submicron particles of dolomite. The result shown that the particle sizes do not vary much from each other, so the optimum grinding time was chose at 2 h, due to small particle size obtained after grinding (8.183 μm) and also less energy is consumed in the grinding process for the production of the ground dolomite. Planetary mill had been chosen due to its capability in producing particle size less than 10μm as well as other filler requirements [12].

Specific surface area analysis

The particle size analysis result was supported by specific surface area using Brunauer Emmett Teller machine. Table 2 above shows that after 2 h grinding, the particle size reduced to submicron size (8.183μm) and there was an increment in specific surface area before and after grinding, 2.211 m^2/g to 2.328m^2/g respectively.

Fourier Transform Infrared Spectroscopy (FTIR)

Figure 1 shows the FTIR spectra of dolomite before and after treatment with stearic acid in a range of wavenumber 650 cm^{-1} and 4000 cm^{-1}. The main difference of the spectra peak can be observed at peak 2917cm^{-1} which was assigned to the C-H stretching vibration mode as per discussed by M. Fuji et. al [13]. The peak was not observed for the raw dolomite spectra; hence it was predicted to be the C-H stretching mode in the modifier. The molecular formula of stearic acid, $CH_3(CH_2)_{16}COOH$ confirms that there is more C-H bonding in the modifier thus it showed that the modification process was successful.

Tensile test

Figure 2(a) showed the decreased of tensile strength with the increasing of filler loading for both composites due to poor interfacial adhesion between dolomite particles and polypropylene matrix. This will initiate micro-cracks that resulting in low tensile strength. The continuous decrease of tensile strength might cause by the inhomogeneous dispersion of filler particles due to the strong tendency of fine particles to agglomerate. Jilken [14] in the previous study explained that this might be due to insufficient amount of stearic acid that was used in the modification process. Figure 2(b) showed that the elongation at break decreased with the increasing of filler loading due to the brittleness of the composites. Dolomite forces PP matrix to deform more than the overall deformation of the composite due to the fact that deformation of filler is much less than of the filler matrix [15]. The elongation at break of treated dolomite was enhanced compared to the composite without treatment, this might due to the existence of stearic acid that only acted as plasticizer or as a lubricant in the composites. Fillers could slide over one another during stretching which resulted in extra extension and elongation. In figure 2(c) it can be observed that the Young's modulus increased with the increasing of filler loading. However no improvement can be seen after treatment of dolomite with stearic acid due to the insufficient amount of stearic acid as discussed in tensile strength result.

Morphology of fractured surface

Figure 3 shows the fracture surface morphology of (a) PP/Dol composites before treatment at (i) 5 wt.%, (ii) 25 wt.%, and (b) after treatment at (i) 5 wt.%, (ii) 25 wt.%. The detachment of dolomite particles from the PP matrix can be clearly observed in figure 3 a(i) and a(ii). At higher filler loading, agglomerations and voids takes place in the matrix. This is resulted from the poor interfacial adhesion between filler and PP matrix. As been explain by Fu [16] the brittleness of composites will be increased with the increased of particulate filler loading if no or very little interfacial adhesion observed in the system. It contributed to the micro-cavitation which will lead to crack propagation. Figure 3 b(i) shows a better and homogeneous dispersion of dolomite in the polypropylene matrix compared to figure 3 b(ii), where the agglomeration and inhomegenous dispersion of dolomite particles is very obvious. This might due to the insufficient amount of stearic acid used to treat the dolomite thus a very obvious agglomerated particles is observed in the fracture surface. This agglomeration resulted decreased in tensile strength and Young's modulus for treated dolomite at higher filler loading (25 wt.%) compared to lower filler loading (5 wt.%), and also when compared to the composite before treatment with stearic acid.

Thermogravimetric analysis (TGA)

Figure 4 shows the TGA curve as a function of both PP/Dol and PP/Sa-Dol composites (5 & 25 wt.%). It can be observed from the graph that the weight loss percentage drop significantly at temperature around 470°C and 700°C-720C. This is due to the decomposition of calcium magnesium carbonate (MgO) and calcium carbonate ($CaCO_3$) respectively. A better thermal stability is achieved for stearic acid treated dolomite for both filler loadings (5 & 25 wt.%) according to the shifted TG curve to a higher temperature (from 700 to 720°C) in the graph confirming the reinforcing role of treated filler in the composites [17].

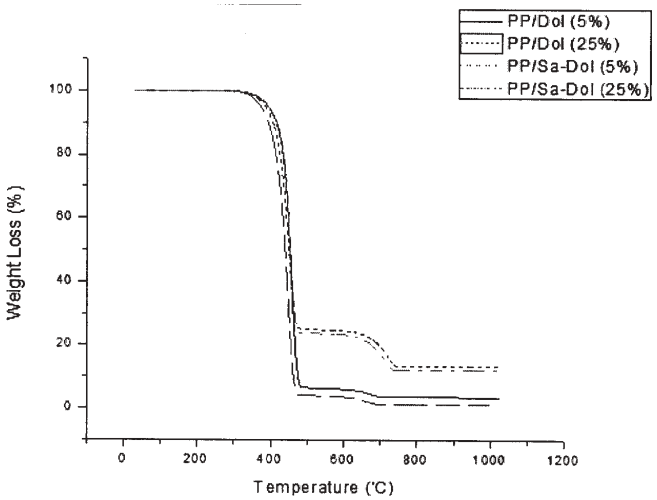

Fig.4.Thermogravimetric analysis (TGA) of untreated dolomite using stearic acid

The reaction of dolomite decomposition is shown in equation below:

$$\text{First peak} : CaMg(CO_3)_2 \rightarrow CO_3 + MgO + CO_2 \quad (1)$$

$$\text{Second peak} : CaCO_3 \leftrightarrows CaO + CO_2 \quad (2)$$

From the TGA graph, the untreated dolomite composites (PP/Dol) is decomposed at 700°C with 93% of weight loss (5 wt.% filler loading) and 96% weight loss (25 wt.% filler loading), on the other hand the weight loss for PP/Sa-Dol after 720°C is around 74% (5 wt.% filler loading) and 76% (25 wt.% filler loading). This might be accounted for by a higher interaction of treated dolomite to the PP matrix [18, 19].

Conclusions

The grinding process for dolomite is proved to reduce the particle size of raw dolomite. This result is supported by particle size analysis and specific surface area analysis, Malvern Mastersizer and BET machine respectively. FTIR analysis confirmed the success of stearic acid treatment to the dolomite particle according the new peak 2917cm^{-1} which was assigned to the C-H stretching vibration mode. The incorporation of dolomite particles into PP/Dol composites had affected the mechanical properties of the composites due to incompatibility between matrix and filler. With treatment using stearic acid, tensile strength did not show any significant increment, but elongation at break had been improved due to better interfacial adhesion between matrix and filler. This might be caused by the plasticizing effect of stearic acid treated dolomite that improved the dispersion of fillers in the composites. SEM micrographs proved better dispersion of dolomite particles at low filler loading for both untreated and treated dolomite, but at higher filler loading, agglomerations of dolomite particles still can be observed even after the treatment. Since this is only the preliminary study, according to the mechanical and morphological properties of PP/Sa-Dol it can be concluded that the amount of stearic acid used in this study is insufficient thus there were no significant changes or improvement can be observed. Thermogravimetric analysis (TGA) shows a better thermal stability for PP/Sa-Dol composite compared to untreated dolomite according to the shifted curve to a higher temperature due to the better nucleation effect of dolomite treated with stearic acid in the PP/Dol composites.

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