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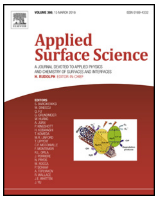

Chemical surface modification of calcium carbonate particles with stearic acid using different treating methods

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ABSTRACT

Calcium carbonate ($CaCO_3$) is often treated with stearic acid (SA) to decrease its polarity. However, the method of application of the SA treatments has a strong influence on $CaCO_3$ thermoplastic composite's interfacial structure and distribution. Several of papers describe the promising effects of SA surface treatment, but few compare the treatment process and its effect on the properties of the final thermoplastic composite. In the current study, we assessed a new SA treatment method, namely, complex treatment for polymer composite fabrication with HDPE. Subsequently, a comparative study was performed between the "complex" process and the other existing methods. The composites were assessed using different experiments included scanning electron microscopy (SEM), void content, density, wettability, differential scanning calorimetry (DSC), and tensile tests. It was observed that the "complex" surface treatment yielded composites with a significantly lower voids content and higher density compared to other surface treatments. This indicates that after the "complex" treatment process, the $CaCO_3$ particles and HDPE matrix are more tightly packed than other methods. DSC and wettability results suggest that the "wet" and "complex" treated $CaCO_3$ composites had a significantly higher heat of fusion and moisture resistance compared to the "dry" treated $CaCO_3$ composites. Furthermore, "wet" and "complex" treated $CaCO_3$ composites have a significantly higher tensile strength than the composites containing untreated and "dry" treated $CaCO_3$. This is mainly because the "wet" and "complex" treatment processes have increased adsorption density of stearate, which enhances the interfacial interaction between matrix and filler. These results confirm that the chemical adsorption of the surfactant ions at the solid-liquid interface is higher than at other interface. From this study, it was concluded that the utilization of the "complex" method minimised the negative effects of void coalescence provides key information for the improvement of existing processes.

1. Introduction

Calcium carbonate ($CaCO_3$) is one of the most popular mineral fillers used in the polymer industry [1] and [2]. However, due to the hydrophilic nature of its surface, $CaCO_3$ is incompatible with hydrophobic polymers such as HDPE [3]. While larger particles can be incorporated into the polymer, the smaller particles by virtue of enhanced particle-particle interactions tend to agglomerate, thus leading to dispersion and performance problems [4]. To overcome this issue, one of the most efficient ways to enhancing the final composite properties is the surface treatment of the filler with a surfactant. The surface treatment can decrease of particle-particle interaction and increase adhesion of matrix/filler. As a consequence, surface coated fillers are used for the production of particulate filled thermoplastic products [5] and [6].

Stearic acid (SA) as a universal and inexpensive surfactant is often used to improve $CaCO_3$ hydrophobic properties [7] and [8]. Several papers have reported the effects of SA surface treatment on the physical properties and thermal behaviour as well as mechanical properties of $CaCO_3$ composites. Lam et al. [9], studied the effect of surface-modified precipitated $CaCO_3$ on properties of $CaCO_3$/PP composites. The study showed that good dispersity and strong adhesion of $CaCO_3$ with PP was achieved due to SA surface

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modification. As a result, thermal stability and mechanical properties of the composite were increased compared to untreated $CaCO_3$ composites. Osman et al. [10], studied the influence of excessive filler coating on the tensile properties of $CaCO_3$/LDPE composites. In their study, it was concluded that it is most advantageous to coat the filler with the optimal amount of surfactant necessary to cover its surface with an organic monolayer. It was found that when excessive SA was used a SA bilayer was formed which counteracted the beneficial effects of the treatment.

SA is made up of two parts: a hydrophobic tail and a hydrophilic head (Fig. 1). During the treatment process, SA is adsorbed on the surface of $CaCO_3$ particles via a chemical reaction between the SA's "head" and calcium cation (Fig. 1). Theoretically, using this process, a monolayer film of hydrophobic molecules is created to cover the $CaCO_3$ particles [11]. However, practically there are many factors that can adversely affect this monolayer formation, such as the treatment method of application [4], the treatment process conditions [12] and [13], the moisture content of $CaCO_3$ [14], $CaCO_3$ particle size [6], $CaCO_3$ concentration [15] or the amount of SA needed to cover the calcite surface with a monolayer [8] and [10]. Hence, complete $CaCO_3$ hydrophobization using SA surface treatment is still a distant goal, this can result in the formation of voids, and void coalescence which is one of the most common defects in composite components [16] and [17]. The presence of voids, even at a very low volume fraction, can significantly damage the material properties [18]. Very fine $CaCO_3$ particles were to be used to minimise the negative effects of void coalescence, but these particles show a strong tendency to agglomerate [19]. Hence, the focus of this study was to develop a SA surface treatment method in order to produce low void $CaCO_3$/HDPE composites.

Currently, there are two methods in commercial use to pre-coat SA onto $CaCO_3$, namely, "dry" and "wet" methods [4] and [8]. With the "dry" method, the SA is added to the filler while it is maintained in a dispersed state, usually by high shear mixing at melting temperatures matching or exceeding of that SA [20]. In the "wet" method, a hot concentrated aqueous suspension of SA is added to a hot aqueous slurry of the filler. Under these conditions, a reaction with the surface of $CaCO_3$ creates a hydrophobic layer on the $CaCO_3$'s surface [4] and [20].

In the current study, we utilised a new treatment based on the wet and dry treatment methods. It is hypothesised that this complex method would achieve better compatibility of $CaCO_3$ particles and reduce voids in $CaCO_3$/HDPE composites. Therefore, HDPE composites which utilise $CaCO_3$ particles coated with SA using different surface treatment was compared. The influence of these SA coating methods on the physical thermal behaviour and mechanical properties of $CaCO_3$/HDPE composites were evaluated.

2. Experimental

2.1. Materials

HDPE [Marlex® HHM 5502BN] used in this study was supplied by Chevron Phillips Chemicals International N.U. Belgium. Ground $CaCO_3$ with the brand name Eglinton GW5 was provided by Omya UK Ltd. Stearic acid was purchased from Sigma Aldrich. Specifications given for each material is in Table 1. Sodium hydroxide was purchased from Sigma Aldrich with a 99.99% purity grade.

$$\underbrace{CH_3(CH_2)_{16}COOH}_{\text{Stearic acid}} \xrightarrow{NaOH} CH_3(CH_2)_{16}COO^- + H^+$$

Scheme 1. The proposed mechanism of hydrolysis reaction occurring in suspension 1.

$$CaCO_3 + H_2O \Longrightarrow HCO_3^- + Ca^{2+} + OH^-$$

Scheme 2. The proposed mechanism of hydrolysis reaction occurring in suspension 2.

2.2. Surface treatment

In all composites, the weight of SA was calculated to ensure 1.5 wt.% of SA was used for all samples.

2.2.1. Dry treatment process

$CaCO_3$ and SA were dry mixed at a ratio of 98.5 wt.% $CaCO_3$ and 1.5 wt.% SA. These components were compounded using an APV MP 19 TC 25 lab scale co-rotating twin screw extruder with 16 mm diameter screws and a 25/1 length-to-diameter ratio.

APV co-rotating extruder screws are designed and manufactured in a modular construction. The required compounding temperature profile was established on the APV extruder by means of six temperature controllers placed along the length of the barrel. A seventh temperature controller was used to regulate the temperature at the die (Table 2). In all cases, the speed of the delivery screws was maintained at such a rate to ensure that the materials were starve fed into the mixing screws. This ensured that in all cases output was independent of screw speed. The resultant extrudate was collected for subsequent tests.

In this step, the high shear mixing and heat was used not only for treatment purposes but also to drive off water formed by the reaction and to ensure all acid is converted to a salt form [4].

2.2.2. Wet treatment process

Two separate suspensions were prepared as outlined by [21] and [12].

- Suspension 1 contained 25 ml of 0.01 mol SA and 250 ml 0.014 mol of NaOH. These suspensions were mixed at 75 °C until the SA had totally dissolved [Scheme 1].

- Suspension 2 consisted of 500 ml of distilled water to which 100 g of $CaCO_3$ was added at a temperature of 75 °C [Scheme 2].
- Subsequently, these two suspensions were mixed together at 75 °C for 15 min. The resultant suspension was filtered and the filtrate was dried in the oven at 50 °C and stored in an airtight container until required [Scheme 3].

2.2.3. Complex treatment process

The complex process was performed using the following three steps:

- Step 1. 294.6 g of $CaCO_3$, 4.5 g of SA and 0.9 g of NaOH were mixed with 3 L of water for 10 min. This step allows all components to mix properly. SA begins to react with $CaCO_3$ during this step.
- Step 2. The resultant mixture was dried in the oven at 75 °C for 48 h. This step allows a higher percentage of SA and calcium cation reaction to take place.

$$CH_3(CH_2)_{16}COO^- + H^+ + HCO_3^- + Ca^{2+} + OH^- \Longrightarrow \underbrace{CH_3(CH_2)_{16}COOCa^+}_{\text{Calcium monostearate}} + HCO_3^- + H_2O$$

Scheme 3. The proposed mechanism of the reaction between SA and calcium cation.