

Characteristics of the treated calcium carbonate particles with stearic acid using different treating methods

Zhi Cao^{a,*}, Michael Daly^b, Lopez Clémence^c, Luke M. Geever^a, Ian Major^a, Clement. L. Higginbotham^a, Declan. M. Devine^a.

^a Materials Research Institute, Athlone Institute of Technology, Athlone, Ireland

^b Mergon International, Castlepollard, Westmeath, Ireland

^c Polytech Grenoble, Grenoble, France

*Corresponding author. Address: Zhi Cao, Innovation partners limited, Midlands research and innovation centre, Athlone institute of technology, Dublin road, Athlone, Co. Westmeath, N37 F6D7. [Tel:+353831006225](tel:+353831006225).

E-mail addresses: caozhitom@gmail.com (Z. Cao), ddevine@ait.ie (D. Devine)

Highlights

- The effects of stearic acid treatment for CaCO₃ are highly influenced by the treatment method of application.
- A new stearic acid treatment method, namely, combination treatment for CaCO₃ was developed.
- The combination treatment was compared with two of the existing methods dry and wet method.
- The negative effects of void coalescence was minimised by the utilization of the combination method.

Keywords: Calcium carbonate, Stearic acid, Treatment method, Void content

Abstract

Calcium carbonate (CaCO₃) 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 their interface 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 composite. In the current study, we assessed a new SA treatment method, namely, combination treatment for polymer composite fabrication with HDPE. Subsequently, a comparative study was performed between the “combination” 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 “combination” surface treatment yielded composites with a significantly lower voids content and higher density compared to other surface treatments. This indicates that the “combination” treatment process can bring the CaCO₃ particles and HDPE matrix much closer together than other methods. DSC and wettability results suggest that the “wet” and “combination” treated CaCO₃ composites had a significantly higher heat of fusion and moisture resistance compared to the “dry” treated CaCO₃ composites. Furthermore, “wet” and “combination” treated CaCO₃ composites have a significantly higher tensile strength than the composites containing untreated and “dry” treated CaCO₃. This is mainly because the “wet” and “combination” 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 solid-liquid interface is higher than at other interface. From this study it was concluded that the utilization of the

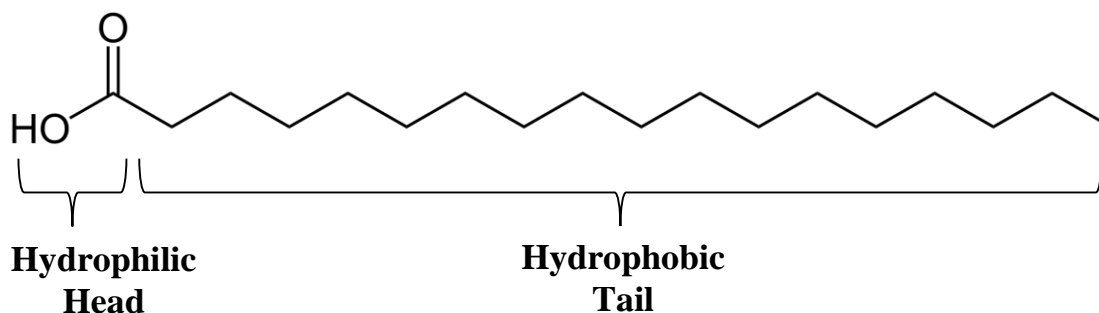
“combination” method minimised the negative effects of void coalescence should provide key information for the improvement of existing processes.

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 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. 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 modification. As a result, thermal stability and mechanical properties of the composite were increased compare 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 (Figure 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 (Figure 1). Theoretically, using this process, a monolayer film of hydrophobic molecules is created to cover for CaCO_3 particles [11].



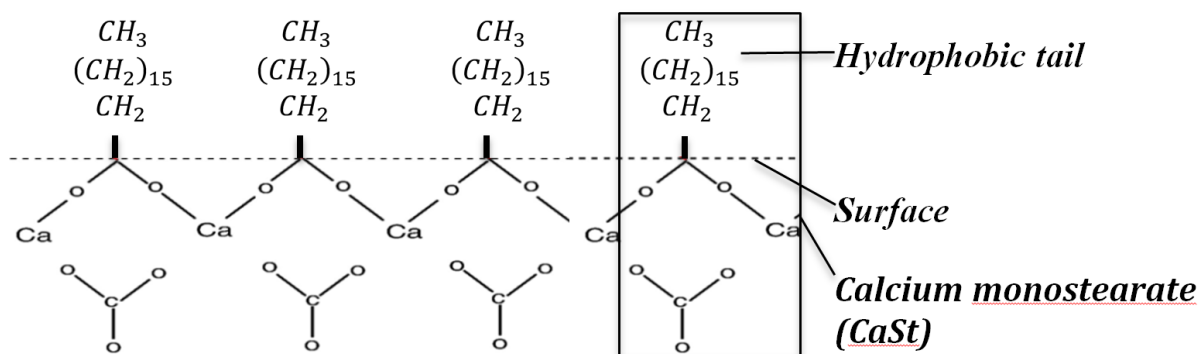


Figure 1: Stearic acid chemical structure and principle of CaCO₃ monolayer surface treatment with stearic acid [12].

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 CaCO₃ [14], CaCO₃ particle size [6], CaCO₃ concentration [15] or the amount of SA needed to cover the calcite surface with a monolayer [8] and [10]. Hence, complete CaCO₃ hydrophobization using SA surface treatment is still a distant goal, this can result in the formation of voids, and void coalescence which are 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 CaCO₃ 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 CaCO₃/ HDPE composites.

Currently, there are two methods in commercial use to pre-coat SA onto CaCO₃, 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 solution of SA is added to hot aqueous slurry of the filler. Under these conditions, a reaction with the surface of CaCO₃ creates a hydrophobic layer on CaCO₃'s surface [4] and [20].

In the current study we utilised a hybrid treatment based on the wet and dry treatment methods. It is hypothesised that this combinations method would achieve better compatibility of CaCO₃ particles and reduce voids in CaCO₃/ HDPE composites. Therefore, HDPE composites which utilise CaCO₃ 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 CaCO₃/ 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 CaCO₃ with the brand name Eglington 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.

Table 1. Main contents specifications

	Density	Appearance Color	Purity Grade	Melting Point
Stearic acid	-	White to Faint Yellow	95%	67.0 - 72.0 °C
High density polyethylene	0.91 – 0.97 g/cm ³	Opaque	High	90- 140°C
Calcium carbonate	2.7 g/cm ³ [7]	White	-	825°C

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

CaCO₃ and SA were dry mixed at a ratio of 98.5 wt. % CaCO₃ and 1.5 wt. % SA. These components were compounded using an APV MP 19 TC 25 lab-scale co-rotating twin-screw extruder with 16mm 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].

Table 2: Reactive extrusion conditions for “Dry” treated CaCO₃ particle production.

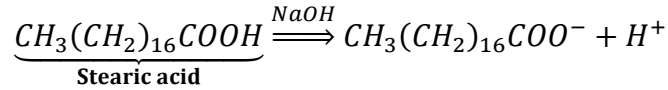
Reactive extrusion	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die	Speed [RPM]
	60 °C	70 °C	80 °C	85 °C	90 °C	95 °C	100 °C	50

2.2.2. Wet treatment process

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

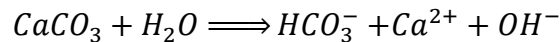
- Solution 1 contained 250 ml of 0.01 mol SA and 250 ml 0.014 mol of NaOH. These solutions were mixed at 75 °C until the SA had totally dissolved [Scheme 1].

Scheme1. Proposed mechanism of hydrolysis reaction occurring in solution 1.



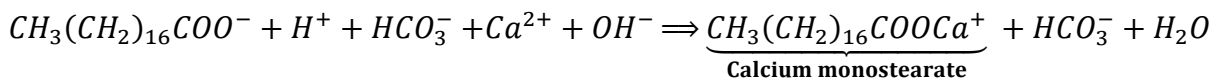
- Solution 2 consisted of 500ml of distilled water to which 100 g of CaCO₃ was added at a temperature of 75 °C [Scheme 2].

Scheme 2. Proposed mechanism of hydrolysis reaction occurring in solution 2.



- Subsequently, these two solutions were mixed together at 75 °C for 15 mins. The resultant solution was filtered and the filtrate was dried in the oven at 50 °C and stored in an airtight container until required [Scheme 3].

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



2.2.3. Combination treatment process

The combination process was performed using following three conservative steps:

- Step 1. 294.6 g of CaCO₃, 4.5 g of SA and 0.9 g of NaOH were mixed with 3 Litres of water for 10 mins. This step allows all components to mix properly. SA begins to react with CaCO₃ during this step.
- Step 2. The resultant mixture was dried in the oven at 75 °C for 48 hours. This step allows a higher percentage of SA and calcium cation reaction to take place.
- Step 3. The dried material from step 2 was compounded with powdered HDPE at a ratio of 1:1 using as APV twin screw extruder. The resultant melt was extruded through a cylindrical die to form a strand. The extrudates were cooled in air prior to granulation. In this step, the extruder was used not only for compounding of CaCO₃ and HDPE into a homogeneous blend, but also further enabling the SA to coat onto CaCO₃ particles. The processing conditions for this process are outlined in Table 3.

Table 3: Reactive extrusion conditions for “Combination” treated CaCO₃ particle production.

Reactive extrusion	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die	Speed [RPM]
	60 °C	70°C	80 °C	90 °C	100 °C	150 °C	180 °C	50

2.3. Composite fabrication

2.3.1. Extrusion Compounding

The compounding of the composites in this study was performed on a Micro 27 laboratory co-rotating twin screw extruder [Leistritz Ltd] with a 27 mm screw diameter and a 38/1 length to diameter ratio. During the compounding process, the temperature profile was increased from 160 °C at the hopper to 200 °C at the die with screw speed of 120rpm was utilised.

CaCO₃ composites were prepared by adding either untreated, dry or wet, treated CaCO₃ and HDPE pellets into the extruder at the throat of the barrel. HDPE was fed into the hopper using a K-Tron feeder. Another K-Tron feeder was filled with uncoated or coated CaCO₃ and the correct feed ratios were set to achieve an 80/20 polymer/ CaCO₃ ratio. These materials were compounded and the resultant composite material was granulated and collected for injection moulding.

Combination coated CaCO₃ composites were prepared using a masterbatch/letdown system. Calcium carbonate masterbatch which containing equal parts of CaCO₃ and HDPE was mixed at a ratio of 2:3 with HDPE to produce a let-down material containing 20 wt. % CaCO₃ and 80 wt. % HDPE. The compositions of all composites are as shown in Table 4.

Table 4: Composition of CaCO₃/ HDPE composites.

Batch name	HDPE [wt. %]	Uncoated CaCO ₃ [wt. %]	CaCO ₃ [dry] [wt. %]	CaCO ₃ [wet] [wt. %]	CaCO ₃ [combination] [wt. %]
PE	100	0	0	0	0
PE-C	80	20	0	0	0
PE-C1	80	0	20	0	0
PE-C2	80	0	0	20	0
PE-C3	80	0	0	0	20

2.3.2. Injection moulding

Injection moulding was carried out on an Arburg™ All-rounder 221 K which has a maximum clamping force of 350 kN and a screw diameter of 25 mm. The theoretical stroke volume for this machine is 49 cm³. The mould used was a family type mould producing type “A” test specimens to ISO294-1 and ISO 6239 international standard. The mould used was maintained at 25°C by means of a separate mould temperature controller unit. All CaCO₃ composite materials were dried for 8 hours at 70 °C prior to injection moulding to remove any moisture retained from the extrusion process. The temperature profile for injection moulding increased from 160 °C at the hopper to 200 °C at the nozzle with injection speed of 100 mm/sec. The holding pressure used was 600 bars with a holding time of 6.5 sec. The cooling time used was 10 sec with a back pressure of 50 bars.

2.4. Characterisation

2.4.1. Scanning electron microscopy

Scanning electron microscopy (SEM) was performed to identify changes induced by the different SA treatment process. Freeze-fracture method was implemented in order to observe these changes in the material composite structure. The experiment included the analysis of the untreated

sample and samples prepared using “dry”, “wet” and “combination” processes. Prior to testing, the samples (ASTM impact bars) were placed in liquid nitrogen for 10 min before being fractured by a Charpy impact machine. After returning to room temperature the samples were prepared for SEM, by ensuring that the orientation of the fractured side was correctly placed onto aluminium pin mount adapter using double sided carbon tape. Furthermore, all samples specimens were sputter coated with gold using a Baltec SCD 005 sputter coater to increase the electrical conductivity. Subsequently, A Mira field emission SEM was used in high vacuum mode with an acceleration voltage of 15 kV, a resolution of 20 μm and a magnification of 2.0 k \times . A back scattered electron (BSE) detector was used for image acquisition.

2.4.2. Void content

The theoretical density and void content of the CaCO_3 / HDPE composites were determined according to ASTM D2734 [22]. For theoretical composite density, the theoretical densities of both the HDPE (0.955 g/cm^3) and CaCO_3 (2.7 g/cm^3) were obtained from the supplier. After the actual density of the composite was determined the weighed sample was placed into a weighed crucible and burned in a 500 $^\circ\text{C}$ muffle furnace for 30 mins until only the CaCO_3 remains. The crucible was cooled and weighed. The HDPE and CaCO_3 contents were calculated as a weight percent from the available data.

The theoretical composite density (T_d) was calculated according to the standard ASTM D2734-09:

$$T_d = 100 / (R / D + r / d) \quad (1)$$

Where: T_d is theoretical composite density; R is the wt% of HDPE; r is the wt% of CaCO_3 ; D is density of HDPE; d is density of CaCO_3 .

The void content of the composites was calculated by comparing the actual density to the theoretical density, and according to the standard ASTM D2734-09:

$$V = (T_d - M_d) / T_d \quad (2)$$

Where: V represents void content (volume %) and M_d represents measured composite density.

2.4.3. Density comparison

Density values of the untreated, “dry”, “wet” and “combination” processes samples were measured according to ASTM standard D 792-08 (Method A) [23] by means of a Sartorius MC201P high sensitivity balance. Prior to density measurements, all samples were dried at 50 $^\circ\text{C}$ for 18 hours. To calculate the density of the composites, the specimen is weighed in air using the balance with a precision of 0.1 mg. Then the specimen is weighed when immersed in distilled water at 21 $^\circ\text{C}$ using a sinker and wire to hold the specimen completely submerged as required. Care was taken to ensure that no air bubbles were trapped prior to taking the measurement. Ten specimens

per batch were assessed. The average of the ten was calculated as composite density. The following equations were formulated to identify the specific gravity and density of the CaCO₃/ HDPE composites.

$$Sg^{21^{\circ}C} = a/(a + w - b) \quad (3)$$

Where: $Sg^{21^{\circ}C}$ is specific gravity of the composites at 21°C; a is the mass of specimen, without sinker, in air; b is the mass of specimen and sinker completely immersed and of the wire partially immersed in gas-free distilled water at 21 °C; W is the mass of totally immersed sinker and partially immersed wire.

$$D^{21^{\circ}C} = Sg^{21^{\circ}C} \times 0.99799 \quad (4)$$

Where: $D^{21^{\circ}C}$ is the density of the composites at 21°C; 0.99799 g/cm³ is density of the water at 21°C.

2.4.4. Wettability

The contact angle was measured using a FTA (First Ten Angstroms, Virginia) 1000 machine. Each sample was measured three times in the same order to obtain a consistent value while using the sessile drop method. For contact angle measurements, a droplet of distilled water was ejected out of the micrometer syringe (GS-1200) onto the sample using a 27 gauge needle. Images of the droplet on the surface of the sample were taken over 20 second duration and the FTA software was used to calculate the angle between a tangent drawn on the water droplet and the surface of the composite. The average of 10 readings was used for each sample.

2.4.5. Thermal properties

A TA instruments 2010 DSC was used throughout the course of this work for thermal characterisation of material. Samples of between 8-10 mg were weighed out using a Sartorius scales with a resolution of 1×10^{-5} g. Samples were then placed in sealed non-hermetic aluminium pans for testing. DSC analysis was performed by cooling the samples to -100°C using liquid nitrogen and heated to 200°C at a rate of 10°C/min. Volatiles were removed from the purging head with nitrogen gas at a flow rate of 30 ml/min. Calibration of the instrument was performed using indium as standard. After each test was completed, the melting point region from the thermograph was analysed to determine heat of fusion (ΔH) and melting point (T_m) of each sample. The crystallinity level (C) of the HDPE matrix can be evaluated from the following equation (5):

$$C = (\Delta H_m / \Delta H_m^0) \times (100/W) \quad (1)$$

where ΔH_m , experimental heat of fusion; W, HDPE content in the CaCO₃/ HDPE mixture; ΔH_m^0 , heat of fusion of the 100% crystalline HDPE found in the literature, that is equal to 293 J/g [24].

2.4.6. Mechanical properties

Tensile tests were carried out using a Lloyd LRX tensometer according to ASTM standard D 638-10. Composites specimens were mounted and strained at a rate of 2 mm/min until failure occurred. Ten specimens per batch were tested and the average strength was calculated.

2.4.7. Statistical analysis

A statistical comparison of the void content, density, contact angle, experimental heat of fusion, the degree of crystallinity and tensile strength was performed. Following assessment of normality of distribution and homogeneity of variance, treatments were compared using a one way ANOVA with a Tukey's Honest Significant Difference Post hoc test to determine differences between individual batches. Differences were considered significant when $p \leq 0.05$. To perform this analysis, the IBM SPSS statistics version 19 software was used.

3. Results and discussion

3.1. Morphology

SEM micrographs of the HDPE composites containing untreated CaCO_3 and SA coated CaCO_3 using different methods are shown in Figure 2. Untreated CaCO_3 particles appeared to have formed agglomerates and exhibited poor intimate contact with HDPE matrix and, as indicated by arrows in Figure 2a, which resulted in debonding between CaCO_3 and the matrix. This effect is as a result of detachment of the unembedded particles during fracture in liquid nitrogen, indicating that there is poor adhesion between the filler and the matrix. These agglomerates are formed due to strong particle-particle interaction between untreated CaCO_3 particles [25]. Similar observation has also been made by other researchers who examined the dispersion of CaCO_3 in polybutylene terephthalate [26] and polypropylene (PP) [27] matrices.

The agglomerates of “dry” coated CaCO_3 particles (Figure 2. b) appeared to exhibit better dispersion within the matrix than untreated particles (Figure 2. a), indicating that the particle-particle interaction is reduced using the “dry” method. However, we did find that debonding on the fracture surface of the composite appeared to have resulted in a large number of voids, which may have been caused by the addition of the “dry” coated CaCO_3 particles (indicated by arrows in Figure 2. b). This phenomenon suggests that the role of the “dry” method on particle–particle interaction may be more important than on particle-polymer interaction. In other words, the main role of the “dry” method is to improve the particle dispersion. The present results are in agreement with the data from Lazzeri et al. who reported that the addition of stearic acid using “dry” method can effectively improve dispersibility of the CaCO_3 / HDPE composites [19].

Composites produced using “wet” coated CaCO_3 (Figure 2. c) particles appeared to yield improved adhesion to the HDPE matrix, which resulted in an apparent reduction in debonding and voids at the fracture interface. This indicates that the “wet” treatment process promotes adhesion between the particles and HDPE matrix thus improving the compatibility between the phases. This may be due to an increase in SA chemical absorption onto the surface using the “wet” coated method in comparison to the “dry” coated method. This phenomena was also reported by Mihajlović et al. [8]. However, agglomerates were observed as indicated by arrows in Figure 2. c.

which indicates indicating poor dispersion and distribution of CaCO_3 particles. These results suggest that the main role of the “wet” treatment method is to improve adhesion between the CaCO_3 particles and HDPE matrix.

Composites prepared using the “combination” coated CaCO_3 (Figure 2. d), it is observed that CaCO_3 particles appeared to have good adhesion with the HDPE matrix as less debonding and voids were observed. This indicates that the “combination” treatment method is more efficient than “dry” treatment method in promoting adhesion between the CaCO_3 particles and HDPE matrix. These results also indicate that there was an increase in SA absorption onto the surface of the CaCO_3 particles using the “combination” coated method in comparison to the “dry” coated method. However, the air voids as indicated by arrows in Figure 2. d. suggests the “wet” treatment method is better than “combination” treatment method in promoting adhesion between the CaCO_3 particles and HDPE matrix. This may be due to the higher SA absorption onto the surface “wet” coated CaCO_3 compare to “combination” coated CaCO_3 . These findings indicate that SA treatment of CaCO_3 does not prevent particles from aggregating, but can effectively reduce the agglomerate particle size and also improve the particle dispersion which can help to reduce the creation of very large voids [19].

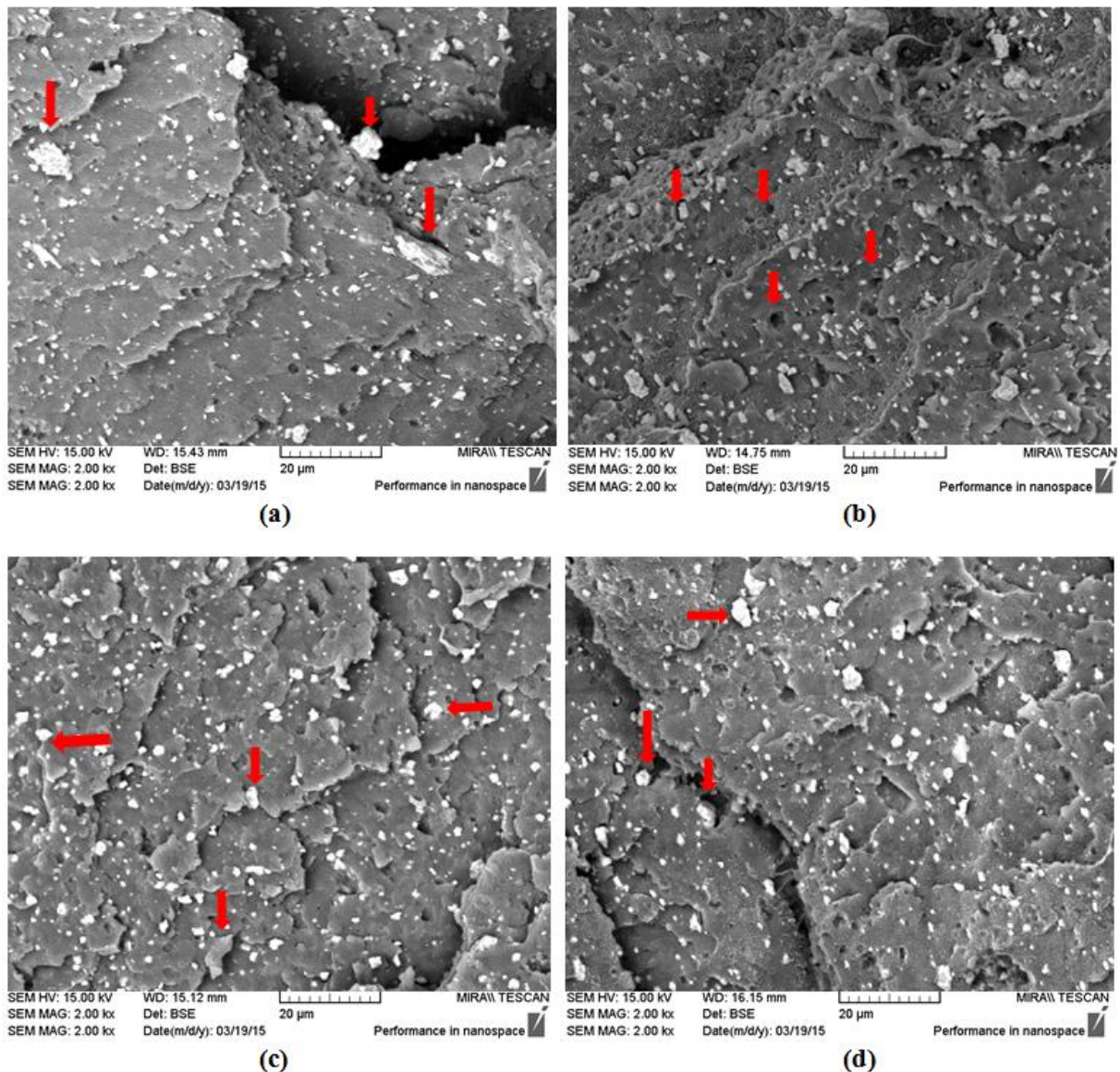


Figure 2. Scanning electron micrographs of CaCO₃/ HDPE composites made with the various treatment methods.

3.3. Void content

Void content is most commonly used to characterize voids in composite. In many cases, it is the only characteristic identified. There are many methods for determining void content including, density measurements, optical image analysis, and ultrasonic attenuation [28]. In this study, density measurements method was used to determine the void content of CaCO₃ composites. It was found that no significant differences in theoretical density between the untreated and the different surface-treated CaCO₃ composites ($p \geq 0.518$). This result has confirmed that all the composite samples contain the same amount of CaCO₃ filler.

The void content (%) of composites containing different surface-treated CaCO₃ and untreated CaCO₃ is presented in Figure 3. The composites containing SA coated CaCO₃ (PE-C1, PE-C2 and PE-C3) have a significantly lower void content than the composite containing untreated CaCO₃ (PE-C) ($p \leq 0.001$). This is mainly because SA treatment of CaCO₃ reduced the agglomerate

particle size and improve the particle dispersion which can help to reduce the creation of voids [19]. There is also some evidence from SEM micrograph (Figure 2. b, c, d.), where less fracture line, less voids and better adhesion between the CaCO₃ particles and HDPE matrix was observed.

The method of application of the SA surface treatments has a significant effect on the void content of the composites. It was found that the composites containing “wet” and “combination” coated CaCO₃ have a significantly lower void content (%) than the composites containing “dry” coated CaCO₃ ($p \leq 0.001$). This is likely due to SA being less chemically absorbed in the “dry” method than in the “wet” method [8]. This indicates that the “wet” and “combination” treatment methods are better than “dry” method in eliminating free volume created by the debonding of the CaCO₃ particles. These results correlate well with the findings from the SEM characterisation (Figure 2. b, c and d.).

Results also show that the “combination” coated method is most effective in removing voids trapped between CaCO₃ and HDPE. The composite samples containing “combination” coated CaCO₃ have a significantly lower void content (%) than the composites containing “wet” coated CaCO₃ ($p \leq 0.001$). This is presumably due to the addition of the fine CaCO₃ particles which were surface treated enabling them to make the internal structure of composite denser and closed [6]. This suggests that the “combination” treatment process can bring the CaCO₃ particles and HDPE matrix much closer together than other methods.

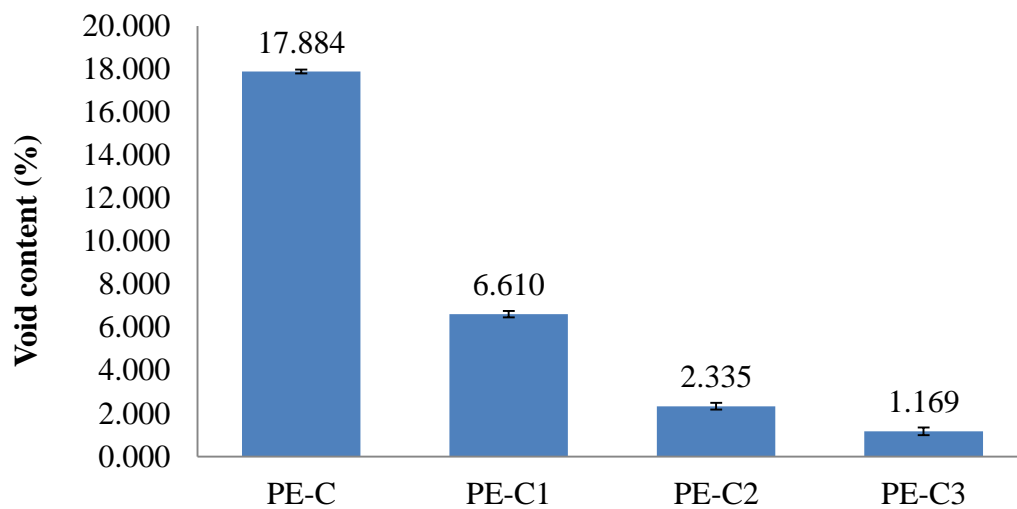


Figure 3: Void content of CaCO₃/ HDPE composites made with the various treatment methods.

3.2. Density comparison

The density of the composite materials is especially relevant because plastic products are often sold on a cost per kilogram basis and a higher density means less raw material input. The density of CaCO₃ is approximately three times greater than HDPE. It was therefore expected that all the CaCO₃ composites would also have higher density compared with pure HDPE. However, our experimental results indicated that no significant differences was found between the untreated CaCO₃ (PE-C) and virgin HDPE ($p \geq 0.666$). This is likely due to the lack of intimate content

between CaCO₃ and HDPE which created free volume in the composite [25] and led to the recorded high void content. This is consistent with the surface characteristics shown using SEM micrograph (Figure 2.a.). It is likely that as the poorly welded CaCO₃ aggregates debonded from the matrix, voids appeared at the surface and the CaCO₃/ HDPE interface and the overall density of composite decreased.

All the HDPE composites containing SA treated CaCO₃ (PE-C1, PE-C2 and PE-C3) have a significantly higher density than the composite containing untreated CaCO₃ (PE-C) ($p \leq 0.001$). This is because the SA surface treatment reduced free volume creation by increasing the extent of dispersion and interfacial interaction between CaCO₃ and HDPE matrix [10] which is supported by the results of void content analysis (Figure 3). There is also some evidence, from SEM micrograph (Figure 2. b, c, d.), of better dispersion and adhesion between the CaCO₃ particles and HDPE matrix.

Results also indicate that the method of application of the SA treatment has significant effect on the density of the composites. The composite sample containing “combination” coated CaCO₃ have a significantly higher density than the composites containing “wet” and “dry” coated CaCO₃ ($p \leq 0.001$). This is mainly because the “combination” method has significantly reduced the free volume in the composite. It can make the internal structure of composite denser than both “wet” and “dry” methods. These facts are strongly supported by Figure 3 showing the composite sample containing “combination” treated CaCO₃ have a significantly lower void content (%) than the composites containing “wet” and “dry” treated CaCO₃.

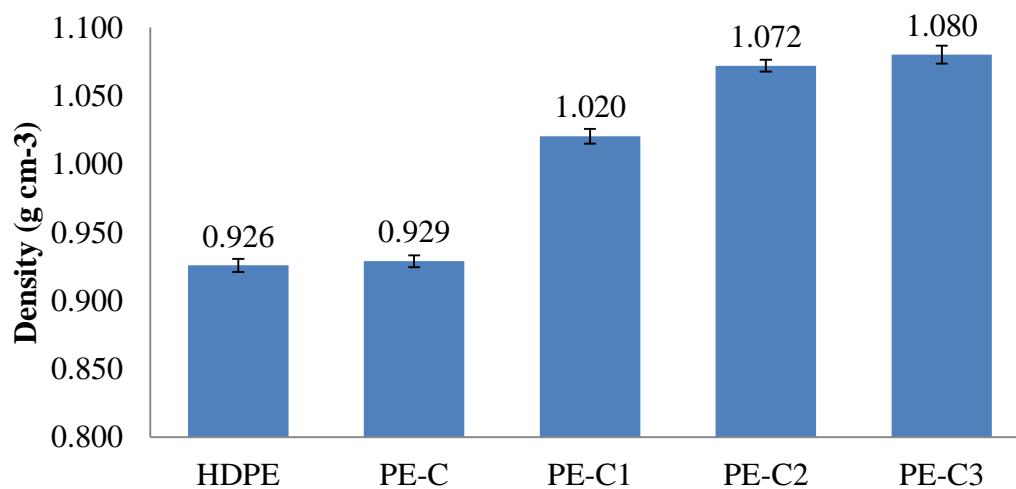


Figure 4: Density of CaCO₃/ HDPE composites made with the various treatment methods.

3.4. Wettability

To determine the hydrophobic characteristic of the CaCO₃/ HDPE composite surfaces, contact angle measurements were conducted. The sessile drop technique to measure contact angles was used in this experiment. The technique of the sessile drop is today the most widely used method [29] and [30]. Contact angle was measured after placement of a drop of water on the composite surface to determine relative wettability [31]. When the contact angle has a value of zero, it results in wetting, whilst if the angle is between 0 and 90°, it results in the spreading of the water

across the material surface. If the contact angle is between 0 and 90°, the material can be classified as hydrophilic due to the molecular attraction. However, if the contact angle is greater than 90°, the material can be classified as a hydrophobic material. This results in the water ‘balling-up’ hence, causing it to run off the surface easily [29].

Ten tests were conducted on the ASTM tensile specimens for each batch and the average was tabulated from the results attained. Figure 5 illustrates the variation of the contact angle measurements of CaCO₃/ HDPE composites. As can be seen, all CaCO₃ composites have a significantly lower contact angle than that of virgin HDPE ($p \leq 0.001$). This was due to the CaCO₃ index at the surface of the composites, and CaCO₃, a hydrophilic material, has a lower contact angle than HDPE, a hydrophobic material. It can also be observed that none of the treatment has made CaCO₃ particles completely hydrophobic. Similar behaviour have been reported by [32].

The composite containing “wet” and “combination” treated CaCO₃ (PE-C2 and PE-C3) has a significantly higher contact angle than the composites containing untreated CaCO₃ (PE-C) ($p \leq 0.001$). This is because the hydrophilic head of the stearate salt attaches to the surface of CaCO₃, while leaving the hydrophobic tail oriented towards HDPE. This resulted in a reduction of the surface wettability of the material [33]. This is confirmed that the “wet” and “combination” methods induce a change on CaCO₃ surface from hydrophilicity to hydrophobicity.

Result also shows that the composite containing “wet” and “combination” treated CaCO₃ (PE-C2 and PE-C3) have a significantly higher contact angle than the composites containing “dry” treated CaCO₃ (PE-C1) ($p \leq 0.001$). Aside from these, no further significant difference were detected ($p \geq 0.296$). This is likely due to the surfactant ions can generally be more chemically adsorbed in the “wet” and “combination” method [8]. It also implies that the “wet” and “combination” methods are effective for obtaining hydrophobic CaCO₃. The “wet” and “combination” treatment methods plays an important role in producing a composite with better resistance towards moisture [33].

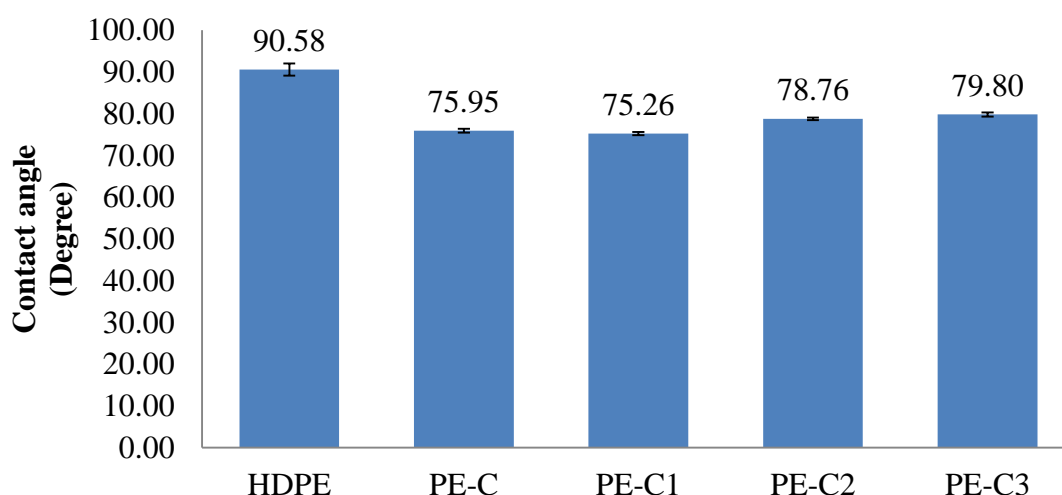


Figure 5: Contact angle measurements of CaCO₃/ HDPE composites made with the various treatment methods.

3.5. Thermal properties

The study of the thermal and crystalline properties of CaCO₃/ HDPE composites was carried out using DSC analysis. An evaluation of the experimentally obtained melting temperatures ranging between -100°C and 200°C is illustrated in the graph at Figure 6. The DSC thermogram indicated that the melting peaks of the composite reduced by up to 3°C in comparison to virgin HDPE. These effects may be due to the lamellar crystallites in the composites which melt at lower temperatures, which indicates that they are thinner than the lamellae in virgin HDPE. Such a thickness dependence of melting of PE crystallites is well documented [34] and [35]. Similar phenomenon were exhibited by Bartczak et al. [36] when CaCO₃ filler particles were added to HDPE.

A better understanding of crystallization characteristics of polymer matrix can service as a guide to manipulate mechanical properties of the composites [37] and [38]. The degree of crystallinity (C) of the HDPE matrix was evaluated from the equation (5). The degree of crystallinity, experimental heat of fusion and melting point are summarized in Table 5. From analysis of this data it was found that all CaCO₃ composites had a significantly higher experimental heat of fusion and degree of crystallinity than virgin HDPE ($p \leq 0.026$), except the “dry” treated CaCO₃ composites (PE-C1) ($p = 0.79$). The “wet” and “combination” treated CaCO₃ composites (PE-C2, PE-C3) had a significantly higher experimental heat of fusion and degree of crystallinity than the “dry” treated CaCO₃ composites (PE-C1) ($p \leq 0.05$).

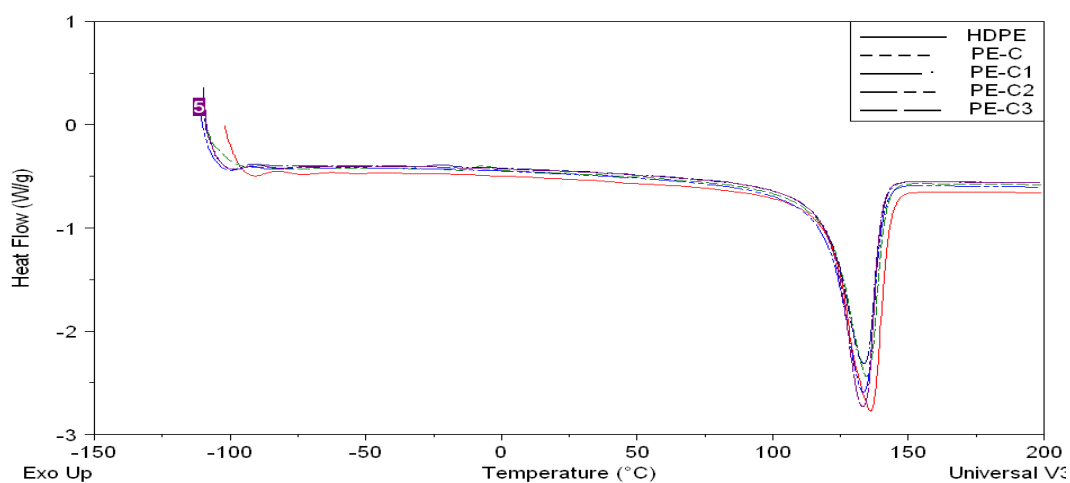


Figure 6: Differential scanning calorimetry thermograms of CaCO₃/ HDPE composites and virgin HDPE.

Table 5: Differential scanning calorimetry melting and the crystallization parameters

	ΔH_m (J/g)	$C = (\Delta H_m / \Delta H^{\circ}_m) \times (100/W)$	T_m (°C)
HDPE	156.9	0.670	136.02
PE-C	170.5*	0.727*	134.57
PE-C1	161.5	0.689	133.62
PE-C2	182.8*, **	0.780*, **	133.33
PE-C3	182.8*, **	0.780*, **	133.12

*Denotes a significant difference with virgin HDPE; **Denotes a significant difference with the “dry” treated CaCO₃ composites; ΔH_m , experimental heat of fusion; W, HDPE content in the CaCO₃-HDPE mixture; ΔH^0_m , heat of fusion of the 100% crystalline HDPE found in the literature, that is equal to 293 J/g [24].

Heat of fusion is the energy required to change a gram of a material from the solid to the liquid state without changing its temperature [34] and [35]. The addition of CaCO₃ significantly increased the amount of energy required to break the solid form of HDPE. These results suggested that the addition of CaCO₃ induced a greater heterogeneous nucleation effect and increased the degree of crystallinity of HDPE. Similar phenomenon was reported by Bartczak et al. [36] and Lazzeri et al. [19].

In the case of the “dry” treated CaCO₃ composites, the average experimental heat of fusion and degree of crystallinity decreased compared to that of “wet” and “combination” treated CaCO₃ composites. These effects are probably due to the insufficient or excess surfactant of CaCO₃ diminishing the nucleating effect. Insufficient surfactant of CaCO₃ cause the formation of agglomerates and excess surfactant can cause the formation of a soft layer at the CaCO₃-HDPE interface at high temperatures, leading to the weak nucleating ability [39].

3.6. Tensile strength

The tensile strength of the composites containing CaCO₃ surface-treated with stearic acid and untreated CaCO₃ is plotted in Figure 7. As can be seen, virgin HDPE had a tensile strength of 29.82 MPa. Batches PE-C contains untreated CaCO₃ and PE-C1 contains “dry” treated CaCO₃ had tensile strengths of 28.09 and 28.52 MPa significantly lower than virgin HDPE ($p \leq 0.001$). These results are due to the poor interfacial interaction between CaCO₃ aggregates and HDPE matrix. Insufficient or excess SA surfactant reduces the mechanical properties, the former because of the formation of agglomerates, and the latter by forming a soft layer at the CaCO₃/ HDPE interface at high temperatures, leading to matrix-filler debonding [39] and [8]. There is also some evidence, from SEM micrograph (Figure 2. a, b.), of the poorly welded CaCO₃ aggregates debonded from the HDPE matrix.

It has been reported that mechanical properties are highly dependent on the surface treatment of the CaCO₃ [27]. With the addition of “wet” and “combination” treated CaCO₃ (PE-C2 and PE-C3) a significant increase in tensile strength was recorded ($p \leq 0.001$). The tensile strength of “combination” treated CaCO₃ composite is 7.04 % higher than untreated CaCO₃ composite. The reasons behind this statistical increase in tensile strength is good interfacial interaction between HDPE matrix and “wet” and “combination” treated CaCO₃ fillers which also enable more stress to be transferred from the matrix to the fillers during external loading [40] and [41]. In doing so, the compatible CaCO₃ particles blocks the movement of macromolecular chains of the HDPE to improve the stiffness and strength [42]. These results also indicate that “wet” and “combination” method enabled the formation of strong bonding between the polar group of the SA and the CaCO₃.

The composite containing “wet” and “combination” treated CaCO₃ (PE-C2 and PE-C3) have a significantly higher tensile strength than the composites containing “dry” coated CaCO₃ (PE-

C1) ($p \leq 0.001$). This is mainly because the “wet” and “combination” treatment processes have increased adsorption density of stearate, which enhances the interfacial interaction between matrix and filler [8]. In “wet” and “combination” treatment system, hydrophilic CaCO_3 and an alkaline solution were used to form a double electric layer. On the border of solid/liquid or mineral/solution, an electric double layer is always formed consisting of the stern and diffused layer [8]. This double electric layer structure can further affect the interaction of CaCO_3 with stearic acid. In the presence of SA, dissociation and neutralization reactions were taking place. As the result of these reactions, the surface precipitation of Ca-stearate can occur by increased concentrations of stearine ions and Ca^+ ion in the electric double layer [8]. All the above results confirm that the chemical adsorption of the surfactant ions at solid-liquid interface is higher than at other interface. Aside from these, no further significant difference were detected between “dry” treated CaCO_3 (PE-C1) and untreated CaCO_3 composites (PE-C) ($p \geq 0.332$).

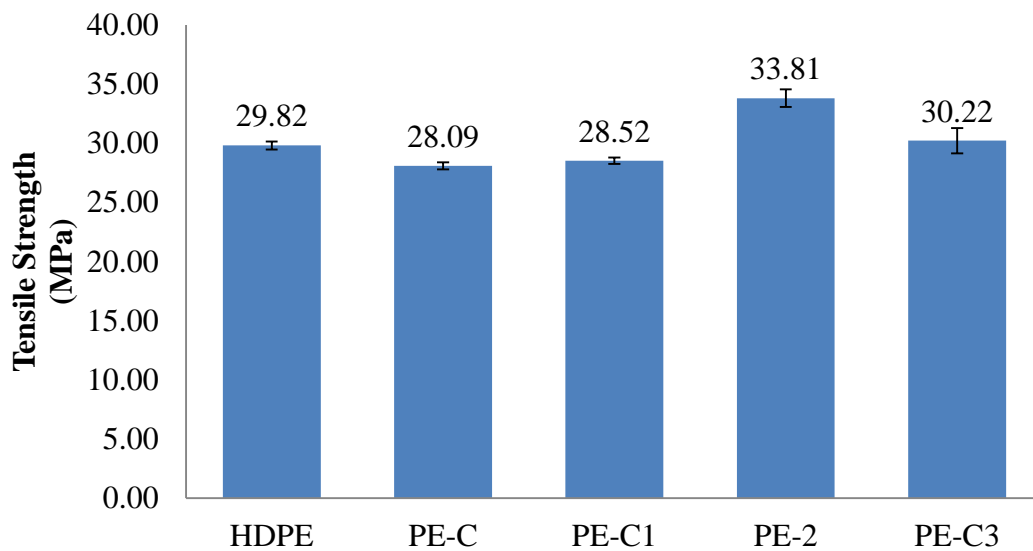


Figure 7: Tensile strength of CaCO_3 / HDPE composites made with the various treatment methods.

4. Conclusions

The present work proposes a new SA treatment method “combination” treatment for the production of CaCO_3 / HDPE composites. The effectiveness of the developed method was evaluated by comparing with two of the existing methods dry and wet method. The effects of these SA surface treatment methods on the physical properties and thermal behaviour as well as mechanical properties of CaCO_3 / HDPE composites were studied. Based on the obtained results and their discussion, the following conclusions can be made:

- The “combination” method can bring the CaCO_3 particles and HDPE matrix much closer together in contrast to the traditional method. The “combination” method is potentially important for composite application where the function of the void contents is a critical factor.

- The “combination” method significantly increased the density of the composite; hence these composites could be used as a direct replacement for HDPE in applications where high density is beneficial.
- The thermal properties and wettability results suggest that the presence of “combination” and “wet” surface treated CaCO₃ significantly increased thermal stability and moisture resistance compare to the “dry” treated CaCO₃ composites.
- For mechanical properties, the composite containing “wet” and “combination” treated CaCO₃ significantly increased tensile strength compare to the “dry” treated and untreated CaCO₃ composites.

In conclusion, the effects of SA surface treatment for CaCO₃ are highly influenced by the treatment method of application. From this study it was established that the utilization of the “combination” method in CaCO₃/ HDPE composites fabrication, delivered superior void coalescence prevention.

5. Acknowledgements

This work was supported by the Athlone Institute of Technology, Presidents Seed Fund and direct funding from Mergon International, Water Street, Castlepollard, Westmeath, Ireland.

6. References

- [1] O. Izgin, M. Aydin, N. Arsu, Preparation of nanocoatings in the presence of precipitated CaCO₃ fillers by UV-curing, *Prog. Org. Coatings*. 76 (2013) 950–954.
- [2] Deepika, S.K. Hait, J. Christopher, Y. Chen, P. Hodgson, D.K. Tuli, Preparation and evaluation of hydrophobically modified core shell calcium carbonate structure by different capping agents, 235 (2013) 581–589.
- [3] P. Rungruang, B.P. Grady, P. Supaphol, Surface-modified calcium carbonate particles by admicellar polymerization to be used as filler for isotactic polypropylene, *Colloids Surfaces A Physicochem. Eng. Asp.* 275 (2006) 114–125.
- [4] M. Xanthos, *Functional fillers for plastics*, 2nd update, Wiley-VCH, Weinheim, 2010.
- [5] A. Buasri, N. Chaiyut, K. Borvornchettanuwat, N. Chantanachai, K. Thonglor, Thermal and Mechanical Properties of Modified CaCO₃/ PP Nanocomposites, *World Acad. Sci. Eng. Technol.* (2012).
- [6] A. Kiss, E. Fekete, B. Pukánszky, Aggregation of CaCO₃ particles in PP composites: Effect of surface coating, *Compos. Sci. Technol.* 67 (2007) 1574–1583.
- [7] E. Yoğurtcuoğlu, M. Uçurum, Surface modification of calcite by wet-stirred ball milling and its properties, 214 (2011) 47–53.
- [8] S.R. Mihajlović, D.R. Vučinić, Ž.T. Sekulić, S.Z. Milićević, B.M. Kolonja, Mechanism of stearic acid adsorption to calcite, *Powder Technol.* 245 (2013) 208–216.

- [9] T.D. Lam, T.V. Hoang, D.T. Quang, J.S. Kim, Effect of nanosized and surface-modified precipitated calcium carbonate on properties of CaCO₃/polypropylene nanocomposites, *Mater. Sci. Eng. A*. 501 (2009) 87–93.
- [10] M.A. Osman, A. Atallah, U.W. Suter, Influence of excessive filler coating on the tensile properties of LDPE–calcium carbonate composites, *Polymer (Guildf)*. 45 (2004) 1177–1183.
- [11] E. Fekete, B. Pukánszky, A. Tóth, I. Bertóti, Surface modification and characterization of particulate mineral fillers, 135 (1990) 200–208.
- [12] W. Chengyu, S. Ye, Z. Xu, P. Yan, B. Hari, W. Zichen, Synthesis of hydrophobic CaCO₃ nanoparticles, (2005).
- [13] Y. Li, Z. Zhao, Y.-T.R. Lau, Y. Lin, C. Chan, Preparation and characterization of coverage-controlled CaCO₃ nanoparticles, *J. Colloid Interface Sci.* 345 (2010) 168–173.
- [14] İ. Özen, S. Şimşek, Vital importance of moisture level in all stages of processing from calcium carbonate coating through polyethylene/calcium carbonate compounding to film generation, 270, Part (2015) 320–328.
- [15] Y. Lin, H. Chen, C.-M. Chan, J. Wu, Effects of coating amount and particle concentration on the impact toughness of polypropylene/CaCO₃ nanocomposites, 47 (2011) 294–304.
- [16] E.A. Birt, R.A. Smith, A review of NDE methods for porosity measurement in fibre-reinforced polymer composites, *Insight Non-Destructive Test. Cond. Monit.* 46 (2004) 681–686.
- [17] P. Del Puglia, M.A. Sheikh, D.R. Hayhurst, Classification and quantification of initial porosity in a CMC laminate, 35 (2004) 223–230.
- [18] A. Zhang, D. Li, H. Lu, D. Zhang, Qualitative separation of the effect of voids on the bending fatigue performance of hygrothermal conditioned carbon/epoxy composites, 32 (2011) 4803–4809.
- [19] A. Lazzeri, S.M. Zebarjad, M. Pracella, K. Cavalier, R. Rosa, Filler toughening of plastics. Part 1—The effect of surface interactions on physico-mechanical properties and rheological behaviour of ultrafine CaCO₃/HDPE nanocomposites, *Polymer (Guildf)*. 46 (2005) 827–844.
- [20] R.N. Rethon, *Particulate-Filled Polymer Composites (2nd Edition)*, 2003.
- [21] S. Mihajlovic, S. Zivko, D. Aleksandra, V. Dusica, J. Vladimir, S. Jovica, Surface properties of natural calcite filler treated with stearic acid, (2009).
- [22] ASTM D2734-09, Standard Test Methods for Void Content of Reinforced Plastics, (n.d.).
- [23] ASTM D792-08, Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement, (2008).
- [24] J. Chen, N. Yan, Crystallization behavior of organo-nanoclay treated and untreated kraft fiber–HDPE composites, *Compos. Part B Eng.* 54 (2013) 180–187.

- [25] W.C.J. Zuiderduin, C. Westzaan, J. Huétink, R.J. Gaymans, Toughening of polypropylene with calcium carbonate particles, *Polymer (Guildf)*. 44 (2003) 261–275.
- [26] G. Deshmukh, S. Pathak, D. Peshwe, J. Ekhe, Effect of uncoated calcium carbonate and stearic acid coated calcium carbonate on mechanical, thermal and structural properties of poly(butylene terephthalate) (PBT)/calcium carbonate composites, *Bull. Mater. Sci.* 33 (2010) 277–284.
- [27] S.M. Zebarjad, M. Tahani, S.A. Sajjadi, Influence of filler particles on deformation and fracture mechanism of isotactic polypropylene, *Proc. Int. Conf. Adv. Mater. Process. Technol. Part 2*. 155–156 (2004) 1459–1464.
- [28] B. Zhang, L. Liu, Z. Wu, D. Wang, L. Ye, Y.W. Mai, et al., Experimental Investigation of Porosity in Carbon/Epoxy Composite Laminates, in: Woodhead Publishing, 2004: pp. 118–123.
- [29] K. Murray, J. Kennedy, B. McEvoy, O. Vrain, D. Ryan, R. Cowman, et al., Characterisation of the surface and structural properties of gamma ray and electron beam irradiated low density polyethylene, *Int. J. Mater. Sci.* 3 (2013).
- [30] L. Hu, P. Dong, G. Zhen, Preparation of active CaCO₃ nanoparticles and mechanical properties of the composite materials, *Mater. Lett.* 63 (2009) 373–375.
- [31] N.M. Stark, L.M. Matuana, Characterization of weathered wood–plastic composite surfaces using FTIR spectroscopy, contact angle, and XPS, 92 (2007) 1883–1890.
- [32] S.-B. Jeong, Y.-C. Yang, Y.-B. Chae, B.-G. Kim, Characteristics of the Treated Ground Calcium Carbonate Powder with Stearic Acid Using the Dry Process Coating System, *Mater. Trans.* 50 (2009) 409–414.
- [33] Z. Hu, X. Zen, J. Gong, Y. Deng, Water resistance improvement of paper by superhydrophobic modification with microsized CaCO₃ and fatty acid coating, *Colloids Surfaces A Physicochem. Eng. Asp.* 351 (2009) 65–70.
- [34] B. Wunderlich, *Macromolecular physics. Vol.1, Crystal structure, morphology, defects*, Academic Press, New York ; London, 1973.
- [35] B. Wunderlich, *Crystal melting*, Academic Press, New York, 1980.
- [36] Z. Bartczak, A.S. Argon, R.E. Cohen, M. Weinberg, Toughness mechanism in semi-crystalline polymer blends: II. High-density polyethylene toughened with calcium carbonate filler particles, *Polymer (Guildf)*. 40 (1999) 2347–2365.
- [37] H. Zhou, *Structure-property relationships: Model studies on melt extruded uniaxially oriented high density polyethylene films having defined morphologies*, Virginia Polytechnic Institute and State University, 1997.
- [38] C.-M. Chan, J. Wu, J.-X. Li, Y.-K. Cheung, Polypropylene/calcium carbonate nanocomposites, *Polymer (Guildf)*. 43 (2002) 2981–2992.

- [39] Y. Lin, H. Chen, C.-M. Chan, J. Wu, Nucleating effect of calcium stearate coated CaCO₃ nanoparticles on polypropylene, *J. Colloid Interface Sci.* 354 (2011) 570–576.
- [40] N. Ning, S. Fu, W. Zhang, F. Chen, K. Wang, H. Deng, et al., Realizing the enhancement of interfacial interaction in semicrystalline polymer/filler composites via interfacial crystallization, *Prog. Polym. Sci.* 37 (2012) 1425–1455.
- [41] M.A. Gunning, O.M. Istrate, L.M. Geever, J.G. Lyons, P. Blackie, B. Chen, et al., The effect of maleic anhydride grafting efficiency on the flexural properties of polyethylene composites, *J. Appl. Polym. Sci.* 124 (2012) 4799–4808.
- [42] J.-Z. Liang, D.-R. Duan, C.-Y. Tang, C.-P. Tsui, D.-Z. Chen, Tensile properties of PLLA/PCL composites filled with nanometer calcium carbonate, *Polym. Test.* 32 (2013) 617–621.