



## Full Length Article

## Mechano-chemical surface modification of calcite by wet-stirred ball milling

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## ABSTRACT

In this study, surface modification of calcite was examined using a laboratory stirred ball mill in wet condition. A fatty acid collector, sodium oleate (oleic acid sodium salt), was used as the modifying agent. Surface modification of the ground calcite sample was studied as a function of sodium oleate dosage, time and pH. Modification efficiency was mainly evaluated by floating test, which measures the active ratio. The effect of surface modification was also investigated using thermogravimetric (TG) and fourier transform infrared spectrometry (FT/IR) analyses, and contact angle measurements. Furthermore, mineralogical and microstructural changes were determined with X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses. The results indicated that hydrophobicity of the powdered calcite increased with increasing sodium oleate dosage, in which the active ratios of 99.0% and 100.0% were obtained with the dosages of 5.0 and 7.5 kg/ton, respectively. Beyond this point, the active ratio values decreased dramatically down to 33.63% for 15.0 kg/ton. Similarly, hydrophobicity values increased with modification time up to the active ratio of 99.27% for 11.5 min. Different to the modifier dosage, additional time resulted in only a very small decline and the active ratio decreased down to 97.70% for 20 min. The best result of 99.27% was obtained with the natural pH of about 9, and the active ratio values substantially decreased below and above this point down to 38.07% for pH 6 and 47.32% for pH 12. Overall results have shown that natural hydrophilic calcite can easily be made hydrophobic using sodium oleate as the surface modifier.

## 1. Introduction

Polymers are nowadays largely used in numerous applications such as various household, construction and engineering products due to their wide range of properties. However, because of some technical and economic reasons, they are rarely used in their pure state. Instead, polymers, which have amorphous or semi crystalline nature, are often mixed with crystalline minerals as particular additives and fillers to lower the cost (extenders) and improve their some physical and mechanical properties (functional fillers) like strength, dimensional stability and surface hardness. In order to meet these specifications, a filler material should have proper shape, size and size distribution, compatible surface characteristics and a high degree of dispersion [1–4].

Calcium carbonate ( $\text{CaCO}_3$ ) is the most commonly used filler in the industries of plastics, rubber, paper, paint and ink due to its worldwide availability in readily usable form, low cost, superior whiteness, inertness and incombustibility along with low oil-adsorbency and water adsorption [3,5,6]. Calcium carbonate is obtained by means of two processes, mainly by grinding of the natural mineral and rarely from synthetic  $\text{CaCO}_3$  prepared by carbonation of a calcium hydroxide solution [4,7]. More than 80% of the total calcium carbonate is provided

by the ground calcium carbonate (GCC), which is extensively used in polymers to improve workability and some physical properties, allow various functionalities and reduce cost of the composites. On the other hand, it very often has adverse effects especially on impact strength due to the agglomeration of hydrophilic  $\text{CaCO}_3$  particles with high surface energy in non-polar polymers. Therefore, it is necessary to make the hydrophilic surface of calcite particles compatible with the organic polymers using a surface modification process to facilitate dispersion as well as to improve water resistance and mechanical properties [3,4,6–9].

Mechano-activated surface modification is a method which takes advantage of mechano-chemical effect during ultrafine grinding. Mechano-chemical effect can be defined as physical and mechanical changes happened close by surface region, in which mineral and modifier get in contact with each other under mechanical forces. Since dry ultrafine grinding needs a very long time and much more energy, the mechano-activated surface modification in wet ultrafine grinding system is considered one of the best methods used to produce surface modified high quality mineral powder. Stirred ball mill, which combines ultrafine grinding together with surface modification, is the most widely used equipment for this purpose [10,11]. Of the various surface

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modifiers, such as silanes, phosphates, titanates, zirconates, etc, monocarboxylic acids with aliphatic hydrocarbon chain (also known as fatty acids and their salts) are the most frequently used to improve calcite's compatibility with, and dispersion in, polymers [1,3,4,8,11,12].

In literature, surface modification of calcium carbonate particles have been studied using sodium stearate [8,10], sodium oleate [11], stearic acid [4,6,7,9,12] and various fatty acids [1]. Rarely dry and mainly wet ultrafine grinding processes were used as the surface modification method in the most of these studies whereas various adsorption processes were preferred in the limited number of them. Generally promising results were obtained in these studies but the optimum modifier dosages used seemed relatively high, varying from 1 to 3% probably due to the very fine sizes of the feed materials. According to the literature data, optimum size for functional filler of rubber products is 100% passing 10  $\mu\text{m}$  and  $d_{50}$  is equal about 1–2  $\mu\text{m}$  [10]. In other words, considering the ultrafine grinding in mechano-chemical treatment, there is no need to keep average feed size down to 3–5  $\mu\text{m}$ . Therefore, in this study, mechano-chemical surface modification of natural ground calcite with comparatively coarser size was examined by wet-stirred ball milling in the presence of sodium oleate as the modifying agent. There is only one study in the related literature used this agent for calcite modification conducted by Yogurtcuoglu and Ucurum [11] in which mean size of calcite particles was 3.58  $\mu\text{m}$ . In addition to modifier dosage and time, pH was also investigated as the processing parameter in this study. Modification efficiency was evaluated mainly by floating test, and also using TG and FT/IR analyses, and contact angle measurements.

## 2. Experimental

### 2.1. Materials

The ground calcium carbonate (GCC) sample used in this study was prepared by crushing and grinding of natural calcite. The major chemical composition of the GCC sample was determined using X-ray fluorescence (XRF) spectrometry and chemical analysis. Loss on ignition (LOI) test was performed in an air oven at 1050  $^{\circ}\text{C}$  for 4 h. Basic physical properties such as particle size and specific gravity were also determined for further characterization. Particle size measurement was done by laser size analysis. Specific gravity was measured with water pycnometer. The major chemical constituents and basic physical properties of the GCC sample are presented in Table 1.

As seen from Table 1, chemical composition of the sample is almost completely composed of calcium carbonate ( $\text{CaO} + \text{CO}_2$ ). The GCC sample also contains trace amounts of  $\text{SiO}_2$ ,  $\text{MgO}$  and  $\text{Fe}_2\text{O}_3$ . Owing to the chemical analysis and the LOI test, it is understood that weight loss during the LOI test is resulted from evaporation of carbon dioxide from the sample. According to the laser size analysis,  $d_{50}$ , average particle

**Table 1**

The major chemical constituents and basic physical properties of the GCC sample.

X-ray fluorescence (XRF)		Chemical analysis	
Constituent	%	Constituent	%
<i>Chemical composition</i>			
$\text{CaO} + \text{CO}_2$	98.96	CaO	55.44
$\text{SiO}_2$	0.18	$\text{SiO}_2$	0.12
MgO	0.60	MgO	0.70
$\text{Fe}_2\text{O}_3$	0.11	$\text{Fe}_2\text{O}_3$	0.03
		LOI ( $\text{CO}_2$ )	43.66
<i>Physical properties</i>			
Average particle size, $d_{50}$ ( $\mu\text{m}$ )			7.32
Specific gravity			2.64

size, of the GCC sample was found as 7.32  $\mu\text{m}$ . Specific gravity was measured as 2.64 which is very close to literature data of 2.71 [10,13].

A fatty acid collector, sodium oleate (oleic acid sodium salt), was used, in this study, for surface modification of the GCC sample. Its molecular formula and weight are  $\text{C}_{18}\text{H}_{33}\text{NaO}_2$  and 304.45 g/mol, respectively. It is a yellow amorphous granules with slight tallow-like odor. It is lighter than a regular solid with a density of about 1.1. It starts to decompose at 232–235  $^{\circ}\text{C}$ . Furthermore, sodium oleate is highly soluble in water (10 g/100 cc) but slightly soluble in ether. It is alkaline in aqueous solution [14]. Diluted solutions of NaOH and  $\text{H}_2\text{SO}_4$  were used for pH adjustments, and distilled water was used through the experiments.

Mineralogical compositions and microstructural characterizations of the GCC sample were determined with X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses. According to the XRD result, the GCC sample consists almost totally of calcite. Based on SEM observations, the  $\text{CaCO}_3$  surface is rough and has a structure consisting of cracks.

### 2.2. Methods

Laboratory modification tests were conducted by a Union Process HD-01/HDDM-01 Attritor with a 750 mL zirconium oxide tank. The attritor has a shaft with agitator disks constructed from stainless steel. Non-metallic media made of zirconium oxide beads (93%  $\text{ZrO}_2$ ) with diameters of 0.35–0.45 mm was used as the grinding medium. 60 g of the GCC sample, 50% pulp density, 1000 rpm of the rotary speed and 280 mL of the grinding media were used as constant, whereas sodium oleate dosage, time and pH were chosen as the processing variables throughout the experiments. At the end of each test, the surface modified sample was first separated from the grinding media and the aqueous phase by sieving and filtration, respectively. The modified sample was then washed with distilled water, and the obtained products were dried at 50  $^{\circ}\text{C}$ .

The modification efficiency was mainly evaluated by floating test, which measures the active ratio, defined as the ratio of the floated product mass to the total mass of the sample. The active ratio can be calculated using the following formula:

$$AR(\%) = \frac{M_F}{M_T} \times 100 \quad (1)$$

In Eq. (1), AR is the active ratio (%),  $M_F$  is the mass of the floated product and  $M_T$  is the total mass of the sample. According to the literature data, the higher the active ratio, the better the modification effect is [4,5,10–12,15]. In the floating tests, 5 g of modified calcite sample were mixed with 250 mL of distilled water in a beaker and stirred vigorously for 10 min. After a reasonable settling time, the floated products were collected, dried at 50  $^{\circ}\text{C}$  and weighed to calculate the active ratio.

The surface modification was further evaluated by thermogravimetric (TG) and fourier transform infrared spectrometry (FT/IR) analyses, and contact angle measurements. TG analysis is an adequate technique for determining organic component adsorbed on the calcite surface [1,4,8,9,11,12,15]. TG analysis was carried out using a temperature range 30–700  $^{\circ}\text{C}$  with a heating rate of 10  $^{\circ}\text{C}/\text{min}$  in  $\text{N}_2$ . FT/IR spectroscopy was used to determine the vibrational modes of functional groups and examine the adsorption mechanism of sodium oleate on the calcite surface. The IR spectra were measured in the range of 4000–400  $\text{cm}^{-1}$  by using the KBr pellet technique [9,11]. Contact angle measurements of the unmodified and modified calcite samples were done by an Attension Theta optical tensiometer [6–8,10,15]. In addition to these evaluation methods, mineralogical and microstructural changes as a result of the modification process were determined with X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses.

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