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## Changes of surface properties of calcite particles with calcium stearate using conventional experimental design and properties of coated calcite

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**Abstract:** Calcite is utilized as a filler mineral in the industries such as plastics, rubber, and paint, to gain products with a variety of features. In order to use a calcite ore as a filler, some specific physical and physico-chemical properties are required such as ultra-fine sizes and conversion of hydrophilic to hydrophobic structure. In the present study, for these purposes, surfaces of the ultra-fine calcite powder ( $d_{50}=2.94 \mu\text{m}$ ) were coated by a mechano-chemical process with calcium stearate [ $\text{Ca}(\text{C}_{17}\text{H}_{35}\text{COO})_2$ ] in a stirred ball mill. The influence of operating parameters such as calcite filling-ratio, ball-filling ratio, operation speed, grinding time and chemical dosage on the active ratio (%) was systematically examined. Then, the properties of modified calcite product were measured and evaluated by contact angle, TGA, DTA, FTIR, and SEM. The results showed that the mechano-chemical technology is very effective for modifying the surface of micronized calcite products using calcium stearate chemical.

**Keywords:** calcite, surface modification, mechano-chemical, calcium stearate, properties of modified calcite

### 1. Introduction

Ground and precipitated calcium carbonates are widely used as performance minerals in the rubber, plastics and paper industries. Both untreated and surface modified forms are used, depending upon the nature of the end product (Katz and Milewski, 1978). Calcite is the most abundant mineral on earth and finds increasing application in the polymer industry. However, the incompatibility of its high energetic hydrophilic surface with the low-energy surface of hydrophobic polymers is a problem to be solved before it can be used as a functional filler. For this and other reasons, the surface of calcite is often rendered organophilic by a variety of surface modifiers such as fatty acids, phosphates, silanes, titanates or zirconates (Rothon, 1995; Krager-Kocsis, 1995; Nakatsuka, 1998; Jancar, 1999). In polymer applications, the calcium carbonate is often blended with polypropylene (PP) homopolymer or polyethylene (PE) to improve process ability and properties such as stiffness and impact resistance of composite materials. For effective mixing and good adhesion characteristics it is desirable that the surface energies of the mineral and polymer are close to each other (Schreiber et al., 1990).

Surface modification is a key process in functional powder preparation, which can be commonly classified into three types: chemical, physical and mechano-chemical. Surface modification with a combined action of modifying reagent and the mechano-chemical effect of ultrafine grinding has been intensively studied in the pigment and filler preparation area (Oprea and Popa, 1980). Mechano-activated surface modification is a modification method of utilizing mechano-chemical effect during ultrafine grinding. Mechano-chemical effect is a physical and mechanical change on the near surface region, where the solids come into contact with each other under mechanical forces (Mohamed and Wakeel, 2000; Frank et al., 2005). Mechano-chemical processes (MCP) use mechanical energy to

activate chemical reactions and structural changes. However, these are not new processes; mechanically activated processes date back to the early history of humankind (e.g., the use of flints to initiate fires). Following these early uses, the field of mechano-chemistry has had a rich history, particularly in Europe, which has led to the use of ball mills for processing a wide range of materials, ranging from minerals to advanced materials (McCormick and Froes, 1998).

In the surface modification process of calcium carbonate, some surfactants as surface modifiers such as silane (Demjeń, 1997), titanate (Monte and Sugerman, 1978), and stearic acid (Hansen et al., 2000; Maged and Suter, 2002; Mihajlović et al., 2009), have been used to make it dispersible in polymer matrix and improve its hydrophobic properties. Among of them, stearic acid is widely used. Monolayer coverage of the calcite surface is achieved by attaching the stearic acid, which makes the material hydrophobic. If it is used as an additive in polymer industry, it improves mechanical properties, dimension stability and surface hardness of polymer matrix (Kovačević et al., 1996; Kovačević et al., 1997). For the practical application, if the amount of fatty acid is low, the desired effect is not achieved, while the use of excessive amount of organic phase leads to processing problems, inferior mechanical properties and increased price. Thus, the optimal amount of fatty acid used for the treatment of calcium carbonate surface is both of a technical and economical issue (Fekete and Pukánszky, 1997).

In the present study, in order to obtain the hydrophobic filler mineral, the surface of the calcite was modified with calcium stearate by the mechano-chemical process. Firstly, the optimum modification variables, such as the powder-filling ratio, ball-filling ratio, speed of stirred mill, modification time, and chemical dosage were determined using conventional experimental design. In the second study, the properties of modified calcite product were measured and evaluated by contact angle, TGA, DTA, FTIR, and SEM.

## 2. Experimental

In this study two samples were tested: micronized calcite (unmodified), and mechano-chemical treated calcite (modified calcite), which had hydrophobic character. The powder sample was taken from Niğde-Turkey region. Some properties of the sample are reported in Table 1. A chemical analysis indicated that the ore was composed of 52.36% CaO. An X-ray diffraction analysis verified that calcite was the sole mineral in the ore (Fig. 1). The mean size of particles in the sample was 2.94  $\mu\text{m}$ . In the present study calcium stearate (>98.5%) [ $\text{Ca}(\text{C}_{17}\text{H}_{35}\text{COO})_2$ ] (molecular weight 323,5468 g/mol) was used.

The grinding and modification machine was a laboratory scale stirred ball mill made of polyurethane with an inner volume of 3000  $\text{cm}^3$ . The grinding media were aluminum balls of 2700

Table 1. Chemical composition of calcite sourced from Niğde-Turkey

Species	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO <sub>2</sub>	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	LOI
%	52.36	0.36	0.02	0.06	0.44	0.02	0.86	0.03	46.23

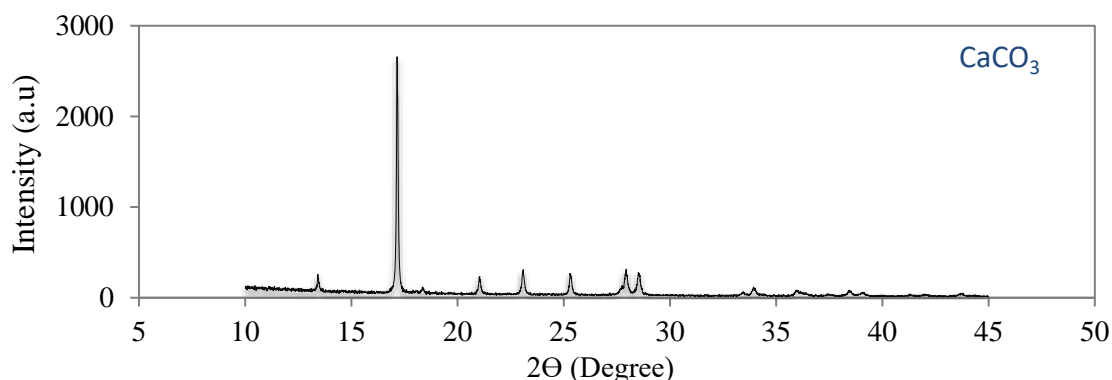


Fig. 1. Powder x-ray diffraction patterns of the starting calcite

kg/m<sup>3</sup> density and three different ball diameters: 1.0, 2.0 and 3.0 mm. The grinding experiment was carried out as a dry batch process, in which samples were taken from the pot at a determined grinding time. After each test, all of the media and ground samples were removed from the mill, and the media were separated from the products by sieving. In order to investigate the effect of experimental variables, such as the ball-filling ratio, powder-filling ratio, grinding operation speed, grinding time (min) and collector dosage (%) on the active ratio, a series of experiments were carried out.

As a measure of hydrophobicity and surface modification, an active ratio of hydrophobic to non-hydrophobic particles was determined using the Eq. 1. The floating test was performed as first characterization study for coated calcite. It is described by Sheng et al. (2006) as follows: floating test is to measure the ratio of floated product to the overall weight of sample after mixing in water and stirring vigorously. The ratio is called active ratio. The higher the active ratio, the better the modification effect is:

$$AR (\%) = [(M_f / (M_s + M_f))] \cdot 100 \quad (1)$$

where  $AR (\%)$  is the active ratio,  $M_f$  is the mass of the floated product and  $M_s$  is the mass of the sink product (Sekulic et al., 2009).

The methods were as follows. Five grams of the final sample was added to 100 cm<sup>3</sup> of distilled water. We measured the ratio of floated product to overall weight of sample after they were mixed in distilled water and stirred vigorously (Price and Ansari, 2004)

The mean particle size, width of PSD and total surface area of the final ultra-fine calcite products were determined. There are several evaluation methods that have been used to represent the width of the PSD of ground product. The cumulative weight passing particle sizes  $d_{20}$  and  $d_{80}$  (Karbstein et al., 1995; Karbstein et al., 1996) are used to evaluate the width of the PSD in mineral processing, and the particle size ratio of  $d_{80}/d_{20}$  is often calculated for the PSD width. The particle sizes  $d_{10}$ ,  $d_{50}$ , and  $d_{90}$  are used for the evaluation of the grinding characteristic of solid materials (Salman et al., 2002; Gorham et al., 2003; Matija and Kurajica, 2010). The particle size ratio of  $d_{90}/d_{10}$  is more useful for representing the PSD width because the size ratio of  $d_{90}/d_{10}$  has a wider range comparison than the ratio  $d_{80}/d_{20}$ . The size ratio  $(d_{90}-d_{10})/d_{50}$  ("span value") also can be used in addition to the ratios  $d_{80}/d_{20}$  and  $d_{90}/d_{10}$  (Karbstein et al., 1996; Nakacha et al., 2004). A decrease in these particle size ratios means a narrower PSD. On the other hand, the steepness ratio can be also defined by the "steepness factor" (SF). The SF can be calculated from the PSD curve of the powder using the following equation:

$$SF = d_{50} / d_{20} . \quad (2)$$

A curve with the greater than 2 is described as "broad" and those with the factor of less than 2 as "narrow" or "steep" (Adi et al., 2007).

The effect of the surface modification was evaluated by the particle size distribution, contact angle, FTIR, TG-DTA and SEM. In this study, the particle size distributions of calcite and modified calcite were measured by using the Malvern Mastersizer 2000. Contact angle measurements in micronized and coated calcite samples were carried out on the CAM- 101 optical contact angle analyzer (KSV Instruments, Finland). The XRD analysis was made with the PANalytical (Empyrean) device. TG-DTA and SEM analyzes were performed by using the Perkin Elmer Pyris 1 and FEI Quanta 400 MK2 instruments, respectively. The vibration modes of functional groups of the compound were determined by the Fourier transforms infrared (FTIR) analysis. The IR spectra were measured in the range of 450–4000 cm<sup>-1</sup> by the Bruker VERTEX 70v.

In order to be able to measure the contact angle of the powder samples, these samples must firstly be converted into pellet form, which is suitable for contact angle measurements. For this purpose, a pellet was prepared under high pressure, using 0.5 g calcite sample. The contact angles were measured by using a goniometer, which is used with a water drop of 6  $\mu$ L and taking Young-Laplace equation into account at the solid-liquid interface.

### 3. Results and discussion

#### 3.1 Influence of calcite powder-filling ratio

The filling ratio of powder has significant influence on the surface modification efficiency of calcite mineral. Under the condition of high filling ratio, the active ratio of hydrophobic products can be

reduced more rationally. However, under low filling ratio conditions, there can be excessive power and chemical consumption and over-grinding in the surface modification process by the stirred mill. The calcite powder-filling ratio was varied between 5 and 20% of stirred mill volume in order to determine the effect of powder-filling ratio on the active ratio (AR%). Experimental conditions were kept constant as shown in Table 2. The results showed that the optimum results were obtained at 15% calcite filling ratio (Fig. 2). As it can be seen from the result, the product had about 75% active ratio.

Table 2. Experimental conditions used in modification tests of calcite-filling ratio

Condition	Variable
Calcite filling ratio (%)	5, 10, 15, 20
Ball filling ratio (%)	30
Operational speed (rpm)	750
Grinding time (min)	15
Chemical dosage (%)	0.75

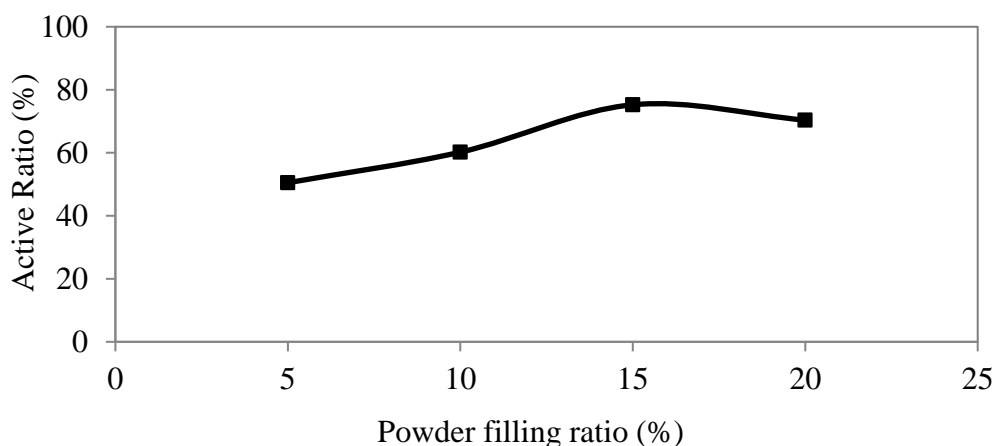


Fig. 2. The effect of calcite filling-ratio on the active ratio

### 3.2 Influence of ball-filling ratio

This study aimed for surface modification rather than grinding. Therefore, investigations at high ball-filling ratios were not conducted. The ball-filling ratio varied between 20 and 40% of stirred mill volume, while other conditions were kept constant (Table 3). It was studied in low ball filling ratio to keep low calcite grinding. Therefore, the maximum value was selected as 40%. The best results were obtained at 35% ball-filling ratio. As it can be seen from the results, the coated product contained about 80.0% active ratio (Fig. 3).

Table 3. Experimental conditions used in modification tests of ball-filling ratio

Condition	Variable
Calcite filling ratio (%)	15
Ball filling ratio (%)	20, 30, 35, 40
Operational speed (rpm)	750
Grinding time (min)	15
Chemical dosage (%)	0.75

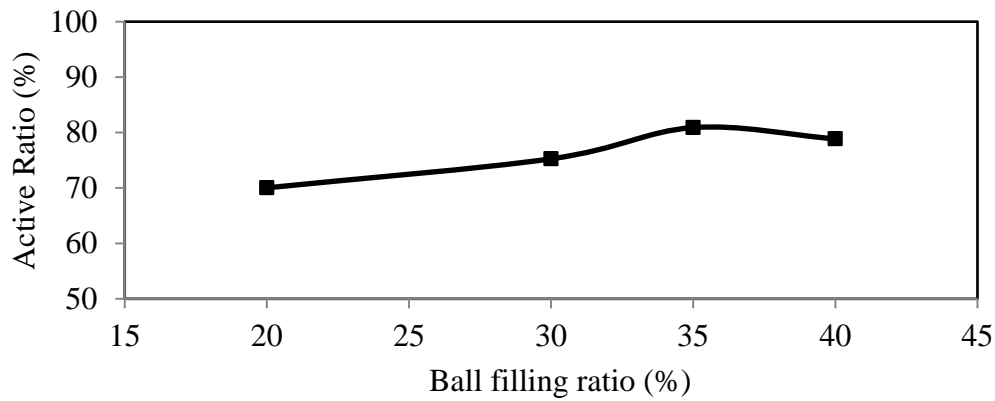


Fig. 3. The effect of ball-filling ratio on the active ratio

### 3.3 Influence of speed of stirred ball mill

The speed of stirred ball mill is an important parameter affecting the active ratio. Fig. 4 shows variation of active ratio as a function of speed of stirred ball mill, between 500 and 1250 rpm (Table 4). The active ratio levels observed were generally low and almost independent of speed. The active ratio tended to increase with increasing the speed up to a value of about 1000 rpm and the variation appeared to show the maximum value at about 90% active ratio.

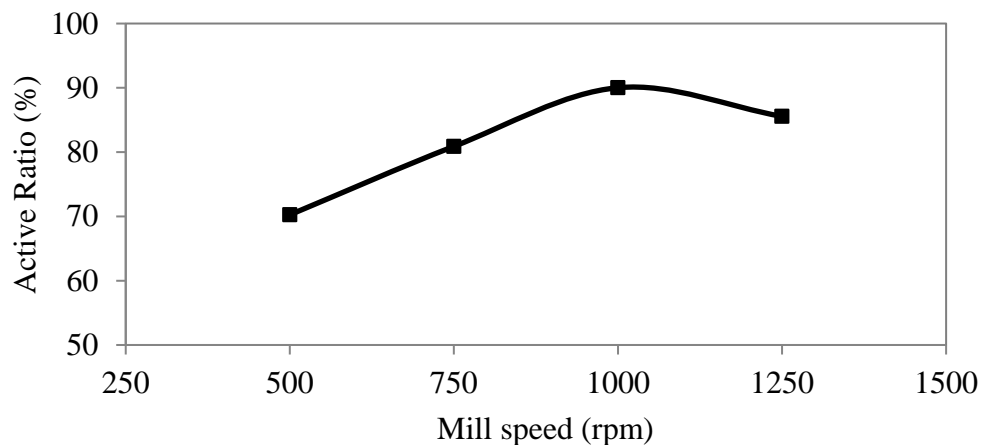


Fig. 4. The effect of mill speed on the active ratio

### 3.4 Influence of modification time

The modification time parameter relates to the particle size with a direct influence on the surface modification recovery. The effect of coating time was investigated in the range from 10 to 30 minutes. For these experiments, calcium stearate dosage was kept at 0.75% of powder. Experimental conditions

Table 4. Experimental conditions used in modification tests of mill speed

Condition	Variable
Calcite filling ratio (%)	15
Ball filling Ratio (%)	35
Operational speed (rpm)	500, 750, 1000, 1250
Grinding time (min)	15
Chemical dosage (%)	0.75

were kept constant (Table 5). Fig. 5 shows that the active ratio increased with increasing modification time up to 15 minutes, apparently going through the maximum at 15 minutes with 90% AR. The active ratio also decreased linearly with an increasing modification time after 15 minutes.

Table 5. Experimental conditions used in modification tests of modification time

Condition	Variable
Calcite Filling Ratio (%)	15
Ball Filling Ratio (%)	35
Operational Speed (rpm)	1000
Grinding Time (min)	10, 15, 20, 30
Chemical dosage (%)	0.75

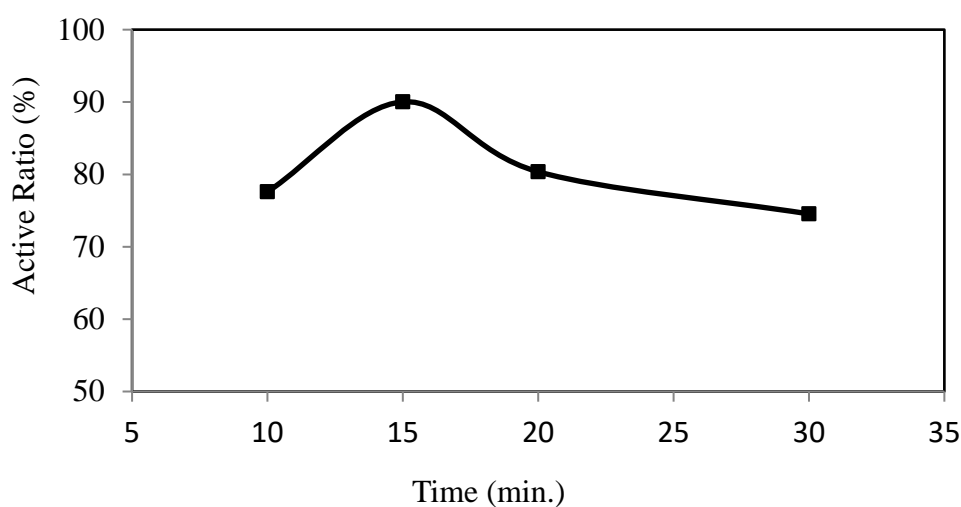


Fig. 5. The effect of modification time on the active ratio

### 3.5 Influence of calcium stearate dosage

The dosage of calcium stearate is the most important parameters in the mineral surfaces modification process, because both product quality and process economic are determined by this parameter. Therefore, six different chemical dosages were studied (Table 6). In addition, the trials showed the impact of calcium stearate addition on the active ratio of the coated calcite product. The active ratio indicated the increase from 78 to about 100% as the dosage of collector was increased from 0.5 to 1.25% of powder. Fig. 6 indicates that the active ratio of hydrophobic calcite increased gradually depending on the amount of calcium stearate and the active ratio (almost 100%) was achieved with 1.10 % calcium stearate of powder by the mechano-chemical surface modification process.

Table 6. Experimental conditions used in modification tests of chemical dosage

Condition	Variable
Calcite filling ratio (%)	15
Ball filling ratio (%)	35
Operational speed (rpm)	1000
Grinding time (min)	15
Chemical dosage (%)	0.5, 0.75, 0.85, 1.0, 1.10, 1.25

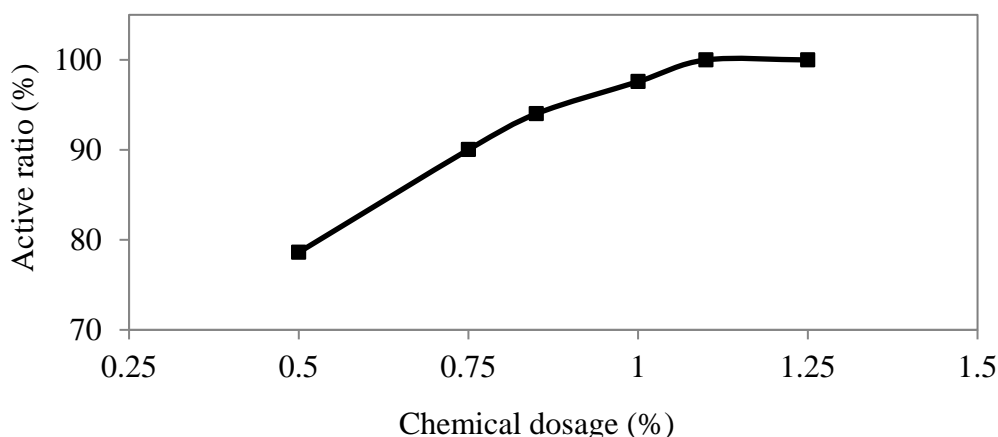


Fig. 6. The effect of chemical dosage on the active ratio

The crushing mechanical force exerted on particles is the motivation to produce the mechano-chemical effect, so its intensity is an important factor influencing the mechano-activated modification effect. This influence was studied through changing the stirrer rotary speed, the mass ratio of grinding media to mineral feeding and the duration of grinding. The specific surface area of the particles increased with the further grinding. Although the agent coverage on the particle surface decreased and the active rate decreased slightly when the agent dosage remained then same, the modification effect was still much better than that of non-ground samples (Ding et al., 2007). It was considered that the surface modification was not fully realized due to over-grinding at the rate of 5%, while the mechanical activation at 20% occupied less than 15% ball-filling ratio. The active ratio of products was increased with increasing the calcite powder-filling ratio up to 15%. At 20%, the active ratio value was sharply decreased. As the amount of powder increased, the collision spaces between the balls and filled and higher rates of breakage were obtained. Eventually, overfilling lead to damping of the collision by powder crushing and agglomeration, the powder bed expanded to give poor collision effect, and the breakage rates decreased (Kolacz, 1999). The active ratio of modified calcite increased with increasing the ball-filling ratio value up to the optimum point (35%), and afterwards active ratio decreased. The influence of the mass ratio of grinding media-to-mineral on modification is very obvious. Apparently, the mechano-activated effect produced during grinding improved the modification effect. It could be seen from the experiment results and corresponding analysis that, there existed a suitable range for the intensity of crushing mechanic force during ultra-fine grinding and simultaneous surface modification of calcium carbonate by chemical addition. If the intensity was too weak, or there was no grinding action, the modification effect would be poor because the mineral surface could not be effectively activated. If the intensity was too high, the modification effect would drop again as the finer particles needed more agent. In addition, the reacted product on the particle surface would be lashed and peeled off (Ding et al., 2007).

The main variable used for acting on the impact rate is the mill speed. It has a direct effect, is easily controllable, and presents little interference with other variables (Almond and Valderrama, 2004). The mill speed had a great effect on the modification of calcite. The mill speed was varied between 500 and 1250 rpm in order to determine the effect of agitation speed on surface modification in this study. The results showed that optimum result were obtained at 1000 rpm. The low speed surface extended the modification time, while the high speed caused excessive grinding. Hence, it caused a low active ratio in the amount of fixed reagent at the high speed. Modification time was varied between 10 and 30 min. The best results were obtained at 15 min. At short (10 min) and long (30 min) modification time the active ratio of concentrate decreased. The 10-minute experimental period appeared to be non-native to the occurrence of mechanical activation. The decrease in the active ratio was due to over-grinding as a result of after 15 minutes of modification. The calcium stearate  $[\text{Ca}(\text{C}_{17}\text{H}_{35}\text{COO})_2]$  agent was used to modify calcium carbonate after the sample was dry-ground to a certain size for a given period. At lower surface coverage of calcite with calcium stearate (0.5%), the active ratio was 78%, while the active ratio over 99.9% was achieved with 1.10% of calcium stearate. Since it is reported in

literature that the higher the active ratio, the better modification effect is (Sheng et al., 2006), the obtained results indicated that with the applied method, high hydrophobicity of the calcite surface was achieved when amount of calcium stearate was 1.10% and 1.25%.

### 3.6 Properties of coated calcite

The particle size of the micronized and coated calcite samples is presented in Fig. 7. As it may be noted,  $d_{10}$ ,  $d_{50}$  and  $d_{97}$  particle size values of micronized calcite were 0.87  $\mu\text{m}$ , 2.94  $\mu\text{m}$  and 10.55  $\mu\text{m}$ , respectively. The coated calcite obtained from the stirred ball had  $d_{10}$ =0.72  $\mu\text{m}$ ,  $d_{50}$ =2.18  $\mu\text{m}$  and  $d_{97}$ =6.60  $\mu\text{m}$ . Table 7 shows PSD values of feed material and modified product. The  $d_{50}/d_{20}$  (SF) values showed a nearly stable trend and two sample had slightly larger values than 2; namely, unmodified and modified calcite showed broad properties according to SF. In addition,  $d_{90}/d_{10}$ ,  $d_{80}/d_{20}$  and Span  $[(d_{90}-d_{10})/d_{50}]$  values gave almost the same results.

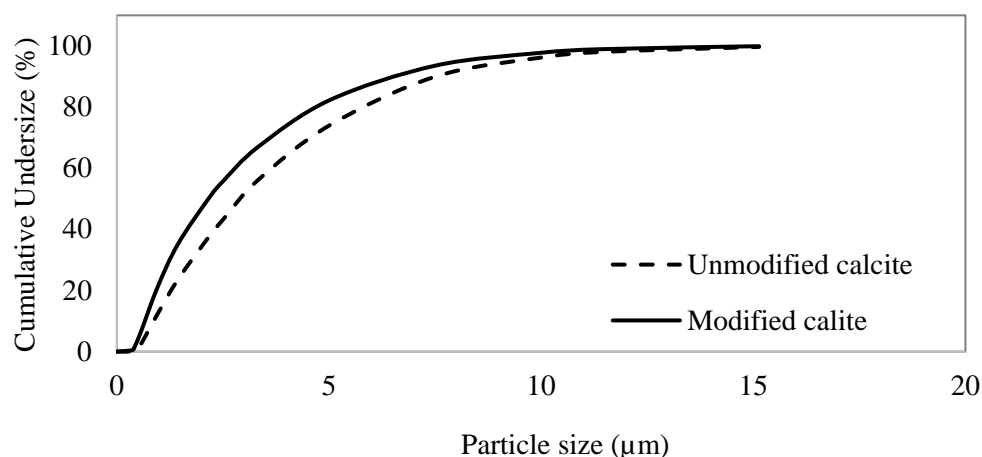


Fig. 7. Cumulative undersize of unmodified and modified calcite powder

Table 7. Some width of PSD values of feed and product

	SF ( $d_{50}/d_{20}$ )	Width of PSD ( $W_{\text{PSD}}$ )		
		$d_{90}/d_{10}$	$d_{80}/d_{20}$	Span $[(d_{90}-d_{10})/d_{50}]$
Unmodified calcite	2.33	8.77	4.57	2.99
Modified calcite	2.20	9.17	4.85	2.70

The DTA and TGA thermal graphs of the unmodified and modified calcite with 1.10% calcium stearate samples are given Figs. 8 and 9. TG curves show different results for the micronized and coated calcite. While, no weight loss was observed in the micronized calcite up to approximately 500 °C because it did not contain an organic compound, the slope of the curve in the coated calcite shows a noticeable change for modified calcite and three main steps are usually visible in the thermal curves in the temperature range of 200-700 °C. The combustion of the organic component was determined by a mass loss. More ahead, the mass lost was started at 200 °C for the sample modified with 1.10% calcium stearate, due to the oxidation of the organic component, while the mass loss from 0 to 200 °C resulted from the loss of moisture (Sekulic et al., 2009). According to the DTA curves for modified calcite in Fig. 9, the mass loss in three temperature intervals were observed: the first in the range from 100 to 300 °C, the second from 300 to 380 °C and the final from 380 to 600 °C. The mass loss in the first temperature range was assigned to desorption of weakly bonded water, which was found in both the unmodified and modified calcite samples. In the second temperature interval, oxidation of the organic component was detected, which was followed with an exothermic peak on the DTA curve. Since the unmodified sample did not contain an organic phase, an exothermic peak was not found in the DTA graph (Sekulic et al., 2009). It can be clearly seen that there was an exothermic reaction in the DTA result of the modified calcite. Thus, both the TG and DTA curves show that the modified calcite had a calcium stearate coating upon it.



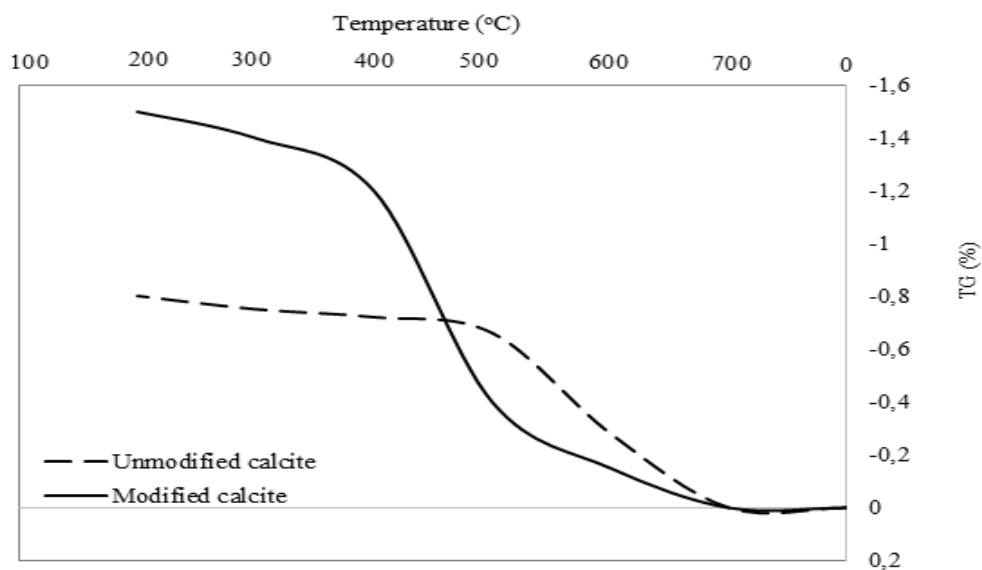


Fig. 8. TGA analysis of unmodified and modified calcites

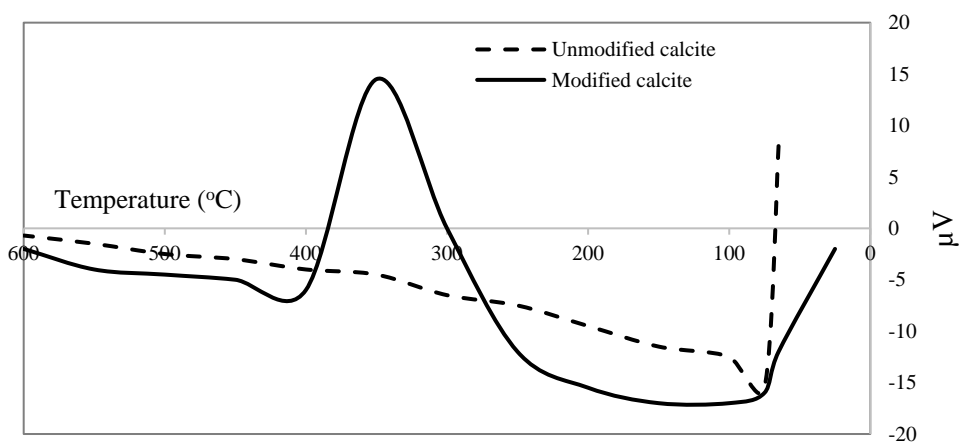


Fig. 9. DTA analysis of unmodified and modified calcites

In this study, the FTIR spectroscopy method was used to investigate the adsorption mechanism of calcium stearate [ $\text{Ca}(\text{C}_{17}\text{H}_{35}\text{COO})_2$ ] on the calcite surface. Initially, FTIR spectra of pure calcium stearate, unmodified and modified calcite were drawn and they were compared with FTIR spectra of  $\text{CaCO}_3$ , which treated with calcium stearate. The results are given in Figs. 10, 11 and 12. Figs.10-11 show the FTIR spectrum of pure calcium stearate, unmodified and modified calcites in the  $0\text{-}4000\text{ cm}^{-1}$  regions. The FTIR results of the unmodified and coated samples are very similar, showing that micronized calcite did not undergo any structural change when coated with calcium stearate. It shows that calcium stearate chemically adsorbed on the  $\text{CaCO}_3$  surface, which interacted with stearate ions, giving the surface Ca-stearate product (Sayan, 2005). This chemisorptions was not reversible and the reaction took place only one direction. A number of different methods have been reported in the literature to determine the quantity of surface-active material on the minerals (Mellgren and Lapidot, 1968).

In the surface modification experiments, the interaction between calcium stearate and calcite is thought to be attributed to chemical adsorption of the anionic group  $[\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-]$  on the calcite surface. The hydrogen bond of a fatty acid is broken if a temperature is increased (Glasstone and Lewis, 1960). Stearic acid forms hydrogen bond with hydroxyl sites on the surface of calcite powder. If adsorption is controlled by the polarity of stearic acid and 2-propanol, (Davydov, 1996) stearic acid adsorbs on the calcite powder surface because the dipole moment of stearic acid is larger than that of 2-propanol (CRC, 1989).

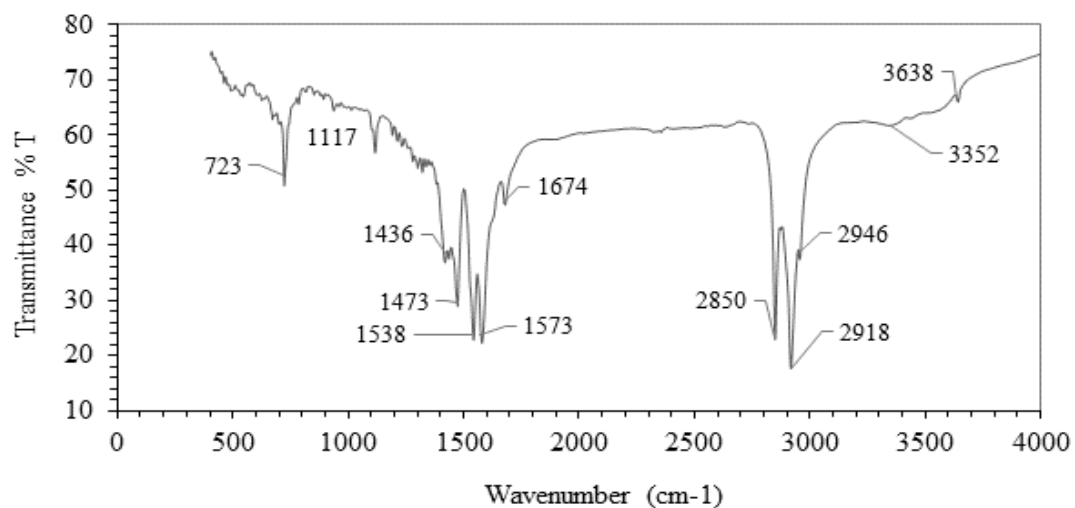


Fig. 10. FTIR analysis of calcium stearate

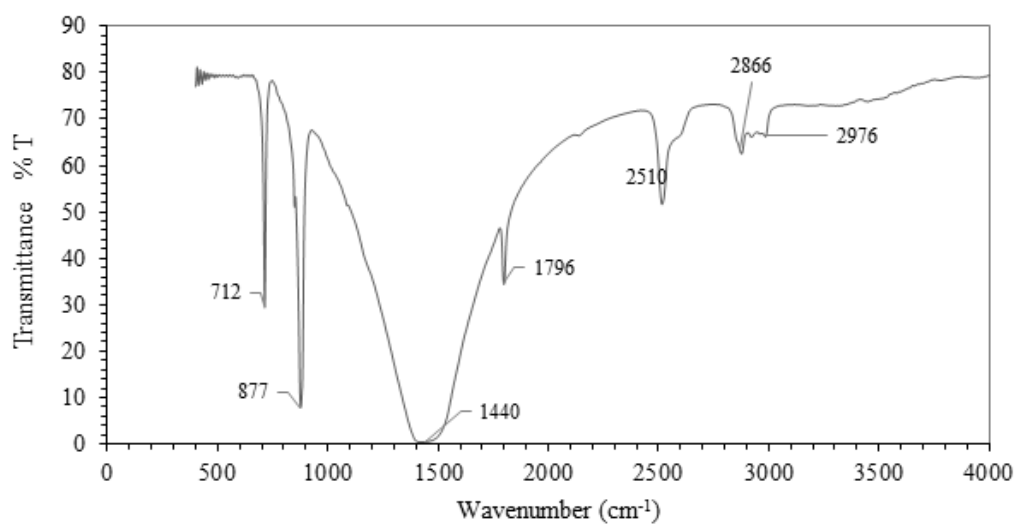


Fig. 11. FTIR analysis of unmodified calcite

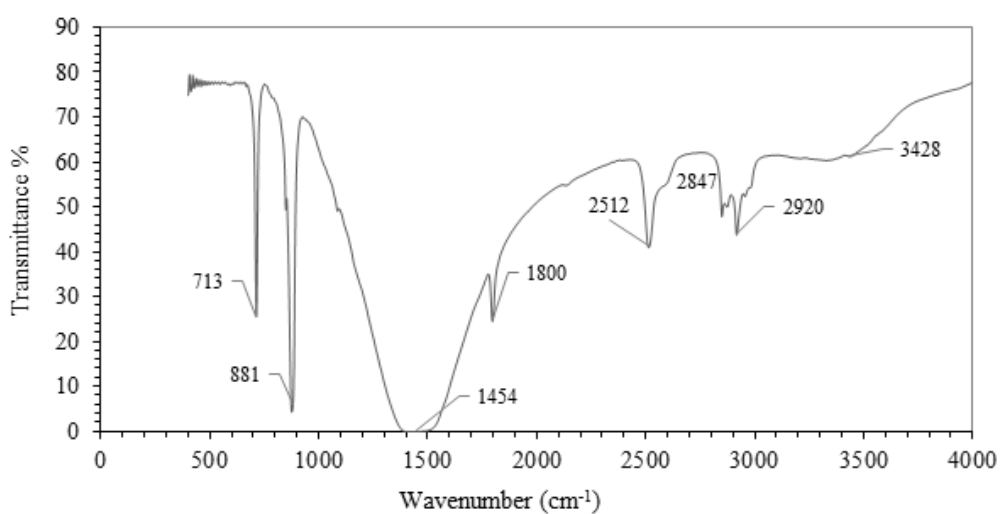


Fig. 12. FTIR analysis of modified calcite

Wettability studies usually involve the measurement of contact angles as the primary data, which indicates the degree of wetting when a solid and liquid interact. The contact angle is defined as the angle formed by the intersection of the liquid-solid interface and the liquid-vapor interface (geometrically acquired by applying a tangent line from the contact point along the liquid-vapor interface in the droplet profile). The interface where the solid, liquid and vapor co-exist is referred to as the "three-phase contact line". Fig. 13 shows that a small contact angle was observed when the liquid spread on the surface, while a large contact angle was observed when the liquid beaded on the surface. More specifically, a contact angle less than  $90^\circ$  indicates that wetting of the surface is favorable, and the fluid will spread over a large area on the surface; while contact angles greater than  $90^\circ$  generally means that wetting of the surface is unfavorable so the fluid will minimize its contact with the surface and form a compact liquid droplet (Yuan and Lee, 2003). The surface contact angle was introduced to discuss the surface properties of calcium stearate, unmodified and modified calcite particles. Contact angles of calcium stearate, unmodified and modified calcite particles were obtained as  $103^\circ$ ,  $48^\circ$  and  $88^\circ$ , respectively (Fig. 14). After surface modification, surface contact angle value of calcite particle sample increases from  $48^\circ$  to  $88^\circ$ , suggesting increased surface hydrophobicity property.

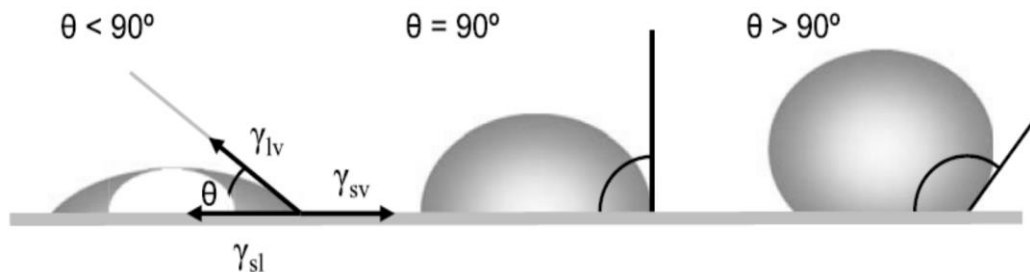


Fig. 13. Illustration of contact angles formed by sessile liquid drops on the smooth homogeneous solid surface (Yuan and Lee, 2003)



Fig. 14. Contact angles of calcium stearate (a), unmodified calcite (b) and modified calcite (c)

Fig. 15 shows SEM images of unmodified and modified calcium carbonate. It can be seen that the surface of calcium carbonate after modification became smooth and uniform due to strong mechano-chemical effects.

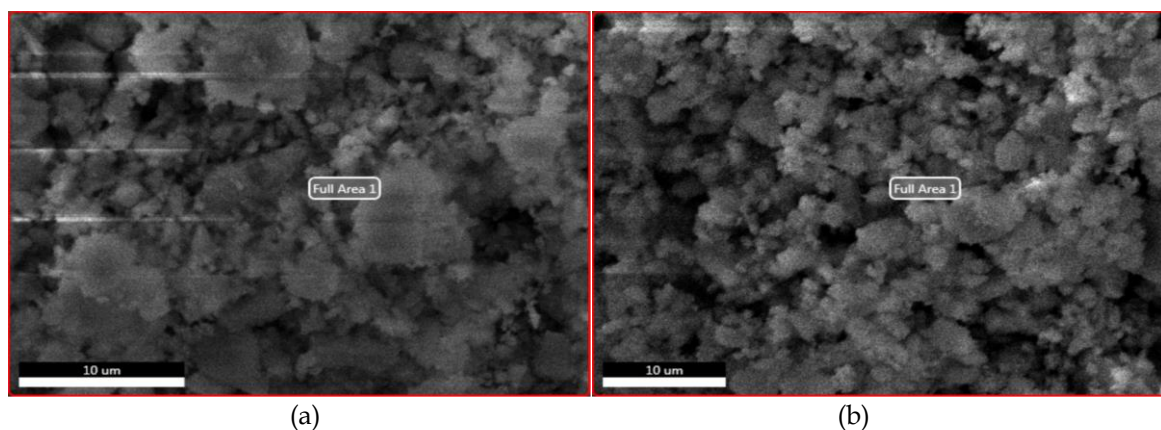


Fig. 15. SEM image of unmodified calcite (a) and modified calcite (b)

#### 4. Conclusions

In this study, firstly, the influence of operating parameters such as the calcite-filling ratio, ball-filling ratio, speed of stirred mill, surface modification time and collector dosage on the active ratio was systematically examined to obtain the hydrophobic calcite product. Secondly, the product was subjected to some analyzes such as TGA-DTA, FTIR, contact angle and SEM. The particle size of coated calcite samples was obtained as  $d_{10}=0.72 \mu\text{m}$ ,  $d_{50}=2.18 \mu\text{m}$  and  $d_{97}=6.60 \mu\text{m}$ . The  $d_{50}/d_{20}$  (SF) values showed a nearly stable trend and two sample had slightly larger values than 2; namely, unmodified and modified calcite showed broad properties according to SF. In addition,  $d_{90}/d_{10}$ ,  $d_{80}/d_{20}$  and Span  $[(d_{90}-d_{10})/d_{50}]$  values gave almost the same results. The results showed that hydrophobic material was obtained by modification of the calcite surface with calcium stearate in the stirred ball mill, and the optimal amount of the chemical needed to cover the calcite surface was 1.1%. The FTIR analysis showed that there was a chemical adsorption process between the chemical and calcite. DTA results showed that there was an exothermic reaction on the coated calcite. TG curves demonstrated that the coated calcite had a layer of calcium stearate coating. After surface modification, the contact angle of calcite particle sample increased from  $48^\circ$  to  $88^\circ$ , suggesting increased surface hydrophobicity property. Electron microscopy (SEM) images of micronized and coated calcite showed that the surface of the calcite after modification appeared to be smooth and uniform. The results showed that the pin mill and calcium stearate chemical were very effective in modifying the surface of the calcite mineral.

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