

## SURFACE PROPERTIES OF NATURAL CALCITE FILLER TREATED WITH STEARIC ACID

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*In order to obtain hydrophobic material, the water suspension of natural limestone with the high content of calcite (>95 %), was treated with different amounts (0.5-4 %) of stearic acid dissolved in chloroform. Thermal analysis showed that at lower initial concentrations of stearic acid (up to 2 %), surfactant molecules are chemisorbed on calcite surface, while at higher initial concentrations acid molecules are additionally physisorbed on mineral surface. XRPD analysis of starting calcite as well as two modified products with 1.5 and 3 % of stearic acid indicated that modification of calcite surface with both amounts of stearic acid, did not cause any changes in the structure of calcite mineral. It was confirmed that long chain stearic acid, in presence of water, alters the calcite surface to strongly hydrophobic, where reaction between stearic acid and  $Ca^{2+}$  ions occurs. Thus, the chemisorption of stearic acid on the calcite surface is responsible for retaining the lower surfactant layer on a charged surface while hydrophobic bonding causes formation of the upper surfactant layer. The optimal amount of stearic acid needed to cover the calcite surface with a monolayer of organic molecules lies between 1.5 % and 2 %.*

### INTRODUCTION

Polymers are often mixed with various particulate additives and fillers in order to produce a new class of materials, termed polymeric composites. This combination of materials lead to the new desirable properties. Thus, mineral fillers are added into the polymer matrix to improve mechanical properties, surface hardness, etc. The industrial importance of calcium carbonate as a filler in composite materials is well recognized and the application in the polymer industry is increasing [1, 2]. Calcium carbonate is usually obtained by grinding of the natural mineral or of synthetic calcite prepared by carbonation of a calcium hydroxide solution [3]. Calcite, the most abundant mineral on earth, is one of the oldest manufactured powder, while the precipitated calcium carbonate was first prepared almost a hundred years ago [4].

However, the incompatibility of its high energetic hydrophilic surface with the low-energy surface of hydrophobic polymers is a problem which need to be solved before calcium carbonate can be used as functional filler [1, 4]. In order to improve dispersibility in polymer media, calcium carbonate surface is often convert into organophilic by a variety of surface modifiers such as silanes, phosphates, titanates, etc. Among others, the most widely used calcium carbonate surface coating is

the treatment with fatty acids, usually stearic acid. As the result of this treatment, a monolayer of hydrophobic organic molecules is attached to the mineral surface. The structure and properties of such organic film have a strong influence on the final properties of the composites because this film represents the interface between the two phases of the heterogeneous material [5-7]. It is well known that when fatty acids are adsorbed onto calcium carbonate surface, they initially form a monolayered array of alkyl chains oriented so that the carboxylic groups are adjacent to the mineral surface. If excess of acid is used, additional acid molecules then may be physisorbed in a second layer, with their chains oriented tail-to-tail to the first molecular layer [8]. For the practical application, if the amount of fatty acid is low, the desired effect is not achieved, while 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 an economical issue [9]. Thermal analysis (thermogravimetry) is the most common method which is used to study the adsorption of organic material by natural minerals [10-12]. Osman and Suter [4] treated calcite surface with different amounts of stearic acid in toluene and used the thermogravimetry for detection of organic contaminations at the calcite surface and for determination of the optimal amount of surfactant

necessary to coat it with an alkyl monolayer. They reported that thermal analysis was able to differentiate between chemisorbed, intercalated (local bilayer), and free acid molecules, which may be present on the surface of calcite fillers.

It is well known that commonly used calcite coating techniques, in a laboratory scale, include dry coating and the solution method. In the solution method, the calcite surface is usually treated with the solution of the acid in a nonpolar solvent. However, Hansen et al. [13] reported that if calcite was wetted with distilled water before it was put into n-decane + stearic acid solution, water film on the calcite surface altered the adsorption of acid on mineral surface. In this study, the hydrophobic calcites were obtained by treatment of water suspension of natural calcite with different amounts of stearic acid dissolved in chloroform, and structure and properties of obtained products were investigated by thermal analysis (DTA/TG/DTG), XRPD analysis, and polarization microscopy.

## EXPERIMENTAL

The natural limestone from Venčac deposit (Aranđelovac, Serbia) was used in these experiments, as a starting material. The <5  $\mu\text{m}$  fraction of the raw material, was used as received, without any further classification. The mineralogical composition of natural limestone showed that it consists primarily of calcite mineral (over 95%), with smaller amounts of opal, limonite-goethite and wollastonite, as measured by X-ray powder diffraction analysis (XRPD). The specific surface area

(SSA) of the starting calcite powder, determined by the Brunauer-Emmett-Teller gas adsorption method (nitrogen), was 4.8  $\text{m}^2/\text{g}$ .

The characteristics of stearic acid used for modification of calcite surface are presented in Table 1. [14]. The amounts of stearic acid used for coating of calcite surface was 0.5, 1, 1.5, 2, 3 and 4%. The modification was performed according to modified procedure published by Rezaei Gomari et al. [15]. In experiments, 10 g of calcite was dispersed in 100 ml of warm distilled water (50°C), and then 10 ml of appropriate amount of dissolved stearic acid in chloroform was added to the calcite suspension. The each suspension was stirred at 4000 rpm, for 15 min, at 50°C. After the modification process, the suspensions were centrifuged at 10000 rpm for 10 min, washed with distilled water, and dried at 50°C. The obtained products were denoted as CS-0.5, CS-1, CS-1.5, CS-2, CS-3 and CS-4.

The effect of surface modification is evaluated by the floating test reported by Sheng et al. [16], which represents the ratio of the floated product to the overall weight of the sample after they are mixed in water and stirred vigorously. The ratio is called active ratio.

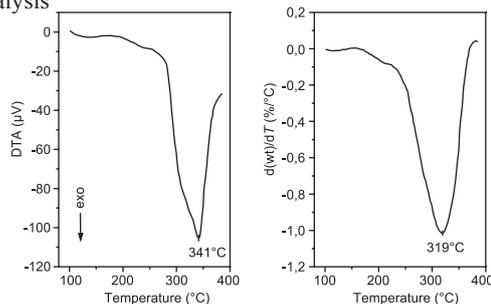
The amount of stearic acid adsorbed onto the calcite surface was followed by thermogravimetry. Thermal analysis was performed on a Netzsch STA 409 EP. Samples were heated (20°C-1000°C) in an air atmosphere, with a heating rate of 10°C  $\text{min}^{-1}$ .

Starting calcite, as well as samples calcites modified with 1.5 and 3% of stearic acid were characterized by XRPD analysis and by polarization microscopy. XRPD analysis was performed on a Philips PW-1710 diffractometer with monochromatic Cu-K $\alpha$  radiation ( $\lambda = 1.54148 \text{ \AA}$ ), in the range of 3-65° 2 $\theta$ , with a step scan of 0.02°. Microscopy analysis was done on a Carl Zeiss, Jena, Model JENAPOL-U polarization microscope in transmitted light by immersion method. For the starting calcite xilol, while for modified calcites water was used as immersion liquid.

Table 1. Characteristics of stearic acid.

Name	Stearic acid
Molecular formula	
Molecular formula	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
Molecular weight, g/mol	284.47
Density, g/ml	0.847
Dissociation constant, pKa	5.7
Solubility in water, g/100 ml	0.034 (25°C), 0.1 (37°C)
Solubility in alcohol, g/100ml	2.5 (cold)
Solubility in ether, $\text{CHCl}_3$ , $\text{CCl}_4$ , $\text{CS}_2$	very soluble

Thermal analysis



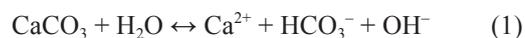
## RESULTS AND DISCUSSION

Since pH has influence on the stearic acid dissociation (see Table 1) and solubility of calcite and promotes reaction between the dissociated acid and calcium ions [17], to follow the modification process, pH of each supernatant after preparation of hydrophobic products was measured. The plot of pH versus the amount of stearic acid used for modification is presented at Figure 1.

As can be seen from Figure 1, pH of solution decreases with increasing the amount of stearic acid used for modification. The acidic and basic characters of the mineral surfaces are indicated by the value of zero zeta potential charge (pHzpc). At pHzpc, the surface is electrically neutral at a particular pH [17]. Several authors reported the zpc of calcite is between pH 8 and

10, depending on the nature and purity of the mineral crystals, the mode of preparation of the mineral for electrokinetic experiments and particularly the size of the crystals [17, 18]. Above this value the calcite surface is negatively charged and below that is positively charged. Hansen et al. [13] reported that precoverage of the calcite surface with water, before the immersion in the n-decane + stearic acid solution improved the adsorption

of acid on the calcite surface likely due to the dissolution of calcite in water and the dissociation of stearic acid. The dissolution of calcite in water is expressed by the following equation:



and as the result of this process, a localized increase of the solution alkalinity occurs. From Figure 1, calcite

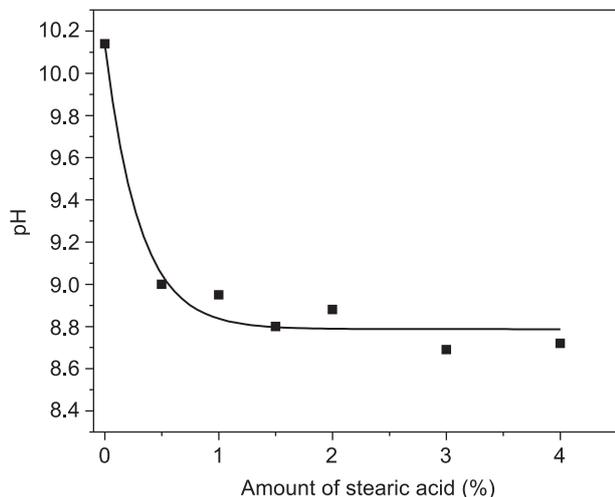


Figure 1. pH versus amount of stearic acid used for modification.

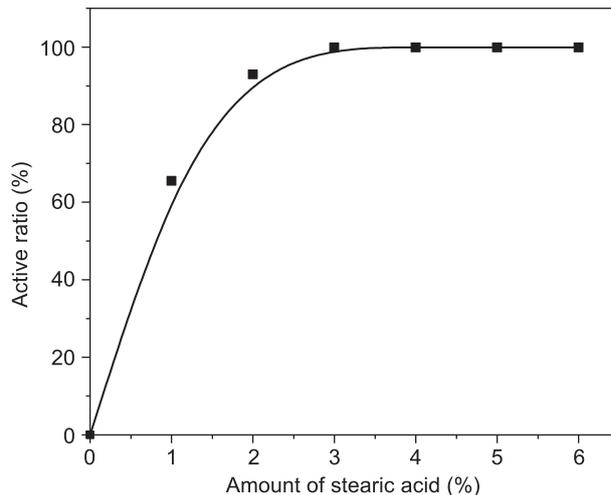


Figure 2. The effect of amount of stearic acid on the active ratio of obtained products.

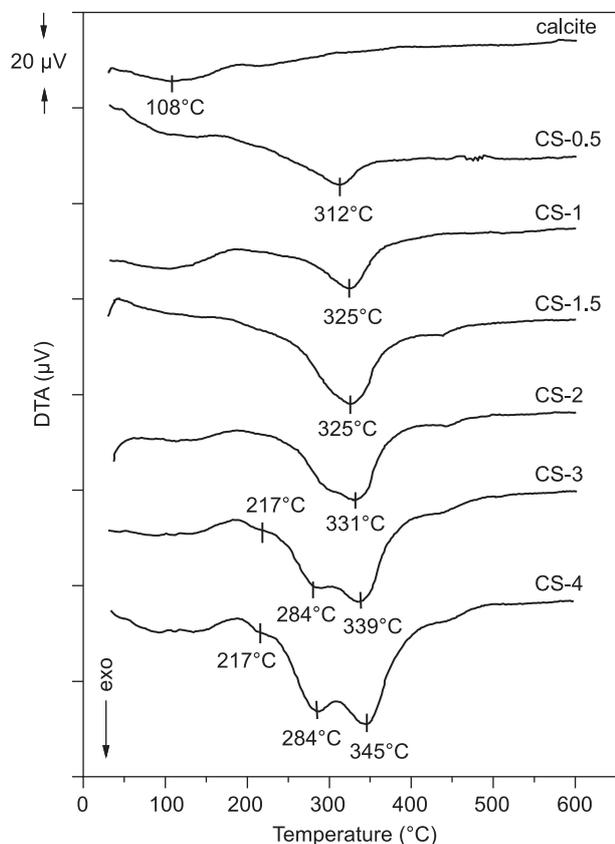


Figure 3. DTA curves of unmodified calcite and calcites modified with different amounts of stearic acid.

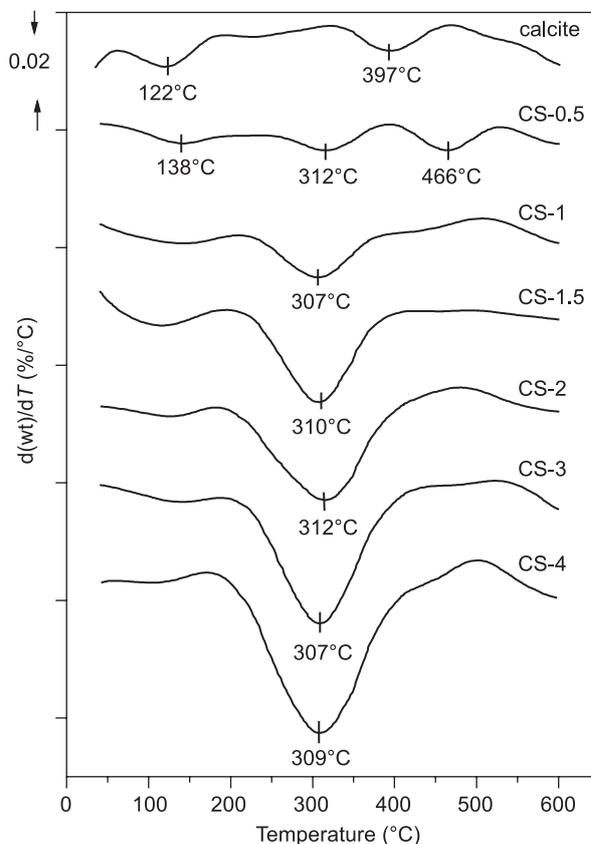
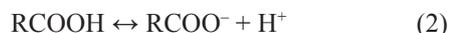


Figure 4. DTG curves of unmodified calcite and calcites modified with different amounts of stearic acid.

surface is slightly basic, while decrease in pH during the modification process indicated the dissociation of stearic acid which resulted in release of protons from acid. Namely, besides the dissolution of calcite in water, in chloroform/water interface, ionization of stearic acid taking place:



Thus, when solution pH increase, ionization of the stearic acid occurs hence the tendency of the anionic groups  $[\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-]$  to dissolve in the water increases and reaches the calcite surface where a chemisorption reaction occurs at the surface of the calcite where calcium stearate is formed [13]. The measurement of pH during the modification process indicated that above mentioned reactions are responsible for adsorption of stearic acid by natural calcite. As the result of this process the hydrophilic calcite surface is changed into a strong hydrophobic.

To investigate the effect of the amount of stearic acid at calcite surface on the hydrophobicity of obtained materials, the active ratio of each product was determined. These results are presented at Figure 2.

As can be seen, from Figure 2., that at lower surface coverage of calcite with stearic acid (0.5%), the active ratio was 65.5%, while the active ratio over 99.9% was achieved with 1.5% of stearic acid. Since is reported in literature that the higher the active ratio, the better modification effect is [19], the obtained results indicated that with the applied solution method, high hydrophobicity of the calcite surface was achieved when amount of stearic acid was  $\geq 1.5\%$ .

The differential thermal analysis (DTA) and derivative thermogravimetric (DTG) curves of the obtained products are presented at Figures 3 and 4. The thermal curves of pure stearic acid are given in Table 1.

Generally, for calcite modified with fatty acids, at thermal curves, two main steps are visible, in the temperature range 25-600°C. The third part starts around 580°C, and corresponds to the decomposition of calcite [15]. The first step, between 25 and 200°C, corresponds to the loss of water, or to the elimination of physisorbed acid that was not removed by the washing procedure, while the main step, between 200 and 400°C corresponds to the oxidation of the organic substance that is chemisorbed at the calcite surface [20]. In order to follow the adsorption of stearic acid by calcite surface, the thermal curves of CSs are divided into two main regions (20-200°C and 200-400°C).

In the first region, for CSs up to 200°C, no endothermic peaks are observed at DTA curves (Figure 3). Additionally, except for CS-0.5, for all modified CSs, no peaks at derivative DTG curves (Figure 4) were observed in this temperature region. The weight loss for all modified calcites in the first temperature region is related to the increased hydrophobicity of calcite surface, and should decrease with increasing the amount

of stearic acid at calcite surface. The plot of weight loss from thermogravimetric curves versus the amount of stearic acid at the calcite surface is presented at Figure 5.

As can be seen from the figure, due to the increased hydrophobicity of modified calcites CSs, the weight loss, in this temperature region, decreases linearly with increasing the amount of stearic acid at calcite surface (coefficient of determination – 0.99). Since the weight loss in the first temperature region corresponds to the loss of water, or to the elimination of physisorbed acid, the linear decrease of weight loss with increasing of amount of stearic acid at mineral surface, as well as the absence of DTG peaks, indicates that, desorption of physisorbed water from partially covered calcite surface, is the major thermal reaction in this temperature region. The second region, between 200°C and 400°C, at DTA curves, is characterized by the exothermic peaks results from the oxidation of organic substance at the calcite surface. For CSs modified with less amount of stearic acid (0.5, 1, 1.5 and 2%), one principal exothermic peak (at the temperature  $> 310^\circ\text{C}$ ) is traced. When the amount of surfactant at calcite surface increased, besides the principal exothermic peak around 340°C, additional exothermic peak at 284°C and a weak shoulder at 217°C can be distinguished for the samples CS-3 and CS-4. The relative intensity of exothermic peaks increases with increasing the amount of stearic acid at the calcite surface. It is noticed that, the position of the principal exothermic peak shifts from 312°C to 345°C, with increasing the amount of stearic acid at the calcite surface. Additionally, it was observed that temperature peak of the stearic acid after adsorption by calcite is shifts toward the temperature peak of the pure surfactant (341°C - Table 1) with increasing the amount of stearic acid used for modification. Since, the degree of adsorption of stearic acid by calcite has an effect on the thermal weight loss of CSs in this temperature range, the weight loss increases from 0.42% for CS-0.5 to 3.15%

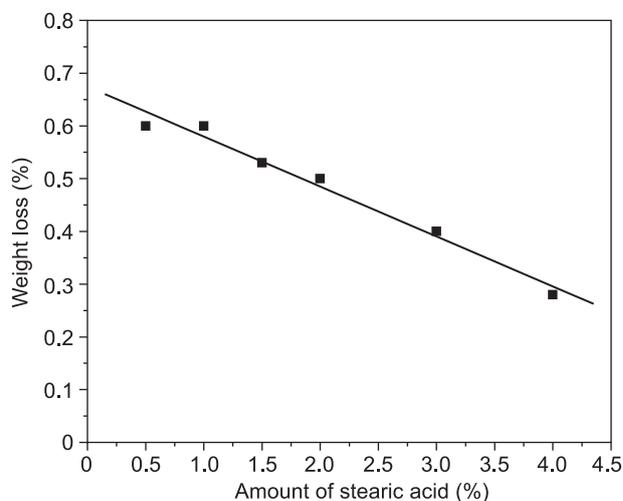


Figure 5. Weight loss in temperature range 20-200°C versus amount of stearic acid at calcite surface.

for the calcite with the highest amount of stearic acid - CS-4 (Table 2). This is in accordance with one intensive derivative peak at  $\sim 310^\circ\text{C}$  on the DTG curves of CSs. The relative intensity of this derivative peak increases with increasing the amount of stearic acid at calcite surface. Thus, from the position of the principal exothermic peak ( $> 310^\circ$ ) at DTA curves, it can be concluded that with applied modification processes, active sites exist at the calcite surface onto which stearic acid is chemisorbed. However, the position and the intensity of the other peaks, indicated the additional interactions between stearic acid and the calcite surface. Namely, fatty acids are initially adsorbed on calcite surface from solution as monomers forming a monolayer, and when the calcite surface is fully covered, the surfactant continues to absorb between the chemisorbed monolayer. Due to the attraction forces between the alkyl chains, the inter-

calated and chemisorbed molecules adopt a tail-to-tail arrangement. Such arrangement leaves the carboxylic groups of the intercalated molecules sticking out of the organic monolayer. Sullivan et al. [21] investigated zeolites modified with different amounts of hexadecyltrimethylammonium (HDTMA) ions by high resolution thermogravimetric analysis (HR-TG) and postulated that HR-TG pyrolysis temperatures should be higher for samples with more strongly bound HDTMA, such as that bound with both coulombic and van der Waals forces at sub-monolayer coverages, while if some of HDTMA is bound only with hydrophobic forces, such as in a bilayer, the pyrolysis temperature should be considerably lower. Also, since, it is well known that weakly bond surfactant from the bilayer can be easily removed from mineral surface by washing with the organic solvents [4], in order to obtain the informations

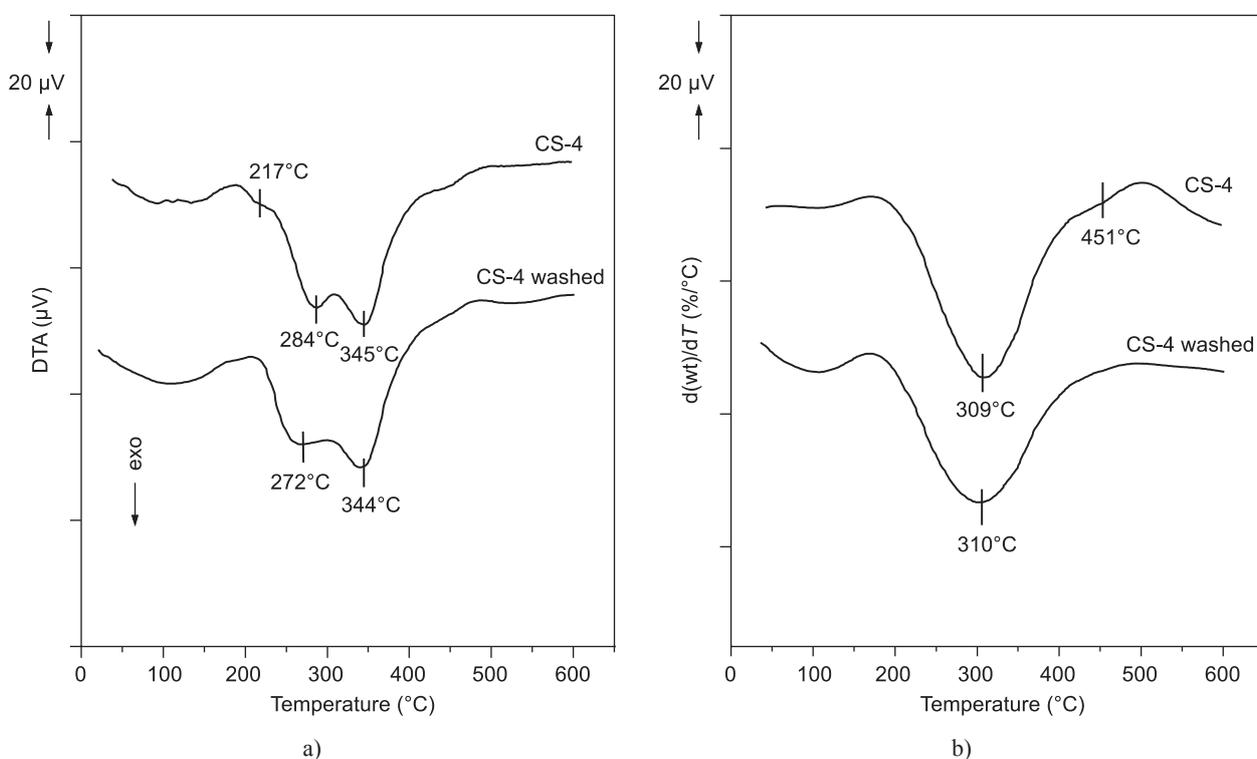


Figure 6. Thermal DTA (a) and DTG (b) curves of CS-4 before and after washing with fresh ethanol.

Table 2. Estimated amount of stearic acid per surface area of calcite.

Sample	Weight loss* (%)	Adsorbed amount ( $\mu\text{mol/g}$ )	Adsorbed amount ( $\mu\text{mol/m}^2$ )	Surface area per molecule ( $\text{nm}^2$ )
CS-0.5	0.42	17.6	3.7	4.50
CS-1	1.10	37.3	7.9	2.15
CS-1.5	1.45	51.0	10.6	1.57
CS-2	1.94	68.1	14.2	1.17
CS-3	2.40	84.4	17.6	0.95
CS-4	3.15	110.7	23.1	0.72

\*Weight loss from TG curves in temperature range  $200^\circ\text{-}400^\circ\text{C}$

about type of bonding of stearic acid at calcite surface, the sample with the highest amount of stearic acid - 4 % (CS-4) was washed several times with fresh ethanol. The thermal curves (DTA and DTG) of sample CS-4 before and after washing are presented at Figures 6a and 6b.

Osman and Suter [4] investigated calcites modified with 0.8, 1 and 2% of stearic acid in toluene by thermogravimetry and found that on DTG curve of calcite modified with 0.8% of stearic acid one decomposition step with the peak maximum at 335°C was observed, while with 1% of stearic acid, an additional decomposition step with the peak maximum at ~ 200°C takes place. When amount of stearic acid was increased to 2%, they noticed a third decomposition step with a peak maximum at 285°C. They observed that peak at 285°C resulted from the use of an excessive amount of surfactant and was identical to that of pure acid. On repeated shaking with fresh toluene or ethanol peak at 285°C quickly disappeared, while peak at 200°C gradually decreased and was more difficult to get rid of, and explained peak at 200°C by the presence of stearic acid molecules which are intercalated between the chemisorbed molecules (local bilayer). From Figure 6a (DTA curves), it can be seen that on repeated shaking of CS-4 with fresh ethanol, the principal exothermic peak at 345°C remains unchanged, peak at 284°C slowly decrease and slightly shift toward lower temperature (272°C), while weak shoulder at 217°C disappeared. From derivative DTG curve (Figure 6b) of washed CS-4 it can be seen that on repeated washing of CS-4 the principal derivative peak at 309°C remains unchanged, while peak at 451°C disappeared. From results showed in this paper, it is possible that for CS-4, peak at 217°C originate from loosely bond stearic acid from the local bilayer, and peaks at ~280°C and ~340°C correspond to the chemisorbed surfactant at calcite surface.

Additionally, it is well known that below and/or equal to the monolayer coverage, the arrangement of alkyl chains at the mineral surface depends on the amount of surfactant used for modification. Sullivan et al. [21, 22] studied the adsorption of hexadecyltrimethylammonium (HDTMA) ions at the zeolite surface and reported that HDTMA orientation depends on the quantity of surfactant at the surface, with close parallel contact between the surfactant and surface at low loading level and with perpendicular orientation at higher loading levels. The weight loss in the second temperature range (200-400°C) is usually used for the calculation the surface concentration of acid molecules [13, 15], and may explain the orientation of alkyl chains at mineral surface, therefore these results are presented in Table 2.

The cross sectional area per adsorbed stearic acid molecule was calculated using the following equation [20]:

$$\sigma = \frac{S_A}{\Gamma \times N_A} \quad (3)$$

where  $\sigma$  is the surface area per molecule ( $\text{nm}^2$ ),  $S_A$  specific surface area of calcite ( $\text{m}^2\text{g}^{-1}$ ),  $\Gamma$  the adsorbed

amount of stearic acid ( $\mu\text{molg}^{-1}$ ) and  $N_A$  is the Avogadro number. From results, presented in Table 2, it can be seen that for modified calcites, the calculated surface area per molecule decreases with increasing the amount of stearic acid at the calcite surface (from 5.42  $\text{nm}^2$  for CS-0.5 to 0.72  $\text{nm}^2$  for CS-4). Rezaei Gomari et al. [20] reported apparent surface area per molecule of stearic acid of 2.80  $\text{nm}^2$  for the dry coating of calcite surface and 1.65  $\text{nm}^2$  for the wet modification. They pointed that these values are in the range of close-packed values (i.e., 1.60-2.50  $\text{nm}^2$ ) for fatty acids. Wright and Pratt [23] suggested, from the calculated molecular area of fatty acids, the value of 2.20-2.60  $\text{nm}^2$  for a perpendicular orientation and above 5.15  $\text{nm}^2$  for the parallel one. It was mentioned above that, in solution monomers of stearic acid are initially adsorbed to the calcite surface, while with excess of surfactant, the bilayer is formed. Accordingly, from the calculated surface area per molecule (Table 2), alkyl chains of stearic acid monomers seems to be positioned close to the calcite surface, for the lowest amount of stearic acid (0.5 %) which is confirmed with higher surface area per molecule, while further addition of stearic acid (1, 1.5 and 2 %) caused rearrangement of alkyl chains to more perpendicular position relative to the calcite surface confirmed with lower surface area per molecule. With the excess of surfactant (3 and 4 %) probably, at the beginning patchy bilayer, and then bilayer is formed.

The starting calcite, as well as the two hydrophobic products CS-1.5 and CS-3 were also characterized by XRPD analysis and polarization microscopy. XRPD patterns of analyzed samples are shown at Figure 7. As can be seen from Figure 7, modification of calcite surface with both amounts of stearic acid, did not cause any changes in the structure of calcite mineral.

Microphotographs of the starting calcite and calcites modified with 1.5 and 3 % of stearic acid are presented at Figures 8a-c.

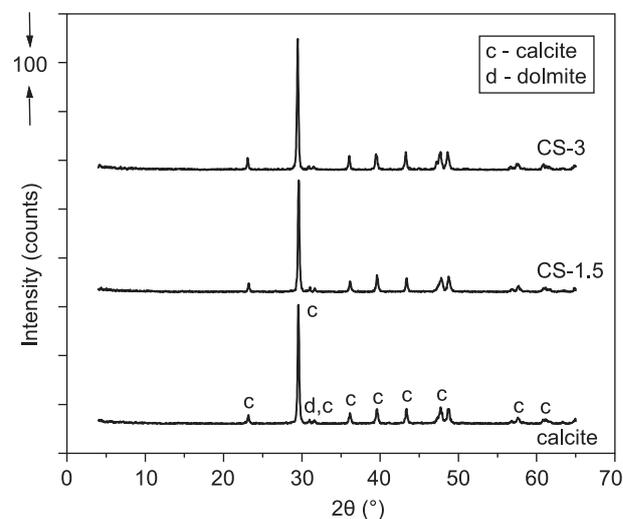
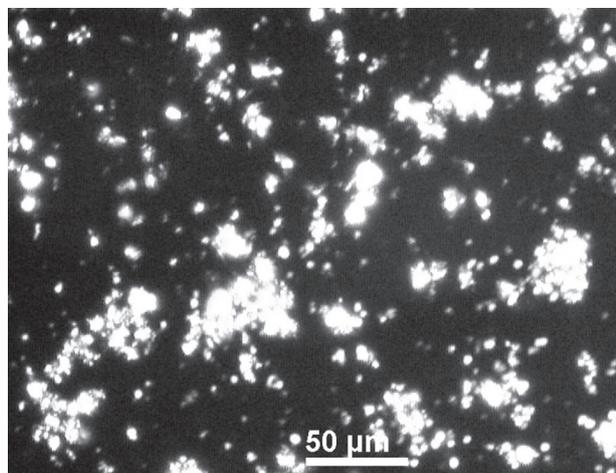
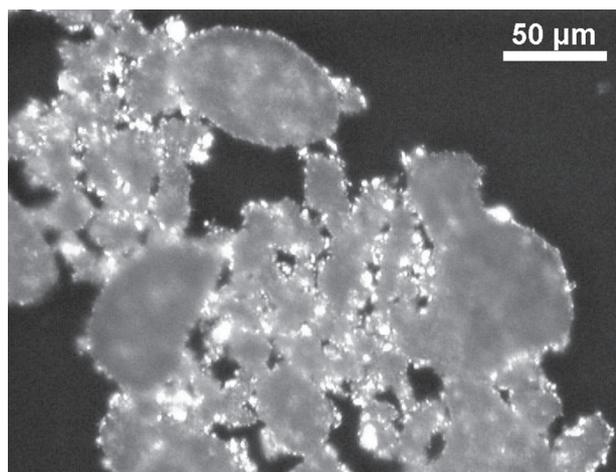


Figure 7. XRPD patterns of calcite, CS-1.5 and CS-3.

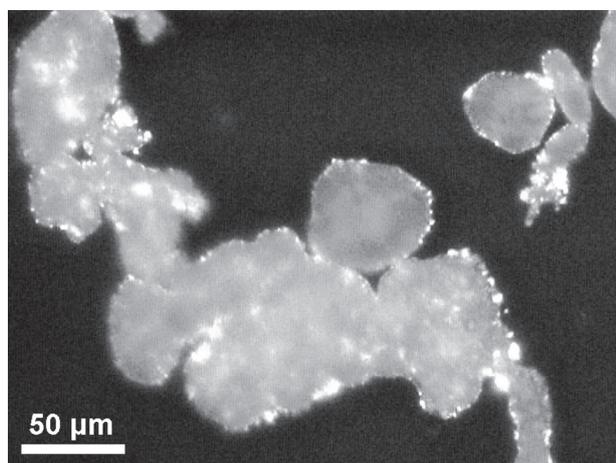
Compared to the starting sample (Figure 8a), in microphotographs of both modified calcites (Figures 8b and 8c) it is obvious that in presence of water as an immersion liquid, particles of coated calcites tend to concentrate, and thus agglomerates are clearly visible. These results



a)



b)



c)

Figure 8. Microphotographs of starting calcite (a), CS-1.5 (b) and CS-3 (c) (20× magnification).

may be another evidence that even with 1.5 % of stearic acid high hydrophobicity of coated product is achieved.

The results reported in this paper showed that hydrophobic material was obtained by modification of calcite surface with stearic acid in warm distilled water, and that optimal amount of stearic acid needed to cover the calcite surface with a monolayer of organic molecules lies between 1.5 % and 2 %. Since, below the monolayer coverage, the high adsorption of stearic acid by calcite is likely due to the dissolution of calcite, in presence of water, as well as, due to the dissociation of acid, results confirmed that chemisorption of stearic acid on the calcite surface is responsible for retaining the lower surfactant layer on a charged surface while hydrophobic bonding causes formation of the upper surfactant layer.

## CONCLUSIONS

Results presented in this paper demonstrate the importance of presence of water in the mechanism of adsorption of the long chain stearic acid onto the calcite surface. Precoverage of the calcite surface with water, before the addition of the chloroform + stearic acid solution, ensure the high adsorption of stearic acid on the calcite. Below the monolayer coverage, the high adsorption was likely due to the dissolution of calcite in water and the dissociation of stearic acid followed by chemisorption of stearic acid on the calcite surface. Thermal analysis showed that at lower initial concentrations of stearic acid (up to 2 %), surfactant molecules are chemisorbed on calcite surface, while at higher initial concentrations acid molecules are additionally physisorbed on calcite surface. From calculated surface area per molecule, it was suggested that alkyl chains of monomers are positioned close to the calcite surface for the lowest amount of stearic acid - 0.5 %, while further addition of stearic acid (1, 1.5 and 2 %) caused rearrangement of alkyl chains to more perpendicular position to the calcite surface. With the excess of surfactant (3 and 4 %), probably at the beginning patchy bilayer and then bilayer is formed. The hydrophobic material obtained by simple modification can find interesting and important application as a filler in polymer industry.

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