



Mechanism of stearic acid adsorption to calcite

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ABSTRACT

This paper presents the interpretation of binding mechanism of stearic acid for calcite surface in two modification methods.

In the “dry” method, a surface dissociation of stearic acid is assumed where H⁺ ion goes to a surface carbonate ion and stearic ion is chemisorbed on primary surface center of –Ca⁺ ion which is only available for chemisorption. The structure of adsorbed layer indicates chemisorption of stearate, but due to steric effects, and the oblique or gauche conformation of hydrocarbon chains. A part of surface –Ca⁺ centers can be blocked, which is explained by the result that physical adsorption dominates over 1.5%.

In the “wet” method, by adding stearic acid, at concentration above the critical concentration of micelle formation in base solution, micelles are formed, and on the other side free stearic acid molecules or molecules from developed micelle dissociate. The resulting stearic ions can be chemisorbed on primary centers of –Ca⁺ ions or participate in ion exchange with OH[–] ions from secondary surface centers. With increasing adsorption density, the adsorbed ions and molecules, due to interactions of hydrocarbon chains, and thickness of double electrical layer, achieve a vertical orientation and keep the trans-conformation of hydrocarbon chains.

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1. Introduction

The ability of limestone to be used as a filler in the polymer industry can be significantly improved by modifying the calcite surface, as the basic mineral in limestone, with surface-active organic modifiers [1–5].

When aiming to obtain a hydrophobic surface of calcite in the modification method, monocarboxylic acids with aliphatic hydrocarbon chain (also known as fatty acids and their salts) are most frequently used as the surfactants. By adsorption of surfactants on calcite, its hydrophilic surface becomes hydrophobic, and therefore compatible with the polymer molecules, which further improves the mechanical properties of final product [6–9].

In many cases, the adsorption is of a mixed nature (i.e. partly chemical and partly physical) [10–12]. Usually, it occurs by formation of multilayers, wherein the first layer is built on the basis of strong chemical forces, with the following layers physically adsorbed over the chemisorbed layer.

In order to better define the adsorption process, mathematical expressions are used that are mainly derived from the example of gas adsorption on a solid adsorbent. A degree of surface coverage (θ) can be used for quantitatively defining the adsorption process. A degree of surface coverage is the ratio of the number of occupied

adsorption places and the number of available adsorption places, so the value is always between 0 and 1. This can be presented numerically by Eq. (1) [10]:

$$\theta = \frac{V}{V_{\infty}} \quad (1)$$

where:

V volume of adsorbate (gas) that is adsorbed
 V_{∞} volume of adsorbate (gas) that completely covers the surface in a monomolecular layer.

Furthermore, degree of surface coverage can be presented by Eq. (2):

$$\theta = k' \frac{x}{m} \quad (2)$$

where: x = mass of adsorbate; m = mass of adsorbent; and k' = coefficient of proportionality.

$$k' = 1 / \frac{x_{\text{monolayer}}}{m} \quad (x_{\text{monolayer}} = \text{mass of adsorbate in a monolayer}) \quad (3)$$

Some studies have shown that each densely packed molecule of fatty acids occupies 0.16 nm² to 0.25 nm² of surface minerals. Rezaei et al. [13] found that during the “wet method” of calcite modification

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with stearic acid, the monolayer adsorption is achieved, where each molecule of stearic acid occupies 0.165 nm^2 . In the case of the “dry method” of modification, one molecule of stearic acid in the statistical monolayer, occupies a calcite surface area of 0.280 nm^2 .

Hence, it was possible to calculate – according to Eq. (4) – the surface of calcite that was available for adsorption of one molecule of stearic acid [14], under set experimental conditions:

$$\sigma = \frac{S_A}{\Gamma \cdot N_A} \quad (4)$$

where:

σ	surface per molecule, m^2
S_A	specific surface of calcite, m^2/g
Γ	adsorbed amount of stearic acid, mol/g
N_A	Avogadro's number, 6.022×10^{23} molecules/mol.

The authors previously published the results of the surface modification of calcite using various concentrations of stearic acid using the “wet process” [14]. This paper describes the method of “dry modification” of calcite with stearic acid as well as the characterization of modified samples. The mechanism of stearic acid binding to the surface of calcite – based on the overall results of modification for both methods – is presented in this paper.

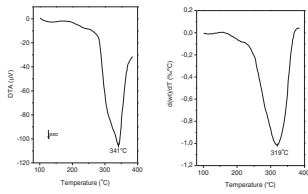
2. Experimental

2.1. Materials and reagents

Limestone from the deposit “Venčac”-Arandjelovac (Serbia) was used in the experimental study as the starting sample: upper grain-size limit of the sample – $10.4 \mu\text{m}$; mean grain diameter (d_{50}) – $6.2 \mu\text{m}$; specific surface area (S) – $4.8 \text{ m}^2/\text{g}$; degree of whiteness – 93.1% ; and moisture content – 0.02% .

The results of chemical analysis have shown that the dominant oxides are CaO (54, 77%) and MgO (0.79%), while the oxides Al_2O_3 , Fe_2O_3 , Na_2O and K_2O are present in trace amounts. Based on the content of CaO and assuming that all MgO is associated with dolomite, it was calculated that the sample has 95.84% of CaCO_3 . The surface-active matter, used in the experiments of calcite modification is technical grade stearic acid, produced by the company “Fluka” – Switzerland. The characteristics of stearic acid used for modification of calcite surface are presented in Table 1 [14].

Table 1
Characteristics of the stearic acid.

Name	Stearic acid
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/100 ml	2.5 (cold)
Solubility in ether, CHCl_3 , CCl_4 , CS_2	Very soluble
Thermal analysis	

2.2. Methods

The “wet method” of calcite modification with stearic acid, as well as the characterization of the obtained products has been described in a previously published paper [14]. To modify calcite with the “dry method”, six samples were prepared per 200 g of calcite, with each sample receiving different levels of stearic acid mass. Mass of stearic acid added to the six samples, calculated for each 100 g of calcite, included 0.5 g; 1 g; 1.5 g; 2 g; 3 g and 4 g. Constant mass of calcite (100 g) was used due to the constant interaction of calcite with the surfactants. According to the stearic acid utilized in the mixture (calcite + stearic acid), the acid concentration in the six samples was: 0.4975%; 0.9901%; 1.4778%; 1.9608%; 2.9126% and 3.8462% respectively. Concentration in the industrial conditions is also expressed in phr units (parts per hundred resin), so that the concentration of stearic acid in relation to calcite will be: 0.5; 1; 1.5; 2; 3 and 4 phr (phr-mass of stearic acid (g) per 100 g of limestone).

The experiments using the “dry method” of calcite surface modification were carried out in a vibrating mill with ring working elements, model “MN 954/3” (manufacturer “KHD Humboldt Wedag” – Germany). The volume of a mill container carrying a sample for modification is 2 dm^3 . The device operates discontinuously in an open-air environment. Modification time is 7 min at 70 °C. The obtained calcite samples, modified by the “dry method”, are denoted as follows: CD-0.5, CD-1, CD-1.5, CD-2, CD-3 and CD-4 (where C = calcite, D = “dry method”, ad number = concentration of stearic acid). Thermal analyses were carried out on the obtained products using the same device as for “wet method” [14].

The thermogravimetric/differential thermal (TG/DT) analysis was carried out in air atmosphere in the temperature range of 20–1000 °C, at a heating rate of 10 °C/min using a Netzsch STA-409 EP analyzer.

The effect of surface modification is evaluated by the floating test reported by Sheng et al. [15], 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.

3. Results and discussion

Thermal analysis of the initial calcite sample, as well as calcite samples modified by “wet” and “dry methods”, were carried out in order to monitor the changes that have occurred in the procedure of calcite modification, i.e. stearic acid adsorption on its surface.

3.1. Differential thermal analysis of modified calcite samples, obtained by the “wet method”

The authors have reported in detail the thermal analyses of calcite samples obtained by the “wet modification method”, in a previously published paper [14]. Only a part of these results will be presented as an introduction to explain the mechanism of stearic acid binding to the surface of calcite.

TG diagrams and weight losses in the various temperature ranges for the starting sample of calcite, and calcite samples modified with stearic acid by the “wet method” are presented in Fig. 1, and DTA curves in Fig. 2.

The main exothermic maximums ($> 310 \text{ °C}$) on DTA curves of calcite, modified by the “wet method” (Fig. 2) are attributed to the chemical adsorbed organic component, stearic ion, $\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-$, and (St^-), which is bound to the positive surface centers in a double electric layer. Since the chemical adsorption provides the strongest bond between the adsorbates and adsorbents, this exothermic maximum at the highest temperature is therefore attributed to the oxidation of the chemically bound organic component.

In the “wet modification method”, in addition to the primary surface ions of calcium ($-\text{Ca}^+$), the secondary active centers for chemisorption can be formed due to the solubility of calcite on the surface. Ion

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