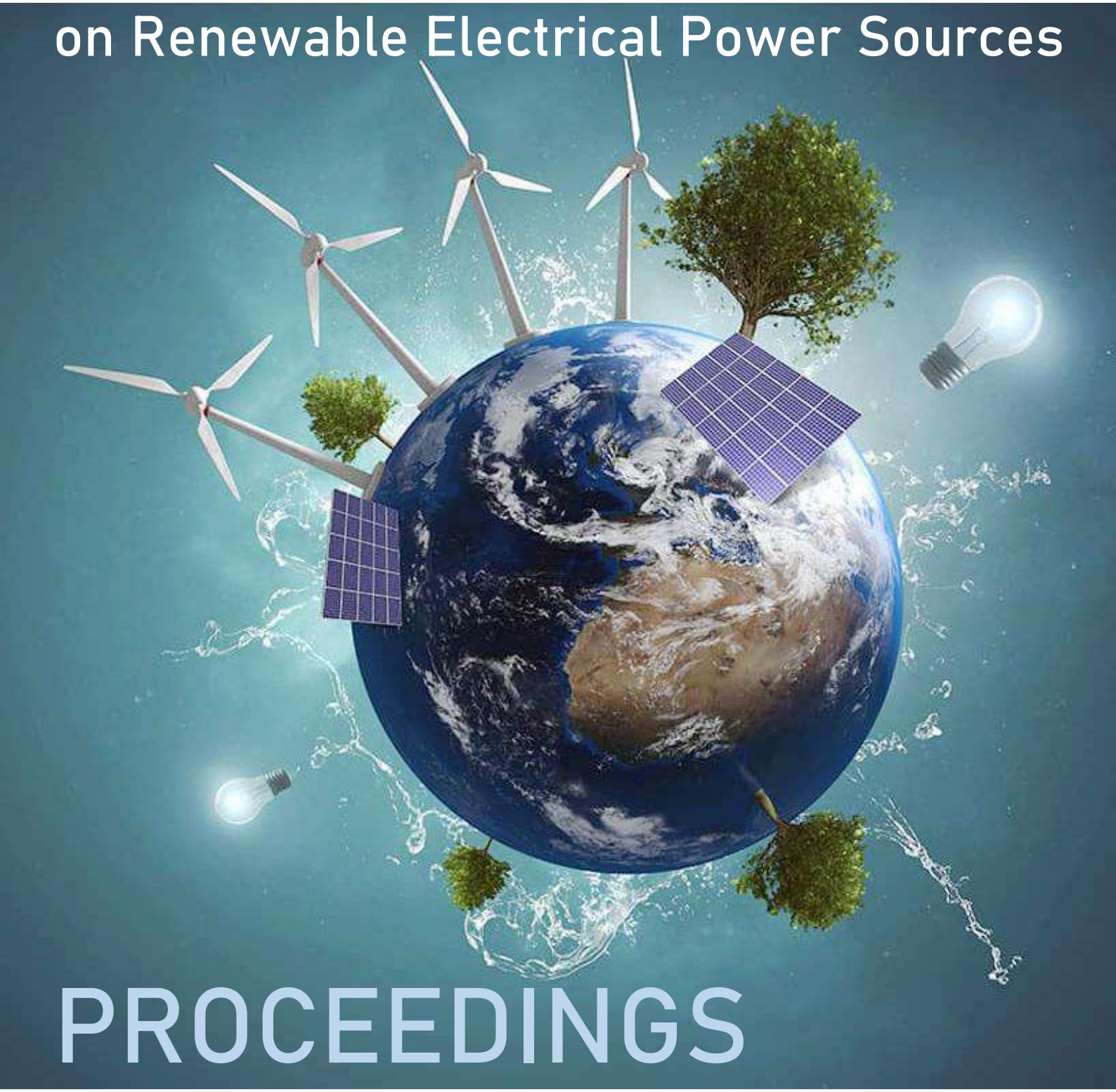
11th International Conference on Renewable Electrical Power Sources



PROCEEDINGS

Editor
Milica Vlahović

Belgrade, November 02-03, 2023

P R O C E E D I N G S

11th International Conference
on Renewable Electrical Power Sources

2023

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11th International Conference
on Renewable Electrical Power Sources

Chamber of Commerce and Industry of Serbia,
Belgrade, November 2 and 3, 2023

Publisher
Union of Mechanical and
Electrotechnical Engineers and
Technicians of Serbia (SMEITS)
Society for Renewable Electrical
Power Sources
Kneza Miloša str. 7a/II,
11000 Beograd

President to the Society
for Renewable Electrical
Power Sources
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Tiraž
100 primeraka

CD umnožava
MT-KOMEX doo, Beograd

ISBN
978-86-85535-16-1

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

502.171:620.9(082)(0.034.2)

INTERNATIONAL Conference on Renewable Electrical Power Sources (11 ; 2023 ; Beograd)
Proceedings [Elektronski izvor] / 11th International Conference on Renewable Electrical Power Sources, Belgrade, November 02-03, 2023 ; [editor Milica Vlahović]. - Beograd : Union of Mechanical and Electrotechnical Engineers and Technicians of Serbia SMEITS, 2023 (Beograd : BEOŽivković). - 1 elektronski optički disk (CD-ROM) ; 12 cm

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Tiraž 100. - Apstrakti. - Bibliografija uz svaki rad.
ISBN 978-86-85535-16-1

a) Енергетски извори -- Одрживи развој -- Зборници

COBISS.SR-ID 129137161

Organizer

Savez mašinskih i elektrotehničkih
inženjera i tehničara Srbije (SMEITS),
Društvo za obnovljive izvore
električne energije

Co-organizer
Institut za arhitekturu i urbanizam Srbije,
Beograd

Privredna komora Srbije,
Beograd

Sponsors

Interplast, Greece

MS Kablovi, Paraćin

Endorsement

MT-KOMEX, Beograd

Održavanje 11. MKOIEE finansijski je pomoglo
Ministarstvo nauke, tehnološkog razvoja i inovacija
Republike Srbije

Република Србија
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FOREWORD

The conditions created by the development of technologies in which modern man lives have led to a complex and paradoxical effect: that by removing obstacles on the way to a more comfortable, simpler, faster and more efficient life and way of working, man also generates numerous misfortunes, attracting dark clouds of threats to the survival of the planet and humanity. The question that concerns and affects all of us - all people, all living beings, systems in which life takes place, large and small, strong and weak - boils down to the problem of the negative impact of man on the environment; this issue invites us to an urgent solution by looking at the causes, proposing solutions, evaluating them, changing approaches and ways of thinking, as well as drawing correct conclusions. Simply put, by adapting nature to one's own needs, man threatens and damages it. That is why, with the joint efforts of all of us, individuals, organizations and states, it is necessary to take all possible measures to immediately prevent the negative effects that are ahead of us.

The importance of renewable sources of electricity, which this international conference focuses on, is noticeable from two angles: the first - it is certain that fossil fuels as a resource will disappear and it is necessary to find alternative sources, the second - the use of renewable energy sources by its essence implies "clean" technology that significantly contributes to reducing CO_2 emissions and thus mitigating climate change and reducing pollution, while encouraging social and economic development in all spheres of life.

The 11th International Conference on Renewable Electrical Power Sources is organized by the Society for Renewable Electrical Power Sources (DOIEE) at SMEITS, with co-organizers: The Institute of Architecture and Urban & Spatial Planning of Serbia (IAUS) and the Chamber of Commerce and Industry of Serbia, with the support of the Ministry of Science, Technological Development and Innovation of the Republic of Serbia.

The registered participants designed their papers according to the given conference topics:
- Energy sources and energy storage;
- Energy efficiency in the context of use of renewable energy sources (RES);
- Environment, sustainability and policy;
- Applications and services.

Eminent authors - scientists, teachers, experts in this field from fifteen different countries: Algeria, Belgium, Bosnia and Herzegovina, China, Croatia, Greece, Hungary, India, Portugal, Saudi Arabia, Serbia, Slovenia, Spain, the United Arab Emirates, and Ukraine, contributed to the conference through sixty-nine papers that were reviewed by the Scientific Committee of the Conference, and after the review process were accepted for presentation at the conference and for publication in the proceedings.

At the end of this short message and at the beginning of the proceedings I believe that it can be proudly said that scientists, researchers, policy makers and industry experts gathered in one place, in order to exchange experiences and knowledge with the aim of promoting scientific and professional ideas and results of research, technology improvement for the use of RES, promoting the rational use of electricity, affirming and proposing inventive solutions in the field of sustainable sources of electricity.

Belgrade, *Milica Vlahović*
November 2023

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<u>Energetska efikasnost u kontekstu primene RES:</u>

<u>Životna sredina, održivost i politika:</u>

Aplikacije:

HIDROFOBIZACIJA KALCITA STEARINSKOM KISELINOM MOKRIM POSTUPKOM

HYDROPHOBIZATION OF CALCITE BY WET METHOD USING STEARIC ACID

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Apstrakt

U ovom radu su prikazani rezultati modifikovanja kalcita stearinskom kiselinom mokrim postupkom. U eksperimentima je kao polazni materijal korišćen prirodni krečnjak sa visokim sadržajem kalcita (većim od 95 %). Površina kalcita je modifikovana različitim količinama stearinske kiseline - 1, 2, 3 i 4 %. Proizvodi su okarakterisani termičkom analizom (DTA/TGA), polarizacionom mikroskopom, IR analizom i „floating" testom. Rezultati su pokazali da se hidrofobnost površine kalcita povećava sa povećanjem količine stearinske kiseline na površini kalcita i da je hidrofobnost dostigla preko 99 % kada je koncentracija stearinske kiseline bila 2 %. Termička analiza je pokazala da se pri početnim koncentracijama stearinske kiseline od 2 % molekuli surfaktanta hemisorbuju na površini kalcita.

Ključne reči: *kalcit, stearinska kiselina, mokri postupak, hidrofobnost.*

Abstract

In this paper, the results of the modification of calcite with stearic acid using the wet method are presented. In the experiments, natural limestone with a high content of calcite (greater than 95 %) was used as the starting material. The calcite surface was modified with different amounts of stearic acid - 1, 2, 3 and 4 %. The products were characterized by thermal analysis (DTA/TGA), polarization microscopy, IR analysis and by the evaluation of a floating test. The results of the floating test showed that hydrophobicity of the calcite surface increased with increasing the amount of stearic acid on the calcite surface and that the hydrophobicity reached over 99 % when the concentration of stearic acid was 2 %. Thermal analysis showed that at initial concentrations of stearic acid of 2 %, surfactant molecules are chemisorbed at calcite surface.

Key words*: calcite, stearic acid, wet method, hydrophobicity.*

1 Introduction

By modification of the calcite surface with surfactants, the limestone employed for PVC production obtains properties that enable the manipulation in the production process, due to the fact that it does not adsorb humidity, and, thus improves blending with PVC. As a result of this process homogeneous mixture is obtained [1].

From this point of view, investigation of the phenomena and mechanism of surface modification of calcite, in order to determine the optimal parameters for obtaining surface-modified calcite, represents the subject of interest of much research [2-5]. The product of the reaction between stearic acid and the calcite surface is a monolayer of hydrophobic organic molecules, which has a strong effect on the final characteristics of the composite because it represents an interphase between the two phases of heterogeneous materials [1].

It is generally accepted that carboxylic acids or their salts react with calcium carbonate to produce a layer of the corresponding calcium salt (calcium stearate in the case of stearic acid) at the mineral surface. Papirer and Fekete found that only one molecule of stearic acid is associated with a Ca^{2+} ion, indicating that the alkyl chains in the monolayer are vertically oriented to the surface of the calcite mineral [6, 7]. The vertical orientation of alkyl chains was confirmed by X-ray analysis. They also showed that applying of stearic acid in concentrations higher than necessary to obtain a monolayer chemisorbed at the calcite surface leads to the formation of multi-layers of physisorbed stearic acid at the mineral surface. It is well known that thermogravimetric analysis (TGA) could be used to confirm the presence of an organic phase at the calcite surface, although it is not used for determining the amount of acid required for the optimal cover of the calcite mineral surface.

Commonly used calcite coating techniques, on a laboratory scale, include dry coating and the wet method. This paper reports the results of investigating the feasibility of the calcite surface modification with stearic acid by the wet method.

2 Experimental procedure

Materials

The natural limestone used in this work was obtained from "Banjakomerc", Serbia. This product is used as filler in the production of PVC elements and pipelines. Stearic acid, a fatty acid, was used as the surfactant for the modification of the calcite surface. Chloroform was used as the organic solvent for stearic acid dissolution.

Modification of the calcite surface

The modification of the calcite was performed using the wet method according to the modified procedure published by Rezaei Gomari [3]: a 10 % aqueous suspension of limestone was treated with an appropriate amount of stearic acid dissolved in chloroform. The concentrations of stearic acid used for coating of the calcite surface were 1, 2, 3, and 4 %. Each suspension was stirred at 4000 rpm, for 15 min, at 50 °C. After the reaction, the suspensions were centrifuged at 10000 rpm for 10 min, washed with distilled water and the obtained products were dried at 60 °C.

Characterization methods

a) Particle size. The granulometric composition of the starting material was determined using a COULTER MULTISIZER. A dilute suspension of the sample in an electrolyte (1 % NaCl) was prepared. Before the granulometric analysis, the sample was dispersed by intensive mixing in a lab mixer for 15 min.

b) Chemical analysis. AAS PERKIN ELMER 703 was used for the determination of the chemical composition of the starting limestone.

c) Microscopic analysis. For identification of the minerals present in starting limestone, qualitative mineral analysis was performed on a polarized light microscope by the immersion method (immersion in xylene for starting limestone, and in water for surface-modified calcite).

d) Determination of the active ratio of the modified calcites. The optimal amount of stearic acid required for the calcite surface modification was determined by the floating test [8] which represents the ratio of the floated product to the overall weight of the sample after mixing in water and vigorous stirring. This ratio, called active is expressed as:

$$I_0 = M_p/(M_p + M_t) \times 100$$

where I_0 is an active ratio (%), M_p is the mass of the floated product and M_t is the mass of the non-floated product.

d) Thermal analysis. Thermal analysis was performed using a NETZESCH 409 EP instrument. The starting calcite as well as surface modified sample were tested in the temperature range from 20 to 1000 °C, at a heating rate of 10 °C/min, under an air atmosphere.

e) IR spectroscopy. The IR spectra were recorded on a HEWLETT PACKARD instrument using the KBr pellet technique, by mixing 1 % of the sample with 99 % of KBr. The samples were investigated in the wavenumber range of 4000 – 2500 cm^{-1}.

3 Results and discussion

The granulometric composition of the starting limestone is given in Table 1. The upper size of the starting limestone was ≈10 □m and the average diameter of D_{50} □ 5 □m.

Table 1. Granulometric composition of starting limestone

Size range, □m	M, %
-18 + 15	0.80
-15 + 10	5.20
-10 + 8	15.80
-8 + 6	31.30
-6 + 5	31.60
-5 + 3	10.87
-3 + 0	4.33
Total	100.00

The chemical composition of the starting limestone ("Banjakomerc") was: CaO - 55.07 %, SiO_2 - 0.57 %, MgO - 0.62 %, Al_2O_3 - 0.038 %, Fe_2O_3 - 0.015 % and loss on ignition - 43.55 %. Based on the amount of CaO, the calculated amount of $CaCO_3$ was 98.29 %.

Mineralogical composition of the investigated limestone was: calcite, opal, wollastonite, getit-limonite, apatite, rutile, and vesuvianite. The sample was mainly in crystal forms (an exception was opal). The main component of the starting sample was calcite (over 95 %), then opal and limonite-getit, which could be observed free or as a cream on the calcite surface, wollastonite and vesuvianite, together with apatite and rutile, were present in traces.

In order to investigate the effect of the stearic acid concentration at the calcite surface on the hydrophobicity of the obtained products, the floating test was performed and the active ratio of each product was determined. The results are presented in Figure 1.

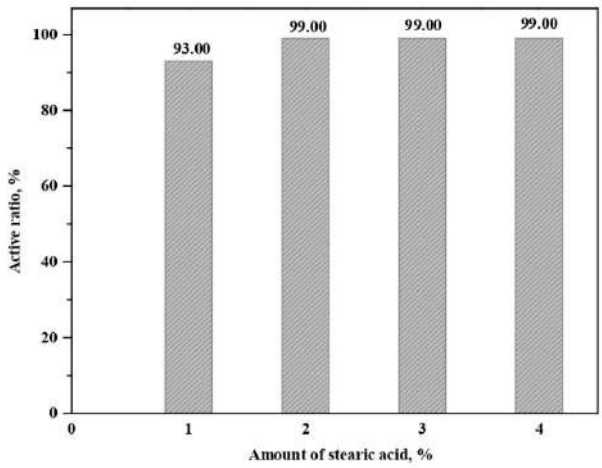
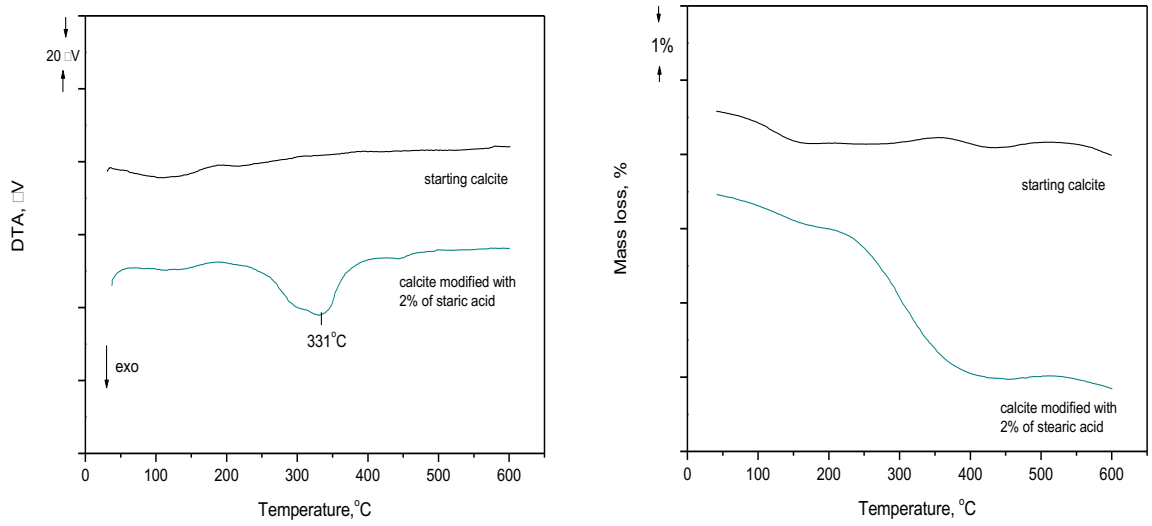


Figure 1. The effect the stearic acid concentration on the active ratio of obtained products

The results presented in Figure 1, showed that with 2 % stearic acid, the active ratio of 99.90 % was achieved and it remained constant with further increase of the stearic acid amount. Hence, 2 % stearic acid was sufficient to obtain a completely hydrophobic calcite surface. Due to this fact, the sample was further characterized by thermal analysis and polarization microscopy.

The thermal (DTA and TG) curves of the starting calcite and the calcite modified with 2 % stearic acid are shown in Figure 2.



a) b)

Figure 2. Thermal: DTA (a) and TG curves (b) of the starting calcite and calcite modified with 2 % stearic acid

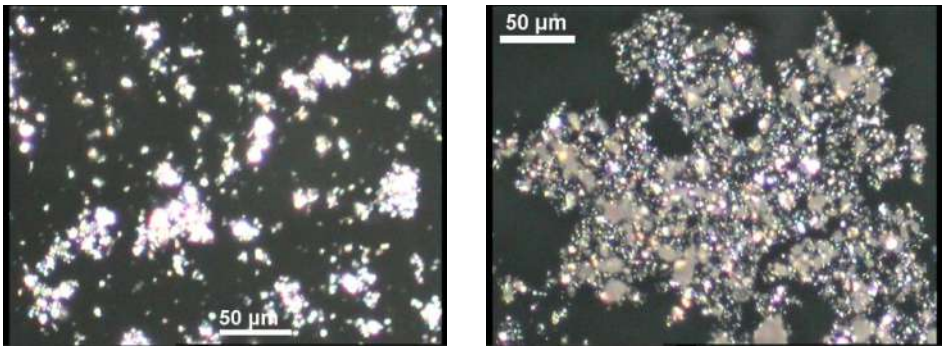
According to the DTA curves in Figure 2a, mass losses in two temperature intervals were observed: the first in the range from 20 to 200 °C and the second from 200 to 400 °C. The mass loss in the first temperature range is assigned to the desorption of weakly bonded water, which was found in both the starting and the modified samples. In the second temperature interval, oxidation of the organic component was detected, which was followed by an exothermic peak on the DTA diagram. Since the starting sample did not contain an organic phase, an exothermic peak was not found on the DTA curve. On the contrary, on the DTA curve of the sample modified with 2 % stearic acid, an exothermic maximum at 331 °C was detected as a result of oxidation of the organic substance present at the calcite surface. The appearance of an exothermic peak in a temperature range of 200-400 °C, and the absence of peaks on the DTA curve of calcite modified with 2 % stearic acid in the first temperature range, indicated that organic substance was chemisorbed at the calcite surface.

The combustion of the organic component was determined by a mass loss. As seen from the TG curves in Figure 2b, the starting sample exhibited insignificant mass loss because it did not contain an organic component. Furthermore, the highest mass loss was found above 200 °C for the sample modified with 2 % stearic acid, due to the oxidation of the organic component, while the mass loss from 0 to 200 °C resulted in a loss of moisture. The mass loss for the starting calcite and calcite modified with 2 % stearic acid is presented in Table 2.

Table 2. Mass loss from TG curves for starting calcite and calcite modified with 2 % stearic acid

Concentration of stearic acid, %	Mass loss, %			
	0-200 ºC	200-400 ºC	400-600 ºC	20-600 ºC
-	0.40	0.07	0.12	0.59
2	0.50	1.94	0.21	2.65

Microphotographs of the starting calcite and calcite modified with 2 % stearic acid are presented in Figure 3.



a) b)

Figure 3. Microphotographs of starting calcite (a), calcite modified with 2 % stearic acid (b)

Compared to the starting sample (Figure 3a), the microphotograph of modified calcite (Figure 3b) indicates that in the presence of water as an immersion liquid, particles of coated calcite tend to concentrate, and thus agglomerates are clearly visible. These results may be another evidence that even with 2 % stearic acid high hydrophobicity of the coated product was achieved.

The starting calcite as well as calcite modified with 3 % stearic acid were additionally characterized by IR spectroscopy. The obtained IR spectra are shown in Figure 4.

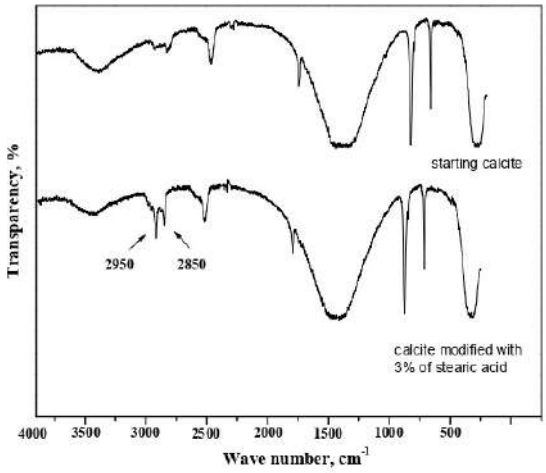


Figure 4. IR spectra of the starting calcite and calcite modified with 3 % stearic acid

According to Figure 4, two intensive bands at 2950 cm^{-1} and 2850 cm^{-1} observed for the calcite modified with 3 % stearic acid, represent asymmetric and symmetric stretching vibrations of

the C-CH_2 bonds of stearic acid. As expected, these peaks are not present in the IR spectra of the started calcite, since it does not have an organic phase.

4 Conclusions

The results presented in this paper show that the hydrophobic product is obtained by modification of the calcite surface with stearic acid using the wet method. The floating test results indicated that 2 % stearic acid was sufficient to obtain the satisfactory hydrophobicity of the product. Thermal analysis showed that at initial concentrations of stearic acid of 2 %, surfactant molecules are chemisorbed at the calcite surface. The hydrophobic material obtained by simple modification can find important applications as a filler in the polymer industry.

Acknowledgments. This work was financially supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Grant No. 451-03-47/2023-01/200023).

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