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Influence of sodium dodecyl sulfate and cetyl trimethylammonium bromide upon calcium carbonate precipitation on bacterial cellulose

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Abstract–Calcium carbonate was deposed on bacterial cellulose (BC) never-dried membranes in the presence of different concentrations of sodium dodecyl sulfate (SDS) and cetyl trimethylammonium bromide (CTAB) by a precipitation reaction between aqueous solutions of calcium chloride ($CaCl_2$) and sodium carbonate (Na_2CO_3) containing, or not, surfactant in their composition. Different shapes of crystals were obtained from rhombohedral ones to flower-like, depending on surfactant type and concentration. From the two surfactants tested, SDS has a greater influence on calcium carbonate morphology than CTAB. The only polymorph obtained in all studied cases was calcite. The composite films BC-calcite were characterized by means of scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and color measurements. The obtained BC-calcium carbonate composites could be used in paper manufacturing.

Key words: Calcium Carbonate, Calcite, Bacterial Cellulose, Sodium Dodecyl Sulfate, Cetyl Trimethylammonium Bromide

INTRODUCTION

Calcium carbonate is one of the most abundant biological minerals and also much used in many industrial applications. Calcium carbonate crystallizes into three different anhydrous crystalline phases: calcite, vaterite and aragonite, with calcite being the most stable. Different organic matrices or additives are used to control the morphology and the polymorphism of calcium carbonate, not only in order to mimic the natural biomineralization process, but also to obtain new composite materials with enhanced properties in comparison with those of raw materials. Among these, polysaccharides as natural biopolymers play the main role. Of the polysaccharides the most studied are alginate, chitin and chitosan, k-carrageenan, alginic acid, starch, dextran, xanthan and cellulose and its derivatives [1-7]. Bacterial cellulose (BC), which is pure cellulose obtained by microbial fermentation, was used as matrix for biomineralization, especially for hydroxyapatite, in relation to bone tissue engineering [8]. It was also used to obtain nanoparticles of CdS, ZnO, platinum or silver for different technical or medical applications [9-13]. From the additives used to influence calcium carbonate crystallization, surfactants must be also underlined. They are used in solution or in emulsion, alone or in different combinations and also as polymer-surfactant mixtures [14-24]. It is difficult to review all the studies which have been conducted to investigate surfactant influence upon calcium carbonate crystallization, but one can briefly affirm that the ionic surfactants are more active as modifiers of calcite crystals morphology and polymorphism than non-ionic surfactants.

Two basic synthetic routes exist to obtain calcium carbonate. The first is a reaction between aqueous solutions of calcium chloride ($CaCl_2$) and sodium carbonate (Na_2CO_3) combined in an equimolar ratio, while the second is the carbonation route [25]. To our best knowledge bacterial cellulose has not been tested as polymer matrix for calcium carbonate deposition. Bacterial cellulose could be used for paper manufacturing, and in this case the interaction between this biopolymer and calcium carbonate could be an interesting research subject. In this paper, a reaction between aqueous solutions of calcium chloride and sodium carbonate combined in an equimolar ratio was used to depose calcium carbonate on a biopolymer, bacterial cellulose. Cetyl trimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) were used as modifiers of calcium carbonate crystal growth. The composite films BC-$CaCO_3$ were characterized by using FT-infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray diffraction (XRD) and color measurements.

EXPERIMENTAL

1. Materials

All chemicals used in the experiments were of analytical grade and used without further purification: calcium chloride ($CaCl_2$), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), cetyl trimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS). All solutions were prepared using high quality deionized water.

2. Synthesis and Purification of Bacterial Cellulose Membranes

The membranes of BC were obtained in static culture. *Acetobacter* sp. strain used in this study was isolated from the traditionally fermented vinegar in the microbiology laboratory of the Chemical Engineering department of Politehnica University of Bucharest. Stock culture was inoculated into modified Hestrin-Schramm medium containing 3% fructose and was incubated for seven days. The obtained gel-like pellicles were purified by boiling in a 0.5 N aqueous

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Table 1. Concentration of aqueous solutions used for calcium carbonate precipitation on bacterial cellulose

	Sample designation				
Type and surfactant concentration	F1	F 2-1	F 2-2	F 3-1	F 3-2
	Without surfactant	CTAB 0.85 mM in $CaCl_2$ solution	CTAB 8.5 mM in $CaCl_2$ solution	SDS 5 mM in Na_2CO_3 solution	SDS 50 mM in Na_2CO_3 solution

Other conditions: Concentration of aqueous solutions used (Na_2CO_3 and $CaCl_2$) was for all samples 0.1 M

solution of NaOH for one hour. The BC thin sheets were then washed with deionized water several times until the pH of the filtrate became neutral and were stored in deionized water at room temperature prior to use.

3. Synthesis of Calcium Carbonate on BC Membranes

The precipitation of $CaCO_3$ on wet bacterial cellulose membrane was carried out at room temperature. In a typical experimental procedure, wet bacterial cellulose gel-like membranes were kept for 10 minutes first in a solution of Na_2CO_3 (0.1 M) and then another ten minutes in a solution of $CaCl_2$ (0.1 M). After soaking in the second solution, the gel membrane became white opalescent. After this, the BC wet membranes were rinsed several times in deionized water and then dried at room temperature. For the experiments in which the surfactants were used as modifiers for crystallization, there were prepared solutions of Na_2CO_3 (0.1 M) or $CaCl_2$ (0.1 M) containing different amounts of CTAB or SDS as it is specified in Table 1.

4. Composites Membranes Characterization

The composite films BC-$CaCO_3$ were examined on a Jasco FT/IR6200 spectrometer with Intron μ Infrared Microscope with ATR-1000-VZ objective. The spectra were the average of 50 scans recorded at a resolution of 4 cm^{-1} in the range from 4,000 to 500 cm^{-1} with a DLATGS detector. Scanning electron microscopy images were obtained with a HITACHI S-2600N scanning electron microscope operating at 20 kV at a magnification of 500-5,000 K. All samples were Au-coated prior to SEM examination. The X-ray diffraction patterns (XRD) were conducted using a Shimadzu XRD 6000 diffractometer with Ni filtered Cu-Kα radiation (40 kV, 30 mA) at 0.02° step in the 2 θ range of 10-80. Color film measurements were done with a spectrophotometer UV-2450 with an integrating sphere (Shimadzu, Japan). The Hunter color scale of lightness (L), a^* (+red/−green) and b^* (+yellow/−blue) values of the films were measured. Standard values were considered those of the white background. Color parameters for the white standard were: L_s=99.85; a_s^*=−5.8 and b_s^*=6.41. Color measurements were replicated three times for each type of film. Calculations were made for D-65 illuminant and 10^0 observer. Total color difference (ΔE) and white index (WI) were calculated as [26]:

$$\Delta E=(\Delta L^2+\Delta a^2+\Delta b^2)^{0.5} \quad (1)$$

$$WI=100-[(100-L)^2+a^2+b^2]^{0.5} \quad (2)$$

where: $\Delta L=L_s-L_{sample}$; $\Delta a=a_s-a_{sample}$; $\Delta b=b_s-b_{sample}$

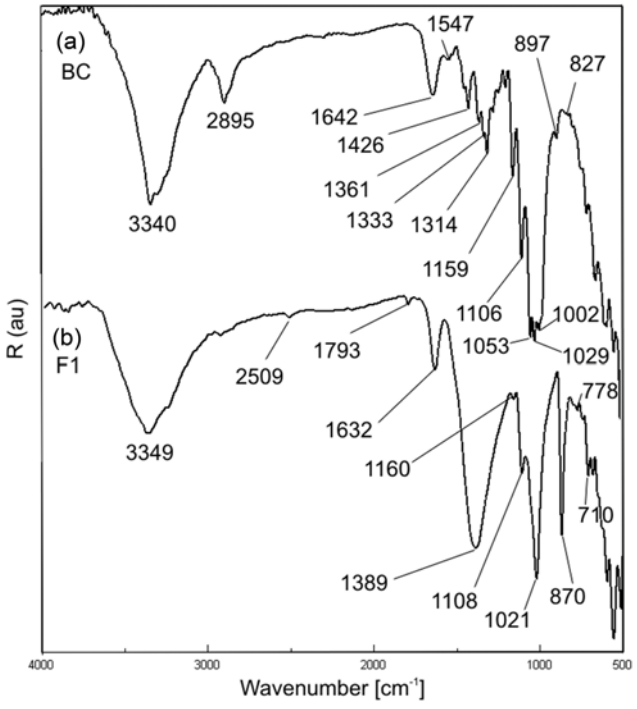

Fig. 1. FT-IR spectra of bacterial cellulose dry film (a) and sample F1 (b).

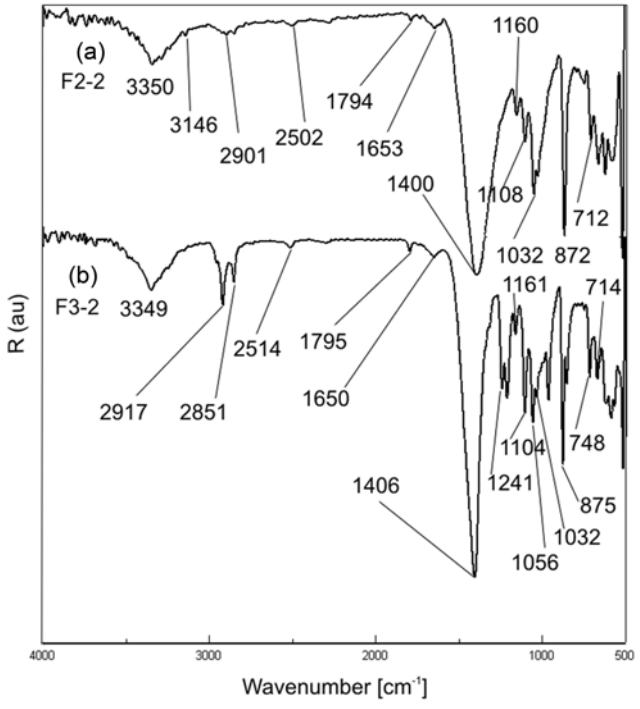

Fig. 2. FT-IR spectra of films: (a) F2-2 and (b) F3-2.

RESULTS AND DISCUSSION

1. Samples FTIR and XRD Characterization

A comparison between FTIR spectra of pure bacterial cellulose dried sheet and the bacterial cellulose-calcium carbonate composite film F1, presented in Fig. 1, reveals some notable differences. These differences must be underlined especially in the regions where bacterial cellulose lacks absorption peaks. The first peaks are those at 2,509 cm^{-1} and 1,793 cm^{-1} which can be assigned to calcite [16, 27]. The band at 1,642 cm^{-1}, which appears due to deformation vibration of the absorbed water molecules in the BC spectrum, is shifted to a lower wavenumber (1,632 cm^{-1}) in the spectrum of BC composite [28]. Very interesting is the peak at 1,389 cm^{-1} in the composite film, a peak which could be assigned to a consociation effect between calcium carbonate and bacterial cellulose. Other peaks which are present in the BC spectrum are shifted in the composite F1 spectrum. Important are also the peaks at 870 cm^{-1} and 710 cm^{-1}, corresponding to absorption bands of calcite [27,29]. The FTIR spectrum presented in Fig. 1(b) confirms that on bacterial cellulose membrane, in the emulsifier absence at room temperature, the polymorph of calcium carbonate deposed is calcite. This assumption is confirmed also by XRD patterns of film F1 (Fig. 3(a)) where all the diffraction peaks assigned to calcium carbonate deposed on BC are characteristic of calcite.

The spectra of composite films BC-calcium carbonate in the presence of high concentrations of CTAB (film F2-2) and SDS (film F3-2) are presented in Fig. 2. These spectra reveal also the peaks which are characteristic of calcite 2,502 cm^{-1} and 1,794 cm^{-1} for F2-2 and 2,514 cm^{-1} and 1,795 cm^{-1} for F3-2. A very sharp peak is registered at 1,400 cm^{-1} for F2-2 and 1,406 cm^{-1} for F3-2 and, as in the case of bacterial cellulose-calcium carbonate composite without surfactant, it could be assigned to calcite formation. The peaks at 872 cm^{-1}, 712 cm^{-1} for F2-2 and 875 cm^{-1} and 714 cm^{-1} for F3-2 are also characteristic peaks of calcite. These assumptions are confirmed by XRD spectra of the composite films obtained in the presence of surfactants (Fig. 3(b), (c)). In Fig. 2(a), which shows

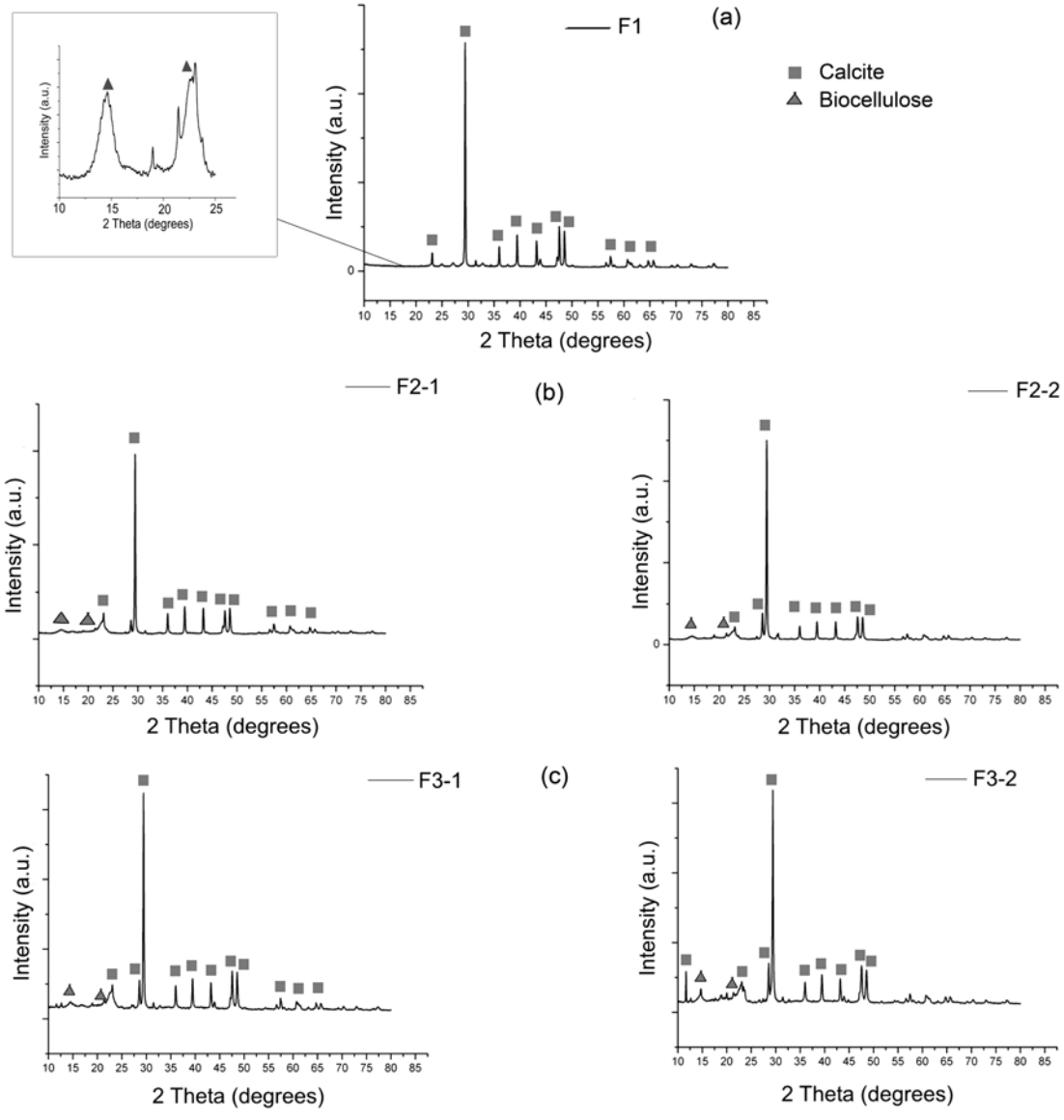

Fig. 3. XRD for all the composites films: (a) F1, (b) F2-1 and F2-2 and (c) F3-1 and F3-2.

the spectrum of composite film F2-2, it is to be noted a band at 2,901 cm^{-1} which could be due to CTAB presence. CTAB exhibits bands due to the symmetric and asymmetric -CH_2 stretching vibrations at 2,914 and 2,846 cm^{-1} [30].

The presence of SDS in the F3-2 composite spectrum (Fig. 2(b)) is more obvious by the peaks at 2,917 cm^{-1} and 2,851 cm^{-1} and possibly by the peak at 1,241 cm^{-1}. For the SDS spectrum, the most important peaks are known at 1,252 cm^{-1} and 1,083 cm^{-1}, which are assigned to symmetric and asymmetric stretching of the sulfate group, and at 2,853 cm^{-1} and 2,924 cm^{-1} due to symmetric and asymmetric stretching and deformation of the methylene groups [31]. These peaks are not all identified in the F3-2 sample spectrum, possibly by an overlap between BC absorption peaks which are presented in the same spectral region. It is obvious that at this high concentration of SDS (film F3-2) the surfactant molecules are adsorbed on the surface of calcium carbonate formed crystals.

Corresponding XRD patterns for all the samples (Fig. 3) exhibit diffraction peaks of calcite, suggesting that the only product obtained when $CaCO_3$ is deposed on bacterial cellulose in the presence or in the absence of surfactants is calcite. Diffraction peaks of bacterial cellulose appear also for all the samples, the main peaks being those at 2θ=14.6 and 2θ=22.5 degrees, as it can be observed from Fig. 3.

2. Morphology Observations by SEM

To observe if the surfactants used have, or have not, an effect on the morphology of $CaCO_3$, SEM images were recorded firstly for the composite film F1 containing calcite deposed in the surfactant absence. Two sorts of crystals are presented at different magnification in Fig. 4, rhombohedral particles and spherical particles, which are entrapped in the bacterial cellulose fibrous structure. In the presence of CTAB, even at low concentration (Fig. 5(a), (b)) the crystal agglomeration is increasing and the irregular intergrown calcite rhombohedral crystals are numerous in comparison with the sample obtained in the absence of CTAB. The number of spherical particles is smaller in comparison with film F1 and at low CTAB concentration (sample F2-1) the spheres are rather ovoid and also consist of irregular intergrown calcite crystals. For high CTAB concentration (sample F2-2), the majority of the particles are rhombohedral and consist of intergrown calcite crystals. Only few spherical particles are observed. For both concentrations of CTAB used in this work, a narrower size distribution of the formed crystals is observed qualitatively in comparison with the mineralized sample obtained in the surfactant absence (F1). CTAB was used also by other researchers as modifier of calcite precipitation, but the studies were done in aqueous solution and not in the presence of a polymeric matrix; that's why the comparison must be reserved, because the working conditions were different [15-17,23]. For example, the conclusion of the study of Yu et al. [15] was that CTAB had no obvious effect on the morphology and polymorph of $CaCO_3$ crystals at room temperature. We consider that in the case of calcium carbonate precipitation on BC in the presence of CTAB, even if the differences are not so impressive, they still exist and the morphology of the crystals obtained in the presence of CTAB on a BC membrane is different. In the presence of surfactant the crystals are more numerous, smaller than in the CTAB absence, with a majority of rhombohedral particles consisting of intergrown calcite crystals and with very few spherical crystals. As it concerns the calcium carbonate polymorphism,

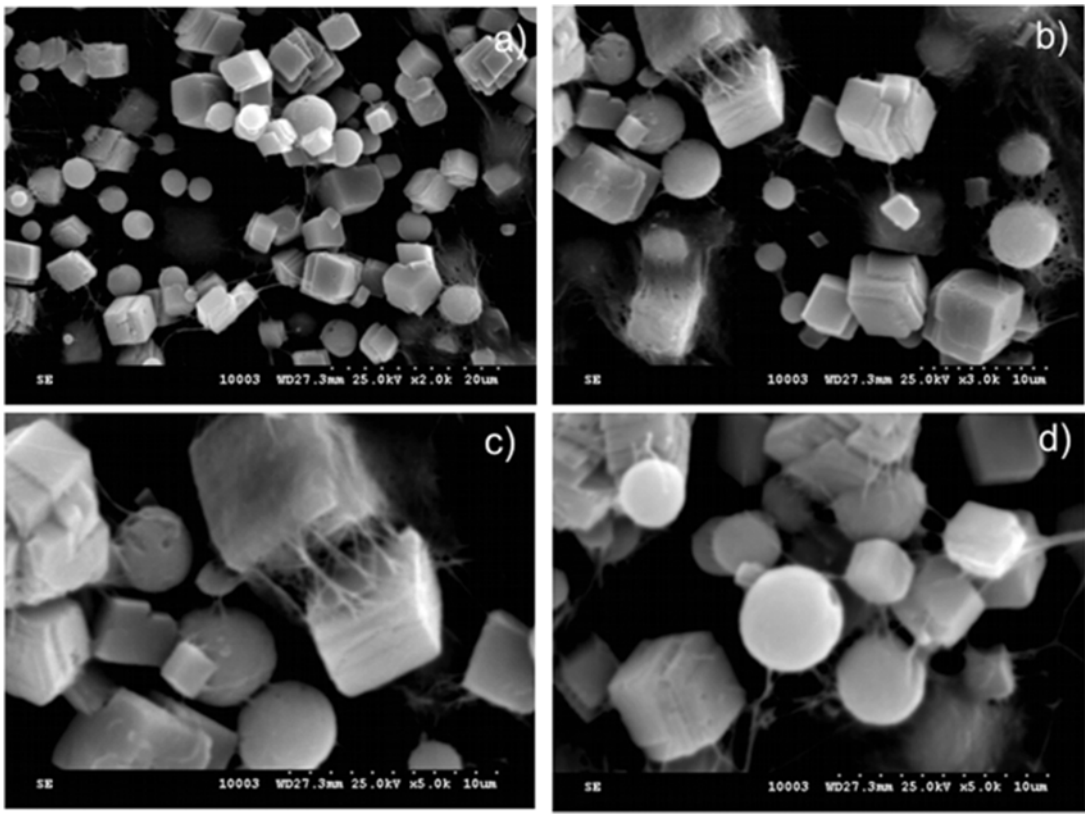

Fig. 4. SEM pictures of film F1: (a), (b) a low magnification; (c), (d) a moderate magnification.

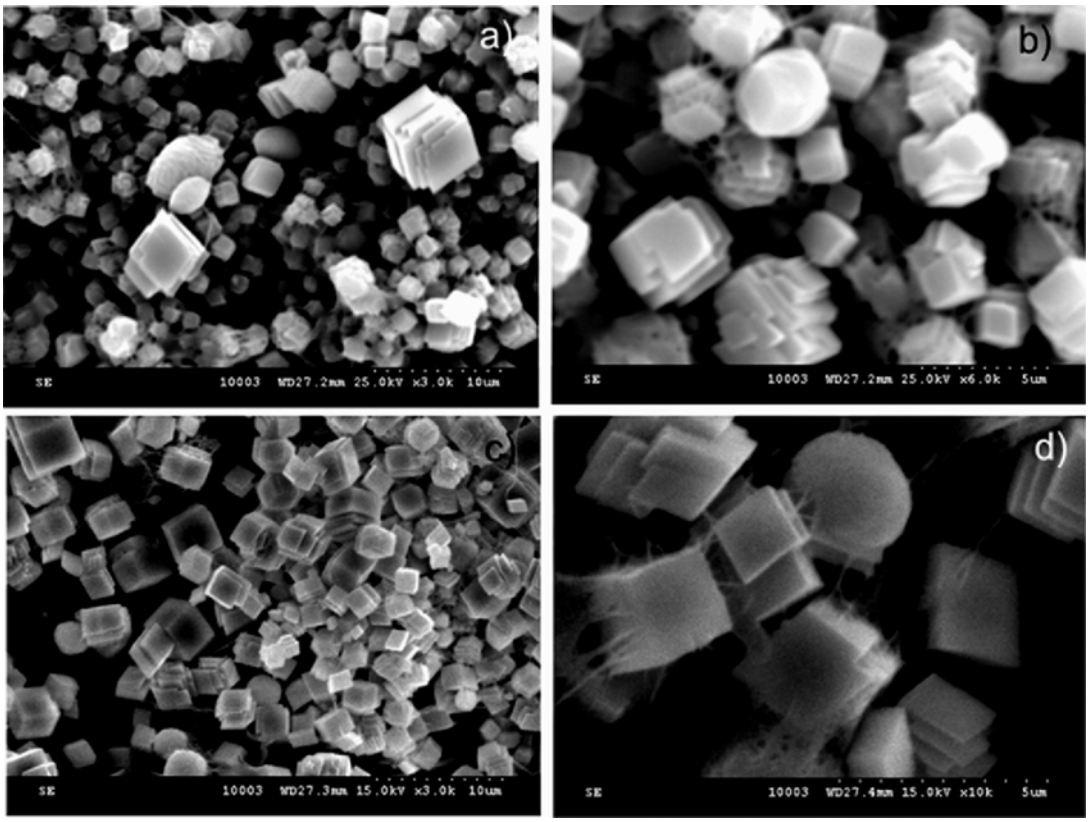

Fig. 5. SEM pictures of films: (a), (b) F2-1 and (c), (d) F2-2.

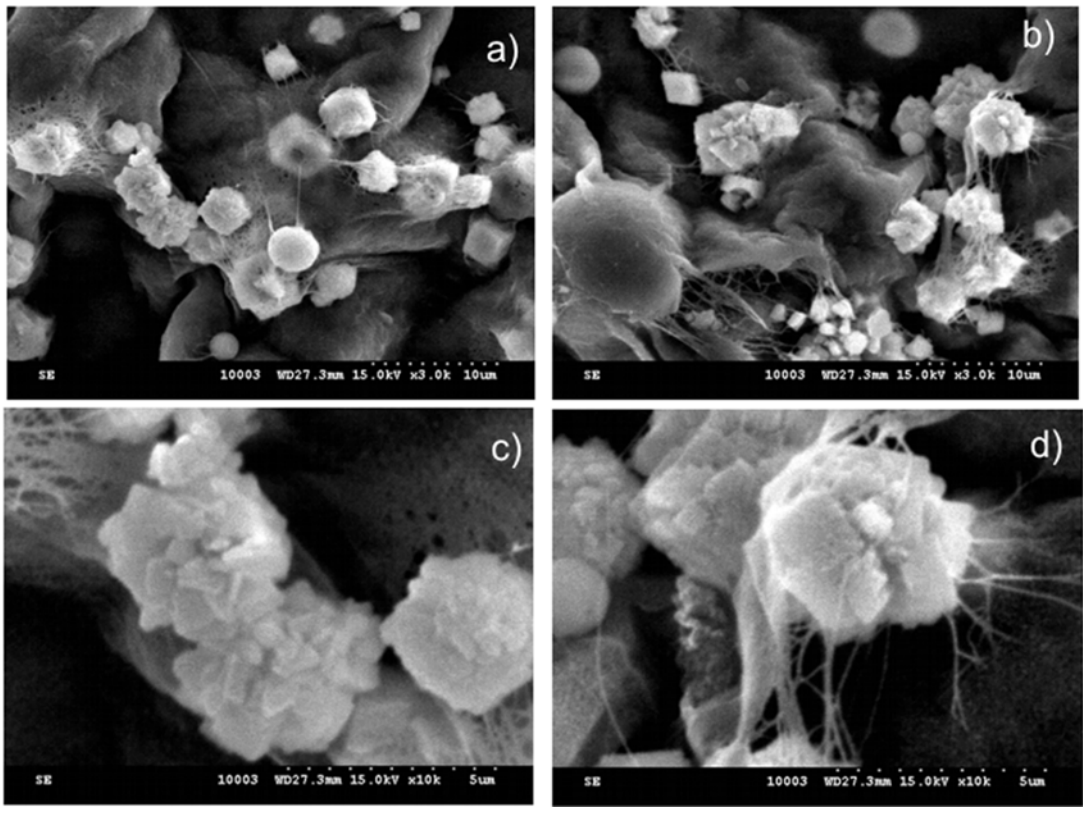

Fig. 6. SEM pictures of film F3-1: (a), (b) top views with a low magnification; (c) detail of image 6(a) with a high magnification showing microstructure of calcite crystals and (d) detail of image 6(b) with a high magnification showing microstructure of calcite crystals.

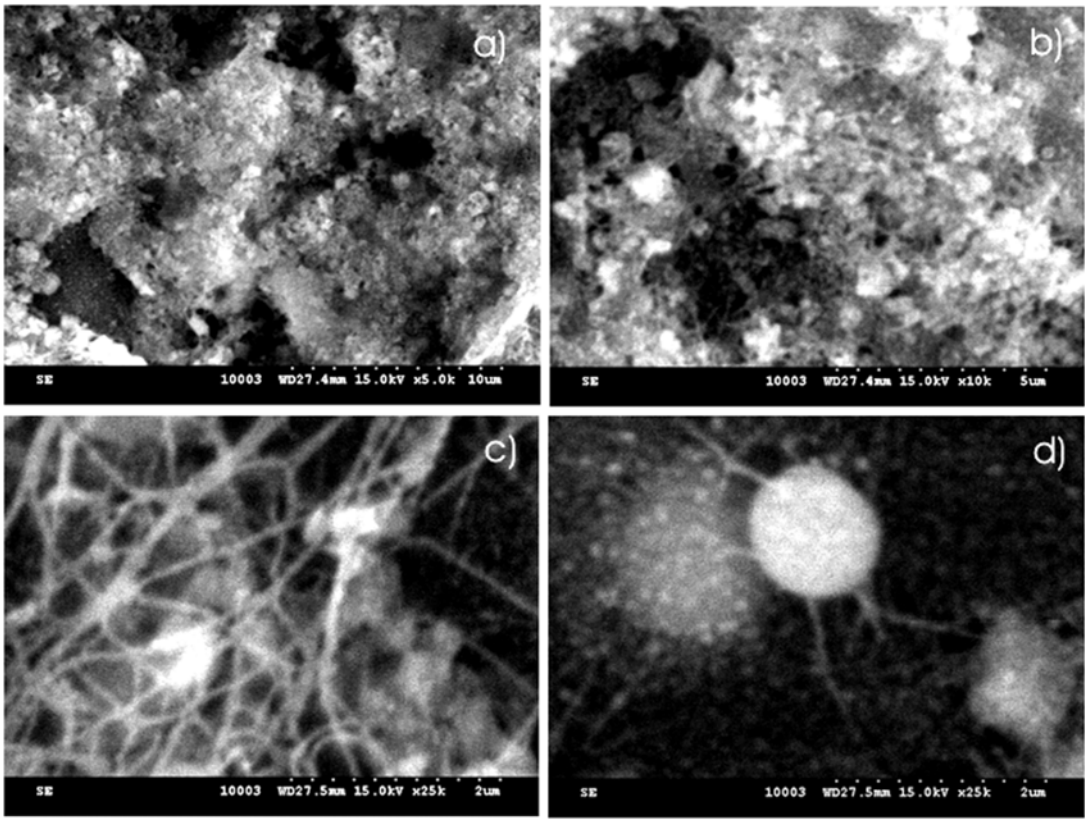

Fig. 7. SEM pictures of film F3-2: (a) view with a low magnification, (b) view with a moderate magnification; (c), (d) views with high magnifications.

our conclusion is that CTAB having a concentration 0.85 mM or 8.5 mM has no obvious influence on the polymorph of $CaCO_3$ crystals deposed on a BC matrix, because XRD patterns for all the composite films obtained in the presence of CTAB reveal the existence of calcite. This conclusion accords with Yu et al. [15].

From Fig. 6, one can observe a more pronounced influence of SDS presence on the precipitation of calcium carbonate on BC matrix. In this case, at a concentration of 5 mM (sample F3-1), which is greater than CMC (critical micellar concentration) of SDS in 0.1 M NaCl (1.5 mM at 25°) [18], the crystals are primarily flower-shaped and only few rhombohedral and spherical particles are obtained (Fig. 6(a) and 6(b)). The formed crystals are entrapped in the BC network and some of them are large crystals. When the concentration is increased 10 times (sample F3-2), very small crystals result which are not clearly seen even at great magnification (Fig. 7(a), (b)). In the BC network are still entrapped also rhombohedral and spherical crystals, but very few (Fig. 7(d)).

It is clear that the presence of SDS changes the crystal shape more than CTAB if we compare the concentration which has the same magnitude order, respectively, samples F2-2 and F3-1. At very high SDS concentration, the aspect of the crystals and their magnitude are changed dramatically, but not the polymorphism of $CaCO_3$, because even in the presence of SDS the polymorph obtained was calcite, as was confirmed by XRD patterns (Fig. 3(c)). Pure calcite is also reported in the literature when SDS is used as modifier of calcium carbonate precipitation in aqueous solutions when its concentration is varied between 0.5 and 5 mM [19]. Very interesting is that at 5 mM SDS concentration Wei et al. [19] observed that the rhombohedral crystals disappeared and monodispersed hollow-spherical particles were obtained. In our studied case we cannot neglect the contribution of bacterial cellulose structure, and for this reason we cannot compare exactly our results with the results obtained for solution precipitation of calcium carbonate in the presence of SDS or in the presence of other anionic emulsifiers as dodecyl benzensulfonic acid [22]. To explain the morphology changes of the calcite crystals is rather difficult because in the studied case there are several factors which influence the result: the presence of the emulsifier in the aqueous solution, the presence of bacterial cellulose, which has highly fibrous structure consisting of ultrafine cellulose microfibrils, and, finally, the lack of agitation. In the case of calcium carbonate precipitation on bacterial cellulose, the pore structures and the tunnels which are created in the BC wet pellicle could be a good environment for crystal growth. BC has also a great water holding capacity ranging from 60 to 700 times its dry weight [32]. In this case many reactions in aqueous solution could be conducted in the gel structure of wet BC. Also, BC could control the crystal growth at nanoscale level, even if for the moment we cannot explain all the facts observed. In the emulsifier presence two interactions are possible: one between BC microfibrils and the emulsifier, while the other interaction appears between the emulsifier and the nuclei of calcium carbonate. The negatively charged head group of anion surfactant molecules could enhance the surfactant adsorption of the molecules on the surface of amorphous $CaCO_3$ as it is already reported [19]. Thus, the greater influence of SDS on the calcite crystal

Table 2. Hunter color parameters and white index for all the studied samples

Sample designation	L^*	a^*	b^*	ΔE	WI
F 1	91.43±0.02	−4.08±0.06	13.38±0.02	10.01±0.03	83.96±0.04
F 2-1	90.26±0.07	−3.91±0.03	15.26±0.02	12.86±0.04	81.47±0.04
F 2-2	94.65±0.07	−5.13±0.03	11.17±0.04	6.76±0.02	86.59±0.02
F 3-1	91.99±0.06	−4.57±0.05	12.41±0.02	9.60±0.04	84.53±0.06
F 3-2	91.34±0.02	−4.25±0.02	12.47±0.01	10.17±0.01	84.23±0.02

Observation: All the measured values are means of three replicates standard deviation

morphology could be explained qualitatively.

3. Color measurement

Table 2 shows the Hunter color parameters for all the composites films. Hunter L^* value, which is a function of lightness, measures the whiteness value of a color and ranges from black at 0 to white at 100. Comparing the Hunter color parameters of the composite BC-calcium carbonate films, there are some differences between them. The L^* value is the highest for film F2-2, resulting in a film with more luminosity and brightness at higher concentration of CTAB. The differences between color parameters of film F2-1 and F2-2 are greater than the differences between films F3-1 and F3-2. This means that the films obtained in the presence of SDS are more uniform from the point of view of the color than the films obtained using CTAB. The color parameters for film F1, obtained in the surfactant absence, are practically similar with the color parameters of films F3-1 and F3-2. For practical applications this is an important fact, because SDS could influence the morphology of the crystals, but has not such an important influence on color parameters.

CONCLUSIONS

Calcium carbonate precipitation is strongly influenced by bacterial cellulose matrix in wet state. The surfactant presence in the aqueous solutions used to precipitate calcium carbonate on bacterial cellulose membranes could also influence the crystal morphology. It is interesting that for all the studied samples the only calcium carbonate polymorph was calcite, even if the concentration of the surfactant was varied in a large range. From the two surfactants tested, one cationic (CTAB) and the other anionic (SDS), the presence of anionic surfactant has a greater influence on the morphology of the obtained crystals. The morphology of the calcite crystals obtained in this work is different from those already reported for the case in which CTAB and SDS were used in aqueous solution for calcium carbonate precipitation. We consider that the differences arise from the presence of bacterial cellulose fibrous structure and high water holding in wet state, which can influence the crystal morphology. The studied system is rather complicated and only future sustained work will be able to explain all the experimental facts observed. From the results already presented in this work, we consider that BC-calcium carbonate composite could be very promising for paper products.

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