

Received March 20, 2013; reviewed, accepted April 15, 2013

CALCIUM CARBONATE MINERALIZATION. PART 1: THE EFFECT OF POLY(ETHYLENE GLYCOL) CONCENTRATION ON THE FORMATION OF PRECIPITATE

**Izabela POLOWCZYK, Anna BASTRZYK, Tomasz KOZLECKI,
Zygmunt SADOWSKI**

Wroclaw University of Technology, Faculty of Chemistry, Department of Chemical Engineering, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland, izabela.polowczyk@pwr.wroc.pl

Abstract: In this study, the role of polymer in precipitation has been examined by studying the effect of poly(ethylene glycol) (PEG) on the formation of calcium carbonate particles. The CaCO_3 particles were characterized by several techniques, such as FTIR, XRD, SEM, and particle size distribution analysis. In the absence of polymer, the mixing of reagents in an aqueous solution led to the formation of calcite crystals. Introduction of poly(ethylene glycol) molecules reduced the rate of crystallization process, and the effect was concentration dependent. In the presence of 0.05, 0.1, and 0.5 % of PEG, after 5 minutes of precipitation initiation, vaterite microspheres appeared in the system and which were transformed into calcite crystals after 24 hours. The calcium carbonate obtained with PEG was characterized by smaller sized particles in comparison with the ones without polymer.

Key words: *calcium carbonate, calcite, vaterite, mineralization, PEG*

Introduction

The crystallization of calcium carbonate (CaCO_3) is of considerable importance in numerous industrial applications as well as in biology. Hence, it is widely used by nature as an inorganic components in exoskeletons and tissues of many mineralizing organisms, giving them strength and shape (Voinescu et al., 2007). There are six CaCO_3 mineral polymorphs including calcite, aragonite, vaterite, CaCO_3 monohydrate, CaCO_3 hexahydrate and amorphous CaCO_3 (Manoli and Dalas, 2000; Li et al., 2010). It has been found that calcite and aragonite have stable thermodynamic structures, while vaterite is thermodynamically unstable so that it is easily transformable to calcite or aragonite in aqueous solution (Li et al., 2010). The

precipitation and stabilization of these polymorphs depend upon the precipitation condition such as degree of supersaturation, pH, ionic medium, and concentration and type of additives (Amjad et al., 2007). The biological system uses organic molecules that function variously as nucleators, cooperative modifiers and as matrices or molds for minerals (Manoli et al., 2002). These organic components are polyanionics and polyacids, which have a high calcium affinity. Avian eggs shells present a unique and interesting model for exploring the process of biomineralization, in which CaCO_3 layers are created by selective nucleation and deposition of calcite crystal by protein. The active sites on the protein recognize calcium ions and induce nucleation of specific polymorph of CaCO_3 and control of the morphology of mineral phase (Lakshminarayanan et al., 2002). Synthesized polymers have also been used in mineralization process. It has been shown that special functional low molecular weight and polymeric additives, such as block copolymers, poly(ethylene glycol) (PEG), polyelectrolyte, polyacrylamide and cellulose, exhibit large influence on the crystallization of CaCO_3 (Xie et al., 2006; Xu et al., 2008; Xu et al., 2011, Sadowski et al., 2010; Su et al., 2010). Among various templates, PEG is of particular interests because its molecules contain hydrophilic groups, which can act as a donor to metal ions to form metal complexes with diverse conformation (Xu et al., 2003). However, up to date the effect of these compounds in precipitation of calcium carbonate is not well understood.

The aim of this paper is to investigate the effect of high molecular weight poly(ethylene glycol) of various concentrations on the crystal growth of CaCO_3 .

Materials and methods

Calcium carbonate precipitation

The poly(ethylene glycol) having an average molecular weight of 5 megagrams/mol from BDH Chemicals was used. Calcium chloride dihydrate (purity > 99%) and disodium carbonate were purchased from Sigma Aldrich. All chemicals used in these syntheses were applied without further purification. The preparation of calcium carbonate was performed according to the method reported in our earlier paper (Sadowski et al., 2010). The solutions of sodium carbonate and calcium chloride (0.1M) with PEG 5000000 (0.01-1%) were prepared one day before the calcium carbonate synthesis and have been stirred overnight. The precipitation experiments were carried out in the Erlenmeyer flasks by mixing a sodium carbonate solution with calcium chloride at the speed of the magnetic stirrer of 300 rpm. After 5 minutes or 24 hours the precipitate was removed from solution by centrifugation. The deposit was collected and washed twice with 100 cm³ of deionized water and dried at 30°C. The experiments were conducted at ambient temperature.

Particle characterization

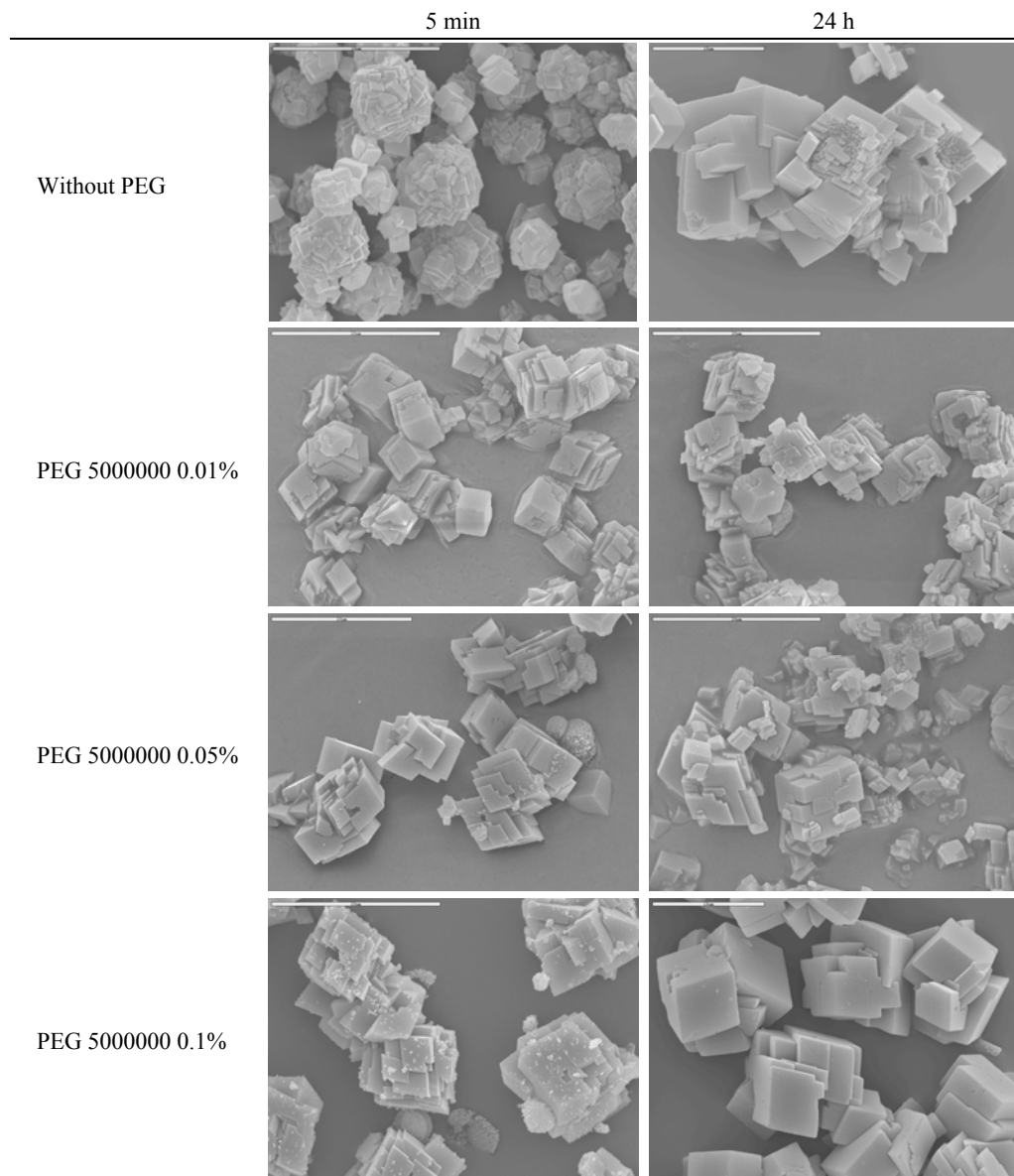
The microstructure of precipitate was observed using a JSM 5800 LV scanning electron microscope (JEOL). The crystallographic structure of calcium carbonates was determined by using an Advance 8D (Bruker) X-ray powder diffractometer with $\text{CuK}\alpha$ radiation. Fourier transform infrared spectroscopy (FTIR) was carried out using PE 1600 FTIR spectrometer (Perkin Elmer). The samples were mixed with KBr powder. The spectra were recorded in a reflection mode from 4000 to 400 cm^{-1} at a resolution of 2 cm^{-1} . Particle size analysis were realized using a Mastersizer 2000 laser diffractometer, equipped with HydroMu dispersion unit (Malvern). These measurements were carried out without and afterwards under operation of ultrasounds in a dispersion unit, so the agglomerates of calcium carbonate could have been broken. The surface area of the samples were measured by the BET method with helium/nitrogen mixture using FlowSorbII apparatus (Micromeritics).

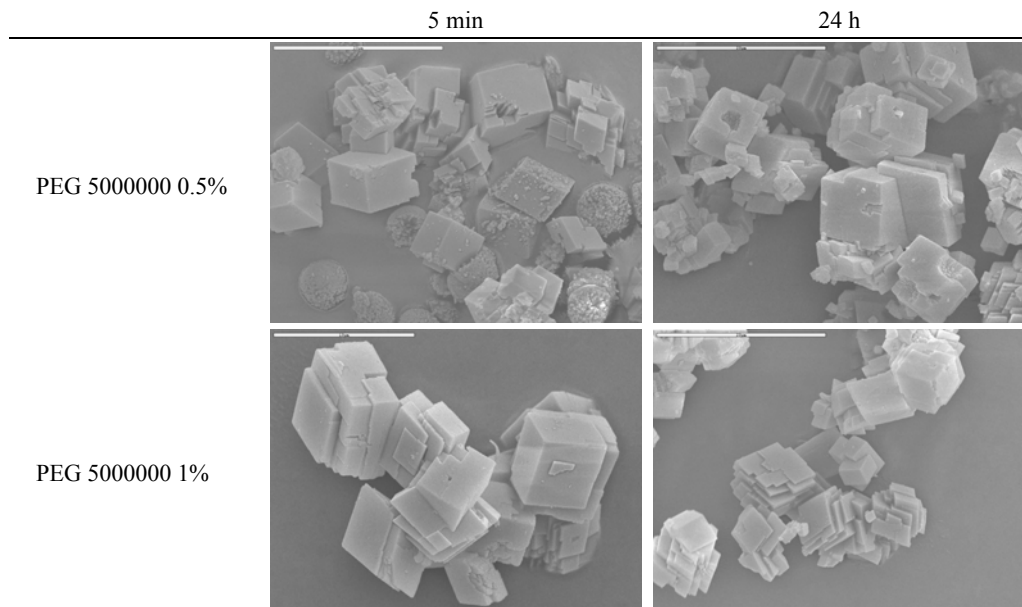
Result and discussion

The morphology and sizes of obtained CaCO_3 precipitates were characterized by the SEM analysis and particle size distribution measurements. In Table 1, the SEM images of calcium carbonate precipitated with the addition of PEG 5000000 and without any additive were collected. The volume median diameters (d_{50}) and quantiles (d_{10} and d_{90}) of particles along with the results of BET specific surface area measurements are shown in Table 2. From these tables one can conclude that CaCO_3 mineralized without PEG polymer formed rhombohedral calcite crystals of an average size of 12.5 and 21.5 μm after 5 min and 24 h of incubation, respectively. Precipitation of calcium carbonates in the presence of various polymer concentration resulted in slight changes of particles diameter after 5 minutes of incubation. In contrast, CaCO_3 precipitates obtained in the presence of PEG but collected after 24 hours of incubation exhibited particles with diameters ranging from 13.4 to 15.9 μm . The slight increase in the particle size observed at a high polymer concentration may be caused by the flocculation effect. The particle formed agglomerates of crystal linked by the polymer molecules, as it can be seen in Table 1. These results indicate that the presence of poly(ethylene glycol) inhibits the growth of CaCO_3 particles in the system. It is known that low and high molecular weight additives can stabilize nonequilibrium morphologies by changing the relative growth rates of different crystal faces through molecular, specific interactions with certain surfaces that modify the surface energy or growth mechanism, or both (Xie et al., 2006). Xie and co-workers (2006) showed that the PEG molecules are able to stabilize and modify crystals. The main cause of the influence of organic additives on the nucleation and crystal growth rates is considered to be the specific adsorption of polymers on the forming faces of calcium carbonate crystals, and the differences in strength of this adsorption interaction because of the nature of polymers (the number and nature of functional groups, including polar ones,

and the molecular weight) determine the final form of the calcium carbonate precipitate (Shestak et al., 2011).

Table 1. SEM images of calcium carbonate particles precipitated in the presence of various concentration of poly(ethylene glycol) after 5 minutes and 24 hours





The PEG is a polymer with the hydrophilic groups ($-\text{CH}_2\text{CH}_2\text{O}-$) which exert the ability to bind calcium as a nucleation site of CaCO_3 and induce the formation of CaCO_3 crystal to adsorption on the special face and inhabitation the crystallization on the orientation (Xie et al., 2006). Additionally, from the SEM images (Table 1), one can see that after 5 minutes of precipitation, regular plate-like structure particles were produced in the presence of PEG 5000000 with at the concentration of 0.01%. At a higher polymer concentration, 0.05, 0.1 and 0.5%, spherical morphologies of carbonates appeared in the system. These microspheres are known as vaterite. Literature data reveal that the individual microsphere of vaterite consists of much smaller nanoparticles and is characterized by high porosity (Kim and Park, 2010). The BET specific surface area results confirm this finding; significantly larger surface areas were obtained for the samples where the vaterite phase were found. From the SEM images it can be observed that the needle-shape structures are also present under that condition. This observation is in agreement with earlier experimental data published in literature. Xie and co-workers (2006) observed that at higher polymer concentrations, the interplay of nucleation and growth becomes more complicated, because the polymorph that is most efficiently nucleated is also the one for which the growth is most effectively stopped. This is why we observe at 0.05 % concentration of polymer a large amount of vaterite in the system.

Figure 1 compares the infrared spectra of CaCO_3 precipitates collected at 5 minute and 24 hours of mineralization in the presence of poly(ethylene glycol) molecules at a concentration of 0.01, 0.05, 0.1, 0.5 and 1.0%. In Figure 1, the spectrum taken at 5 minute exhibits a split in the band around 1320 and 1419 cm^{-1} . The two split carbonate

Table 2. Specific surface areas BET and diameters of calcium carbonate particles precipitated in the presence of various concentration of poly(ethylene glycol)

Sample name	Time	BET S.A. [m ² /g]	d_{10} [μm] no-ultrasounds/ ultrasounds	d_{50} [μm] no-ultrasounds/ ultrasounds	d_{90} [μm] no-ultrasounds/ ultrasounds
Without PEG	5min	0.99	9.8/6.6	22.7/12.5	47.2/23.2
	24h	0.74	16.4/7.9	32.6/21.5	59.3/40.4
PEG 5000000 0.01%	5min	0.73	7.7/6.2	17.4/12.7	36.5/23.1
	24h	0.71	8.9/6.5	20.4/13.4	39.4/24.5
PEG 5000000 0.05%	5min	1.19	9.5/8.2	18.8/14.7	33.7/24.4
	24h	0.74	9.2/6.0	19.3/13.6	40.6/25.1
PEG 5000000 0.1%	5min	1.37	8.7/7.0	21.0/15.7	41.4/29.1
	24h	0.56	11.0/8.2	23.6/15.6	44.5/28.0
PEG 5000000 0.5%	5min	1.39	6.9/7.6	15.6/13.6	30.2/23.9
	24h	0.56	9.9/7.9	21.0/15.8	44.8/30.8
PEG 5000000 1%	5min	0.52	7.8/6.3	17.9/12.7	81.2/23.4
	24h	0.62	8.4/6.8	18.3/14.9	35.3/30.4

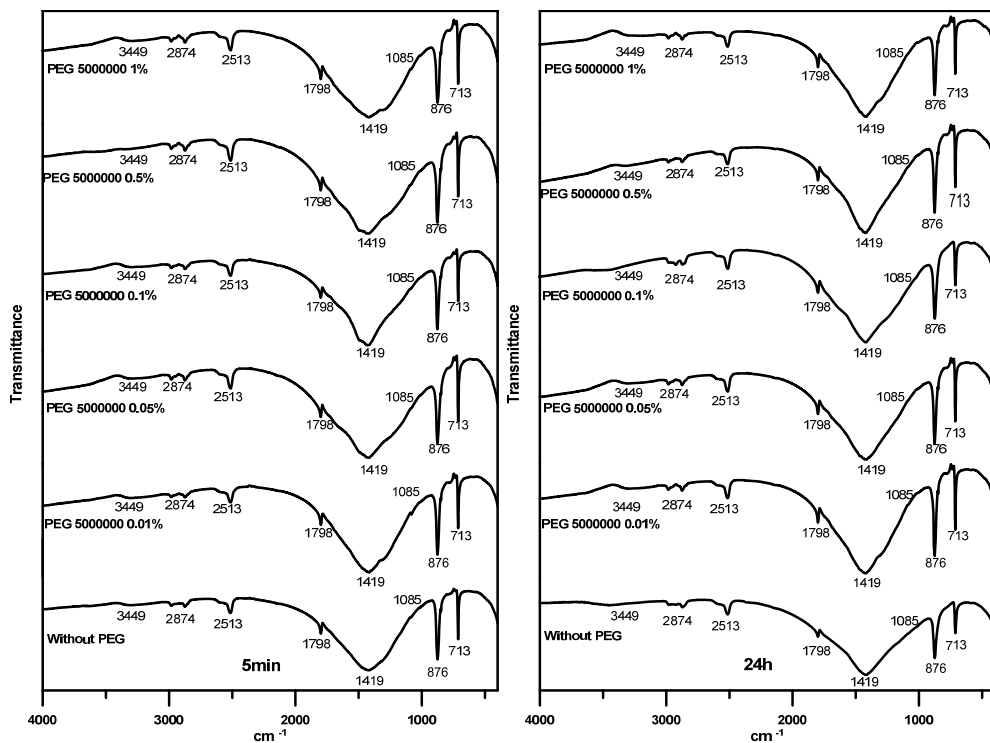


Fig. 1. FTIR spectra of calcium carbonate precipitated after 5 minutes and 24 hours in the presence of various concentration of poly(ethylene glycol)

absorptions appear in ACC or the vaterite phase by an asymmetric stretch of carbonate ions, according to literature data (Addadi et al, 2003; Kim and Park, 2010). These results suggest that the addition of polymer preserves the vaterite phase transition into calcite. The FTIR spectrum of calcium carbonate obtained after 24h revealed a characteristic spectrum of calcite crystal based on the in-plane band and on the out-plane band at ~ 712 and ~ 875 cm^{-1} respectively, and anti-symmetry stretch at ~ 1420 cm^{-1} characteristic of calcite (Menahem and Mastai, 2008; Xu et al., 2011; Wang et al., 2009).

The powder diffraction patterns presented in Figure 2 also evidenced calcite phase creation, mostly. With the elliptical marks, the small vaterite picks appearing in the calcium carbonate precipitated within 5 min in the presence of 0.05–0.5% of PEG concentration were distinguished. Without the addition of poly(ethylene glycol) as well as at very high (1%) concentration, only calcite was formed. Also leaving the particles in solution for one day resulted in vaterite phase extinction.

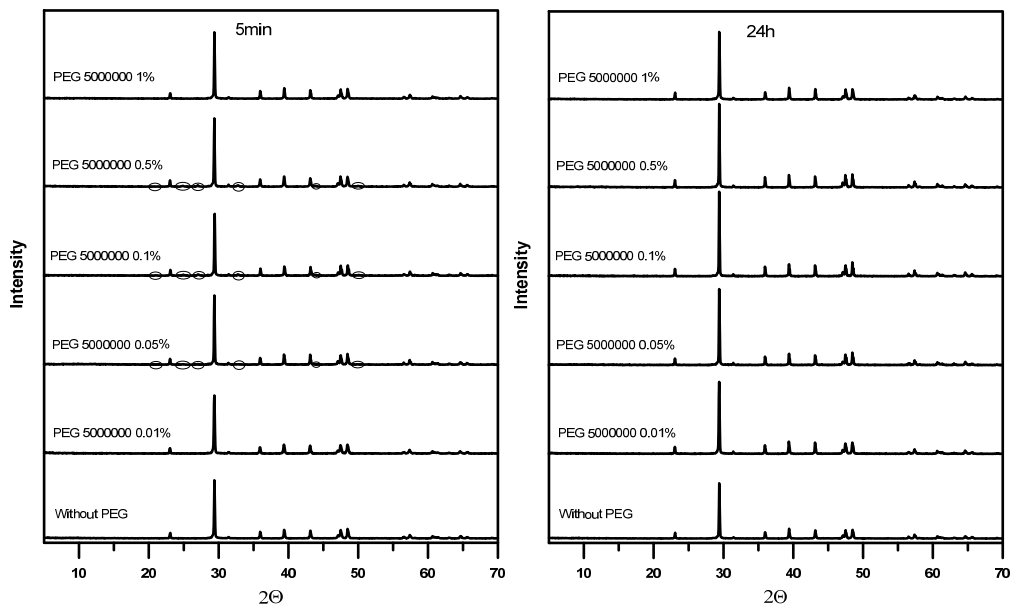


Fig. 2. XRD patterns of calcium carbonate crystals obtained at various concentration of poly(ethylene glycol) after 5 minutes and 24 hours precipitation

The quantitative analysis of powder diffraction data has been performed using the ReX ver. 0.7.0 computer program (Bortolotti et al., 2009). The software is free for personal and non-commercial use, and along with a short tutorial and is available at <http://www.rexpd.com>. The results of analysis for calcium carbonate precipitates after 5 minutes are shown in Table 3. Calcite was the only phase found in calcium carbonate after 24 h.

Table 3. Calcite and vaterite contents in calcium carbonate precipitated after 5 minutes in the presence of various concentration of poly(ethylene glycol)

Sample name	CaCO ₃ form	vol.%	wt.%
Without PEG	calcite	100	100
	vaterite	0	0
PEG 5000000 0.01%	calcite	100	100
	vaterite	0	0
PEG 5000000 0.05%	calcite	98.6	97.0
	vaterite	1.4	3.0
PEG 5000000 0.1%	calcite	94.8	89.4
	vaterite	5.2	10.6
PEG 5000000 0.5%	calcite	95.5	90.8
	vaterite	4.5	9.2
PEG 5000000 1%	calcite	100	100
	vaterite	0	0

Conclusions

The calcium carbonate crystals precipitated in the presence of PEG polymer are predominantly calcite. Small amount of vaterite phase has been obtained at the concentration of polymer 0.05–0.5%. Without polymer addition only calcite phase was formed. PEG 5000000 can affect the morphology of CaCO₃ crystals as well as a size distribution of precipitate. The smallest particles were obtained in the presence of 1% of the polymer in the solution. The largest surface areas have been obtained for samples having the vaterite phase. The possible mechanism of formation of calcium carbonates crystals is proposed below. In the aqueous solution, Ca²⁺ and CO₃²⁻ firstly form ACC, which quickly transforms into vaterite and calcite within minutes. At the same time the polymer molecules adsorb on the surface of the particles. They inhibit the growth of crystal during the process resulting in formation small particles. This mechanism is similar to that described in literature in the presence of other polymer such as pluronic (Zhao et al., 2012). Both polymers possess the same functional group, ethylene oxide (EO), which can interact with calcite surface.

Acknowledgements

The work was financed by a statutory activity subsidy from the Polish Ministry of Science and Higher Education for the Faculty of Chemistry of Wrocław University of Technology for 2012/2013 (S20072/Z0307).

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