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Polymerization Process-Method for Control of Crystal Nucleation of Calcium Carbonate

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We report based of the new concept for controlling crystal polymorphs of $CaCO_3$, entitled "latent inductor method", [10] the results obtained by developing the crystallization in the same time with polymerizations process of methyl methacrylate. The crystalline form of product is discussed reported to analytical results obtained by FT-IR spectroscopy, X-ray, SEM. We discuss, in the same time, the particularity of polymeric assistant of crystallization process.

Keywords: crystallization of $CaCO_3$; latent inductor; polymer; polymorph crystal control

INTRODUCTION

Calcium carbonate is one the most abundant mineral in nature. Such industrial and biomedical applications require well defined calcium carbonate particles with narrow size distribution, uniform shape and defined crystal structure. In this idea, a considerable researches works has been devoted to elucidating the relationship between the synthesis condition and properties of obtained calcium carbonate particles. The operating parameters, such reactant concentration, pH values,

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additives, mixing, admixing and operation mode are inter-related, the mechanism of calcium carbonate precipitation still seem clouded [1–3].

Crystalline morphology, dimension and orientation of $CaCO_3$ are determined by the presence of protein matrix or other macromolecular systems. The growth and organization modalities are placed to the organic- inorganic interface. Organic sequences involve the structural information for inorganic nucleation. By consequence, those determine the growth of different polymorph $CaCO_3$: vaterite, aragonite, calcite [4,5].

Particularly, the role of organic additives on the calcium carbonate nucleation and control of growth are not yet fully understood. It is therefore interesting to examine the addition of chemicals on the carbonation process [6–8]. Although crystallization of minerals in presence of various additives and synthetic polymers has been investigated as model of biomineralization, for additive are put in evidence only two specifically functions [9]:

a) they could inhibit crystal growth by binding to the growth site of the crystals;
b) they can induce the heterogeneous nucleation, controlling and stabilizing the precipitated polymorph.

In this conditions has been take shape the idea to study the selective interactions of additives at different stage of nucleation process, where has not been investigated in details. A new concept for controlling crystal polymorphs of $CaCO_3$ by addition of synthetic additives are developed [10]. The key point of this method is to using a "latent inductor" for crystal nucleation. In this concept, the latent inductor as its inactive state does not affect nucleation and growth of crystal. After the inactive state is transferred to an active state by a stimulus, the active inductor can induce nucleation and growth of the crystal.

Another method is the interfacial reaction whence make spherical particles of calcium carbonate [11] in mixed crystal forms of calcite and vaterite were found to comprise the spherical hallow particles.

The goal of this article is discussion regarding results obtained by modification of the interfacial method. This modification consist in the developing in the same time the control of polymorph growth by a latent inductor method. We discuses the dimensional distribution and the influence of the major factors which affect the morphological structure and dimension of $CaCO_3$ particles.

EXPERIMENTAL

Materials

We used methyl methacrylate (MMA) from Merck, purified by rectification on reduced pressure; such monomer, potassium persulphate (PSK), by Fluka, as initiators, toluene (T) from Reactivul SA, purified by normal pressure rectification, as monomer–polymer solvent, calcium nitrate, calcium chloride and potassium carbonate, analytical pure, from Merck, such component for obtained $CaCO_3$.

Experimental Techniques

a) Synthesis

All synthesis has been developed at 30°C under stirring at pH = 8.

General working procedures involve the transformation of MMA in poly(methyl methacrylate) (PMMA) in the same time with mineralization process of $CaCO_3$. We used the interfacial reaction modified with latent inductor method. Firs, was dissolved in T the MMA (2,81 mole/l). Second a potassium carbonate (1 mole/l) and ammonium persulphate aqueous solutions was added to the toluene solution thus that the volume ratio water/oil = 3:7. Then, this mixture was emulsified by magnetic stirring for 20 min at 30° C. Last, calcium salt solution (chloride or nitrate), with a know concentration so that has been respected the molar ratio indicated in the Table 1, was poured under stirring in the obtained emulsion. We extract the sample at different reaction time. The mineralization process evolution have assessing by optical microscopy.

Figure 1 show a potential mechanism to produce calcium carbonate particle.

a) Analysis

The obtained crystal phases were characterized by FTIR analysis, using a Bruker Equinox 55 apparatus, X ray diffraction, using a Shimadzu XRD apparatus and scanning electron micrograph (SEM) using a HITACHI apparatus.

RESULTS AND DISCUSSIONS

The firs experimental series used K_2CO_3 and $Ca(NO_3)_2$ (Table 1a) as basically materials for calcium carbonate synthesis. Figure 2 reveal the optical images obtained from the analyzed samples at established time of reaction.

TABLE 1 Investigate Composition Substrate and the Main Process and Dimensional Characteristics

Nr.	CO_3^{2-} : Ca^{2+}	x_{MMA}*	$x_{Ca^{2+}}$	η (%)	d_{max} (μm)** 10 min	40 min	70 min	1440 min
a) $K_2CO_3 + Ca(NO_3)_2$								
1	2 : 1,5	0,008	0,4200	1,993	2 (86,67)	2, (88,40)	2 (84,88)	–
2	2 : 1,0	0,0093	0,3307	1,433	2 (54,60)	2, (78,54)	2 (76,53)	–
3	1 : 2,0	0,0093	0,6600	1,575	1 (78,57)	1 (57,23)	1 (81,43)	1 (55,93)
4	2 : 0,1	0,0132	0,0470	11,11	1 (74,19)	1 (72,72)	1 (61,63)	–
5	1 : 1,0	0,0140	0,4930	1,23	2 (91,41)	2 (93,53)	2 (94,15)	–
6	1 : 0,5	0,0184	0,3272	14,967	1 (50,00)	1 (99,71)	1 (65,91)	–
7	1 : 0,1	0,0250	0,0890	6,974	1 (72,91)	1 (61,08)	1 (55,31)	–
b) $K_2CO_3 + CaCl_2$								
1	0,5 : 0,4	0,030	0,430	1,131	2 (95,70)	2 (76,10)	2 (74,65)	3 (47,91)
2	1,0 : 0,4	0,020	0,280	4,474	2 (75,40)	2 (54,89)	–	2 (46,16)
3	1,5 : 0,4	0,015	0,205	5,864	2 (75,52)	2 (71,57)	2 (57,64)	3 (46,57)
4	2,0 : 0,4	0,012	0,168	9,500	2 (55,53)	2 (63,31)	2 (56,87)	2 (44,71)

*in all cases the MMA concentration in the substrate was 2,81 10^{-2} mol/l.

**bracket values are the frequency of volume density for the indicate dimension of diameter.

For all investigated substrates, the increasing of reaction time is accompanied by apparition of the high mineral organization, consequences of aggregation phenomenon. In the same time is evidently that the increasing of CO_3^{2-}/Ca^{2+} ratio have a consequence formation of the particles with large diameters just in the starting point of process.

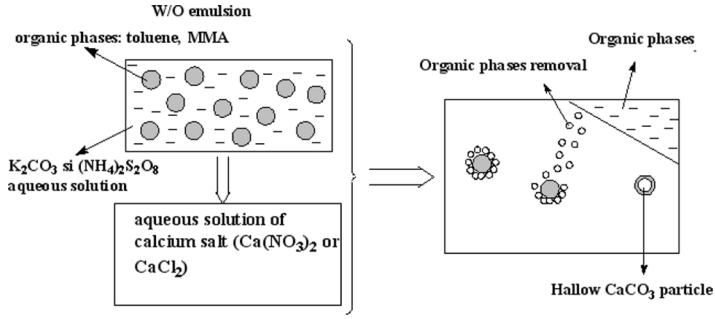


FIGURE 1 Predicted mechanism to produce calcium carbonate by latent inductor method/interfacial reaction method.

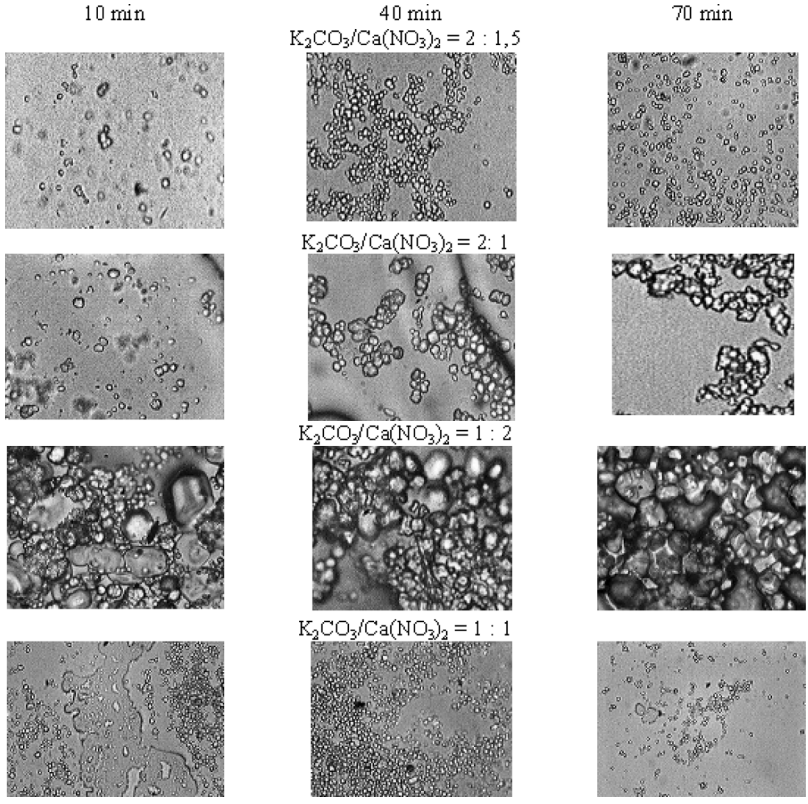


FIGURE 2 Optical micrographs for calcium carbonate synthesized by $Ca(NO_3)_2$.

The Figure 3 exemplified the microscopic photos for the evolution of mineralization process in the second experimental series which used K_2CO_3 and $CaCl_2$ (Table 1b) as basically materials for calcium carbonate synthesis.

Comparing with the firs series is evidently than in this case the mineralization process starting with large diameters for calcium carbonate particles. In the same time we remark a more uniform distribution for the crystallization zones determined by organically phases. Similar with the previous case, the reaction time favors the agglomeration structures.

The yield of process is a consequence of substrate composition (CO_3^{2-}/Ca^{2+} ratio) as well as counter-ion nature for calcium salt. Thereby, for $Ca(NO_3)_2$ case we obtain a maximum value of yield for

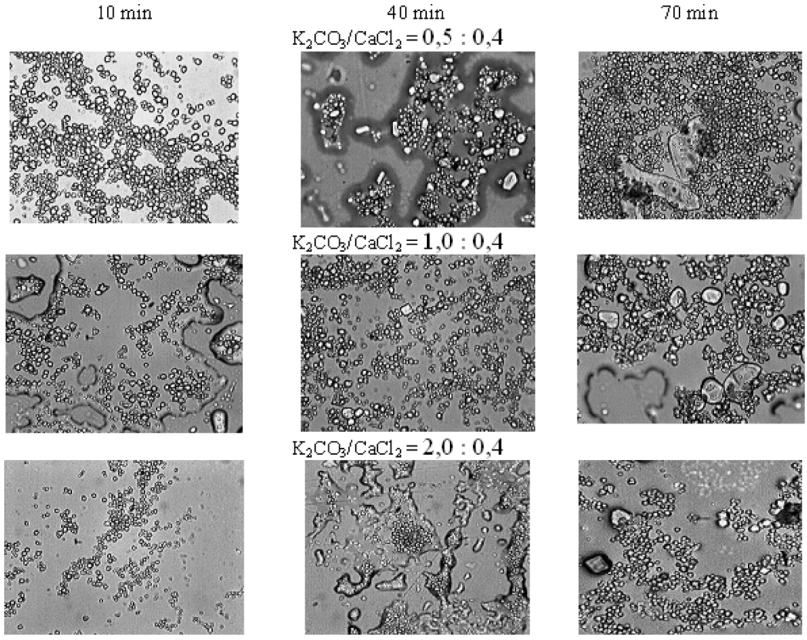


FIGURE 3 Optical micrographs for calcium carbonate synthesized by $CaCl_2$.

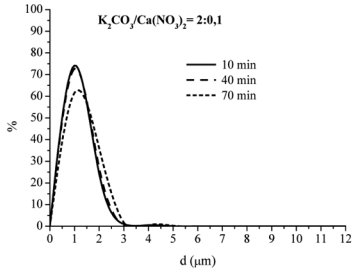
$x_{Ca^{2+}} = 0,322$ and $x_{MMA} = 0,0184$, which correspond a 1μm for diameter value. The decreasing a yield in the same time with increasing of Ca^{2+} and MMA concentrations is duet, probably to the modification of the dimensional populations. If we expect an increasing of the yield value, the evolution of dimensional distribution of particles population have as consequences a colloidal dissolution of $CaCO_3$.

For experiments with $CaCl_2$ we can observe a continuous increasing of reaction yield reported to Ca^{2+} and MMA concentration (see Table 1). Therefore, counter- ion of calcium ion is very important factor regarding the microstructure organization which presume or not the diversification of the dimensional populations.

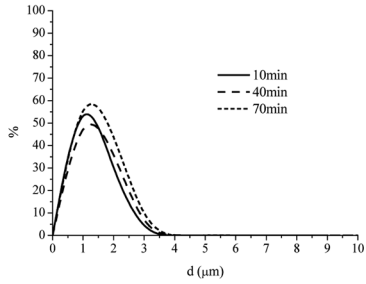
Granulometric curves showed in the Figures 4 and 5, mark out in the both analyzed cases a mono-modal distribution. The population frequencies with the same dimension is a consequence of ionic ratio CO_3^{2-}/Ca^{2+} and reaction time. The curves maxima is a consequence of ion ration CO_3^{2-}/Ca^{2+} and reaction time.

We remark a narrow distribution for main ionic ratio and the enlargement of distribution frequency curve with reaction time.

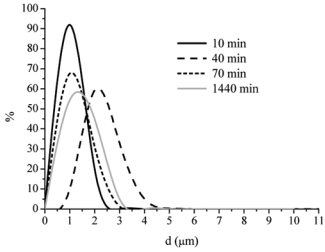
We remark a particular dimensional evolution for $K_2CO_3/Ca(NO_3)_2 = 2{:}1{,}5$ feed ($d_{max} = 2\,\mu m$) which conserve the dominant



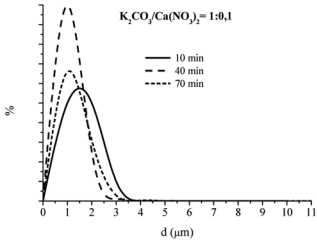
(a) $K_2CO_3/Ca(NO_3)_2$ = 2 : 0,1



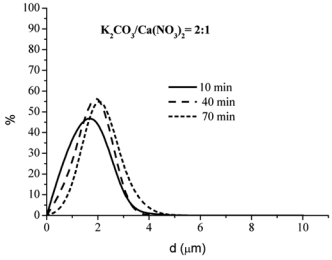
(b) $K_2CO_3/Ca(NO_3)_2$ = 1 : 0,5



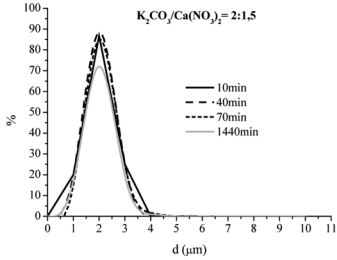
(c) $K_2CO_3/Ca(NO_3)_2$ = 1 : 0,2



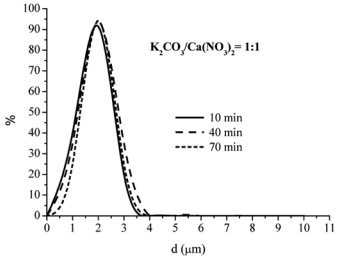
(d) $K_2CO_3/Ca(NO_3)_2$ = 1 : 0,5



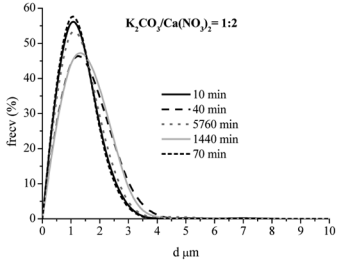
(e) $K_2CO_3/Ca(NO_3)_2$ = 2 : 1



(f) $K_2CO_3/Ca(NO_3)_2$ = 2 : 1,5



(g) $K_2CO_3/Ca(NO_3)_2$ = 1 : 1



(h) $K_2CO_3/Ca(NO_3)_2$ = 1 : 2

FIGURE 4 Granulometric curves for synthesis of calcium carbonate starting to $K_2CO_3/Ca(NO_3)_2$.

dimension of particles regardless of reaction time. One the other hand a particular evolution are register for the substrate $K_2CO_3/Ca(NO_3)_2 = 2:1$ and $K_2CO_3/Ca(NO_3)_2 = 1:0,5$ characterized practically by the same value of molar ration of Ca^{2+} (0,3307 and 0,3272, respectively). Therefore the value of medium diameter and dimensional distribution in time are different (see Table 1a). This phenomena will be explained by modification of MMA molar ration in the reaction feed. Thus, practically, doubling the x_{MMA} ($K_2CO_3/Ca(NO_3)_2 = 1:0,5$) the maxima value of diameter decrease (see Table 1a and Fig. 4).

A displacement for a great value of maximum diameter, when change the counter- ion of calcium (Fig. 5, Table 1b), are accompanied by the increasing of the distribution frequencies of the diameters with 1 μm for the short time of reaction, with a maxima for equimolar substrate (see Fig. 5 and Table 1b).

These aspects suggest in the first time an aggregation of the $CaCO_3$ particles, consequence of the increasing of the carbonate ions concentration on the interface. In the second time, we can affirms that

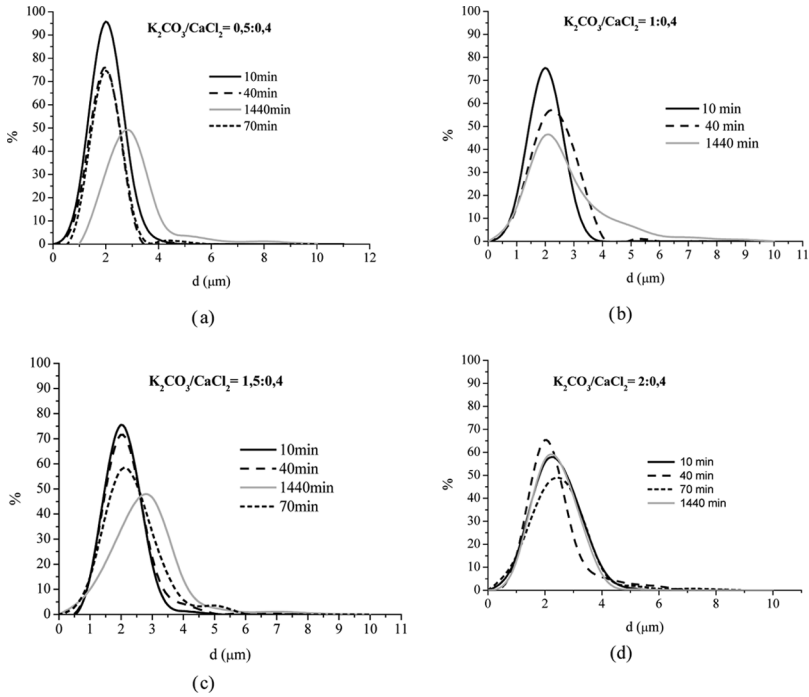


FIGURE 5 Granulometric curves for synthesis of calcium carbonate starting to $K_2CO_3/CaCl_2$.

the increasing of the reaction time favors the $CaCO_3$ growth on the initial crystallite surface. Have been an optimal value of the population concentration on whereon the calcium carbonate particles precipitate.

In all cases, the assistance of the organic fraction on the apparition and the growth of the calcium carbonate, after mineralization starting, not affect the particle dimension. Will be affected only the distribution frequency of the dimensional population. If a short reaction times the distribution of dimensional population are narrow and characterized by high values of distribution frequencies (Fig. 5). Increasing of reaction time determine a widening of distribution curve and diminution of distribution frequencies. That will be explained by changing of dimensional population: diminution of majority population is accompanied by increasing of the minority population and in the same time the emergence of superior dimensional populations (Fig. 6).

FT-IR analysis (Fig. 7) put in all cases the vibration bands at 1387–1400 cm^{-1} and 868–871 cm^{-1}. That are characteristic to the stretching vibration and the asymmetric deformation of $CaCO_3$, respectively. is set off by The vibration band from 700–715 cm^{-1} are determinant for the morphological differences. Thus, for utilization of $CaCl_2$, we remark the peak at 711–713 cm^{-1} with is specific to calcite. Displacement of vibration bands is a consequence of orientation angle in the mineralization process. The same peaks are specific for substrates based on $Ca(NO_3)_2$ One exception are registered for the substrate $CO_3^{2-}/Ca^{2+} =$ 1:0,5, whereon a peak at 747, 714 cm^{-1} appear. This is specific of vaterite.

The Figure 8 present the SEM photos for $CaCO_3$ particles. The mean particle was a little less than 2 μm in appearance including many small particle. The surface appears to be closely packed with rhombohedral and octahedral forms (see detail at 20 nm in the Fig. 8).

In the X-ray diffraction pattern spectra (Figs. 9 and 10), the peak at $2\Theta = 28–30^{\circ}$ correspond to pure calcite. The other peaks are all attributed to vaterite crystal form. According to the literature dates [11] the vaterite-to-calcite ration can be about 50% but is depends on the concentration and nature of calcium salt with their optimum concentration to obtain the maximum ratio. These concentration have been reported to affect also the synthesis yield of particles. The literature information predicted that the surface energy was associated with the mineralization mechanism. External surface were hydrophobic and internal surface were hydrophilic. This is probably because the two- sidedness of the interfaces aligns calcium carbonate particles.

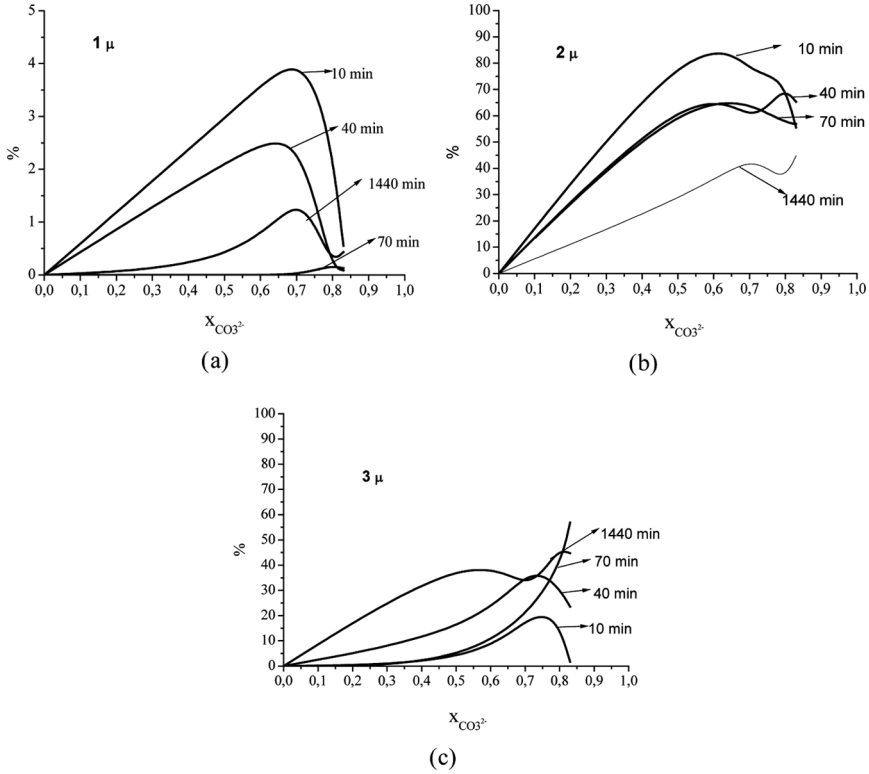


FIGURE 6 Distribution curves of dimensional population for calcium carbonate synthesis starting to $K_2CO_3/CaCl_2$.

Role of Organic Phases in the Calcium Carbonate Formation

The MMA polymerization developed simultaneous with mineralization process of calcium carbonate dispose the orientation of the crystals.

The formation of calcium carbonate appear onto organic droplets surface. The crystallization form is determined by the electrostatic potential of the organic phase, which change at polymerization evolution. In the same time the induction period is very important: by the induction time we comprehend the time of initiator decay, whence in all case is the same: 3 minutes. The formed oligomers in the first stages behave a tension active agents and adsorb on the surface the calcium carbonate. By consequence, increasing the PMMA concentration involve an increase of the specific area and the decreasing of

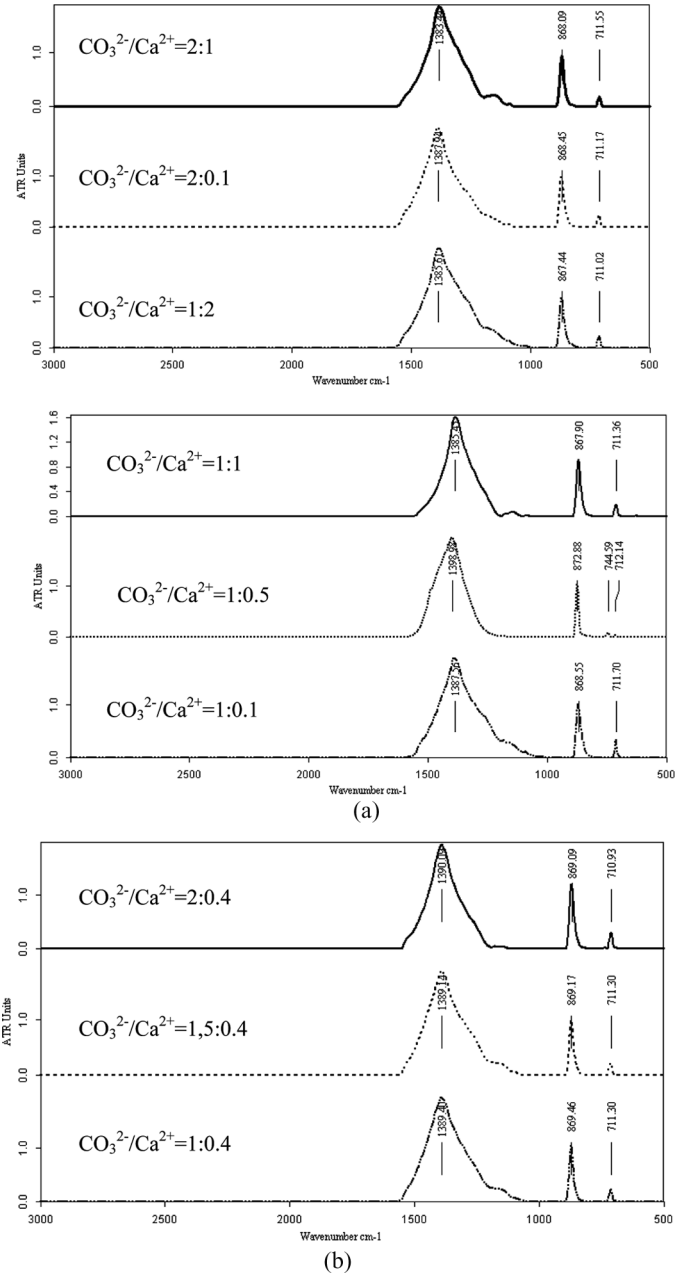


FIGURE 7 FT-IR spectra of synthesized $CaCO_3$.

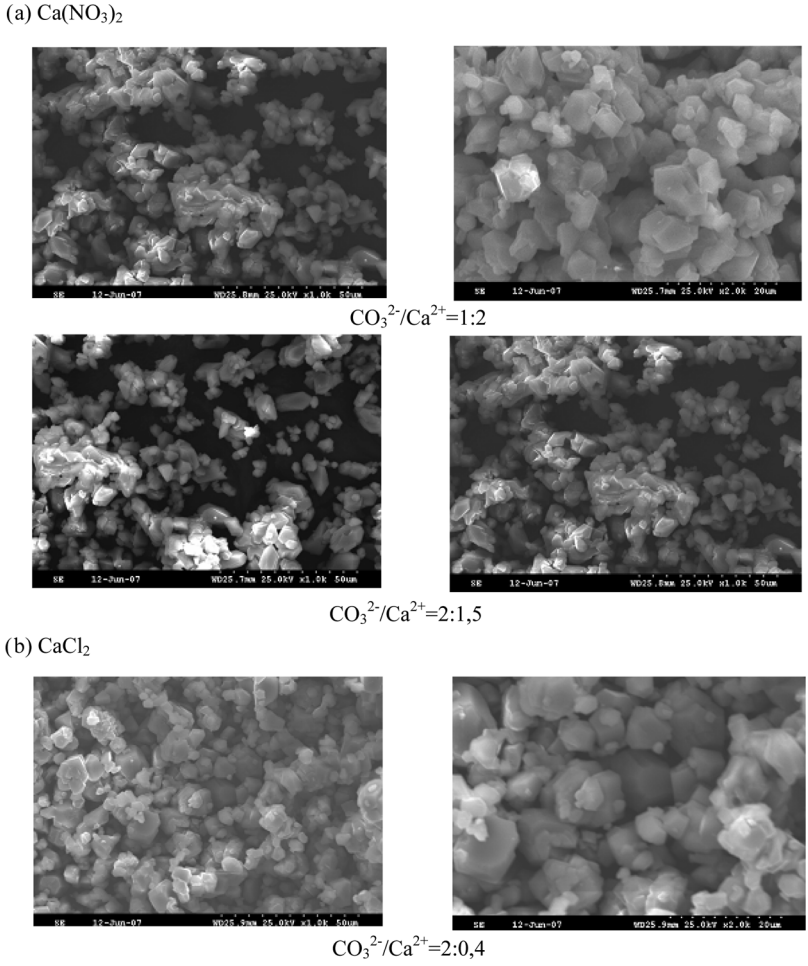


FIGURE 8 Scanning electron micrographs of calcium carbonate prepared by mixed method's.

the crystallite size (primary particles). So, we can talk of the transfer for the polymerization place and crystallization process: for the interface organic/aqueous on the powder surface, preserving the calcium carbonate morphology. The aggregation process are a consequence of the incompatibility of the modified organic phases (MMA → PMMA) in the consumption monomer time, therefore an increasing of the polymer chains whence determine the phase separation phenomena.

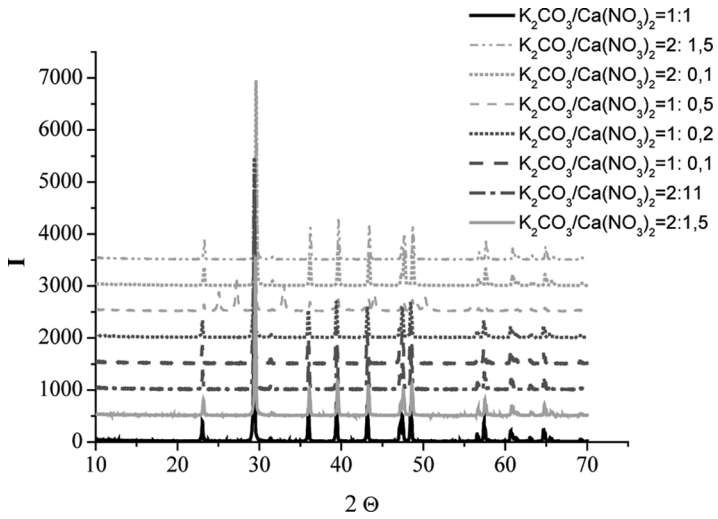


FIGURE 9 X-ray diffraction patterns of calcium carbonate synthesized starting to $Ca(NO_3)_2$.

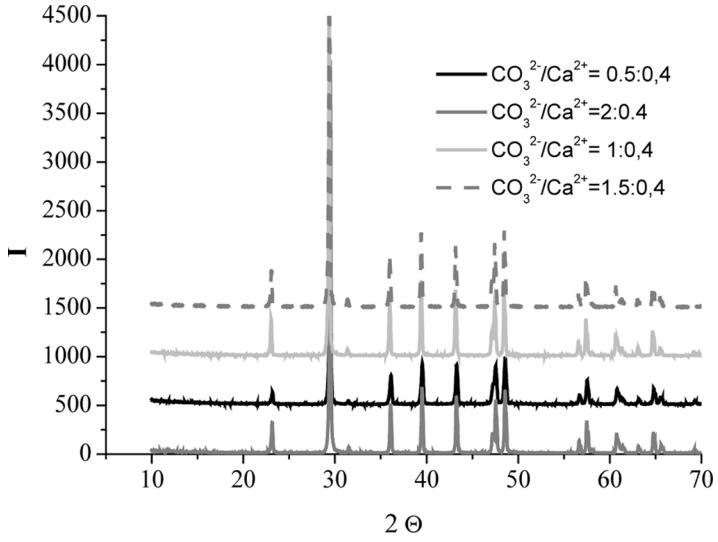


FIGURE 10 X-ray diffraction patterns of calcium carbonate synthesized starting to $CaCl_2$.

CONCLUSIONS

Methacrylic monomers can be used as a latent active surfactant based here electrostatic energy. In the binding moment on the calcium carbonate surface the electric charge in the external field of the involved atoms, increase. The dimension, density and morphological form of calcium carbonate are the results of the corroborative effect of the incubation time and concentration of active compounds in the substrate. Comparing of the individual techniques used for the calcium carbonate synthesis (interfacial method and latent inductor method) by there mixing up we can obtain the complex morphology only by substrate composition modification. Further investigations are in progress.

REFERENCES

[1] Manoli, F., Kanakis, J., Malkaj, P., & Dalas, E. (2002). *J. Cryst. Grow.*, *236*, 363.
[2] Sims, S. D., Didymus, J. M., & Mann, S. (1995). *J. Chem. Soc. Chem. Comm.*, 1031.
[3] Gower, L. B. & Odom, D. J. (2000). *J. Cryst. Grow.*, *210*, 719.
[4] Kato, T., Sugawara, A., & Hosoda, N. (2002). *Adv. Mat.*, *14*(12), 869.
[5] Dalas, E. & Koutsoukos, P. G. (1989). *J. Colloid Interface Sci.*, *127*, 273.
[6] Kanakis, J. & Dalas, E. (2000). *J. Cryst. Grow.*, *219*, 277.
[7] Manoli, F. & Dalas, E. (2001). *J. Cryst. Grow.*, *222*, 293.
[8] Naka, K. & Chujo, Y. (2001). *Chem. Mater.*, *13*, 3245.
[9] Belcher, A. M., Wu, X. H., Christensen, R. J., Hansma, P. K., Stucki, G. D., & Morse, D. E. (1996). *Nature*, *381*, 56.
[10] Naka, K., Keum, D.-K., Tanaka, Y., & Chujo, Y. (2000). *Chem. Comm.*, *2000*, 1537–1538.
[11] Nakahara, Y. & Fountai Kogaku kai-hi. (1995). *J. Soc. Pow. Techol.*, *32*(2), 97.