

Effects of (complementary) Polyelectrolytes Characteristics on Composite Calcium Carbonate Microparticles Properties

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This study follows the possibility to tune the thermal stability of some CaCO₃/polymer composites by crystal growth from supersaturated solutions controlled by polymer structure or by using nonstoichiometric polyelectrolyte complexes (NPECs). As the ratio between the organic and inorganic parts in the composites controls the Ca²⁺/polymer network crosslinking density, the CaCO₃/polymer weight ratio was kept constant at 50/1, varying the initial concentration of the polyanions solutions (0.05 or 0.06 wt.%), the NPECs molar ratio, n⁺/n⁻ (0.2 or 0.4), or the inorganic precursors concentration (0.25 or 0.3 M). Poly(2-acrylamido-2-methylpropanesulfonic acid-co-acrylic acid) (PSA) and chondroitin-4-sulfate (CSA) were used as polyanions. Some NPEC dispersions, prepared with the same polyanions and poly(allylamine hydrochloride) (PAH), were also used for calcium carbonate crystallization. The characteristics of the prepared composites were investigated by scanning electron microscopy (SEM), flow particle image analysis (FPIA), particles charge density (CD), zeta-potential (ZP). The thermal stability of the composite particles was investigated as compared to bare CaCO₃ microparticles prepared at the same initial inorganic concentrations.

Keywords: CaCO₃/polymer composites, polyanions, polyelectrolyte complexes, thermal stability

Calcium carbonate is one of the most abundant materials on the planet and has been used for various polymer composites. CaCO₃ exists in three types of crystalline form: calcite, the most stable form with trigonal-rhombohedral structure, aragonite, of orthorhombic crystal structure, and vaterite, which exists in hexagonal form. The properties and applications of CaCO₃ depend on the morphology, polymorphism, particle size, and chemical purity of the crystals. A well-known application of CaCO₃ is its use as filler for plastics, aiming to improve some product properties - physical, rheological, thermal and mechanical. CaCO₃ has received an increased attention due to its wide range of potential applications and its low cost [1,2]. Thermal stability is the key factor used to evaluate the application area of materials and thus the thermal stability of polymers and composites need to be investigated to meet application requirements.

Many studies showed a correlation between calcium carbonate growth characteristics and the structure of the additive organic molecules [3-7]. However, difficulties in understanding their respective roles arise from the complexity in studying such mechanisms in the solid-liquid systems and the large ability of the CO₃²⁻ anions to form different supramolecular structures.

Numerous studies have been carried out to understand the influence of organic molecules on CaCO₃ particle growth, and various additives including surfactants [8], macromolecules [9-14], amino acids [15], extracts [16,17], ionic liquids [18], etc., have been investigated. Recent studies discuss the use of nonstoichiometric polyelectrolyte complexes (NPEC) as templates in controlling CaCO₃ crystals growth [19,20]. The NPEC dispersion characteristics, such as molar ratio, particles size and charge density slightly affect the CaCO₃/NPEC composite particles surface morphology, electrokinetic

parameters and the polymorphic content. CaCO₃/NPECs composite microparticles also show increased microparticles resistance against EDTA as chelating agent, the arrangement of preformed NPECs into the composites and the Ca²⁺ ions bridges formed between shorter anionic chains remained uncompensated by the cationic polymer probably conducting to a dense network matrix [20].

In this context, the aim of this study was to investigate the possibility to tune the thermal stability of some CaCO₃/polymer composites by crystal growth from supersaturated solutions controlled by polymer structure or by using NPECs. As the ratio between the organic and inorganic parts in the composites controls the Ca²⁺/polymer network crosslinking density, in this study the CaCO₃/polymer weight ratio was kept constant at 50/1, varying the initial concentration of polyanions solutions (0.05 or 0.06 wt.%), the molar ratio of NPECs, n⁺/n⁻ (0.2 or 0.4), or inorganic precursors concentration (0.25 or 0.3 M). Two polyanions were used: poly(2-acrylamido-2-methylpropanesulfonic acid-co-acrylic acid) (PSA) which is a synthetic, flexible polymer, and chondroitin-4-sulfate (CSA), a sulphated glycosaminoglycan with a semi-rigid macromolecular chain. Some NPEC dispersions, prepared with the same polyanions and poly(allylamine hydrochloride) (PAH) as polycation, were also used for calcium carbonate crystallization. Scanning electron microscopy (SEM) was used to provide particles morphology, and flow particle image analysis (FPIA) to evidence their mean size and circularity. Polymer presence into the composite particles was evidenced by particles charge density (CD) and zeta-potential (ZP). The thermal stability of the composite particles was investigated as compared to bare CaCO₃ microparticles prepared at the same initial inorganic concentrations.

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Sample code	[Na ₂ CO ₃]= [CaCl ₂], M	CaCO ₃ , g/100 mL	Polymer, wt.%	Polymer, g/100 mL	CaCO ₃ /Polymer, g/g
C _{0.25}	0.25	2.5	-	-	-
C _{0.25} /PSA _{0.05}	0.25	2.5	0.05	0.05	50/1
C _{0.25} /CSA _{0.05}	0.25	2.5	0.05	0.05	50/1
C _{0.3}	0.3	3	-	-	-
C _{0.3} /PSA _{0.06}	0.3	3	0.06	0.06	50
C _{0.3} /CSA _{0.06}	0.3	3	0.06	0.06	50
			n ⁺ /n ⁻		
C _{0.25} /(PSA/PAH) _{0.2}	0.25	2.5	0.2	0.0484	51.65/1
C _{0.25} /(PSA/PAH) _{0.4}	0.25	2.5	0.4	0.0493	50.71/1
C _{0.25} /(CSA/PAH) _{0.2}	0.25	2.5	0.2	0.0472	52.97/1
C _{0.25} /(CSA/PAH) _{0.4}	0.25	2.5	0.4	0.0482	51.87/1

Table 1
CaCO₃/POLYANION
COMPOSITES
PREPARATION
CONDITIONS

Experimental part

Materials

CaCl₂·2H₂O and Na₂CO₃ from Sigma-Aldrich were used as received. The PSA copolymer, which contains 55 mol-% 2-acrylamido-2-methylpropanesulfonic acid and 45 mol-% acrylic acid, was synthesized and purified according to ref. [21]. CSA from bovine trachea was purchased from Sigma and used as received. PAH of low molar mass from Fluka was used without further purification.

Preparation of CaCO₃/polymer composites

The formation of CaCO₃/polyanion composites was carried out in glass beakers, at 25 °C, according to the procedure already published [19]. The CaCO₃/polymer weight ratio was close to 50/1 for all samples, as shown in table 1.

For NPEC preparation, the concentration of polyanions aqueous solution was 1.7 x 10⁻³ and 10⁻³ M for PSA and CSA, respectively, whereas PAH aqueous solutions concentration was 5 x 10⁻³ M. Dispersions of NPEC were prepared by mixing the solutions of oppositely charged polyelectrolytes in appropriate proportions, according to the desired mixing molar ratio, n⁺/n⁻ (0.2 or 0.4). After mixing, the formed dispersions were stirred 60 min and were characterized and used in composite preparation after 24 h.

The composites were prepared by solving Na₂CO₃ in the polyanion aqueous solution or in the NPEC dispersion. Equal volumes of as prepared solutions or dispersions were rapidly mixed with a CaCl₂ aqueous solution, with Na₂CO₃ and CaCl₂ having equal concentrations. The mixtures were stirred for 1 min on a magnetic stirrer and then kept under static conditions for 30 min. The obtained microparticles were separated by filtration, intensively washed with water and finally washed with acetone and dried in oven at 40 °C, for 1.5 h. Samples with the same inorganic concentration and without polymer were prepared for comparison purposes.

Characterization of composite microparticles

The particles shape and surface were examined by using a FEI Phenom Desktop Scanning Electron Microscope, in high vacuum mode. To avoid electrostatic charging the particles were sputtered with gold.

The particles size distribution of the carbonate particles was evaluated using the Sysmex Dynamic Flow Particle Image Analyzer 2100. To obtain correct values, the Sysmex FPIA 2100 image analyser was checked before starting the main experiment by using certified size standards.

The electrokinetic potential of carbonate samples was measured by means of ZetaSizer Nano ZS (Malvern, UK) operating at the 633 nm wavelength. The instrument measured the electrophoretic mobility of the particles. From the electrophoretic mobility the apparent zeta-potential values (ζ_{app}) were calculated by the Smoluchowski's equation. The presented values are average values of at least three independent measurements performed for each sample on 0.5 mg/mL aqueous dispersions.

The concentrations of the charged groups in microparticles dispersion were determined by titration using the Müttek PCD 03 (BTG Instruments GmbH, Herrsching, Germany) particle charge detector. The charge density was calculated from the amount of standard solutions [poly(sodium ethylenesulfonate) or poly(diallyldimethyl ammoniumchloride), with a concentration of 10⁻³ mol×L⁻¹] necessary to reach the zero value of the streaming potential. All measurements were run at room temperature.

The thermogravimetric analysis (TGA) was performed on a STA 449 F1 Jupiter device (Netzsch, Germany). Approximately 10 mg of each sample were heated in an open alumina crucible, in nitrogen atmosphere, with a flow rate of 50 mL min⁻¹ and a heating rate of 10°C min⁻¹. Samples were heated in the 30-700°C temperature range.

Results and discussions

The ratio between the organic and inorganic parts in the CaCO₃ based composites plays an important role in the inner structure of the materials, controlling the polymer network crosslinking density, the nature of the inorganic polymorphs or the ratio between polymorphs. Therefore, in this study the CaCO₃/polymer weight ratio was 50/1, as obtained by changing either the initial concentration of the polyanion solutions (0.05 or 0.06 wt.%) or molar ratio, n⁺/n⁻ (0.2 or 0.4), or the inorganic precursors concentration (0.25 or 0.3 M). Similar samples, prepared with the same polymers but with different concentrations, were studied in a previous paper [19], and the main observation was

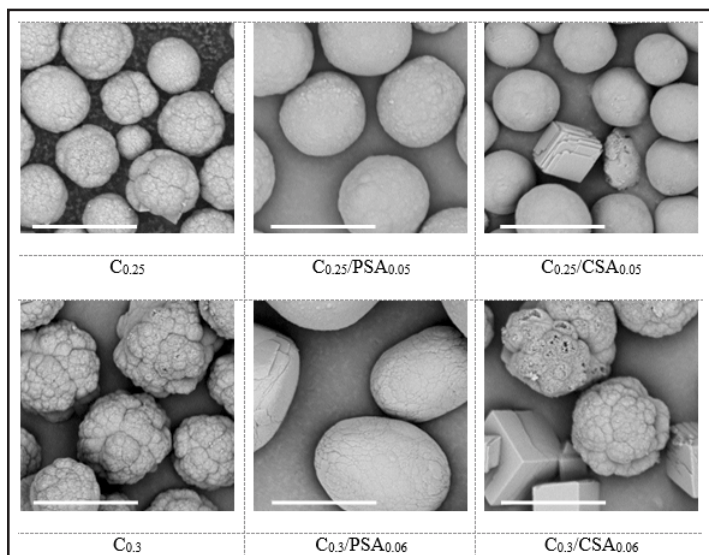


Fig. 1. SEM images of CaCO_3 /polyanion particles prepared with initial concentration of the polyanions solutions (0.05 or 0.06 wt.%) and the inorganic concentration (0.25 or 0.3 M); scale bar - 10 μm

that by increasing the inorganic concentration from 0.05 M to 0.3 M the particles sizes increased, irrespective of polyanion structure. In this study, the polymer concentration was decreased up to 0.05 and 0.06 wt.%, closer to the total weight polymer concentration in the NPEC dispersions, aiming to obtain samples with a similar CaCO_3 /polymer weight ratio.

Some SEM images of the polyanion based samples as well as samples prepared without polymer and the same inorganic concentration are shown in figure 1.

As shown in figure 1, the increase on the initial inorganic concentration increases the particles size, irrespective of polymer presence or its structure. Moreover, even if the PSA synthetic polymer has a more flexible backbone as compared to the semi-rigid one of CSA, the composite particles size looks similar for the same inorganic ratio. Usually, calcite crystallizes as rhombohedral particles, whereas vaterite particles exhibit a spherical shape. Therefore, taking into account the microparticles shape observed in the images included in figure 1 one may assume that PSA favours the formation of vaterite polymorph, whereas the presence of cubic and spherical

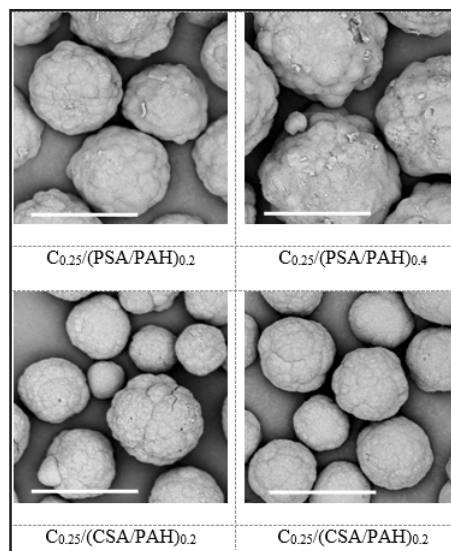


Fig. 2. SEM images of CaCO_3 /NPEC particles prepared with NPEC molar ratio of 0.2 or 0.4, and the inorganic concentrations of 0.25 M; scale bar - 10 μm

particles in CSA based composites suggests the formation of both calcite and vaterite polymorphs, irrespective of inorganic concentration.

The morphology of CaCO_3 /NPEC composite particles observed by SEM is shown in figure 2.

As shown in figure 2, particles surface morphology is similar for all NPEC based samples, irrespective of polyanion structure and NPEC molar ratio, and differs from that of the particles prepared with polyanion (fig. 1). These observations are in agreement with the results obtained when microparticles were prepared with NPEC based on the same polyanions and chitosan and the same ratio between the polymers [19]. However, larger particles were obtained when PSA was used in NPEC formation, most probably due to the higher flexibility of the free parts of the polyanion in excess that allows the formation of larger nets by crosslinking their ionic charges with calcium divalent ions.

Particles size distribution for each sample, determined by dynamic image analysis, are shown in figures 3 and 4, the results on the mean and modal particles sizes being summarized in table 2.

Sample code	Mean diam, μm	Mode diam, μm	Mean circularity
C0.25	7.13	5.07	0.831
C0.25/PSA0.05	7.22	6.97	0.915
C0.25/CSA0.05	6.95	6.34	0.951
C0.3	8.69	6.07	0.849
C0.3/PSA0.06	11.38	10.89	0.885
C0.3/CSA0.06	10.14	9.68	0.859
C0.25/(PSA/PAH)0.2	11.70	10.12	0.836
C0.25/(PSA/PAH)0.4	11.92	9.43	0.815
C0.25/(CSA/PAH)0.2	8.09	6.83	0.871
C0.25/(CSA/PAH)0.4	8.45	7.43	0.881

Table 2
MEAN AND MODE DIAMETER AND CIRCULARITY DETERMINED BY FPIA

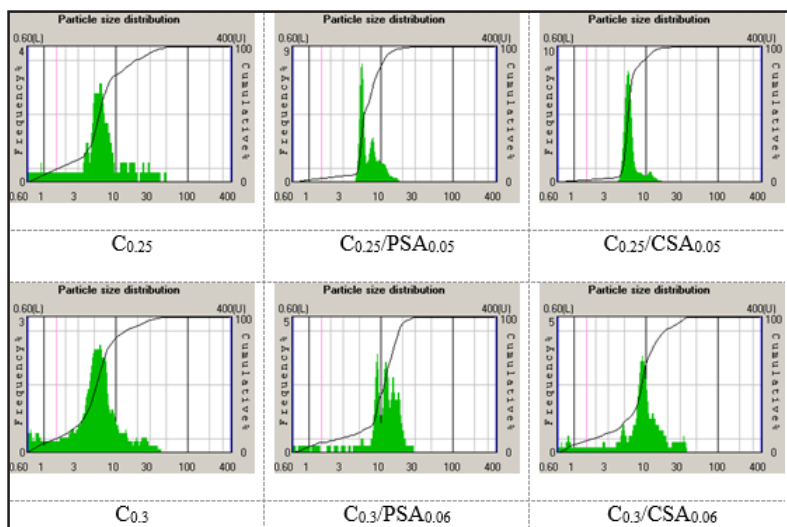


Fig. 3. Particles size distribution obtained by FPIA measurements of CaCO_3 /polyanion microparticles

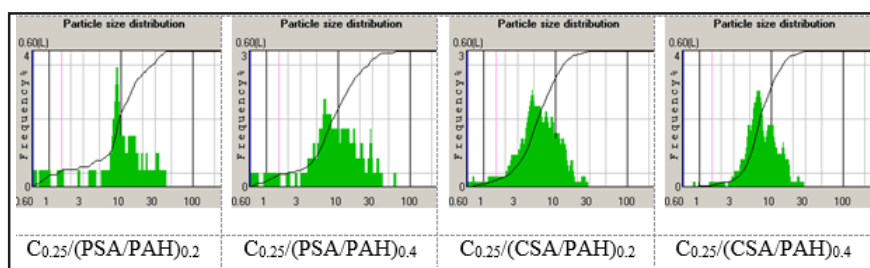


Fig. 4. Particles size distribution obtained by FPIA measurements of CaCO_3 /NPEC microparticles

As shown in figure 3, the particles size dispersity decreases when the polyanions were used in composites preparation, as compared to the samples prepared without polymer and the same inorganic concentration. This may be an evidence for a good control of the crystallization played by the polyanion templates. However, the particles size distribution looks wider when NPECs were used (fig. 4). To further sustain the particles size distribution, the values of mean and modal diameter included in table 2 can be considered. As shown by all graphs in figures 3 and 4, non-symmetric distribution curves for the particles size were obtained for each investigated sample. Therefore, the mean and mode diameter have different values, as shown in table 2. Usually, mean diameter is a calculated value similar to the concept of average, whereas the mode diameter is the highest peak of the frequency distribution and represents the particle size (or size range) most commonly found in the distribution. Even if the mode diameter is not as commonly used, it can be descriptive and can be a further evidence of particles size distribution broadness: closer mean and mode values can be ascribed to a narrow size distribution. Therefore, as values in table 2 show, the closer values were obtained for samples prepared with both polyanions and the lowest inorganic concentration (0.25 M). At the same time, the circularity values for that two samples are the closest to 1 (ascribed to the spheres) whereas for the other samples the values are lower than 0.9, suggesting the presence of rhombohedral or egg-shaped particles.

Since all the polymers involved in particles formation contain ionic groups, one should expect the overall particles charge density and surface zeta potential to be influenced by the amount of included polymer. Table 3 summarizes the complementary electrokinetic measurements carried out on the composites, namely the particles charge density (CD) and the zeta-potential values (ZP).

The CaCO_3 /polymer ratio is almost constant in the composite particles (~50/1, table 1) but the initial precursors concentrations varied in sample preparation.

Table 3

PARTICLES CHARGE DENSITY (CD) AND ZETA-POTENTIAL (ZP) OF CaCO_3 COMPOSITE PARTICLES

Sample code	CD, meq/g	ZP, mV
C _{0.25}	-28.30	-7.6
C _{0.25} /PSA _{0.05}	-257.46	-24.2
C _{0.25} /CSA _{0.05}	-205.99	-20.3
C _{0.3}	-41.47	-9.7
C _{0.3} /PSA _{0.06}	-294.76	-26.8
C _{0.3} /CSA _{0.06}	-239.52	-23.1
C _{0.25} /(PSA/PAH) _{0.2}	-156.79	-16.7
C _{0.25} /(PSA/PAH) _{0.4}	-124.44	-13.7
C _{0.25} /(CSA/PAH) _{0.2}	-113.64	-13.6
C _{0.25} /(CSA/PAH) _{0.4}	-94.94	-11.1

Accordingly, increasing precursor's concentration in the initial mixture increased the CD and ZP values. However, the highest increase of both CD and ZP values has been obtained when polyanions were involved in composite preparation. At the same time, for the same initial concentrations higher values were obtained when PSA was used, which can be an evidence of the higher amount of this polymer included in the composites even if the same amount as CSA has been used in the initial mixtures. The differences should be understood taking into account the molar mass of the polyanions (279 and 463 g/mol for PSA and CSA, respectively), for the same weight (0.05 or 0.06 wt.%) the PSA aqueous solution containing a higher number of molecules and thus a higher solution charge density. Lower CD and ZP values were obtained for NPEC based composites, as compared to polyanion based composites.

During NPECs nanoparticle formation, part of polyanion charges are compensated by polycation ones, and therefore the CD and ZP values of NPECs dispersions are lower than that of the corresponding polyanion solution. Moreover, the higher the n^+/n^- value, the higher content in polycation and thus the lower CD and ZP values are obtained. This trend is also observed in the NPEC based composites, higher values being obtained for the same molar ratio when PSA was used.

Even if CD and ZP values can be indirectly ascribed to the polymer content in the NPECs based composites, the results are not relevant. In this case, the polyanion charges already compensated by the polycation cannot be determined by the above mentioned methods, but only the free polyanion charges in excess. Therefore, to avoid the method limits, thermogravimetric measurements were performed, comparing the weight loss at 500°C of composite microparticles to that of CaCO_3 ones. Thus, to further demonstrate polymers presence into the composite, in figures 5 and 6 the TGA plots of CaCO_3 /polymer composites with various contents in CaCO_3 , as compared to the TGA curves of CaCO_3 are presented. Tables 4 and 5 summarize the thermogravimetric data for all investigated samples.

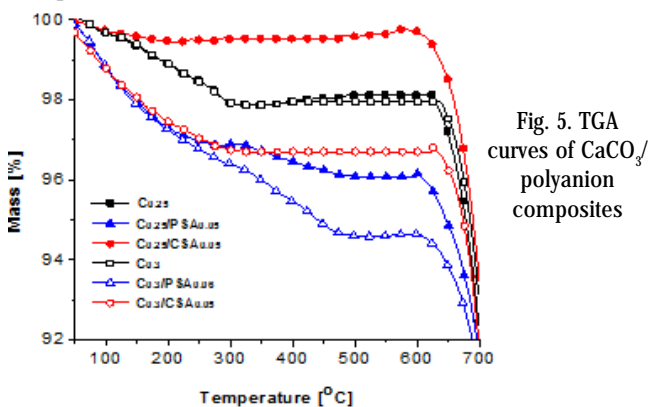


Fig. 5. TGA curves of CaCO_3 /polyanion composites

Samples $C_{0.25}$ and $C_{0.3}$ are thermally stable up to about 500°C (fig. 5), the ~1.8 % weight loss of both samples (table 4) being ascribed to the removal of intrinsic water content on the particles. The thermal decomposition recorded above 600°C, with the highest mass losses, corresponds to material degradation to CaO [22,23]. The increase of precursors concentration determines a slight decrease in intrinsic water content (1.78 % and 1.84 % for $C_{0.25}$ and $C_{0.3}$, respectively), also reflected in the mass residues differences recorded at 700°C (91.85 % and 92.58 %).

The thermal behaviour of the polyanion-based composite samples depends on the structure of polymers. Thus, the thermal degradation of CaCO_3 /PSA composites takes place in three stages. During the first degradation step, in the temperature range 50–180°C, the loss of adsorbed water molecules takes place simultaneously with the first polymer decomposition step with transformation of vicinal carboxylic groups on the backbone to anhydride structures and the degradation of sulfonic groups with elimination of SO_2 [24]. The second decomposition region, between 325 and 475°C (table 4), is the main polymeric decomposition step, when fragmentation of anhydride rings and depolymerisation reactions take place. Taking into account that the third decomposition step, above 600°C, corresponds to CaCO_3 degradation, the polymer content can be ascribed to the mass loss at 550°C as compared to samples prepared with the same inorganic concentration but without polymer. Thus, even if the ratio CaCO_3 /PSA is constant, an increase of polymer concentration in the crystallization system leads to an increase of polymer content in the composite microparticles.

The semi-rigid structure of CSA determines a slightly improved thermal stability of the corresponding composites (table 4), as compared to microparticles based on PSA, with a more flexible backbone. Actually, CSA does not decompose below 600°C, the mass loss at 550°C being

		(°C)	(°C)	(°C)	(%)	(%)	(%)
$C_{0.25}$	I	40	77;188;281	293	1.69	1.78	92.58
	II	613	643	697	5.50		
$C_{0.25}/\text{PSA}_{0.05}$	I	68	80	188	3.15	3.91	91.29
	II	326	367	475	0.70		
	III	602	643	695	4.78		
$C_{0.25}/\text{CSA}_{0.05}$	I	73	82	100	0.40	0.41	92.98
	II	605	628	694	6.60		
$C_{0.3}$	I	68	75;167;217;281	290	1.58	1.84	91.85
	II	596	630	694	6.23		
$C_{0.3}/\text{PSA}_{0.06}$	I	54	79	133	3.52	5.40	90.81
	II	325	437	465	1.79		
	III	603	643	695	3.71		
$C_{0.3}/\text{CSA}_{0.06}$	I	51	74	233	2.98	3.03	91.86
	II	626	650	689	5.04		

Table 4
THERMOGRAVIMETRIC DATA OF CaCO_3 /POLYANION COMPOSITES

T_i – onset thermal degradation temperature; T_{max} – temperature that corresponds to the maximum rate of decomposition for each stage evaluated from the peaks of the DTG curves; T_f – endset thermal degradation temperature; W_m – mass loss; W_{m550} – mass loss at 550°C; W_{rez700} – percentage of residue remained at 700°C.

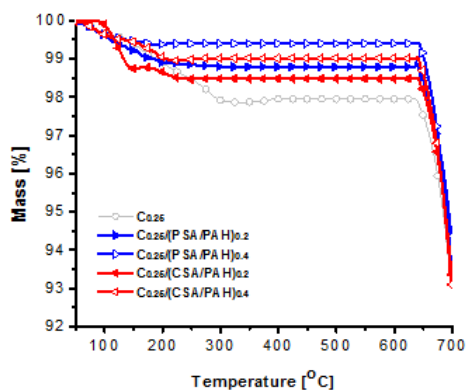


Fig. 6. TGA curves of CaCO₃/NPEC composites

Sample	Stage	T _i (°C)	T _{max} (°C)	T _f (°C)	W _m (%)	W _{m 550} (%)	W _{rez 700} (%)
C _{0.25} /(PSA/PAH) _{0.2}	I	95	116	140	1.18		
	II	186	189	232	0.30	1.82	92.08
	III	603	644	692	5.44		
C _{0.25} /(PSA/PAH) _{0.4}	I	67	82	111	0.47		
	II	160	190	208	0.46	1.05	92.58
	III	600	643	692	6.32		
C _{0.25} /(CSA/PAH) _{0.2}	I	54	79	177	1.12	1.15	93.91
	II	608	673	689	4.70		
C _{0.25} /(CSA/PAH) _{0.4}	I	64	77	106	0.38	0.45	93.03
	II	600	644	691	6.51		

Table 5
THERMOGRAVIMETRIC DATA
OF CaCO₃/NPEC
COMPOSITES

T_i – onset thermal degradation temperature; T_{max} – temperature that corresponds to the maximum rate of decomposition for each stage evaluated from the peaks of the DTG curves; T_f – endset thermal degradation temperature; W_m – mass loss; W_{m 550} – mass loss at 550°C; W_{rez 550} – percentage of residue remained at 700°C

ascribed only to the removal of adsorbed and/or combined water molecules from inorganic/organic phases.

Usually, the formation of NPECs improves the thermal stability as compared to that of the corresponding polyelectrolytes [25].

Therefore, as shown in figure 6, the thermal stability of composites based on NPEC increased as compared with composites prepared with the corresponding polyanions, their stability being higher than that of C_{0.25}. Increasing the polycation content, meaning increasing the intrinsic polyanion/polycation charge compensation, increases composites thermal stability, irrespective of polyanion structure, the NPECs thermal decomposition taking place above 600°C, in parallel with CaCO₃ degradation to CaO.

Conclusions

This study focussed on the synthesis, characterization and thermal stability of some CaCO₃/polymer composites obtained by crystal growth from supersaturated solutions and controlled by polymer structure (PSA - a synthetic, flexible polymer, and CSA - a sulfated glycosaminoglycan with a semi-rigid macromolecular chain) or by using NPECs (with the same polyanions and PAH). The CaCO₃/polymer weight ratio was kept constant at 50/1, varying the initial concentration of the polyanions solutions (0.05 or 0.06 wt.%), the molar ratio of NPECs, n⁺/n⁻ (0.2 or 0.4), or the inorganic precursors concentrations (0.25 or 0.3 M). The thermal behaviour of the polyanion-based composite samples depends on the structure of polymers. The semi-

rigid structure of CSA determines a slightly improved thermal stability of the corresponding composites, which do not decompose below 600°C, the mass loss up to 550°C being ascribed only to the removal of adsorbed and/or combined water molecules from inorganic/organic phases. The composites prepared with NPECs showed the highest thermal stability, irrespective of the polyanion used in their preparation and irrespective of molar ratio between charges.

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