NOI COMPOZITE ANORGANIC/ORGANICE OBȚINUTE PRIN PROCESUL GELCASTING CA PRECURSORI PENTRU MATERIALELE CERAMICE POROASE

NEW INORGANIC/ORGANIC COMPOSITE OBTAINED BY GELCASTING PROCESS AS PRECURSORS FOR POROUS CERAMICS MATERIALS

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A series of new inorganic/organic composites were synthesized by polymerization of acrylic acid in a concentrated aqueous suspension of alumina powder, using N,N'-methylenebisacrylamide as crosslinker. The inorganic/organic composites were characterized by scanning electron microscopy (SEM), thermal analysis (TGA/DTG), infrared spectroscopy (FTIR) and X-ray diffraction (XRD). Composite materials, with a volumetric shrinkage ranging from 50 to 87% depending on the acrylic acid concentration, were obtained. By increasing the acrylic acid **concentration,** ***the compressive strength increased up to 230 MPa. It was demonstrated that these composite systems can form porous alumina ceramic materials with ~80% porosity after burning off the organic network.***

O serie de noi materiale composite anorganic/organice au fost sintetizate prin polimerizarea acidului acrilic într-o suspensie apoasă concentrată în alumină, utilizând ca reticulant N,N'-metilenebisacrilamida. Compozitele anorganic/organice au fost caracterizate prin microscopie electronica de baleiaj (SEM), analiză termică (TGA / DTG), spectroscopie în infraroşu (FTIR) şi difracție de raze X (XRD). Au fost obținute noi compozite, cu o contracție volumetrică de la 50 la 87%, în funcție de concentrația de acid acrilic. Prin creşterea concentrației de acid acrilic, rezistența la compresiune a crescut până la 230 MPa. A fost demonstrat faptul că din aceste sisteme se pot obține materiale compozite poroase cu o porozitate de ~ 80% în urma procesului de arderea a rețelei polimerice.

Keywords: *gelcasting, polymeric composites, alumina, acrylic acid, sintering, porous ceramics*

1.Introduction

Porous ceramics, due to the possibility of controlling the final porosity and permeability and also due to their high temperature and chemical stability properties [1-4] can be used for many important applications such as hot gas particle filters, catalytic supports, membrane supports, sensors, piezoelectric ceramics, light-weight structural parts for high temperature applications and also biomedical and construction materials [1-3,5].

Gelcasting is an attractive and new processing approach for producing of porous ceramics from preceramic polymer composites [4]. The syntheses of porous ceramic materials by polymers precursor process presents an increasing interest in recent years [2,5-8]. First gelcasting process was used to fabricate dense composites materials, and then the process was amended to fabricated porous ceramics too. The gelcasting process consists in a slurry made from ceramic powder dispersed in a water based monomer solutions and then cast into a mould, were the monomer polymerizes in-situ to keep the particles of ceramics in a rigid and homogenous gelled part. After the gel was formed, the green bodies can be removed from the mould, then dried and sintered in controlled conditions [7-11].

The gelcasting process presents many advantages such as: high strength of the green bodies which permits the forming of complex shapes, the low content of the organic additives used, the short processing time, the homogenous distributions of the organic additives and easier organic additives removal [2,4,7,10-13].

A variety of ceramic systems, such as: alumina [9-11], silicon nitride [11,12], zirconia [11], cordierite [4], silicon carbide [14], hydroxyapatite [15] oxide nanoparticles [16] were used to obtain

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ceramic porous materials through the gelcasting process. Also in the literature there are a variety of potential monomers that can be used in gelcasting process, as for example: acrylamide [13,14,16], methacrylamide [8,15], methacrylic acid [9] as monofunctional monomer and poly(ethylene glycol) diacrylate or dimethacrylate, N,N '- methylene bisacrylamide [8,10,13-15] as difunctional monomers. As a free-radical initiator: ammonium persulphate with N,N,N',N' – tetra-methylethylenediamine [10,14,15] or potassium persulphate [13] were used.

The present paper investigates the preparation conditions and properties of some new inorganic/organic composite materials obtained by gelcasting process, based on alumina and polyacrylic acid crosslinked with N, N'-methylene bisacrylamide, in order to obtain new porous ceramic materials. Potassium persulphate and sodium metabisulphite were used as redox initiator system. From the literature data the alumina gelcasting systems have been intensively researched. But, from our knowledge the systems based on acrylic acid initiated by the KPS / MS system redox was not used. The use of the acrylic acid presents a great advantage because it is a non neurotoxic monomer as for instance acrylamide. Also, the used initiation system allows that the polymerization reaction take place at room temperature, making our method economically and technologically more advantageous than other radical initiation systems. The acrylic acid plays two roles: one as network polymers who keep the immobilized inorganic particles and the second role as porogen agent. For this reasons there is no need to use a different porogen agent in the system. The properties of these composites and the capacity to form porous ceramics after burning off the organic network will be also highlighted.

2. Experimental

2.1. Materials

The employed alumina sample in this study was from commercial source (Alum Tulcea S.A) and was used as received. Table 1 shows the chemical composition (as determined by EDAX analysis) of the alumina powder (Al) produced in Tulcea, Romania.

Table 1

Characteristics of the use alumina

Caracteristicile aluminei utilizate

EDAX Quantitative Results *Rezultate EDAX cantitative*		
Element *Elemente*	Wt (%) *% masic*	At (%) *% atomic*
O	33,66	46,12
Al	66,34	53,88

Acrylic acid (AA), ALDRICH, 99% was used as binder phase. The AA was distilled under vacuum in order to remove the polymerization inhibitor and stored in the freezer. The *N*, *N′* - methylene bisacrylamide (MBA), SIGMA-ALDRICH, 99% was used as crosslinking agent. Potassium persulfate (KPS), ACROS ORGANIICS, 99% and sodium metabisulfite (MS), ACROS ORGANICS, 97% were used as initiators. Excepting AA, all reagents were used without further purification. In this work, if not other noted, % are weight percents.

An aqueous solution of ammonium polyacrylate (NH_4PAA) was used as phase dispersant. The NH_4PAA dispersant was prepared in the laboratory using the following procedure:

A solution of 20% acrylic acid (AA) in distilled water was prepared. The solution was purged for 15 minutes with nitrogen in order to remove any dissolved oxygen. Then aqueous solutions of KPS and MS, were added, so that the concentration of redox initiation system (KPS=MS) was 0.5% relative to acrylic acid. The polymerization proceeded in a thermostat oil bath at $45^{O}C$ for 60 min. After polymerization, the pH value of polyacrylic acid solution was 3. The pH was increased at 8 with a concentrated solution of 25% ammonia (NH_3).

2.2. Preparation of inorganic/organic composites via gelcasting process

Ceramic suspensions were prepared by adding alumina powder - 45 % (wt) relative to water - to an aqueous solution of NH_4PAA in distilled water. The concentration of the NH_4PAA dispersant was 17 % (wt) relative to alumina. The monomer concentration was varied in the limits 20-35 % wt AA relative to alumina.

The suspension was mechanical stirred for one hour, for an optimal dispersion of particles and a dispersant adsorption into clays particles surface. Distilled acrylic acid (AA), N,N'-methylenebisacrylamide (MBA) and the KPS/MS redox initiation system were added in the polymerization reaction flask. After homogenization, the suspension was cast into 10 mm diameter glass vials. The vials were then sealed by septa plastics and kept at room temperature so that the polymerisation can proceed. The vials were broken after two hours, and the resulting green bodies were cut into small cylindrical-shaped pieces, about 1 cm thickness. The green bodies were dried for 24 hours at room temperature and then at $105^{O}C$, in an oven at atmospheric pressure, to constant weight. In the following, the new inorganic/organic composite materials were designated as Al (XAA) where X represents the wt% of AA monomer relative to alumina. The inorganic/organic composites were pyrolyzed at atmospheric pressure, by heating at a heating rate of 10°C/min till 1500 ^{O}C, and maintaining at this temperature during 4 h.

2.3. Determination of the density, the volumetric shrinkage and porosity of the inorganic/organic composites

To determine the density and the volumetric shrinkage of the undried and respectively dried inorganic/organic composites, a piece of cylindrical form was taken from each sample. The diameter and height of the body were measured. Samples weights were determined using an analytical balance.

The density of the undried and respectively dried inorganic/organic green body composites was determined according to equation (1):

$$\rho_{GB} = \frac{w_{GB}}{V_{GB}}[g/cm^3] \quad (1)$$

Where (w_{GB}) is the weight of the inorganic/organic composites, and the (V_{GB}) is the volume of inorganic/organic composites.

The volume was determined according equation (2):

$$V_{DB} = \frac{3{,}14\times(d_{GB}{}^{2})\times h_{GB}}{4}[cm^3]; \quad (2)$$

Where (d_{GB}) is the diameter of the inorganic/organic composites and the (h_{GB}) is the height of the inorganic/organic composites.

The volumetric shrinkage was determined according equation (3):

$$SV = \frac{V_{GB} - V_{DB}}{V_{GB}}\times 100[\%]; \quad (3)$$

Where (V_{GB}) is the volume of undried inorganic/organic composites and the (V_{DB}) is the volume of dried inorganic/organic composites.

Density and porosity of porous ceramic materials obtained by gelcasting process were determined by Archimedes' method. Water was used as the immersion liquid

2.4. Characterization

The IR spectrum of the samples was recorded on a Bruker VERTEX 70 instrument by averaging 32 scans with 4 cm^{-1} resolution, using the KBr pellet technique.

Thermal gravimetric analyses (TGA) were performed using Q500 TA Instruments. The thermographs were obtained at a heating rate of 10^{O}C/min, using 5-10 mg of sample. The experiments were made under 100 ml/min nitrogen flow.

Scanning electron microscopy (SEM) analyses of the porous ceramic materials surface were carried out on a FEI Quanta 3D FEG.

The X-ray diffractograms of the inorganic/organic composites were recorded on a Rigaku Ultima IV operating at 40 kV and 30 mA. The 2θ angle varied from 3^{O} to 30^{O} using a 0.02^{O} step size.

The compression properties of the dry inorganic/organic composites were measured on an Instron 3382 instrument, equipped with a 100 kN cell at room temperature (25±1 °C).

3. Results and discussion

The gelcasting technology consists in crosslinked polymer aqueous gels obtained by using an organic monomer solution that can be in situ polymerized, to form a strong macromolecular gel network, with incorporated alumina particles, defined by the mould [17 - 19]. In this work AA is the chain building monomer and MBA is the chain branching or crosslinking monomer. After addition of free radical initiator system (KPS/MS) to the solution, the monofunctional monomer (AA) reacts to form long chains which are occasionally branched by the incorporation of the (MBA) difunctional monomer. The result is a very high molecular weight polymer (PAA-co-MBA) that fills the space and traps the water molecules among its branches. The result is a polymer–water gel where alumina particles are immobilized. The green body composites were sintered at a temperature of 1500ºC for 4h in a furnace at atmospheric pressure.

3.1. Infrared Spectroscopy (FTIR) Analysis

The FTIR spectra of the Al, poly (AA-co-MBA) and Al-poly (AA-co-MBA) composites are shown in Figure 1.

The FTIR spectrum of the alumina sample displays three peaks at 642 cm^{-1}, 603 cm^{-1} and 456 cm^{-1} corresponding to the Al–O stretching vibrations [20]. The FTIR spectrum of poly (AA-co-MBA) showed peaks at 2924 cm^{-1} and 2851 cm^{-1} corresponding to the CH_2 stretching vibrations [21,22], the peaks at 1725 cm^{-1} are due to protonated carboxylate groups forming a cyclic dimmer , while the peaks near 1570 and1420 cm^{-1}

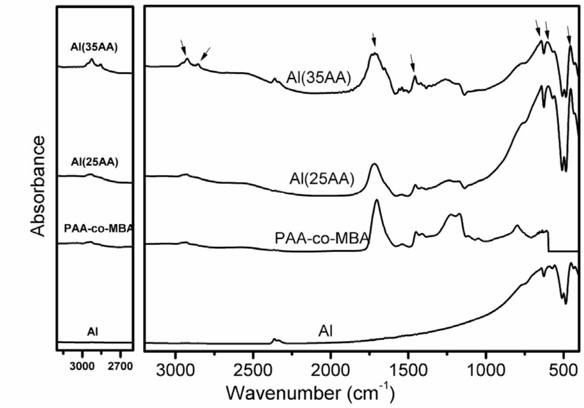

Fig. 1 - FTIR spectra of Al, poly (AA-co-MBA) and Al-poly (AA-co-MBA) composites with 25% wt AA and 35% wt AA. / *Spectrul FTIR al Al, poli (AA-co-MBA) şi al compozitelor Al-poli (AA-co-MBA) cu 25% masic AA şi 35% masic AA faţă de alumină.*

corresponds to the asymmetric and symmetric C-O stretching vibration of carboxylate groups [22].

The FTIR spectrum of alumina/poly (AA-co-MBA) composites, with different AA contents, showed all characteristic peaks of alumina and acrylic polymers. The characteristic peaks to the carboxylic group R-COO$^-$ of the polymers are the most relevant. Also, by decreasing the concentration of the acrylic acid monomer in the composite preparation from 35 to 25%, the relative intensities of the carboxylate groups peaks decreases.

3.2. Thermal behaviour

TG and DTG curves of Al, poly (AA-co-MBA) and Al/poly (AA-co-MBA) composites formed by gelcasting are given in Figure 2 and 3. The thermal degradation behaviour of poly (AA-co-MBA) shown in Figure 2 is very complex [23].

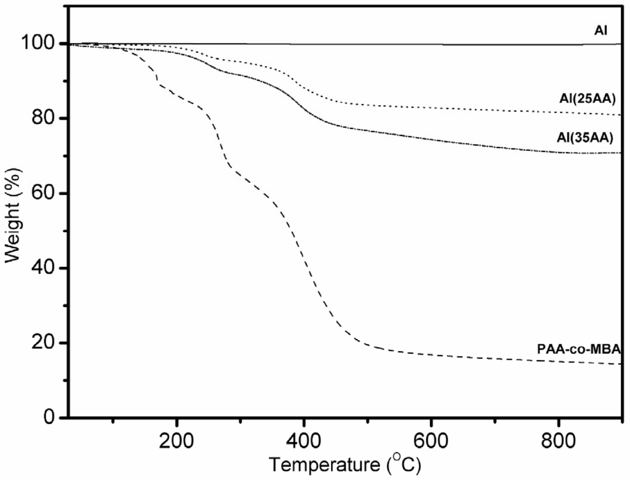

Fig. 2 - The TGA curves of Al_2O_3 , poly (AA-co-MBA) and Al- poly (AA-co-MBA) green body with 25% wt AA and 35% wt AA
Curbele TGA ale Al_2O_3, ale poli (AA-co-MBA) şi ale compozitelor uscate pe bază de Al- poli (AA-co-MBA) cu 25% masic AA şi 35% masic AA.

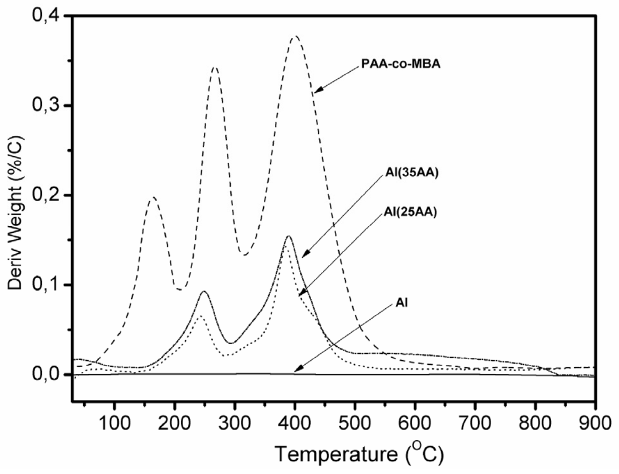

Fig. 3 - The DTG curves of Al_2O_3 , poly (AA-co-MBA) and Al- poly (AA-co-MBA) green body with 25% wt AA and 35% wt AA
Curbele DTG ale Al_2O_3, ale poli (AA-co-MBA) şi ale compozitelor uscate pe bază de Al- poli (AA-co-MBA) cu 25% masic AA şi 35% masic AA.

Three degradation stages were observed [24, 25]. The first stage at 80-160°C was accompanied by 14.26 % weight loss associated with the release of water. The second stage between 160-335°C is characterized by a 22.99% weight loss probably assigned to the dehydration of carboxylic acid followed by decarboxylation. The third stage was noticed at 350-399°C and characterized by a 45.7% weight loss due to the chain scission of the main chain.

The TG and DTG analyses of the samples with different concentrations of monomer are shown also in Figure 2 and 3. The new composites TG results indicated weight losses between 19-30%. Weight loss increased with the increase of monomer concentration. These analyses highlighted the two processes of decomposition: the first process occurred at a temperature closed to that of polyacrylic acid (about 250°C) and the second took place at temperatures lower than that of polyacrylic acid (about 390°C). Maximum reduction of the second process was more pronounced at higher monomer concentration.

3.3. Shrinkage behaviour

The results displayed in Figure 4 showed the influences of monomer content on density and volumetric shrinkage.

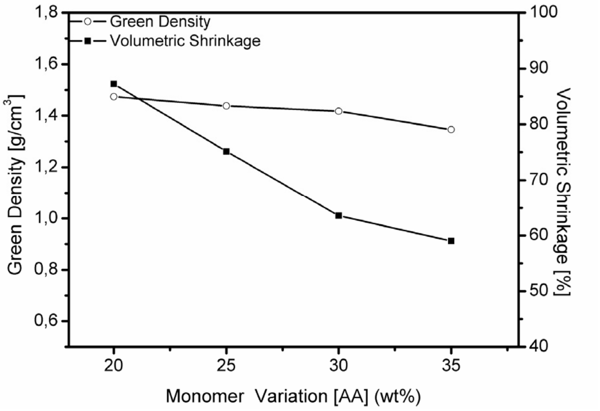

Fig. 4 - Influence of the monomer concentration over the density and over the volumetric shrinkage / *Influența concentrației de monomer asupra densității şi asupra contracției volumetrice.*

The density of inorganic/organic composites, obtained before the drying process is practically not influenced by the variation of monomer concentration. Polymer composite gel presented density values between 1.3 to 1.5 g/cm^3, closed to water density (used as solvent). Figure 4 shows the influence of monomer concentration on the volumetric shrinkage of resulting green body composites, obtained after the drying process at 105°C. The volumetric shrinkage of the inorganic/organic composites decreases from 59 to 87%, as the monomer content increases ([AA] =20-35%). The explanation of this fact could be the crosslinking density augmentation (produced by higher monomer contents). Between 20-30 % [AA] monomer the croslinked polymer is insufficient for the stabilization of the matrix which entraps the alumina powders. At greater monomer content the macromolecular network becomes more compact and the structure of the composite is more stable, the ceramic particles being distributed more uniformly [26, 27].

3.4. Mechanical properties

The stress – strain curves of the inorganic/organic composite materials studied are presented in Figure 5. The compression strength of dry green body composites shows the highest value: 230 MPa at 35 % (wt) monomer concentration and the lower value: 39 MPa at 20 % (wt) monomer concentration.

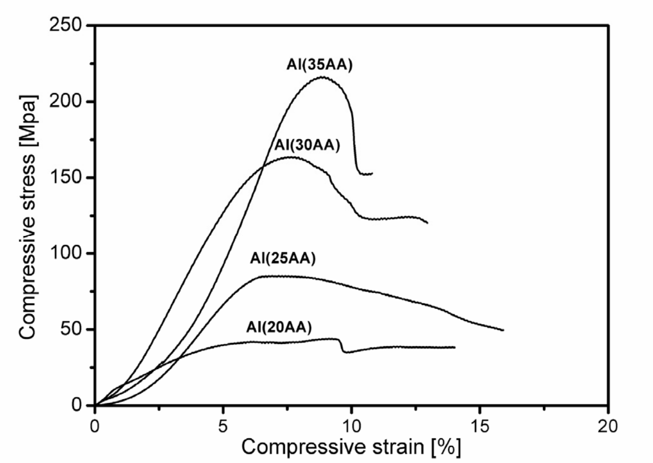

Fig. 5 - The stress – strain diagrams of the Al- poly (AA-co-MBA) green body with 20% wt AA, 25% wt AA, 30% wt AA and 35% wt AA / *Curbele de deformare la compresie ale compozitelor pe bază de Al- poli (AA-co-MBA) cu 20% masic AA, 25% masic AA, 30% masic AA şi 35% masic AA.*

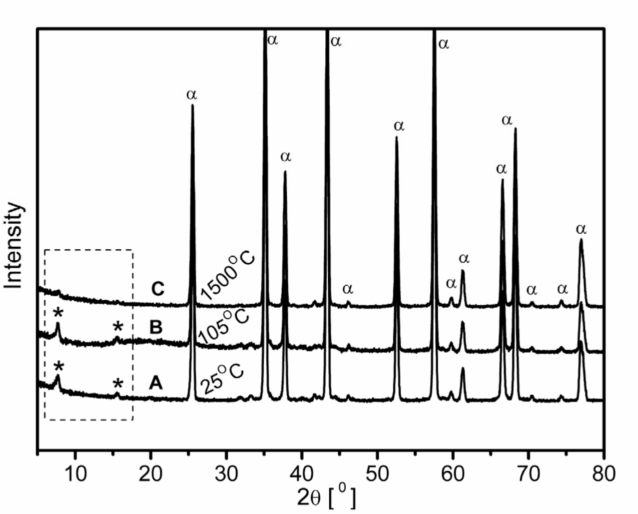

Fig. 6 - XRD patterns of the specimens with (A) - Al_2O_3, (B) Al- poly (AA-co-MBA) green body with 25% wt AA dried at 105°C and (C) – sintered body with 25% wt AA at 1500°C (* - traces of impurities) / *Difractogramele XRD ale probelor (A) - Al_2O_3, (B) materialelor compozite uscate la 105°C pe bază de Al - poli(AA-co-MBA) cu 25% masic AA şi (C) – materialelor ceramice sinterizate la 1500°C cu 25% masic AA.*

The possible explanation is that at a higher concentration of monomer, the network structures of gel are very homogeneous and compact and so, the gel network structures are more stable and stronger as it is suggested also by Juanli Yu. et all [26].

Also the distribution of alumina powders in composites could be more uniform at greater organic content. This explanation is supported by the literature data which show that the distribution of ceramic powders in the green materials gives a series of excellent properties and plays an important role in determining the characteristic of the final product [28, 29].

3.5. X-ray Diffraction (XRD)

The XRD diffractograms of the Al_2O_3 and Al_2O_3-poly (AA-co-MBA) composite dried at 105°C are shown in Figure 6 and 7.

The XRD diffractograms indicate that there was no phase transformation detected between Al_2O_3 and alumina/poly (AA-co-MBA) composites. The X-ray analyses showed that α - Al_2O_3 phase was the major crystalline phase, but also was observed traces of some impurities. However, when the sintering temperature was 1500°C, the X-ray analyses showed only the presence of α - Al_2O_3 phase, no other phases was observed (Figure 6, curve C). The X-ray diffractions of alumina/poly (AA-co-MBA) composites, with different AA contents showed all characteristic peaks of the same α phase when the sintering temperature was 1500°C (Figure 7). This confirmed that the monomer variation used in the gelcasting process had no influence in the phase composition of the investigated material.

3.6. Porosity of sintered bodies

The water displacement – Archimedes method shows slightly higher sintered porosity than it was obtained by weight measurements. The simplest method for adjusting the porosity is to adjust the monomer concentration. Previous studies [21,22] reported that the porosity of porous ceramics generally increases with monomer concentration increasing and decreased with filler content increasing. As shown in figure 8 the sintered bodies at 1500° C followed the general trend between porosity and monomer concentration. The porosity increased from 50% to 87% by the increasing of monomer content from 20 to 35 vol%. The porosity decreases due to excessive volumetric shrinkage of the specimens during heat-treatment. Figure 8 also shows open porosity of sintered bodies as a function of monomer concentration. It can be seen that the open porosity increased slightly with the increasing of the monomer concentration. The difference between total porosity and open porosity, closed porosity generally increased with increasing of the total porosity of sintered bodies. The reaction

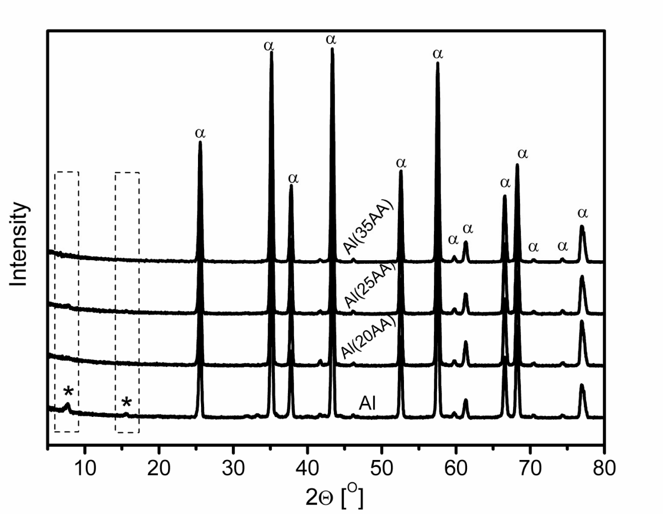

Fig. 7- XRD patterns of the specimens with different monomer concentration, sintered at 1500^{O}C for 4h (* - traces of impurities) / *Rezultatele analizelor XRD ale materialelor compozite, cu diferite concentrații de monomer, sinterizate la temperatura de 1500°C, timp de 4h.*

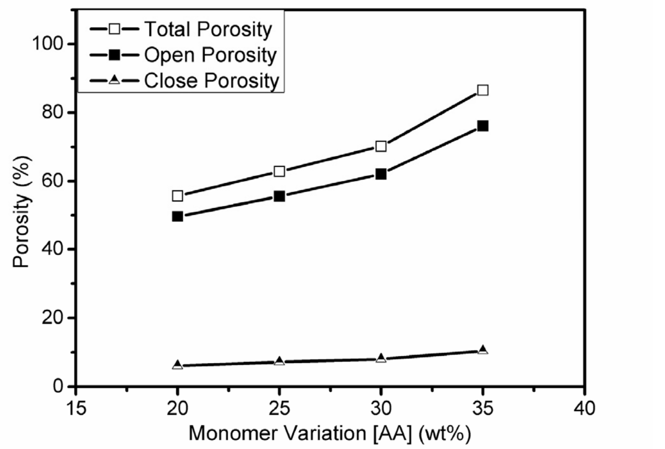

Fig. 8 - Influence of the monomer concentration over the porosity of the sintered bodies at 1500^{O} C / *Influența concentrației de monomer [AA] asupra porozității finale a materialelor ceramice sinterizate la 1500°C.*

based on the organic matter decomposition evolves quite large amount of gaseous by-products, which decreases the formation of closed porosity and is more favourable for increasing the open porosity. All this affirmations are in good agreements with the SEM images of sintered bodies with various monomer concentrations (Figure 9).

The pore size distributions of the sintered bodies, obtained by using SEM image analysis, are illustrated in Figure 9. SEM images provide information about pore morphology and pore size. One can observe an increase in the pore diameter and a change in the pore number of the sintered body with the increasing of monomer concentration. It may be noticed that the sintered body prepared with 35 wt% AA monomer content has more pores that are interconnected with others, causing opened pores.

4. Conclusions

A new system with low-toxicity based on poly (acrylic acid) gels was successfully applied to prepare green body alumina composites. FTIR experiments confirmed the obtaining of polymer composites with alumina particles. The optimum concentration of monomer that leads to high strength machinable green bodies with a good dispersion of alumina was 35 wt% relative to alumina. Higher monomer loadings have also good green mechanical properties and are good candidates for the formation of highly-porous ceramics after burning out the polymer network. Porosity data of the sintered body display that porous ceramic with higher porosity can be obtained by using the gelcasting process based on alumina and polyacrylic acid.

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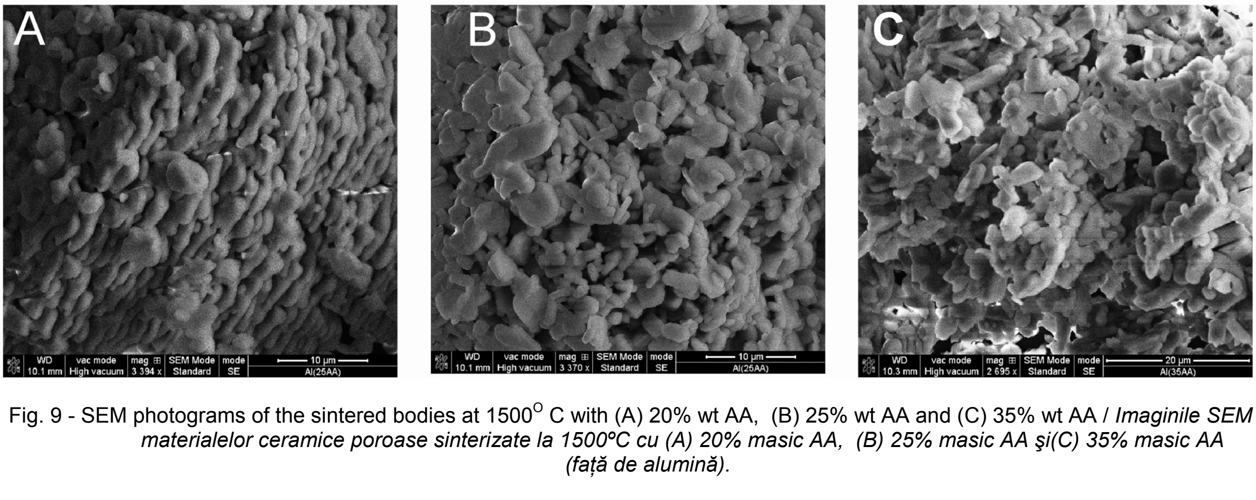

Fig. 9 - SEM photograms of the sintered bodies at 1500^{O} C with (A) 20% wt AA, (B) 25% wt AA and (C) 35% wt AA / *Imaginile SEM ale materialelor ceramice poroase sinterizate la 1500°C cu (A) 20% masic AA, (B) 25% masic AA şi(C) 35% masic AA (față de alumină).*

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