

DRAGAN RAJNOVIC<sup>1</sup>  
 SEBASTIAN BALOS<sup>1</sup>  
 LEPOSAVA SIDJANIN<sup>1</sup>  
 MIROSLAVA RADEKA<sup>1</sup>  
 SNEZANA PETROVIC<sup>2</sup>  
 DMITAR ZORIC<sup>2</sup>  
 JONJAUA RANOGAJEC<sup>2</sup>

<sup>1</sup>Faculty of Technical Sciences,  
 University of Novi Sad, Novi Sad,  
 Serbia

<sup>2</sup>Faculty of Technology, University  
 of Novi Sad, Novi Sad, Serbia

SCIENTIFIC PAPER

UDC 666.3.017

DOI 10.2298/CICEQ101119007R

## THE INFLUENCE OF POLYMER ADDITION ON FLEXURAL STRENGTH, FRACTURE MODE AND POROSITY OF TRADITIONAL CERAMICS

*The usage of air-swept milling of raw materials is the most efficient method for preventing the negative lime-blowing process of ceramic roofing tiles. However, after air-swept milling the clay minerals lose water which has to be returned back before the shaping procedure. Addition of surface active materials could increase hydrophilicity of the raw material and reduce needed time for re-wetting through the control of meso-, micro- and nanoporosity of the clay material. In view of that, the object of this research was to study the influence of polyethylene glycol (PEG600) on porosity, mechanical properties and fracture surface characteristics of traditional ceramic materials. It was founded that with the addition of polyethylene glycol (PEG600) to traditional clay materials it is possible to achieve desired porosity, from meso, through micro and up to nano, without degrading the mechanical properties of the final products.*

*Key words: polymer addition; traditional ceramics; mechanical properties; porosity; microcracks.*

The properties of raw material mixtures (clay mineral compositions, feldspars, carbonates, quartz) are of decisive importance for the process of sintering and therefore for the quality of the final product in the production of structural clay products [1]. Raw material mixtures with significant carbonate content need a particular approach since carbonates play the role of stabilizer and mineralizer, but could also present the starting point for the most dangerous failures. The calcite particles, which are decomposed during the firing process into calcium oxide, increase mechanical and physical properties of the final product only when the crystalline phases (gehlenite, anorthite and wollastonite) are formed at temperatures above 870 °C. These forms are the result of CaO reactions with Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, the components of the clay minerals [2]. Otherwise, the CaO particles (when the grain size is >1 mm) as a part of the final product structure, in the presence of the humidity, rapidly react and form portlandite, Ca(OH)<sub>2</sub>. This effect is known as "lime blowing" [3] and

is deleterious for the final properties of the structural clay products.

The carbonates can be efficient stabilizers if their particles are finely ground and surrounded by clay minerals. Unfortunately, even the recent types of the fine roller mills in a semi-wet preparation method are not able to grind the shelly-limestone particles to a degree which would permit their complete thermal decomposition and the formation of crystalline phases. Usage of an air-swept mill for drying and grinding raw materials turns out to be the most efficient method for preventing the lime-blowing process of ceramic roofing tiles. Grinding and drying (stream of the hot air up to 750 °C, time of contact with raw material several seconds) activate thermally and mechanically the clay minerals and partly decompose the carbonates. After such structure changes, a raw material powder was obtained with clay minerals which enter all future thermal reactions with a higher energy level than the ordinary one after a semi-wet preparation method.

However, after air-swept milling the clay minerals lose water that has to be returned back before the shaping procedure. Considering this fact, the raw material after the air-swept mill has to be stored in order to restore the water content from the surrounding humidity. This is time-consuming process and it is limited by the characteristics of the industrial line.

Corresponding author: D. Rajnovic, Faculty of Technical Sciences, University of Novi Sad, Trg D. Obradovića 6, 21000 Novi Sad, Serbia.

E-mail: [draganr@uns.ac.rs](mailto:draganr@uns.ac.rs)

Paper received: 19 November, 2010

Paper revised: 4 February, 2011

Paper accepted: 24 February, 2011

It is expected that through addition of the surface active materials (SAM) the storage time could be diminished. The surface active materials react with clay minerals, changing the amount of micro and meso porosity of the raw material powder [4]. The clay minerals adsorb the organic ions of the SAM enlarging their basal spacing [5] and allow faster absorption of the water. In this way, the air-swept mill material might regain their hydrophilicity in much shorter time. On the other hand, introducing a SAM into the raw material mixture could lead to a decrease of mechanical properties of the final clay product. Namely, unwanted defects, like cracks or gas bubbles might be introduced into the microstructure [4,6].

In view of that, the object of this research was to study the porosity, mechanical properties and the fracture surface of SAM added traditional ceramics. This article presents one of the valorization ways of the original clay raw material batch (before the air-swept milling and drying) based on the application of polyethylene glycol (PEG 600) with the idea to control meso-, micro- and nanoporosity, as well as to increase rheological (green samples) and mechanical properties (dried and fired samples) [7]. The idea was to study the clay/polymer system (PEG600) for its future industrial application in the structural clay production based on the air-swept milling and drying procedure that could be a promising technological segment.

## EXPERIMENTAL

### Material

Three model systems were produced in laboratory conditions and analyzed as dried and fired products. The raw material with a relatively large amount of carbonates (calcite and dolomite, 13 mass%), illite-montmorillonite clay minerals, quartz, and feldspars was used as a base (Tables 1 and 2). To this material a defined quantity of polyethylene glycol (HO-CH<sub>2</sub>-(CH<sub>2</sub>-O-CH<sub>2</sub>)<sub>*n*</sub>-CH<sub>2</sub>-OH) with molecular weight 600 (PEG 600, Baker, Germany) as polymer surface active material (SAM) was added. The produced materials were designated as: 0%PEG - control system without polymer addition; 1%PEG and 5%PEG - with 1 and 5% mass addition of PEG 600 (polyethylene glycol), respectively.

### Procedure

The clayey raw material (water content of 19.50 mass%), was prepared by semi-wet mill procedure in industrial conditions (company Potisje a.d., member of Tondach group, Kanjiža, Serbia). The defined quantity of PEG 600 (1 or 5 mass%) was added, without any extra quantity of water, in laboratory conditions to a mass of 5 kg of the clayey raw material, in order to obtain raw material batches of demanded plasticity. The mixing temperature ( $\approx 100$  °C) of the formed batches was over the melting temperature of the PEG600 (melting temperature 20-25 °C, flash point 210 °C). The samples of the defined dimensions (10 mm×10 mm×55 mm) were shaped on laboratory scale (laboratory extruder, 8 bar).

Table 1. Phase composition (mass%) of the clayey raw material

Quartz	26
Feldspars <sup>a</sup>	17
Illite + muscovite	26
Kaolinite	6
Montmorillonite	5
Chlorite	6
Calcite	7
Dolomite	6
$\Sigma$	99

<sup>a</sup>Orthoclase, low temperature plagioclase

The weight gain measurements were performed to determine water uptake due to capillary condensation. The formed samples were initially dried at 105±5 °C for 20 h in order to determine dry weights. They were then placed in three chambers of defined relative humidity (RH) value. The RHs values in the chambers were adjusted with 500 ml of a saturated aqueous solution containing: K<sub>2</sub>SO<sub>4</sub> (150 g/l for obtaining 97 to 99% RH), (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (900 g/l for 80 to 82% RH) and NaCl (400 g/l for 75 to 76% RH). The samples were periodically removed, weighted and returned to chambers for further soaking. The incubation period of the samples was 21 day.

The samples stored in the chamber with a RH value range of 75 to 76% were chosen for the future firing procedure in a laboratory kiln with a heating rate of 400 °C/h and a holding time of 1 h at 960 °C.

Table 2. Particle size composition (mass%) of the clayey raw material

Composition	Particle diameter, mm						
	>1.0	1-0.8	0.8-0.5	0.5-0.2	0.2-0.1	0.1-0.063	<0.063
Original raw material before grinding procedure	0.59	0.05	0.16	0.28	0.95	2.05	95.92
Semi-wet prepared raw material after grinding procedure	0.01	0.11	0.26	0.26	0.96	2.65	95.75

## Characterization

The amount of micro- and mesoporosity was additionally evaluated indirectly, based on the experiments with the salt saturated aqueous solutions, which determine RH values in the chambers. The increase of weight of samples, accommodated to specified RH value, is attributed to capillary condensation in pores with radius in the range of roughly  $2 \times 10^{-9}$  to  $10^{-7}$  m. The Kelvin equation shows the relationship between the capillary pore radius, the place of water condensation, and relative humidity:

$$r = -\frac{2\sigma \cos \theta}{\rho RT \ln \phi} \quad (1)$$

where  $\sigma$  is the surface tension of water [N/m],  $\phi$  - relative humidity [%],  $\theta$  - wetting angle [°],  $r$  - capillary radius [m],  $\rho$  - density of water [ $\text{kg/m}^3$ ],  $R$  - gas constant for water vapor [J/kg K], and  $T$  - absolute temperature [K].

The values of the capillary radius were derived from the Kelvin equation using relative humidity values of 75, 81 and 98%, and the results are presented in Table 3 [8]. The moisture content of the dried samples was determined based on the weight loss measurements after heating at 105 °C for 20 h.

Table 3. Relation between the relative humidity value (RH) of the storage chambers and pore radius values (capillary condensation takes place in the pores of the corresponding pore radius) [8]

RH / %	97-99	80-82	75-76
$r_{\text{pores}}$ / nm	22	8	4.5

Furthermore, after drying and heating process the textural characterization of the samples was done with a mercury intrusion porosimeter (model 2000, porosimeter WS, Carlo Erba, Rodano, Milano, Italy). Mechanical properties, *i.e.*, flexural strength was obtained by three point bend test at tensile machine Toyoseiki AT-L-118B, with measuring range from 0 to 1000 N. At least five samples were tested as dried and fired products. The fracture surfaces were examined visually and by means of SEM JEOL JSM 6460LV operating at 20 kV.

## RESULTS AND DISCUSSION

### Characteristics of raw materials

The mineral composition of the standard raw material mixture characterizes the presence of the clay minerals (illite, montmorillonite, chlorite and kaolinite) and a large amount of carbonates (calcite and dolomite) as well as the presence of feldspars and

quartz, Table 1. The results of particle size distribution indicate the fact that more particle size are less than 0.063 mm after the semi-wet grinding mill procedure, Table 2.

### Characterization of the dried samples

The dried samples were characterized considering the presence of micro- and mesoporosity and the mechanical properties. The amount of nanoporosity was evaluated indirectly based on the experiments with the saturated aqueous solutions. The mass increase of the samples is related with the amount of the pores, the radius of which corresponds to the pore size in which the capillary condensation happens, Table 4.

Table 4. Relation between the relative humidity value (RH) of the air in the storage chambers and the moisture content ( $\Delta m$  / %) of the samples (the sample moisture content was determined based on weight loss ( $t = 105$  °C,  $\tau = 20$  h))

Dried sample system	RH / %		
	97-99	80-82	75-76
0%PEG	7.99±0.26	3.0±0.03	2.5±0.01
1%PEG	7.71±0.18	3.28±0.04	3.4±0.02
5%PEG	10.93±0.32	3.38±0.03	2.97±0.02

The results presented in Table 4 indicate that in the case of the system 5%PEG the amount of pores with the radius value of 22 nm significantly is increased. The amount of pores with  $r \leq 8$  nm is increased in the case of the same samples, but more prominent role has PEG 600 in the case of the samples 1%PEG. The presence of these pores could provide the quantity of water (by the condensation of water vapors) necessary for achieving the desirable rheological properties of the raw batch during the shaping procedure.

The pore radius distribution, determined by mercury porosimetry, indicates that the presence of PEG 600 changed the pore size distribution of the dried samples porosity as well as their total porosity (Figure 1 and Table 5). Namely, the amount of pores in the range of 0.008-0.016  $\mu\text{m}$  is the highest for the system 5%PEG (Figure 1), which is very approached to the results presented in Table 4 for the relative humidity values (RH) in the range of 97-99% ( $r_{\text{pores}} \approx 22$  nm). The differences in pore size distribution among the three studied systems are also evident for larger pores (system 0%PEG: 64-120 nm, system 1%PEG: 120-250 nm, system 5%PEG: 8-16  $\mu\text{m}$ ).

It was found that flexural strength of the dried samples was slightly increased for the systems with polyethylene glycol addition (Table 6). This increase

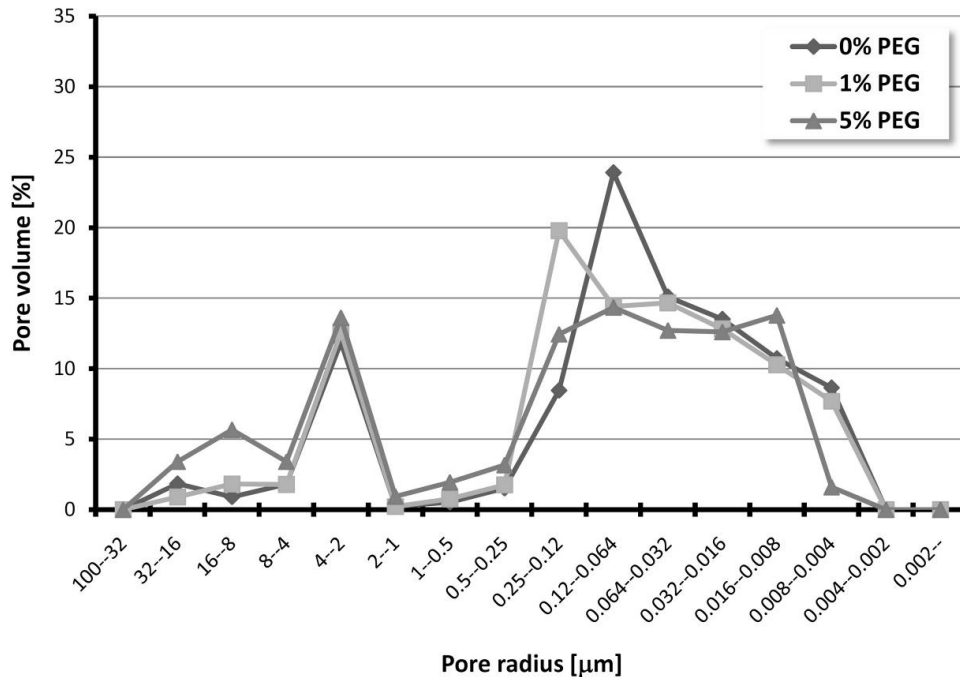


Figure 1. Pore size distribution of the dried samples.

could be contributed to expected increase in hydroplasticity of the polymer added samples. However, the macroscopic and microscopic examination of the dried systems showed that a significant level of microcracks was present in all samples (Figure 2), with the most pronounced cracks present in the system 5%PEG. The observed increase in microcracks quantity however did not produce significant increase in the total porosity (Table 5). The large microcracks were in the range from 0.1 to 0.5 mm for the system without polymer addition, from 0.5 to 1 mm for the system with 1%PEG and from 0.5 to 2 mm for the system with 5%PEG, Figure 3. This suggests, in conjunction with the flexural strength and the total porosity results, that the hydroplasticity of the dried material was increased based on the polymer addition, but the rheological properties were harmed, resulting in matching mechanical properties.

Table 5. Total porosity of the dried samples determined by Hg porosimetry

Dried sample system	0%PEG	1%PEG	5%PEG
Total porosity, %	17.01±0.85	18.50±0.76	18.26±0.98

Table 6. Flexural strength of the dried samples

Dried sample system	0%PEG	1%PEG	5%PEG
Flexural strength, MPa	8.2±1.1	9.1±0.4	8.8±1.2

### Characterization of the fired samples

The total porosity of the selected fired ceramic systems is presented in Table 7. This value was diminished by the addition of PEG 600. The characteristics of pore size distribution (Figure 4) distinguish the systems with polymer addition (1%PEG and 5%PEG) from the system without polymer (0%PEG) considering the quantity of the pores in the range of 4-

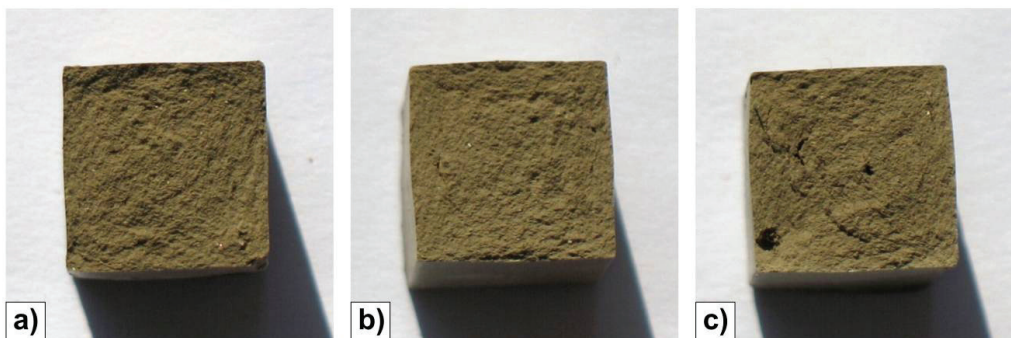


Figure 2. Macrophotographs of the fracture surface of the dried samples: a) 0%PEG; b) 1%PEG; c) 5%PEG.

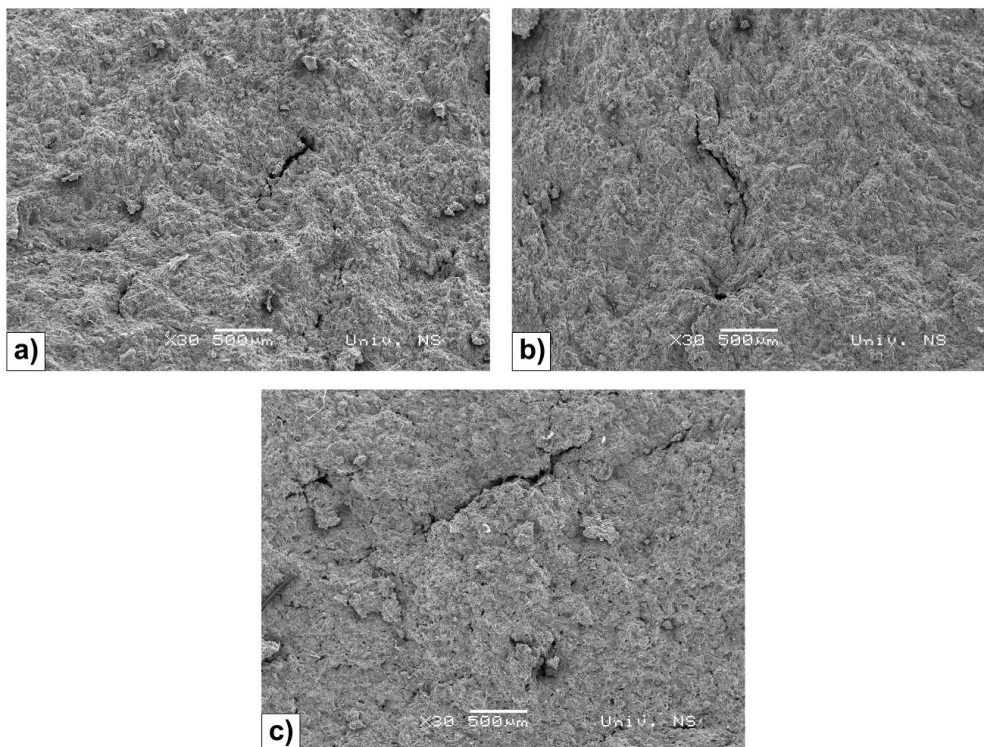


Figure 3. Increase of microcracks at the fracture surface of the dried samples prepared with the addition of PEG 600 (SEM): a) 0%PEG - 0.1-0.5 mm crack length; b) 1%PEG - 0.5-1 mm; c) 5%PEG - 0.5-2 mm.

Table 7. Total porosity of the fired samples determined by Hg porosimetry

Fired sample system	0%PEG	1%PEG	5%PEG
Total porosity, %	26.04	25.85	25.33

-120 nm as well as in the range of 2-4 μm. Namely, the presence of large pores (2-4 μm) decreases and the number of small ones (4-120 nm) increases (Figure 5). On the other hand, the main pore size interval remains identical (0.12 to 1 μm) for all systems (Figure 6).

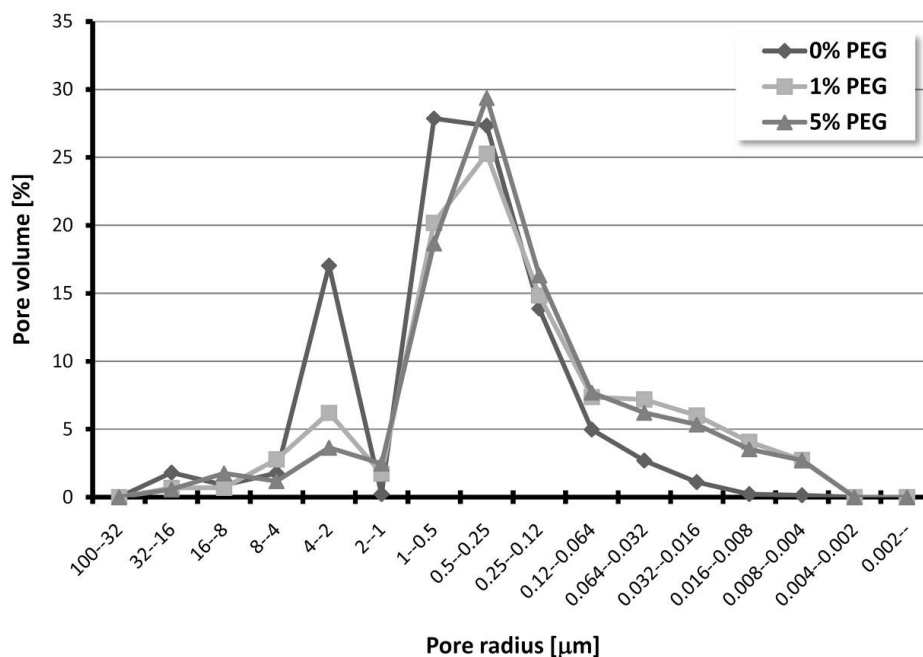


Figure 4. Pore size distribution of the fired systems.

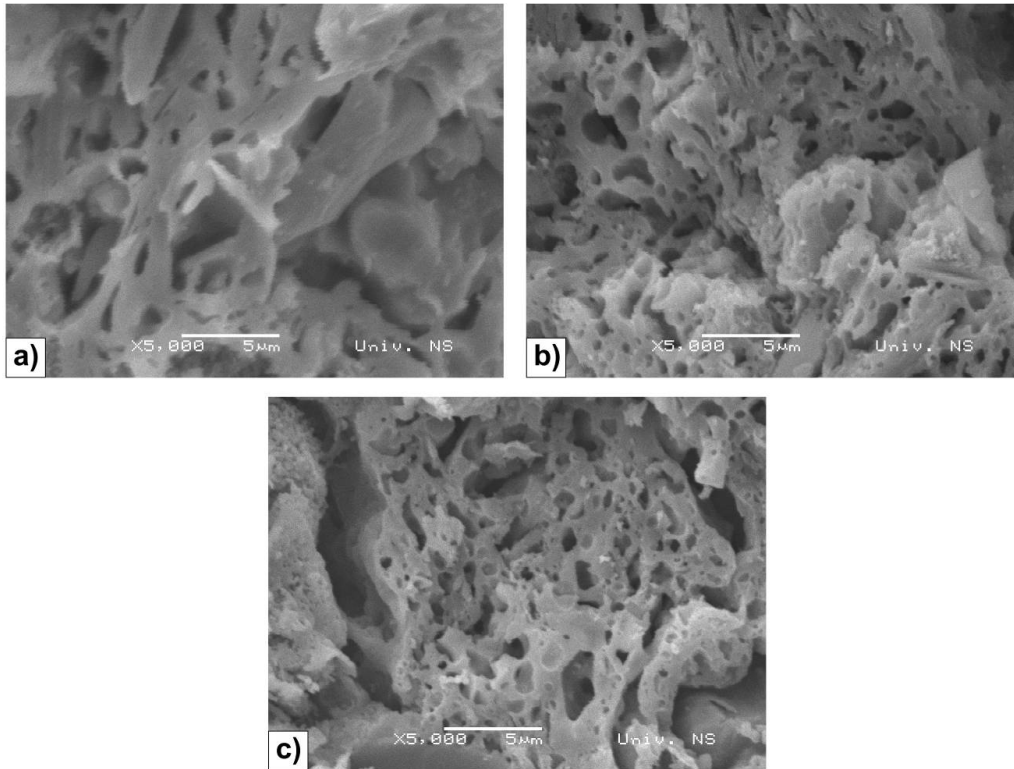


Figure 5. PEG 600 addition decrease the large and increase the small pore radius (SEM): a) 0%PEG; b) 1%PEG; c) 5%PEG.

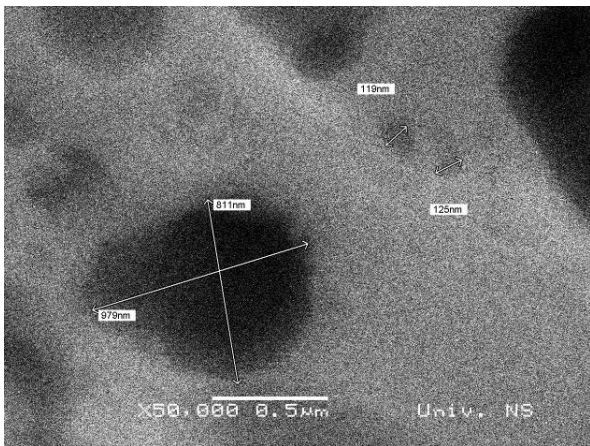


Figure 6. Main pore size interval 0.12 to 1 μm of the fired systems.

The flexural strength of the fired samples was at the level of 30 MPa with a slight increase in the case of the polymer added samples (Table 8). On the fracture surface of the system 5%PEG a gray coloring was noticed due to appearance of the reduction atmosphere during the firing process, Figure 7. Comparing the fracture surface of the dried (Figure 3) and the fired samples (Figure 8) an additional small increase of microcracks was noticed after firing process. The highest amount of cracks was present in the system with 5%PEG (average size of crack length

Table 8. Flexural strength of the fired samples

Fired sample system	0%PEG	1%PEG	5%PEG
Flexural strength, MPa	28.9±1.7	29.4±2.5	31.4±1.0

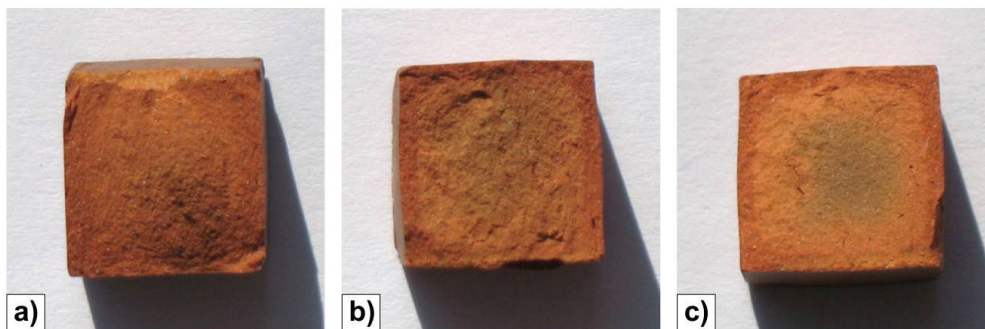


Figure 7. Macrophotographs of the fracture surface of the fired samples: a) 0%PEG; b) 1%PEG; c) 5%PEG.

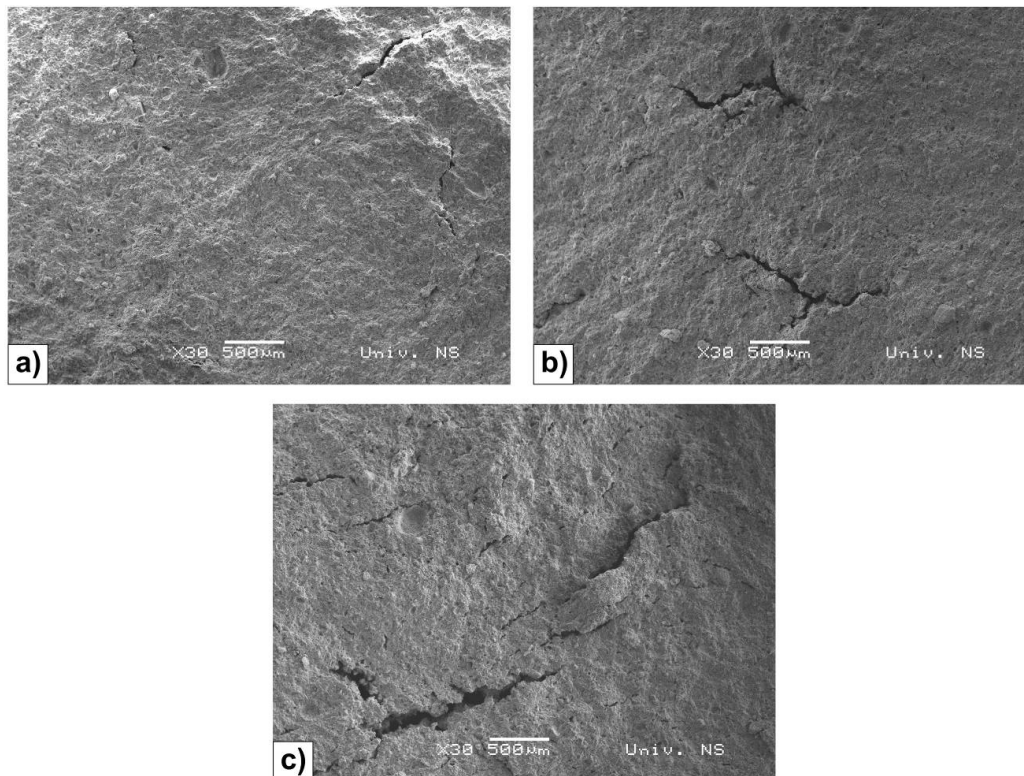


Figure 8. Increase of microcracks at the fracture surface of the fired samples prepared with the addition of PEG 600 (SEM):  
 a) 0%PEG - 0.3-1 mm crack length; b) 1%PEG - 0.5-1.5 mm; c) 5%PEG - 0.5-2.5 mm.

0.5-2.5 mm), followed by 1%PEG (0.5-1.5 mm), while the system 0%PEG (no polymer added) had the lowest (0.3-1 mm) amount of cracks (Figure 8). The negative influence of microcracks on mechanical properties has been well documented in literature [6,10-13]. Nevertheless, in this case the flexural strength of the polymer added samples remained at the approximately same level, or was slightly increased, in spite of the larger amount of microcracks. This behavior could be only contributed to do microstructure changes caused by PEG 600 addition and to alteration of the pore size distribution, the decrease of the large pores presence (2-4  $\mu\text{m}$ ) and the increase of the number of small ones (4-64 nm).

## CONCLUSION

According to the obtained results it was found that the effect of polyethylene glycol (PEG600) addition on clay material properties is dual:

- The amount of pores is changed at meso-, micro- and nanolevel, namely the micropores presence (2-4  $\mu\text{m}$ ) is decreased while the number of small ones (4-64 nm) is increased, since the PEG600 reacts with the clay minerals enlarging their basal spacing and hence increasing the hydrophilicity and microstructure strength.

- Size and density of cracks at the macrolevel are increased. However, the mechanical properties remain the same due to dominant microstructure toughening effect of polymer on micro and nanolevel.

## Acknowledgment

This work was supported by Ministry of Education and Science, Republic of Serbia.

## REFERENCES

- [1] S. Freyburg, A. Schwartz, *Ziegeltechnisches Jahrbuch* (2007) 59-73
- [2] A. Escardino, J. Garcia-Ten, C. Feliu, *J. Eur. Ceram. Soc.* **28** (2008) 3011-3020
- [3] G. Cultrone, E. Sebastian, K. Elert, M.J. de la Torre, O. Cazalla, C. Rodriguez-Navarro, *J. Eur. Ceram. Soc.* **24** (2004) 547-564
- [4] P. Colombo, *J. Eur. Ceram. Soc.* **28** (2008) 1389-1395
- [5] L.B. de Pavia, A.R. Morales, F.R.V. Diaz, *Appl. Clay Sci.* **42** (2008) 8-24
- [6] H.S. Kim, J.H. Kim, K. Ikeda, *Br. Ceram. Trans.* **102** (2003) 133-137
- [7] L. Heller-Kallai, in *Handbook of Clay Science*, F. Bergaya, B.K.G. Theng, G. Lagaly Eds., Elsevier, 2006, p. 289-308

- [8] Ju. G. Frolov, Kurs koloidnoj hemii (Poverhnostnie javlenija i duspersnie sistemi), Hemija, Moskva, 1982, p. 135 (in Russian)
- [9] Z-H. Wena, Y-S. Han, L. Liang, J-B. Li, Mater. Charact. **59** (2008) 1335-1338
- [10] T. Fett, J. Eur. Ceram. Soc. **25** (2005) 543-547.
- [11] Y. Sakaida, K. Tanaka, JSME Int. J. Ser. A **46** (2003) 30-39
- [12] L.J. Vandeperre, J. Wang, W.J. Clegg, Philos. Mag. **84** (2004) 3689-3704
- [13] L. Sidjanin, J. Ranogajec, D. Rajnovic, E. Molnar, Mater. Des. **28** (2007) 941-947.

DRAGAN RAJNOVIC<sup>1</sup>  
SEBASTIAN BALOS<sup>1</sup>  
LEPOSAVA SIDJANIN<sup>1</sup>  
MIROSLAVA RADEKA<sup>1</sup>  
SNEZANA PETROVIC<sup>2</sup>  
DMITAR ZORIC<sup>2</sup>  
JONJAJA RANOGAJEC<sup>2</sup>

<sup>1</sup>Faculty of Technical Sciences,  
University of Novi Sad, Novi Sad,  
Serbia

<sup>2</sup>Faculty of Technology, University  
of Novi Sad, Novi Sad, Serbia

NAUČNI RAD

## UTICAJ DODAVANJA POLIMERA NA SAVOJNU ČVRSTOĆU, KARAKTER LOMA I POROZNOST KOD TRADICIONALNE KERAMIKE

*Upotreba tehnike suve prerade sirovinskog kompozita u proizvodnji glinenog crepa je najefikasniji metod za sprečavanje pojave „kokičanja“ krečnjaka kod eksploatacije finalnog proizvoda. Međutim, nakon suve prerade dolazi do gubitka vode kod glinenih minerala koju je potom potrebno nadoknaditi tokom procesa oblikovanja. Radi skraćivanja vremena odležavanja ponovo ovlaženog opekarskog praha korišćene su površinski aktivne supstance koje povećavaju hidrofilitnost praha putem obrazovanja sistema kontrolisane mezo, mikro i nano poroznosti. Ispitan je uticaj dodavanja polietilen glikola (PEG600) glinenom opekarskom prahu na poroznost, mehaničke osobine i karakter loma tradicionalnog glinenog crepa. Utvrđeno je da se dodavanjem polietilen glikola (PEG600) postiže željena mezo-, mikro- i nano-poroznost materijala, bez smanjenja mehaničkih osobina finalnog proizvoda.*

*Ključni reči: dodatak polimera; tradicionalna keramika; mehaničke osobine; poroznost; mikroporsline.*