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Applicability of the Waste Fibres in Cement Paste

Regina KALPOKAITĖ-DIČKUVIENĖ [*], Irena LUKOŠIŪTĖ, Kristina BRINKIENĖ, Arūnas BALTUŠNIKAS, Jūratė ČĖSNIENĖ

Laboratory of Materials Research and Testing, Lithuanian Energy Institute, Breslaujos 3, LT-44403 Kaunas, Lithuania

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Fibres produced from waste catalyst together with commercially available polypropylene fibres were incorporated into ordinary Portland cement paste. The effects of fibre content as well as a mix of different type of fibres on mechanical and physical properties of wet and dry samples were investigated. The results showed that presence of fibres reduced compressive strength of the plain cement in wet and dry state. Contrary, when the combination of 1.5 wt% waste and 1.5 wt% polypropylene fibres was used flexural strength of cement mixture increased by up to 9 % at the age of 28 days. It was observed that addition of 1.5 wt% of only waste fibres improved flexural strength after long hydration period as well. However, the lowest mechanical strength results showed samples with 3 wt% of waste fibres. It was also observed that higher content of waste fibres reduced porosity of the cement mixture and consequently, decreased water absorption capacity. Presence of fibres reduced drying shrinkage of samples and they were lower than plain cement after 28 days of hydration.

Keywords: fibre, catalyst waste, polypropylene, cement, strength, water absorption.

1. INTRODUCTION

Nowadays industry and municipal generates a huge amount of different types of wastes that are recycled or stored in disposal landfill. One of the solutions of utilization of the waste is their or their of sub-products incorporation into concrete industry [1 – 4]. Prior to disposal various thermal processes have been proposed for treating of wastes [5].

Recycled plastics, glass, cellulose, ceramic, wood or metal fibres exhibit different properties such as lightweight, durability, chemical resistance, and thermal or electrical insulation. These properties can be useful for the production of new composite materials. The effect of adding cellulose-recycled fibres, recycled polyethylene terephthalate (PET), acrylic fibres, waste metallic and glass fibres on mechanical or thermal properties of cement paste or concrete was studied in [2, 3, 6 – 11]. Polypropylene fibres (PP) (up to 1 % by volume) are used in concrete due to low cost, outstanding toughness, enhanced shrinkage cracking resistance and mechanical strength [7, 8, 10, 12, 13]. Composites containing hybrid of glass and acrylic fibres result in better flexural strength and can be a replacement of asbestos [9]. It was also found that waste acrylic fibres reinforced mortars have physical, mechanical and durability properties similar to the mortar reinforced with glass or PP fibres [8]. Recycled PET fibres reinforced concrete has slightly lower thermal resistance, but higher compressive strength in comparison with PP fibres reinforced concrete [7]. Contrary, addition of the waste metallic fibres to the cement matrix does not improve the post-cracking behaviour of material. However it was observed that the use of a mix of short and long waste metallic fibres increases flexural strength and ductility of the composites [2]. According to [10, 13] reinforcement of concrete with a mix of different types of fibre like carbon and steel or PP gives even better mechanical strength results than with monotype fibre.

Fibres produced by thermal plasma technique also can be reused as additives or recycled as secondary raw material [14, 15]. It was observed [14] that addition of 1 % – 2 % of thermally transformed rock and glass fibres in stoneware tile mixes give promising results regarding the technological properties of the fired product. Mechanical strength of concrete reinforced with fibres produced from incinerator ashes is similar to the results with the glass fibre [15]. On the other hand, ceramic fibres are much more durable in ordinary Portland cement than glass fibres are [16, 17].

Previous our results showed [18] that ceramic fibre produced by thermal plasma technique has thermally and chemically resistant mullite phase. Moreover, incorporation of these fibres into refractory concrete was useful due to reduction of cracks formation and increase flexural strength after prolonged thermal treatment at high temperature [19]. Meanwhile, the main objective of this experimental study is to explore the possibility of utilization of the fibres produced from waste catalyst in ordinary Portland cement paste.

2. EXPERIMENTAL DETAILS

The materials used for mix production were ordinary Portland cement type CEM I 42.5 N (enterprise “Akmenes cementas” Lithuania), polypropylene fibres (Belmix®BM12), fibres produced from waste catalyst [20] referred as waste fibres (Table 1) and deionised water.

Table 1. Properties of the fibres

Type	Diameter (μm)	Length (mm)	Density (kg/m^3)
Waste fibres (WF)	2 – 10	12	2210
Polypropylene (PP)	34	12	910

[*]Corresponding author. Tel.: +370-37-401984, fax: +370-37-351271.
E-mail address: *regina@mail.lei.lt* (R. Dičkuvienė)

The water to cement ratio of 0.4 was constant for all mixes. Fibres were added to the cement paste as the percentage of 0.75 %, 1.5 % and 3 % by weight of cement (Table 2). The cement paste without fibre was moulded as a reference material. According to [8] fibres were dry-mixed with the cement for 3 min to obtain the uniform fibres dispersion in the matrix. Then the required amount of water was added and the materials were mixed for the period of 3 min. Each type of freshly mixed paste was cast into prismatic (20 mm × 20 mm × 100 mm) samples for flexural, drying shrinkage and compressive strength tests. All samples were formed and cured in moulds for 24 h above the water. Then they were taken from the moulds and cured in water for 6, 13 and 27 days at the ambient temperature of (20 ±2) ºC. Samples of each mix were divided into two parts before mechanical tests. One part of samples was dried in oven at 105 ºC until the constant weight was reached.

Table 2. Cement pastes proportions

Paste code and label	Fibre to cement (wt %)		Cement (wt %)	Water to cement (w/c)
	WF	PP		
PC	–	–	100	0.4
0.75WF	0.75		100	0.4
1.5WF	1.50		100	0.4
3.WF	3.00		100	0.4
0.75PP	–	0.75	100	0.4
1.5PP	–	1.50	100	0.4
3PP	–	3.00	100	0.4
0.75WF0.75PP	0.75	0.75	100	0.4
1.5WF1.5PP	1.50	1.50	100	0.4

The mechanical tests were done by the Zwick Roell universal test machine of the capacity up to 50 kN and equipped with the testExpert® program. Both flexural and compressive strength tests were evaluated at sample ages of 7, 14 and 28 days according to LST EN 196:2007. Flexural strength tests were performed with the wet and dry samples at the rate of 0.2 mm/min. Then broken specimens were used for compressive strength tests performed at the rate of 0.5 mm/min. Values were expressed as average of 6 measurements.

Apparent density and apparent porosity results were obtained through the Archimedes method using water as the immersion liquid (in accordance with ISO 5017:1996). Water absorption test was performed on the cubic specimens (20 mm × 20 mm × 20 mm) who were cured in water for 28 days. Then dried until the constant weight was reached and the dry mass (M_d) for each sample was recorded. After that they were totally immersed in water at 20 ºC until they achieved constant saturated mass (M_s). The absorption capacity was calculated in percentage as a ratio of difference of saturated (M_s) and dry (M_d) mass to dry (M_d) mass.

Drying shrinkage test was performed with three prismatic specimens to each series of tested samples. They were removed from moulds after 24 hours after formation and put into measuring apparatus at ambient temperature of (20 ±2) ºC. Measurement apparatus consists of a measurement attachment and a base with adjustment screws. The measurement attachment is formed by a dial gauge, which reads accurately to 0.01 mm, rigidly mounted in a measuring frame. Reference rod was used as a standard length against which gauge readings were tested. The readings of the length were taken after 3, 7, 14 and 28 days. By statistical analysis, coefficient of variance defined as the percentage ratio of the standard deviation to the mean value was evaluated for all test results. In this study, coefficient of variance for flexural strength varied from 7.24 % up to 9.11 %; for compressive strength varied from 6.52 % up to 8.47 %; for water absorption test, apparent porosity and density was in a range from 1.89 % up to 2.38 %.

Scanning electron microscopy (JEOL, JSM 5600) was used to analyse the microstructure of the material. X-ray diffraction (XRD) patterns were obtained using Cu-K_α radiation (DRON-6) source. The existing phases were identified by the commercial Search Match program.

3. RESULTS AND DISCUSSION

The results of mean values of the flexural strength are presented in Figures 1 and 2 for the wet and dry samples respectively. It can be seen that flexural strength of the wet plain cement mix sharply increases up to 14 days and slightly after (Fig. 1). The same flexural strength growth shows samples with WF fibre addition. Contrary, strength of samples with hybrid fibre system rises sharply only after 14 days, meanwhile samples with PP fibres increases gradually during all hydration periods. At early age of hydration the higher was content of PP fibre the higher was flexural strength of wet cement mix which is in accordance with [2, 12]. Contrary, presence of 0.75 % and 3 % of WF fibre reduced strength by up to 19 % and 11 % respectively (Fig. 1). At the same age 3 % of hybrid fibre system enhanced flexural strength of plain cement paste by up to 23 % and by up to 28 % with 3 % of PP fibre. These only two groups of samples showed the highest strength results and after 28 days. Comparing with reference material flexural strength was 9 % and 3 % higher for 1.5WF1.5PP and 3PP respectively (Fig. 1).

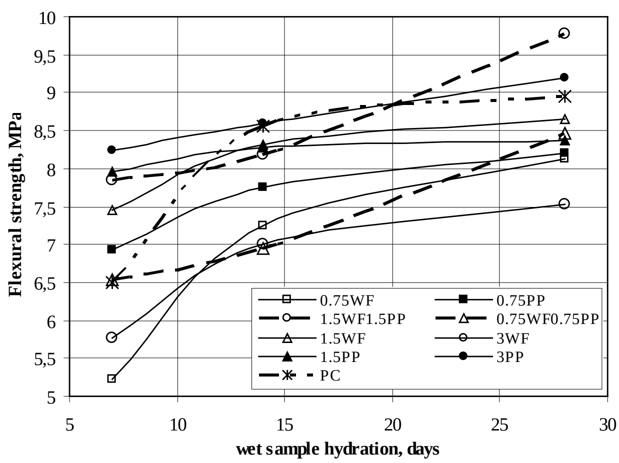


Fig. 1. Flexural strength of the wet cement paste as a function of sample aging time

Flexural strength of all samples tested increased when they were dried (Fig. 2). Dependences for the samples with PP fibres as well as with hybrid fibre system have the same character like in wet state. Contrary, flexural strength of the samples with 1.5 % of WF fibres sharply increased after 14 days of hydration (Fig. 2), and enhanced flexural strength of cement mix by up to 6 % at 28 day age. Meanwhile sample with 3 % of WF addition repeated character of the curve of the plain cement mixture, but the strength was one and a half lower and furthermore, the lowest from all tested samples.

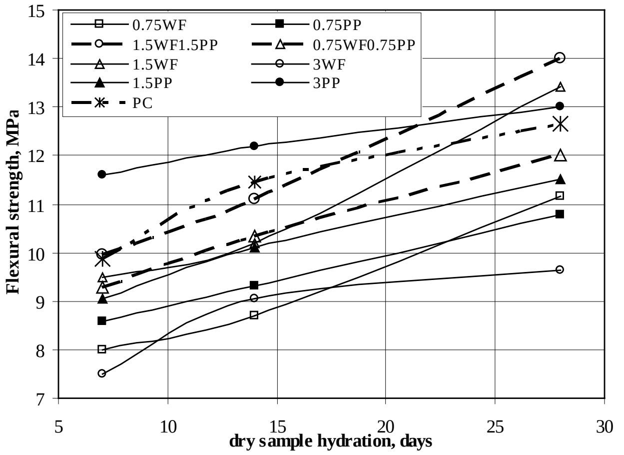


Fig. 2. Flexural strength of the dry cement paste as a function of sample aging time

Presence of 3 % of PP enhanced flexural strength of cement mix in all hydration period investigated, however it was only 3 % higher than reference material at 28 day age. The higher flexural strength (by up to 11 %) at the same age was indicated for sample with the hybrid fibre system (1.5WF1.5PP) and it was the best result obtained.

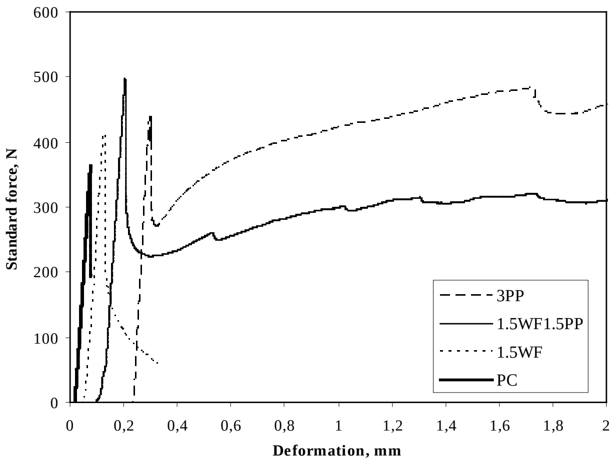
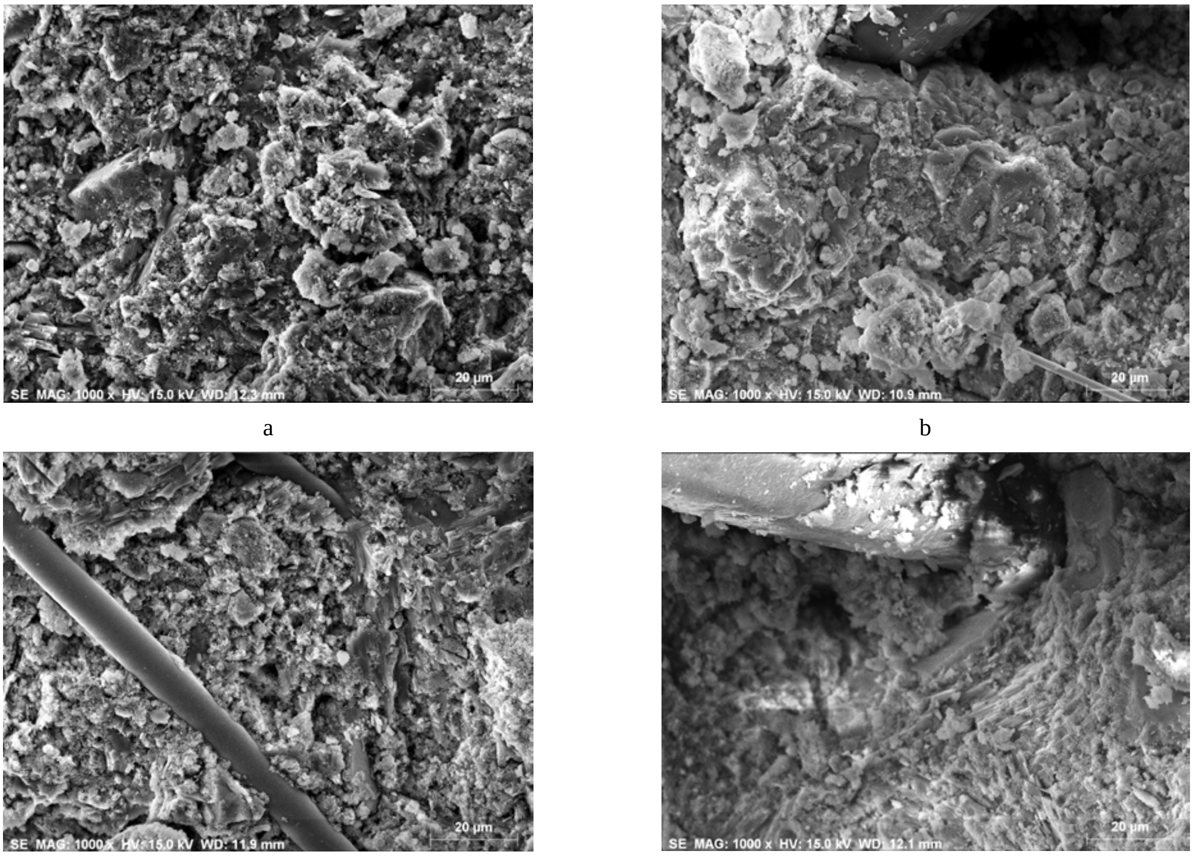


Fig. 3. Typical flexural load-deformation curves of the cement paste with and without fibre addition

Such a sharp increment in flexural strength could be related with fibres properties as well as their distribution in the material. Useful information gives load-deflection curves (Fig. 3). The initial linear response of curves up to first crack formation shows that material strained without damage. Beyond the flexural yield point, the maximum strain exceeded the strain capacity of the cementitious matrix causes the formation of local, randomly distributed, microcracks throughout the area of maximum strain in the



a b c d

Fig. 4. Microstructure of the cement paste at 28 days age: a – PC, b – 1.5WF1.5PP, c – 1.5WF and d – 1.5PP

sample. As the load increased the microcracks propagate and coalesced into more extensive damage (Fig. 3 first peak). However, the added fibres resisted the microcrack growth and resulted in the observed response (area after the first peak) which may be characterized by the sharp drop in the stiffness. Moreover, presence of 3 % of PP fibres showed fibre bridging across the macrocrack resulted in residual load capacity after the macrocrack formation. Consequently higher flexural strength of samples with 3 % of PP fibres was achieved not due to the matrix (small first peak), but due to fibres ability to withstand load (second wide peak), which is in agreement with [10]. Contrary, presence of smaller (more than three times) in diameter WF fibres leads to densification of the material (Fig. 4, Fig. 5) and consequently, toughness improvement. Distribution of WF and PP fibres can be observed in SEM micrographs (Fig. 4 b, d), where only small part PP fibres are visible in the top of figure. When hybrid fibre system was used reduction of porosity up to 6 % (Fig. 6) as well as slight increment in density was achieved at the age of 28 days (Fig. 5). On the other hand, it was noticed [2, 8, 13] that combination of fibres with different dimension and type controls cracks at different size levels in different zones of the sample, therefore increase in flexural strength was observed.

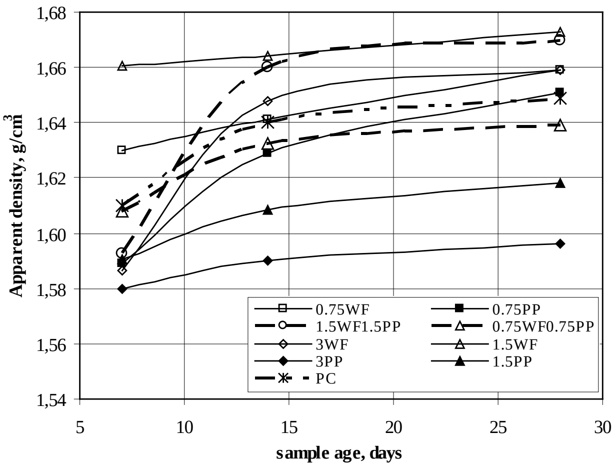


Fig. 5. Apparent density of the cement paste as a function of sample aging time

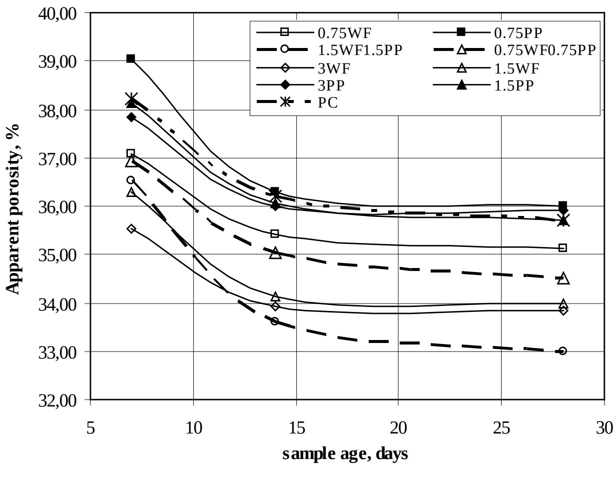


Fig. 6. Apparent porosity of the cement paste as a function of sample aging time

Analysis of wet and dry cement mixtures with fibre showed that compressive strength (Fig. 7 and Fig. 8) of the plain cement mix was the highest at all hydration periods investigated. It was observed that fibre type had no influence on compressive strength and strength decreases with the increasing fibre content which is in accordance with [2, 8]. In wet state hybrid fibre system as well as 3 % of fibres reduced compressive strength of the cement paste up to twice at early age of hydration (Fig. 7). Lower reduction up to 12 % was found for samples with 1.5 % of fibre addition (Fig. 7), while presence of 0.75 % of fibre reduced compressive strength up to 24 %. At the age of 28 days results divided into two groups – lower reduction (8 % – 13 %) gave samples with less than 2 % fibre addition, whereas decrease of (24 % – 27 %) was obtained for samples with 3 % of fibre (Fig. 7).

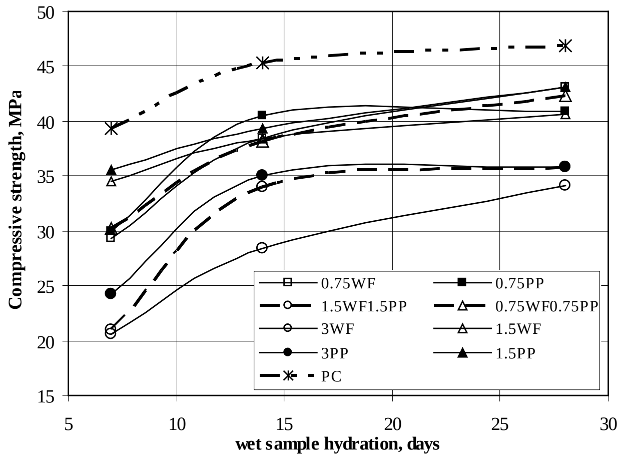


Fig. 7. Compressive strength of the wet cement paste as a function of sample aging time

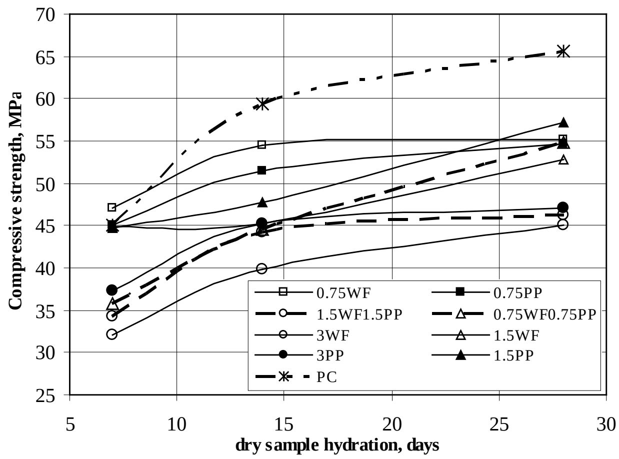


Fig. 8. Compressive strength of the dry cement paste as a function of sample aging time

Dry samples with less than 2 % of fibres at 7 day age exhibited approximately the same compressive strength as the reference material (Fig. 8). Contrary, at the same age from 17 % up to 28 % lower compressive strength was achieved for dry samples with hybrid fibre system as well as with 3 % of WF or PP fibre (Fig. 8). It was observed that compressive strength of dry samples with hybrid fibre system as well as the plain cement mix increased up to one and a half time after long hydration period. However, presence of fibre was still detrimental and reduced strength of samples with various types and content of fibre from 13 % up to 31 % at 28 days age (Fig. 8). Like in a wet state the lowest values were obtained for the dry cement paste with 3 % of WF fibre.

Such reduction in compressive strength could be attributed to the crystallization processes of the material during hydration. X-ray analysis (Fig. 9) showed that dry samples with the fibre had the same crystalline phases as the plain cement: alite – $3CaO{\cdot}SiO_2$ (C_3S), belite – $2CaO{\cdot}SiO_2$ (C_2S) and portlandite – $Ca(OH)_2$ (CH); but with the lower intensities at 28 days age.

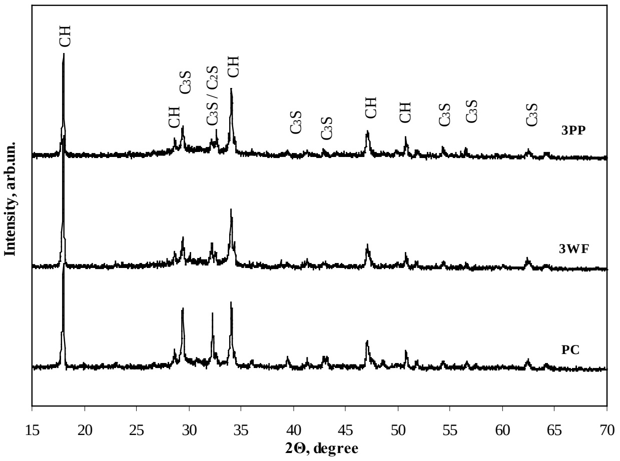


Fig. 9. XRD patterns of cement pastes at 7 days age

According to [21, 22] the main hydration period so-called induction period takes up to several hours and is responsible for the formation of dense C-S-H gel shells with a thickness of a few tens of nm. As C-S-H gel grows outward from the cement particles, it does not take the form of a monolithic solid phase but instead develops an internal system of tiny pores, called gel pores. Although the liquid water in the gel pores is not part of the solid C-S-H phase in a chemical sense, it is physically isolated and thus cannot undergo further chemical reaction with the cement minerals. This is the main reason for the range of water contents of C-S-H gel. The C-S-H gel, including its internal gel pores, occupies significantly more volume than the original C_3S and C_2S mineral that it replaces. C-S-H formation on the surface of alite and their growth is responsible for the layers of C-S-H gel expantion and interconection into continuous phase, causing the setting of cement paste and strength development [22]. On the other hand, part of water, which is not consumed in chemical reactions, is enclosed in microstructure and is responsible for the porosity and thus for the mechanical properties [21]. So, it could be assumed that incorporation of fibres affected C-S-H formation or growth and therefore lower compressive strength was achieved.

According to [3, 8, 21] water absorption reduces due to presence of fibres as well as with the increasing test age. It was observed (Fig. 10) that the water absorption of samples with PP fibres was higher than of the plain cement up to the age of 14 days. Contrary, samples with WF fibres determined lower absorption capacity than the reference material at various aging time. There is some interdependence between the porosity and water absorption of the samples. Comparison of the results shows that mixes with lower porosity (Fig. 6) absorbed lower amount of water (Fig. 10), thus they are potentially more durable. Samples with 3 % of mixed fibres absorbed up to 7 % less amount of water than the plain cement and it was the best result.

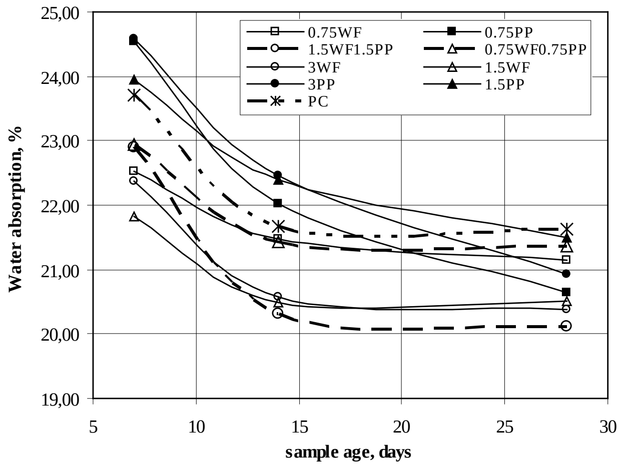


Fig. 10. Water absorption capacity of the cement paste as a function of sample age

Results of drying shrinkage are summarized in Table 3. Drying shrinkage of all samples was intensive up to 7 days and thereafter it increased slightly. The results show that drying shrinkage increases with the increasing content of fibres and they are slightly depending on the type of fibres used. It was also observed that drying shrinkage of the plain cement was the lowest after first 3 days, but it was the highest after 28 days. Shrinkage of others fibrous samples were lower than the plain cement and did not exceed 0.4 % value at 28 days age.

Table 3. Results of drying shrinkage

Cement paste code	$\Delta L/L$, %			
	3 days	7 days	14 days	28 days
PC	–0.16	–0.33	–0.37	–0.40
0.75WF	–0.18	–0.31	–0.35	–0.37
1.5WF	–0.19	–0.32	–0.36	–0.36
3WF	–0.20	–0.33	–0.37	–0.39
0.75PP	–0.18	–0.33	–0.37	–0.37
1.5PP	–0.19	–0.34	–0.36	–0.38
3PP	–0.19	–0.35	–0.37	–0.39
0.75WF0.75PP	–0.16	–0.31	–0.35	–0.36
1.5WF1.5PP	–0.17	–0.32	–0.35	–0.36

4. CONCLUSIONS

The following conclusions may be drawn:

– Incorporation of only WF into Portland cement reduced flexural strength of wet and dry cement mix. However, it was found optimum (1.5 %) content of WF when increment of flexural strength by up to 6 % was obtained after 28-days of hydration.
– Due to PP fibres ability to withstand load ant their combination with much smaller in diameters WF fibres results in increament of flexural strength of cement paste. Thus, flexural strength of hybrid fibre

system (1.5 % WF with 1.5 % PP) at the age of 28 days was 9 % and 11 % higher than reference paste in wet and dry state respectively.

- Compressive strength of wet and dry cement mix reduced with the addition of fibre as well as with the increase of fibre content. The lowest results showed samples with addition of 3 % WF.
- Presence of higher content of WF as well as hybrid fibre system reduced porosity and water absorption capacity of the cement paste. The mixed fibre system (1.5 % WF with 1.5 % PP) showed the best results and reduced water absorption by up to 7 % at 28 days age.
- The obtained results showed the possibility of application of the fibres produced from waste catalyst in ordinary Portland cement paste when a flexural strength is preferable.

REFERENCES

1. **Vieira, S. C., Ramos, A. S., Vieira, M. T.** Mullitization Kinetics from Silica- and Alumina-rich Wastes *Ceramics International* 33 2007: pp 59 – 66.
2. **Meddah, M. S., Bencheikh, M.** Properties of Concrete Reinforced with Different Kinds of Industrial Waste Fibre Materials *Construction and Building Materials* 23 2009: pp. 3196 – 3205.
3. **Asokan, P., Osmani, M., Price, A.** Improvement of the Mechanical Properties of Glass Fibre Reinforced Plastic Waste Powder Filled Concrete *Construction and Building Materials* 24 2010: pp. 448 – 460.
4. **Gopalakrishnan, R., Govindarajan, D.** Compressive Strength and Electron Paramagnetic Resonance Studies on Waste Glass Admixtured Cement *New Journal of Glass and Ceramics* 1 2011: pp. 119 – 124. http://dx.doi.org/10.4236/njgc.2011.13017
5. **Gomez, E., Amutha Rani, D., Cheeseman, C. R., Deegan, D., Wise, M., Boccaccini, A. R.** Thermal Plasma Technology for the Treatment of Wastes: A Critical Review *Journal of Hazardous Materials* 161 2009: pp. 614 – 626. http://dx.doi.org/10.1016/j.jhazmat.2008.04.017
6. **Bentchikou, M., Guidoum, A., Scrivener, K., Silhadi, K., Hanini, S.** Effect of Cellulose Fibre on the Thermal and Mechanical Properties of Cement Paste *Proc. International Conference RILEM* 2 2004: pp. 724 – 730.
7. **Fraternali, F., Ciancia, V., Chechile, R., Rizzano, G., Feo, L., Incarnato, L.** Experimental Study of the Thermo-Mechanical Properties of Recycled PET Fibre-reinforced Concrete *Composite Structures* 93 2011: pp. 2368 – 2374. http://dx.doi.org/10.1016/j.compstruct.2011.03.025
8. **Pereira-de-Oliveira, L. A., Castro-Gomes, J. P., Nepomuceno, M. C. S.** Effect of Acrylic Fibres Geometry on Physical, Mechanical and Durability Properties of Cement Mortars *Construction and Building Materials* 27 2012: pp. 189 – 196. http://dx.doi.org/10.1016/j.conbuildmat.2011.07.061
9. **Jamshidi, M., Ramezanianpour, A. A.** Laboratory and Industrial Investigations on Hybrid of Acrylic and Glass Short Fibres as an Alternative for Substituting Asbestos in Hatschek Process *Construction and Buildings Materials* 25 2011: pp. 298 – 302.
10. **Sukontasukkul, P., Pomchiengpin, W., Songpiriyakij, S.** Post-crack (or Post-peak) Flexural Responce and Toughness of Fiber Reinforced Concrete After Exposure to High Temperature *Construction and Building Materials* 24 2010: pp. 1967 – 1974.
11. **Siddique, R., Khatib, J., Kaur, I.** Use of Recycled Plastic in Concrete: a Review *Waste Management* 28 2008: pp. 1835 – 1852.
12. **Nili, M., Afroughsabet, V.** The Effect of Silica Fume and Polypropylene Fibres on the Impact Resistance and Mechanical Properties of Concrete *Construction and Building Materials* 24 2010: pp. 927 – 933.
13. **Chen, B., Liu, J.,** Residual Strength of Hybrid-Fiber-Reinforced High-Strength Concrete after Exposure to High Temperatures *Cement and Concrete Research* 34 2004: pp. 1065 – 1069.
14. **Gualtieri, A. F., Foresti, E., Lesci, I. G., Roveri, N., Gualtieri, A. M., Dondi, M., Zapparoli, M.** The Thermal Transformation of Man Made Vitreous Fibers (MMVF) and Safe Recycling as Secondary Raw Materials (SMR) *Journal of Hazardous Materials* 162 2009: pp. 1494 – 1506. http://dx.doi.org/10.1016/j.jhazmat.2008.06.066
15. **Yang, Sh.-Fu., Wang, T., Lee, W. Ch., Sun, K., Tzeng, Ch.** Man-Made Vitreous Fiber Produced from Incinerator Ash using the Thermal Plasma Technique and Application as Reinforcement in Concrete *Journal of Hazardous Materials* 182 2010: pp. 191–196.
16. **Ma, Y., Zhu, B., Muhua, T.** Properties of Ceramic Fiber Reinforced Cement Composites *Cement and Concrete Research* 35 2005: pp. 296 – 300.
17. **Canal, C., Ginebra, M. P.** Fibre-Reinforced Calcium Phosphate Cements: a Review *Journal of the Mechanical Behaviour of Biomedical Materials* 4 2011: pp. 1658 – 1671.
18. **Kalpokaitė-Dičkuvienė, R. Kėželis, R., Čėsnienė, J., Brinkienė, K., Baltušnikas, A., Milieška, M.** Microstructure Analysis of Fibrous Material Manufactured by Plasma Spray Method *Materials Science* (*Medžiagotyra*) 15 (3) 2009: pp. 262 – 265.
19. **Kalpokaite-Dickuviene, R., Cesniene, J., Brinkiene, K.** Influence of Fibres Content on Performance Parameters of Refractory Concrete *Mechanika* 18 (5) 2012: pp. 498 – 502.
20. **Milieška, M., Kėželis, R., Kalpokaitė-Dičkuvienė, R., Čėsnienė, J., Brinkienė, K., Mėčius, V.** Application of Plasma Technology for Nanofiber Formation from Oil Refinery Waste (Zeolite) *Power Engineering* 54 (4) 2008: pp. 54 – 58.
21. **Stark, J.** Recent Advantages in the Field of Cement Hydration and Microstructure Analysis *Cement and Concrete Research* 41 2011: pp. 666 – 678. http://dx.doi.org/10.1016/j.cemconres.2011.03.028
22. **Gallucci, E., Mathur, P., Scrivener, K.** Microstructural Development of Early Age Hydration Shells around Cement Grains *Cement and Concrete Research* 40 2010: pp. 4 – 13. http://dx.doi.org/10.1016/j.cemconres.2009.09.015