

Polypropylene fiber reinforced cement mortars containing rice husk ash and nano-alumina

Ehsan Mohseni^{1*}, Mojdeh Mehrinejad Khotbehsara¹, Farzad Naseri², Maryam Monazami³ and Prabir Sarker⁴

¹ Department of Civil Engineering, University of Guilan, Rasht, Iran

² Department of Civil Engineering, Islamic Azad University-East Tehran Branch, Tehran, Iran

³ Department of Civil Engineering, University of Shahrood, Shahrood, Iran

⁴ Department of Civil Engineering, Curtin University, Perth, Australia

*Corresponding Author: Mohseni@msc.guilan.ac.ir;

Ehsan.mohseni172@gmail.com

Tel: +98 9125590423

Abstract

This paper presents the effects of incorporating two supplementary cementitious materials: rice husk ash (RHA) and nano-Alumina (NA) in polypropylene fiber (PPF) reinforced cement mortars. RHA is an agricultural waste material and thus recycling of this material has substantial economic and environmental benefits. Compressive strength, flexural strength, water absorption and drying shrinkage of the hardened composites were investigated. The interfacial transition zone and the microstructures were studied by using Scanning Electron Micrograph (SEM) and X-ray Diffraction (XRD) analysis. A slight increase in compressive strength of mortar was observed by using up to 10wt% of RHA as a replacement of cement. However, addition of nano-Alumina helped the compressive strength of mortar remain approximately equal to that of the control specimen even when 20 or 30wt% RHA was used. Addition of polypropylene fibers resulted in significant increase in the flexural strength of the mortar specimens. It was also observed that NA and PPF could reduce water absorption by pore blocking effect. The positive interactions between polypropylene fibers and RHA resulted in the lowest drying shrinkage of the fibrous mortar containing RHA. XRD analysis showed that the intensity of Alite and Belite phases decreased and new peak of portlandite produced with the addition of NA. The addition of RHA enhanced the late strength of the cement composites. Consequently, the combined addition of RHA, NA and PPF has resulted in increasing of flexural strength and reduction in both water absorption and drying shrinkage of SCMs.

Key words: Polypropylene fiber; Rice husk ash; Nano- Al_2O_3 ; Compressive and flexural strength; Water absorption; Drying shrinkage.

35
36
37

1. Introduction

38

Concrete can be made greener by using waste materials that reduce its environmental impact such as the reduction of CO_2 emission in cement production. According to the European Cement Association, the concrete technology today allows for new buildings to be built with 60% less energy use and CO_2 emissions over the lifecycle of the building than conventional buildings constructed 20 years ago [1]. In the mix design, there are also extra steps taken to improve the sustainability of a structure with a long life cycle. Fly ash, blast furnace slag, recycled concrete, power plant waste, rice husk ash, waste glass, red mud, burnt clay, etc. are some of the waste materials used in concrete. Rice husk ash (RHA) is a carbon neutral green product and several ways are currently being used for disposing them [2-4]. Annually a large amount of rice is produced in the rural areas of different countries such as Iran, Malaysia, Thailand, Bangladesh, India, Pakistan, Myanmar etc. Huge quantities of rice husk are produced during the processing of this rice. The rice husk is used as fuel which generates the rice husk ash. Incorporating rice husk ash in concrete as a cement replacement has many environmental and economic advantages. RHA is a good pozzolan that can be used to make concrete. Using rice husk ash in concrete has been examined by many researchers around the world. The initial and important reviews on the use of RHA in concrete focused on the mechanical performance of concrete [2-9]. However, recent studies have mostly worked on the concrete properties when RHA with additional admixtures were incorporated [10-14]. Using wood fiber waste (WFW), rice husk ash (RHA), and limestone powder waste (LPW) as cement replacement materials in lightweight concrete blocks was studied by Torkaman et al. in 2013 [10]. The results indicated that the bulk density and water absorption of concrete samples were significantly reduced by the addition of RHA. Sharma [11] reported that up to 10% mass of cement can be replaced by RHA that is mixed with plastic fibers with nearly equivalent compressive strength.

39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

RHA was incorporated in different types of concrete such as normal concrete, self-consolidating concrete and high performance concrete [12-18]. Madandoust [12] reported that the use of 20wt% RHA in normal concrete reduced the early-age strength development. Safiuddin et al. [13] investigated the flowing ability of self-consolidating concrete and its binder paste and mortar components with rice husk ash. The results showed good improvement in the flow ability of the mixtures when the rice husk ash was added to the binder. The test results revealed that the w/b ratio and RHA content significantly influenced the flowing abilities of the binder pastes, mortars and concretes. However, using RHA may also decrease the flowing ability

66
67
68
69
70
71
72
73
74

of the self-compacting concretes. In another study, Safiuddin et al. [14] showed that the flowing ability of mortar mixtures decreased as the amount of RHA was increased. Robler et al. [15] reported that due to the mesoporous structure of RHA, it absorbs free water, so the w/b ratio in the cementitious matrix is reduced and the compressive strength is increased consequently.	75 76 77 78 79
Nanoparticles have been recently used as a cement replacement to tailor the mechanical properties of concrete [19-24]. These particles increase the cement hydration and act as a filler to reduce the porosity of mortar. Noorvand et al. [20] examined the effect of nano-TiO ₂ in black rice husk ash concrete. The results showed improvement in both mechanical and micro-structural properties of mortars with black rice husk ash. In their study, the compressive strength was found to increase by up to 18% when black rice husk ash and nanoparticles were used in the mortar. However, the compressive strength decreased by about 27% when black rice husk ash was used singly.	80 81 82 83 84 85 86 87 88
Polypropylene fiber (PPF) was incorporated in concrete for many years to enhance the flexural properties and also restrain the progression of cracks [25-31]. It also improves the strength of concrete against impacts and fatigue. Medina [30] reported that the cracking control ability of PPF on the exposed concrete surface reduced water permeability and CO ₂ diffusion. It also increased porosity and reduced bulk density and the ultrasonic modulus of natural pozzolan cement concretes.	89 90 91 92 93 94
The ingress of various ions from the environment and its movement through building materials are the main reasons for deterioration of structures. So, the control of the permeability of concrete plays an important role in providing resistance to aggressive environment [32]. In this study, a novel combination of nano-alumina (NA), RHA and PPF was used in concrete. The aim was to partially replace Portland cement by RHA and make mixtures of improved properties in hardened stages by the addition of NA and PPF.	95 96 97 98 99 100 101 102
2. Experimental program	103
2.1 Materials	104
Natural river sand and ordinary Portland cement type I conforming to ASTM C778 [33] and ASTM C150 [34], respectively were used. According to the ASTM standard, rice husk ash (RHA) can be used as a pozzolanic material with cement [35]. The particle size distribution curve of RHA is given in Fig. 1. The physical properties of RHA substantially depend on the burning conditions. Particularly, the temperature and period of burning influence on the microstructure and crystallinity of RHA [36]. The partial burning of rice husks produces black RHA whereas the	105 106 107 108 109 110 111

complete burning results in either white or gray RHA. Hwang & Chandra [37] 112
suggested that burning rice husk at temperatures below 700°C provides amorphous 113
silica. In this study the husk was sourced from Rasht, Iran and an electric kiln was 114
used to burn the rice husk pellets. Heating cycles were conducted by an electric 115
system with a heating rate of 5°C/min. Each sample was held at temperatures 116
between 500 and 700°C for 6 hours. The XRD results illustrate that when the RHA 117
was burned within 300°C to 700°C, it turned into amorphous silica. For instance, the 118
XRD pattern of the ash indicates the presence of noncrystalline silica as seen in Fig. 119
2. RHA is mainly composed of silica, which constitutes 91% of the total mass. This 120
amount of silica is seen as Quartz in XRD diagram of RHA. The chemical 121
composition and physical properties of cement and RHA are given in Table 1. Nano- 122
Al₂O₃ in dispersed suspension form with an average particle size of 20 nm, specific 123
surface area of 200m²/g and purity of higher than 98% was used in this study. Fig. 2- 124
a and 2-b show the XRD diagrams of the nano-Al₂O₃ and RHA. The scanning 125
electron micrographs (SEM) of nano-Al₂O₃ and RHA are given in Fig. 3. It can be 126
seen from these figures that nano-Al₂O₃ particles are spherical while the RHA 127
particles are of irregular shape. In order to achieve the desired fluidity and better 128
dispersion of the nanoparticles, a polycarboxylate type superplasticizer (SP) 129
conforming to ASTM C494 [38] with a density of 1.03 g/cm³ was utilized. The 130
content of superplasticizer was adjusted for each mixture to keep the slump flow of 131
mortars 25±1 cm. 132

Polypropylene fibers (PPF) produced from recycled raw materials was chosen 133
because of its high resistance to corrosion and chemical leaching, its resilience 134
against impact and freezing, and its environmental benefits. A photograph of the 135
fibres is shown in Fig. 4 and the properties of the fibres are given in Table 2. The 136
fibres with a length of 6 mm and a diameter of 20 micron making an aspect ratio of 137
300 was utilized at a dosage of 0.3% by volume. 138

2.2 Mix proportions 139

Twenty six mixtures were prepared with different amounts of RHA, NA, PPF and 140
SP. The percentage of RHA was varied between 0 and 30% by weight of the total 141
binder. The percentage of nanoparticles was 0, 1, 2 and 3%, and PPF was used in 0 142
and 0.3% of the binder. The amount of SP varied between 0.2 and 1% by weight of 143
the binder. The water to binder ratio (w/b) was kept constant at 0.49 for all mixtures. 144
Detailed mix proportions of the mortars are given in Table 3. In labeling of the 145
mixtures, the number after RHA, NA and PPF represents the percentage of rice husk 146
ash, Nano-Alumina and Polypropylene fibres respectively. 147

2.3 Production of specimens 148

Nanoparticles may not always show a uniform distribution in the mixture due to 149
their large surface area [39]. As this could directly affect the physical and 150

mechanical properties of the mortars, the specimen production procedure used in this study was carried out in accordance with the ASTM C305 standard [40]. However, some change in the mixing procedure was necessary due to presence of nanoparticles. Masks and gloves were used to avoid direct contact with the fine particles during the mixing. First, the cement and RHA were dry mixed in the mixer at a moderate speed (80rpm) for 1 min. Then, these components were mixed at a high speed (120rpm) for 90 seconds with the nanoparticles, 90% of the water and the specified amount of fibers. The sand was then gradually added over a period of 30 seconds while the mixer was running at a moderate speed (80rpm). Eventually the superplasticizer and remaining water were added and stirred at high speed (120rpm) for 30 seconds. After this, the mixture was allowed to rest for 90 seconds and then mixing was continued for 1 minute at a high speed (120rpm). This mixing procedure was followed to facilitate the distribution of the nanoparticles and the fibers in the mortar.

Fresh mortar was cast into 50×50×50 mm cubes for compressive strength and water absorption tests and in 50×50×200 mm steel moulds for flexural and shrinkage tests. The specimens were compacted using a tamping rod to exclude the air bubbles from the mortar. The specimens were demoulded 24 hours after casting and cured in water at 23±3 °C until they were tested.

2.3 Test procedure

Compressive strength test was conducted in accordance with the ASTM-C109 standard [41] using a hydraulic testing machine at a loading rate of 1350N/s. The three-point (i.e. center-point) loading flexural test was carried out with the span of 180mm and at a loading rate of 44N/s. The compressive and flexural strength results were determined at 28 and 90 days of curing. The average value of the test results of three specimens was reported.

The water absorption test was carried out at 28 days of age. Saturated surface dry specimens were kept in an oven at 110°C for 72 hours. After determination of the initial weight, the specimens were immersed in water for 72 hours. The final weight was then determined and the absorption was calculated to assess the permeability of the mortar specimens. The absorption value was obtained by taking an average of the test results of two specimens.

To determine the drying shrinkage, (50×50×200) mm prisms were tested in accordance with ASTM C157-89 [42]. Two gauge studs were inserted at the two ends (along the center axis) of each specimen immediately after casting of the specimens. The specimens were demoulded 24 hours later and placed in water for 7 days. After this the specimens were removed from water and the initial dial gauge readings were taken immediately. Then the specimens were stored in dry room of the laboratory with temperature of 23±2°C and a relative humidity of 50±4%. The

length change tests were taken at ages (7, 28, 60 and 90) days. The length change of specimens was measured by means of a length comparator conforming to the requirement of ASTM C490-00a [43]. The specimen was rotated slowly in the measuring device, while the measurement of length was being made. The accuracy of the dial gauge of the measuring device was 0.002 mm. The average value of four readings from two prisms was adopted for each mix.

3. Results and discussion

3.1. Compressive strength

The compressive strength values of mortar specimens are given in Table 4 and the variations of strength with age are plotted in Fig. 5. The results show a slight increase in compressive strength by the addition of RHA up to 10wt% and a reduction in strength with further increase in the RHA content. The improvement in the strength of mortars incorporating RHA, especially at later ages is due to its pozzolanic action. The calcium silicate hydrate (CSH) gel produced by the reaction of the high silica content of RHA with the $\text{Ca}(\text{OH})_2$ generated from the hydration of cement contributes to the continued increase of strength at the later ages. Similar effect of RHA was also observed in previous works [12]. Giaccio et al. [44] showed in the experiments that incorporating RHA as 10wt% of the binder improved the compressive strength of concrete samples. Gastaldini et al. [45] also reported enhancement in compressive strength, when RHA was used as partial replacement of cement. However, excessive amounts of RHA could decrease the compressive strength. Figs. 6-a, 6-b and 6-c show the SEM images of control specimen, a specimen with 10%RHA, and a specimen with 10%RHA and 3%NA, respectively. The solid phase of mortar is composed of 5 parts: C-S-H, C-H, ettringite, monosulfate and residual unhydrated cement. These 5 parts are different in their volume fraction, density, dimensions, morphology and Christianity. So characterization is usually done by SEM micrograph, especially for understanding the morphology and dimensions of solid parts. Unreacted materials are materials that do not resemble to any products of the hydration. The black spaces in SEM photos are the capillary pores which are decreased, when nano- alumina is added. As a definition, capillary pore is the space which is not taken up by the cement and hydration products (dependent on w/c); 2.5-50nm in size in well-hydrated concrete. These pores are irregular in shape, also size and amount are related to w/c and degree of hydration. Micropores with diameter less than 50 nm are more crucial for drying shrinkage and creep and macropores with diameter more than 50 nm are more significant for strength. As it is seen in Fig. 6-b, the amount of pores is reduced by the addition of RHA in comparison with that of the specimen without RHA as shown in Fig. 6-a. However, couple of unreacted particles can be clearly seen in Fig. 6-b.

Using nanoparticles fostered the compressive strength of specimens substantially.	230
The effect of nanoparticles in mortars can be summarized in the following 3 steps:	231
1. Nano-Alumina works as fillers to fill the pores, so the compactness of samples is enhanced [46]. As it can be seen in SEM images of the specimen with RHA and NA in Fig. 6-c, there are fewer and smaller pores and the microstructure is more compacted when NA is added. This is due to the fact that nanoparticles are expected to affect the kinetics and hydration of cement substantially and yield greater filling of voids of cement-based composites in comparison with the mineral additives in virtue of their larger surface area and greater electrostatic force.	232 233 234 235 236 237 238
2. Hydration of cement is a sum of chemical reactions between cement and water. A third type of material may affect the hydration process. High specific surface of nano-alumina particles accelerates the hydration process by rapid dissolution of cementitious compounds. This led to the formation of clusters of calcium aluminosilicate (C-A-S-H) gel.	239 240 241 242 243
3. Nanoparticles make the cement matrix homogenous and makes the structure compacted. As it is shown in Fig. 6-c, there are less unhydrated cement and more homogenous cement matrix in comparison with the control sample.	244 245 246
Table 4 also shows that when the amount of RHA is 30%, using NA more than 2 % has an inverse effect and decreases the compressive strength. When a mixture contains 30% RHA, for the rest of 70% cement, homogeneous hydrated microstructure cannot be formed, because the nanoparticles cannot be well dispersed. By addition of excessive amount of nanoparticles, they replace part of the cementitious materials, nonetheless this does not affect the strength and the excess silica will leach out and cause a deficiency in strength. Dispersion of nanoparticles is the main reason of the formation of homogeneous structure that is an important factor in compressive strength of a specimen. So despite the best result was achieved when 3% NA was used, using 2% NA gives the best average mechanical and economical results.	247 248 249 250 251 252 253 254 255 256 257
As expected, the results also show that addition of PPF did not have a significant effect on the compressive strength of samples. Also in some specimens like RHA20NA3 addition of PP decreases the compressive strength slightly. According to the Table 5, RHA10NA3PP0.3 showed the best result, as the increase percentage was 18.2 and 20.1 at 28 and 90 days respectively.	258 259 260 261 262
Also the outstanding impact of age on improvement of compressive strength can be seen in Table 4. In all samples, percentage of decrease was lowered or the percentage of increase was heightened, when the curing time increased from 28 days to 90 days. In the mixtures with RHA, the amount of cement is lower than in the control sample. So at the early ages, the structure was less compact and the volume	263 264 265 266 267

of pores increased as the amount of RHA increased. As the age of curing increased, the pozzolanic reactions increased that caused a higher density of the product. Presence of nanoparticles was the other way of filling the pores when RHA is incorporated. The similar comparison was also reported by Chao-Lung et al. [47]. The results are similar between early age and 28 days of curing. As a result, the process of improving compressive strength and the pozzolanic reactions are started at early ages and continued at least up to the age of 90 days.

3.2. Flexural strength

The flexural strength results are presented in Table 5, while the variation of flexural strength with time is shown in Fig. 7. The results indicate the outstanding effect of adding PPF in the improvement of flexural strength. It can be seen that the mixes with PPF and RHA showed higher values in comparison with that of the control sample. Also, flexural strength of specimens incorporating nanoparticles in most cases was higher than that of the control sample. However, these particles strengthen the weak region that is between cement paste and RHA. The SEM images of specimens incorporating RHA, NA and PPF, which are given in Figs. 9-a and 9-b, confirm this statement. The nanoparticles fill the pores especially porous portlandite crystals which array in the interfacial transition zone (ITZ) between cement matrix and RHA.

It can be seen in Table 4 that the addition of 30wt% RHA lowered the flexural strength up to about 14%. Instead the addition of 0.3% PPF boosted flexural strength up to 14%, which was equal to the value for the control sample. By comparison of Fig. 6-b and Fig. 8-a, it is evident that using PPF can balance out the negative effects of RHA incorporation. As it is shown, PPF in mortars look like very small bars that can control the crack propagation.

The results also show that when the amount of RHA is 30%, adding nanoparticles more than 2% lowers the flexural strength by about 1.5%. This result was also obtained in compressive strength test. The effect of aging on improvement of flexural strength is also evident. In all samples the percentage decrease was improved when specimens were tested after 90 days of curing.

It is verified that specimens that were not reinforced with PPF exhibited brittle failure. These failures started with micro cracks in the cement-aggregate interface that then propagated as the load increased. The PPF reinforced specimens, however, exhibited ductile failure. The initial cracks started in the cement matrix, but they did not propagate as fast as in the case of plain mortar specimens. This is due to the reinforcing ability of PPF to limit cracking from its unique high strength bond with the cementitious materials. Microscopic analysis of mortar fracture surface (Fig. 9a and 9b) shows that micro cracks exist at the aggregate-matrix interface of the plain mortar specimen even before any load has been applied to the mortar. The formation

of such cracks is due primarily to the strain and stress concentrations resulting from the incompatibility of the elastic moduli of the aggregate and paste components. On the other hand, the strong bond between the fibers and cement paste in the PPF reinforced mortar specimen reduces such cracks (Fig. 9c). The composite system of mortar reinforced with PPF is assumed to work as if it were unreinforced until it reaches its “first crack strength.” It is from this point that the reinforcing fibers take over and hold the mortar together.

Typical flexural load displacement response of different mixtures containing 0.3% PPF and 3% nano- Al_2O_3 at 90 days are represented in Fig. 10. The test was controlled automatically by computer with a constant cross head movement of 1mm/min. As it is evident, unreinforced mortar demonstrated brittle behavior. The samples fully fractured with the increase of mid span displacement after peak load, while fiber reinforced mortar exhibited ductile behavior. Study of the load-displacement curve showed that mortar containing nano- Al_2O_3 was obviously more brittle than that of control mortar, however, integrating PP fibers somewhat compensated this shortage. A relatively big increase was observed when increasing the PPF content to 0.3%. When cracks occurred and propagated, the fibers were able to bridge across the cracks, preventing the crack-face separation. The fibers sustained the load until they pulled out from the matrix. This mechanism provides an additional energy absorption which led to a stable fracture process and higher fracture energy. The presence of nano- Al_2O_3 enhanced the efficiency of the transfer of load from matrix to fiber by increasing the friction coefficient between the fiber and the matrix. Hence the sample containing PP fibers and nano- Al_2O_3 showed a higher peak-load with long post-peak curve as compared to the other samples, as shown in Fig. 10. When enough PPF is distributed in the matrix to bridge any growing micro crack, the additional energy is consumed in breaking or pulling out the fibers, hence, leading to higher failure load and toughness to the material.

3.3 Water absorption test

Water absorption of concrete is a measure of the capillary forces exerted by the pore structure that causes fluids to be drawn into the body of the materials [48].

The experimentally obtained results are presented in Fig. 11. Each of them is the mean value of three samples tested at 28 days of curing. In general, the results showed small reductions in the absorption values when RHA was added.

Using fine particles such as RHA leads to the segmentation of large pores and fosters nucleation sites for precipitation of hydration products in cement paste. However, the replacement of cement by RHA up to 10% also reduced the water absorption of specimens. Addition of RHA more than 10% leads to an increment of water absorption. The increase in water absorption in samples with a relatively high content of pozzolans is associated with the decrease of ordinary Portland cement,

which reduces the hydration products in specimens. As shown in Fig. 6, it was observed that the incorporation of RHA in mortars could lead to extensive pore refinement in both the matrix and the interfacial zones. The resulting pore refinement can effectively decrease the water permeability.

However increase in the amount of nano-Alumina and also PPF further reduced the water absorption. Due to very high specific surface area, the nanoparticles contained some free water on the surface, which resulted in continuous hydration that made the matrix more compacted. This seems like that external curing time for mortar samples. The percentage of water absorption is related to the porosity of the hardened mortar which is engaged by water in a saturated state [5].

3.4 Drying shrinkage

Fig. 12 shows the variations of drying shrinkage over time for mortars made with different percentages of RHA and PPF. The drying shrinkage of mortars is highly related to the stiffness of aggregates and their porosity. As seen from the figure, both RHA and PPF reduced the drying shrinkage of the mortar mixtures. All the specimens started to shrink gradually after removal from water. This is in virtue of the modification of pore size distribution and the interfaces beside the rapid loss of moisture from the surface of the specimens having high cement content. The results show that drying shrinkage values increased with time and the rate decreased after about 10 weeks of age. The drying shrinkage of the mortars with RHA after 90 days ranged from 801 to 843 microstrains. Mortars made with RHA exhibited lower drying shrinkage after 90 days compared with that of the control specimen. Drying shrinkage (after 90 days) decreased by 5% to 12% when RHA increased from 10% to 30%. The variation in shrinkage with water content may be introduced by the difference in types of water lost at a wide range of stages of drying. It is also associated with the modulus of elasticity of the sample. Mortar with high water content has a lower strength and lower modulus of elasticity and hence has a greater tendency to shrinkage. Due to the higher surface area of RHA in comparison with cement, such fine particles (RHA) can absorb more water, which leads to reduction of water content and consequently the drying shrinkage is reduced. On the other hand, incorporating PPF also reduced the drying shrinkage of mortars. At 90 days, the drying shrinkage values were 729, 680, 651 and 622 microstrains for mixtures PP0.3, RHA10PP0.3, RHA20PP0.3 and RHA30PP0.3, respectively. Malhotra et al. [49] concluded that polypropylene fiber reinforced high volume fly ash concrete has very low drying shrinkage property. Liu et al. [50] and Salih and Al-Azaawee [51] stated that polypropylene fiber mixed into cement mortar decreased its dry-shrinkage. They concluded that the reduction in drying shrinkage increased with the increasing volume fraction of fibers. Kirca and Sahin [52] supported this finding and reported that the use of polypropylene fibres restrained the movements in micro level by bridging and stitching the fine cracks. This is attributed to the ability of

polypropylene fibers to minimize the density of cracks, crack length and width, which can limit the shrinkage. 386
387

3.5 X-ray Diffraction 388

Fig. 13 illustrates the XRD analysis of mortar with and without Al_2O_3 nanoparticles at 7 days of curing. Ettringite, portlandite, Alite and Belite were found to be major phases for the specimens. Changes in peak height and formation of new peaks were found at 7 days. Intensity of Alite and Belite phase decreased and a new peak of portlandite (2 theta of 16, 28 deg.) were found. However, no other new crystalline phase was found with nano- Al_2O_3 addition. The results indicate that, $\text{Ca}(\text{OH})_2$ crystals (portlandite) which needs for formation of C-S-H gel appears in mortars containing nanoparticles, while for sample without nanoparticles, it is not appeared demonstrating synergic influence of nanoparticles on formation of subsequent C-S-H gel. 389
390
391
392
393
394
395
396
397
398

Conclusion 399

The following conclusions are drawn from the current study on mortars with incorporation of RHA, nano- Al_2O_3 and polypropylene fibers: 400
401

- The addition of RHA increased the 28-day compressive strength of samples up to 1% from their original level when cement was replaced by 10% RHA. Nevertheless addition of 20% and 30% RHA decreased compressive strength by up to 11% and 14%, respectively. However, this rate decreased at the age of 90 days. 402
403
404
405
- The addition of RHA reduced the 28-day flexural strength of samples up to 2%, 11%, and 14% from their original level when cement was replaced by 10%, 20% and 30% RHA. However, higher strength development was observed at 90 days when RHA content was increased from 10% to 30%. Incorporation of nano- Al_2O_3 enhanced the compressive and flexural strengths of samples containing 10% and 20% RHA. However, strength of the specimens containing 30% RHA enhanced when cement was replaced by 2% nano- Al_2O_3 . The most advantageously effective amount of nano- Al_2O_3 was 3% by weight of the binder. For instance, the compressive strength increased up to 18% and 20% when 3% nano- Al_2O_3 was added to samples with 20% RHA at 28 and 90 days, respectively. Also, the 28-day and 90-day flexural strengths were enriched by up to 34% and 41% respectively, when 3% nano- Al_2O_3 was added to the samples with 10% RHA. Therefore, incorporation of nano- Al_2O_3 compensated the strength loss caused by 10% and 20% cement replacement by RHA. Furthermore, the strength development from 28 to 90 days was more in samples containing RHA at all levels. 406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
- Water absorption of the specimens slightly decreased by the addition of 10% RHA and the values were same as that of the control sample with further increase of RHA up to 30%. Water absorption further decreased with the increase of nano- Al_2O_3 dosage up to 3%. 421
422
423
424

- Incorporation of polypropylene fiber enhanced the flexural strength of samples remarkably. The 28-day and 90-day flexural strengths increased by 18.6% and 23.1% respectively when 0.3% PPF was added to mixtures containing 10% RHA and 1% NA. 425
426
427
428
- SEM images confirmed the formation of denser microstructure with nano- Al_2O_3 addition. The densification of the microstructure is attributed to the formation of additional CSH by the RHA and CASH by the Al_2O_3 . The compact microstructure improved bonding of the fibres with the matrix, which improved the flexural strength of the mortar specimens. 429
430
431
432
433
- Presence of RHA and PPF in mortars, both separately and together reduced drying shrinkage. The positive interaction between polypropylene fibers and rice husk ash resulted in the lowest drying shrinkage of the fibrous mortars. 434
435
436

References 437

- [1] The European Cement Association, CEMBUREAU, Activity Report 2013, www.cembureau.eu 438
439
- [2] Goncalves M.R.F. Thermal insulators made with rice husk ashes: Production and correlation between properties and microstructure, Construction and Building Materials, 2007;21:2059–2065 440
441
442
- [3] Faiziev S, Synthesis of ceramic compounds utilizing woody waste materials and rice husk, Construction and Building Materials Materials Science Forum Vols. 437-438 (2003) pp 411-414 21 2059–2065. 443
444
445
- [4] Basha E A, Hashim R, Mahmud H B and Muntohar A S, Stabilization of Residual Soil with RHA and Cement, Construction and Building Materials, 2005;19:6:448-453. 446
447
448
- [5] Al-Khalaf, Moayad N., and Hana A. Yousif. "Use of rice husk ash in concrete." International Journal of Cement Composites and Lightweight Concrete 6, no. 4 (1984): 241-248. 449
450
451
- [6] Nehdi, Moncef, J. Duquette, and A. El Damatty. "Performance of rice husk ash produced using a new technology as a mineral admixture in concrete." Cement and concrete research 33, no. 8 (2003): 1203-1210. 452
453
454
- [7] Ismail, Muhammad Shoaib, and A. M. Waliuddin. "Effect of rice husk ash on high strength concrete." Construction and Building Materials 10, no. 7 (1996): 521-526. 455
456
457
- [8] Mehta, Povindar K. "Properties of blended cements made from rice husk ash." In ACI Journal Proceedings, vol. 74, no. 9. ACI, 1977. 458
459

[9] Ganesan, K., K. Rajagopal, and K. Thangavel. "Rice husk ash blended cement: assessment of optimal level of replacement for strength and permeability properties of concrete." <i>Construction and Building Materials</i> 22, no. 8 (2008): 1675-1683.	460 461 462
[10] Torkaman, Javad, Alireza Ashori, and Ali Sadr Momtazi. "Using wood fiber waste, rice husk ash, and limestone powder waste as cement replacement materials for lightweight concrete blocks." <i>Construction and Building Materials</i> 50 (2014): 432-436	463 464 465 466
[11] Sharma, R. K. "Effect of substitution of cement with rice husk ash on compressive strength of concrete using plastic fibres and super plasticizer." <i>KSCE Journal of Civil Engineering</i> 18.7 (2014): 2138-2142.	467 468 469
[12] Madandoust, Rahmat, Malek Mohammad Ranjbar, Hamed Ahmadi Moghadam, and Seyed Yasin Mousavi. "Mechanical properties and durability assessment of rice husk ash concrete." <i>Biosystems Engineering</i> 110, no. 2 (2011): 144-152.	470 471 472
[13] Safiuddin, Md, J. S. West, and K. A. Soudki. "Flowing ability of self-consolidating concrete and its binder paste and mortar components incorporating rice husk ash." <i>Canadian Journal of Civil Engineering</i> 37, no. 3 (2010): 401-412.	473 474 475
[14] Safiuddin, Md, J. S. West, and K. A. Soudki. "Flowing ability of the mortars formulated from self-compacting concretes incorporating rice husk ash." <i>Construction and Building Materials</i> 25, no. 2 (2011): 973-978.	476 477 478
[15] Rößler, Christiane, Danh-Dai Bui, and Horst-Michael Ludwig. "Rice husk ash as both pozzolanic admixture and internal curing agent in ultra-high performance concrete." <i>Cement and Concrete Composites</i> 53 (2014): 270-278.	479 480 481
[16] Kishore, Ravande, V. Bhikshma, and P. Jeevana Prakash. "Study on strength characteristics of high strength rice husk ash concrete." <i>Procedia Engineering</i> 14 (2011): 2666-2672	482 483 484
[17] Memon, Shazim Ali, Muhammad Ali Shaikh, and Hassan Akbar. "Utilization of rice husk ash as viscosity modifying agent in self compacting concrete." <i>Construction and building materials</i> 25, no. 2 (2011): 1044-1048.	485 486 487
[18] Van Tuan, Nguyen, Guang Ye, Klaas Van Breugel, Alex LA Fraaij, and Danh Dai Bui. "The study of using rice husk ash to produce ultra high performance concrete" <i>Construction and Building Materials</i> 25, no. 4 (2011): 2030-2035.	488 489 490
[19] Madandoust, R., E. Mohseni, S.Y. Mousavi and M. Namnevis, 2015. An experimental investigation on the durability of self-compacting mortar containing nano-SiO ₂ , nano-Fe ₂ O ₃ and nano-CuO. <i>Construct. Build. Mater.</i> , 86: 44-50.	491 492 493

[20] Noorvand, Hassan, Abang Abdullah Abang Ali, Ramazan Demirboga, Nima Farzadnia, and Hossein Noorvand. "Incorporation of nano TiO ₂ in black rice husk ash mortars." <i>Construction and Building Materials</i> 47 (2013): 1350-1361.	494 495 496
[21] Mohseni, E., M.M. Ranjbar, M.A. Yazdi, S.S. Hosseiny and E. Roshandel, The effects of silicon dioxide, iron(III) oxide and copper oxide nanomaterials on the properties of self-compacting mortar containing fly ash. <i>Magaz. Concrete Res.</i> 2015;67;20:1112-1124	497 498 499 500
[22] Yang, J., E. Mohseni, B. Behforouz and M.M. Khotbehsara, An experimental investigation into the effects of Cr ₂ O ₃ and ZnO ₂ nanoparticles on the mechanical properties and durability of self-compacting mortar, <i>International Journal of Materials Research</i> , 106;8;886-892.	501 502 503 504
[23] Khotbehsara M.M., Mohseni E, Yazdi M.A, Sarker P, and Ranjbar M.M, Effect of nano-CuO and fly ash on the properties of self-compacting mortar. <i>Construct. Build. Mater.</i> , 2015;94:758-766.	505 506 507
[24] E. Mohseni, M.M. Ranjbar and K.D. Tsavdaridis, Durability Properties of High-Performance Concrete Incorporating Nano-TiO ₂ and Fly Ash, <i>American Journal of Engineering and Applied Sciences</i> 2015, 8;4:519.526.	508 509 510
[25] Bayasi, Ziad, and Jack Zeng. "Properties of polypropylene fiber reinforced concrete." <i>ACI Materials Journal</i> 90, no. 6 (1993).	511 512
[26] Bayasi, Ziad, and Jack Zeng. "Properties of polypropylene fiber reinforced concrete." <i>ACI Materials Journal</i> 90, no. 6 (1993).	513 514
[27] Mydin, Md Azree Othuman, and Sara Soleimanzadeh. "Effect of polypropylene fiber content on flexural strength of lightweight foamed concrete at ambient and elevated temperatures." <i>Advances in Applied Science Research</i> 3, no. 5 (2012): 2837-2846...	515 516 517 518
[28] Ramezaniyanpour, A. A., M. Esmaili, S. A. Ghahari, and M. H. Najafi. "Laboratory study on the effect of polypropylene fiber on durability, and physical and mechanical characteristic of concrete for application in sleepers." <i>Construction and Building Materials</i> 44 (2013): 411-418	519 520 521 522
[29] Alhozaimy, A. M., P. Soroushian, and F. Mirza. "Mechanical properties of polypropylene fiber reinforced concrete and the effects of pozzolanic materials." <i>Cement and Concrete Composites</i> 18, no. 2 (1996): 85-92.	523 524 525
[30] Flores Medina, N., G. Barluenga, and F. Hernández-Olivares. "Enhancement of durability of concrete composites containing natural pozzolans blended cement	526 527

through the use of Polypropylene fibers." <i>Composites Part B: Engineering</i> 61 (2014): 214-221.	528 529
[31] Bagherzadeh, Roohollah, et al. "An investigation on adding polypropylene fibers to reinforce lightweight cement composites (LWC)." <i>Journal of Engineered Fibers and Fabrics</i> 7.4 (2012): 13-21.	530 531 532
[32] Salas, Andres, et al. "Comparison of two processes for treating rice husk ash for use in high performance concrete." <i>Cement and concrete research</i> 39.9 (2009): 773-778.	533 534 535
[33] ASTM C778-13 (2011) Standard Specification for Standard Sand, in: <i>Annual Book of ASTM Standards</i> , ASTM, Philadelphia, PA.	536 537
[34] ASTM C150 (2011): Standard specification for Portland cement, in: <i>Annual Book of ASTM Standards</i> , ASTM, Philadelphia, PA.	538 539
[35] ASTM C311 (2011) Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete, in: <i>Annual Book of ASTM Standards</i> , ASTM, Philadelphia, PA.	540 541 542
[36] Nagataki, S., "Mineral admixtures in concrete: state of the art and trends" <i>Proceedings of V. Mohan Malhotra Symposium on Concrete Technology: Past, Present, and Future</i> , SP-144, P.K. Mehta, ed., American Concrete Institute, Farmington Hills, Michigan, USA, 1994, pp.447-482.	543 544 545 546
[37] Hwang, CL & Chandra, S., "The Use of Rice Husk Ash in Concrete", in S Chandra (ed.), <i>Waste materials used in concrete manufacturing</i> , William Andrew, 1997.	547 548 549
[38] ASTM C494 (2011) Standard Specification for Chemical Admixtures for Concrete, in: <i>Annual Book of ASTM Standards</i> , ASTM, Philadelphia, PA.	550 551
[39] Sobolev K, <i>Nanomodification of cement</i> , in: <i>NSF Workshop on Nanomodification of Cementitious Materials, Portland Cement Concrete and Asphalt Concrete</i> , Florida, USA, 2006.	552 553 554
[40] ASTM C305 (2011) Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency, in: <i>Annual Book of ASTM Standards</i> , ASTM, Philadelphia, PA.	555 556 557
[41] ASTM-C109 (2011) Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (using 50 mm [2 in.] Cube Specimens), in: <i>Annual Book of ASTM Standards</i> , ASTM, Philadelphia, PA.	558 559 560

[42] ASTM C157/C157M (2003) Standard Test Method for Length Change of Hardened Hydraulic Cement Mortar and Concrete, in: Annual Book of ASTM Standards, ASTM, Philadelphia, PA.	561 562 563
[43] ASTM C490-00a (2003) Standard Practice for Use of Apparatus for Determination of Length Change of Hardened Cement Paste, in: Annual Book of ASTM Standards, ASTM, Philadelphia, PA.	564 565 566
[44] Zerbino, R., G. Giaccio, and G. C. Isaia. "Concrete incorporating rice-husk ash without processing." <i>Construction and building materials</i> 25, no. 1 (2011): 371-378.	567 568
[45] A.L.G. Gastaldini, G.C. Isaia, T.F. Hoppe, F. Missau, A.P. Saciloto, Influence of the use of rice husk ash on the electrical resistivity of concrete: A technical and economic feasibility study, <i>Construction and Building Materials</i> 2009; 23:3411–3419.	569 570 571 572
[46] Mohseni, E., B.M. Miyandehi, J. Yang and M.A. Yazdi, 2015. Single and combined effects of nano-SiO ₂ , nano-Al ₂ O ₃ and nano-TiO ₂ on the mechanical, rheological and durability properties of self-compacting mortar containing fly ash. <i>Construct. Build. Mater.</i> , 84: 331-340.	573 574 575 576
[47] Chao-Lung, Hwang, Bui Le Anh-Tuan, and Chen Chun-Tsun. "Effect of rice husk ash on the strength and durability characteristics of concrete." <i>Construction and building materials</i> 25, no. 9 (2011): 3768-3772.	577 578 579
[48] Hall C (1989) Water sorptivity of mortars and concretes: a review. <i>Mag Concr Res</i> 41(147):51–61.	580 581
[49] Malhotra VM, Caretta AGG, Bilodeau A. Mechanical properties and durability of polypropylene fiber reinforced high-volume fly ash concrete for shotcrete applications. <i>ACI Mater J</i> 1994;91:478–86.	582 583 584
[50] Liu L-F, Wang P-M, Yang X-J. Effect of polypropylene fiber on dry-shrinkage ratio of cement mortar. <i>Jianzhu Cailiao Xuebao J Build Mater</i> 2005;8:373–7.	585 586
[51] Salih SA, Al-Azaawee ME. Effect of polypropylene fibers on properties of mortar containing crushed bricks as aggregate. <i>Eng Technol</i> 2008;26:1508–23.	587 588
[52] Kirca O, Sahin M. The influence of using polypropylene fiber on durability of white concrete. In: <i>5th National concrete congress, durability of concrete, Istanbul; 2003: 375–82.</i>	589 590 591
	592

Table 1: Chemical composition and physical properties of cement and RHA

593

	Constituents (wt.%)	Cement	RHA
Chemical composition	SiO ₂	21.75	91.15
	Al ₂ O ₃	5.15	0.41
	Fe ₂ O ₃	3.23	0.21
	CaO	63.75	0.41
	MgO	1.15	0.45
	SO ₃	1.95	0.62
	K ₂ O	0.56	6.25
	Na ₂ O	0.33	0.05
	L.O.I	2.08	0.45
Physical properties	Surface area (cm ² /g)	3105	4091
	Specific gravity (g/cm ³)	3.15	2.07

594

Table 2: Properties of polypropylene fiber

595

Unit weight (g/cm ³)	0.9-0.91
Reaction with water	Hydrophobic
Tensile strength (MPa)	300-400
Elongation at break (%)	100-600
Melting point (°C)	175
Thermal conductivity (W/m/K)	0.12
Length (mm)	6
Diameter (µm)	20

596

597

598

599

600

601

602

603

604

605

Table 3: Mix details of mortars

Sample ID	Cement (kg/m ³)	RHA (kg/m ³)	NA (kg/m ³)	PPF (kg/m ³)	Water (kg/m ³)	Sand (kg/m ³)	SP (kg/m ³)
CO	450	0	0	0	220	1430	0.9
RHA10	405	45	0	0	220	1415	1.8
RHA10NA1	400.5	45	4.5	0	220	1410	1.8
RHA10NA2	396	45	9	0	220	1400	1.8
RHA10NA3	391.5	45	13.5	0	220	1395	1.8
RHA20	360	90	0	0	220	1400	2.25
RHA20NA1	355.5	90	4.5	0	220	1390	2.25
RHA20NA2	351	90	9	0	220	1385	2.25
RHA20NA3	346.5	90	13.5	0	220	1380	2.25
RHA30	315	135	0	0	220	1380	3.25
RHA30NA1	310.5	135	4.5	0	220	1375	3.25
RHA30NA2	306	135	9	0	220	1370	3.25
RHA30NA3	301.5	135	13.5	0	220	1360	3.25
PP0.3	450	0	0	2.7	220	1430	1.5
RHA10PP0.3	405	45	0	2.7	220	1415	2.25
RHA10NA1PP0.3	400.5	45	4.5	2.7	220	1410	2.25
RHA10NA2PP0.3	396	45	9	2.7	220	1400	2.25
RHA10NA3PP0.3	391.5	45	13.5	2.7	220	1395	2.25
RHA20PP0.3	360	90	0	2.7	220	1400	3.25
RHA20NA1PP0.3	355.5	90	4.5	2.7	220	1390	3.25
RHA20NA2PP0.3	351	90	9	2.7	220	1385	3.25
RHA20NA3PP0.3	346.5	90	13.5	2.7	220	1380	3.25
RHA30PP0.3	315	135	0	2.7	220	1380	4.5
RHA30NA1PP0.3	310.5	135	4.5	2.7	220	1375	4.5
RHA30NA2PP0.3	306	135	9	2.7	220	1370	4.5
RHA30NA3PP0.3	301.5	135	13.5	2.7	220	1360	4.5

Table 4: Compressive strength of mortars

614

Sample ID	Compressive strength (MPa)			
	28 days	% of increase or decrease	90 days	% of increase or decrease
CO	45.1		50.2	
RHA10	45.3	0.44	50.3	0.2
RHA10NA1	45.6	1.11	51.1	1.8
RHA10NA2	50.3	11.5	57	13.5
RHA10NA3	52.6	16.6	59.6	18.7
RHA20	40.1	-11.1	45.7	-9.0
RHA20NA1	41.6	-7.7	47.3	-5.8
RHA20NA2	43.2	-4.2	49.1	-2.2
RHA20NA3	46.7	3.5	53.1	5.8
RHA30	38.7	-14.2	44.1	-12.1
RHA30NA1	40.1	-11.1	45.7	-9.0
RHA30NA2	40.3	-10.6	45.9	-8.6
RHA30NA3	39.6	-12.2	45.3	-9.8
PP0.3	46.9	4.0	53.4	6.4
RHA10PP0.3	45.4	0.6	51.9	3.4
RHA10NA1PP0.3	47.2	4.7	53.4	6.4
RHA10NA2PP0.3	51.6	14.4	58.4	16.3
RHA10NA3PP0.3	53.3	18.2	60.3	20.1
RHA20PP0.3	41.6	-7.8	47.3	-5.8
RHA20NA1PP0.3	41.9	-7.1	47.5	-5.4
RHA20NA2PP0.3	42.9	-4.9	48.9	-2.6
RHA20NA3PP0.3	45.9	1.8	52.1	3.8
RHA30PP0.3	39.5	-12.4	45	-10.3
RHA30NA1PP0.3	40.2	-10.9	45.7	-9.0
RHA30NA2PP0.3	41.6	-7.8	47.3	-5.8
RHA30NA3PP0.3	40.9	-9.3	46.3	-7.8

615

616

617

618

619

620

Table 5: Flexural strength of mortars

621

Sample ID	Flexural Strength (MPa)			
	28 days	% of increase or decrease	90 days	% of increase or decrease
CO	6.76		7.78	
RHA10	6.64	-1.8	7.8	0.3
RHA10NA1	6.75	-0.1	7.92	1.8
RHA10NA2	7.55	11.6	8.84	13.6
RHA10NA3	7.89	16.7	9.24	18.8
RHA20	6.02	-10.9	7.08	-9.0
RHA20NA1	6.24	-7.7	7.33	-5.8
RHA20NA2	6.48	-4.1	7.61	-2.2
RHA20NA3	7.01	3.6	8.23	5.9
RHA30	5.81	-14.1	6.84	-12.1
RHA30NA1	6.02	-10.9	7.08	-9.0
RHA30NA2	6.05	-10.5	7.11	-8.6
RHA30NA3	5.94	-12.1	7.02	-9.8
PP0.3	7.97	17.9	9.72	24.9
RHA10PP0.3	7.72	14.2	9.44	21.3
RHA10NA1PP0.3	8.02	18.7	9.72	24.9
RHA10NA2PP0.3	8.77	29.7	10.63	36.6
RHA10NA3PP0.3	9.06	34.0	10.97	41
RHA20PP0.3	7.07	4.6	8.61	10.7
RHA20NA1PP0.3	7.12	5.3	8.65	11.2
RHA20NA2PP0.3	7.29	7.8	8.90	14.4
RHA20NA3PP0.3	7.80	15.4	9.48	21.8
RHA30PP0.3	6.72	-0.5	8.19	5.3
RHA30NA1PP0.3	6.83	1.0	8.32	6.9
RHA30NA2PP0.3	7.07	4.6	8.61	10.7
RHA30NA3PP0.3	6.95	2.8	8.43	8.4

622

623

624

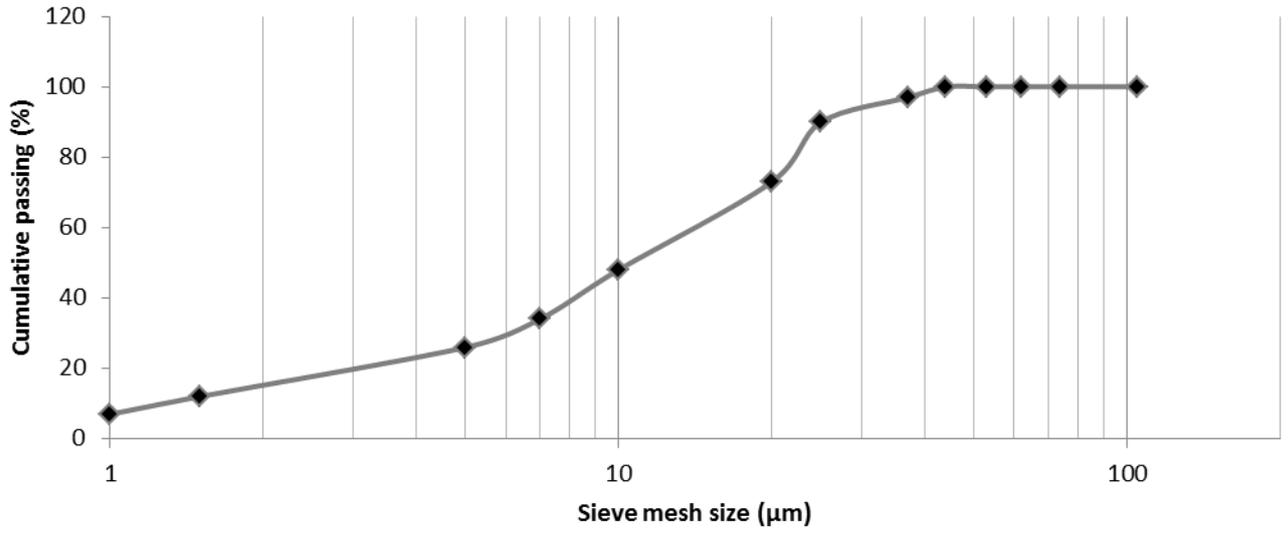
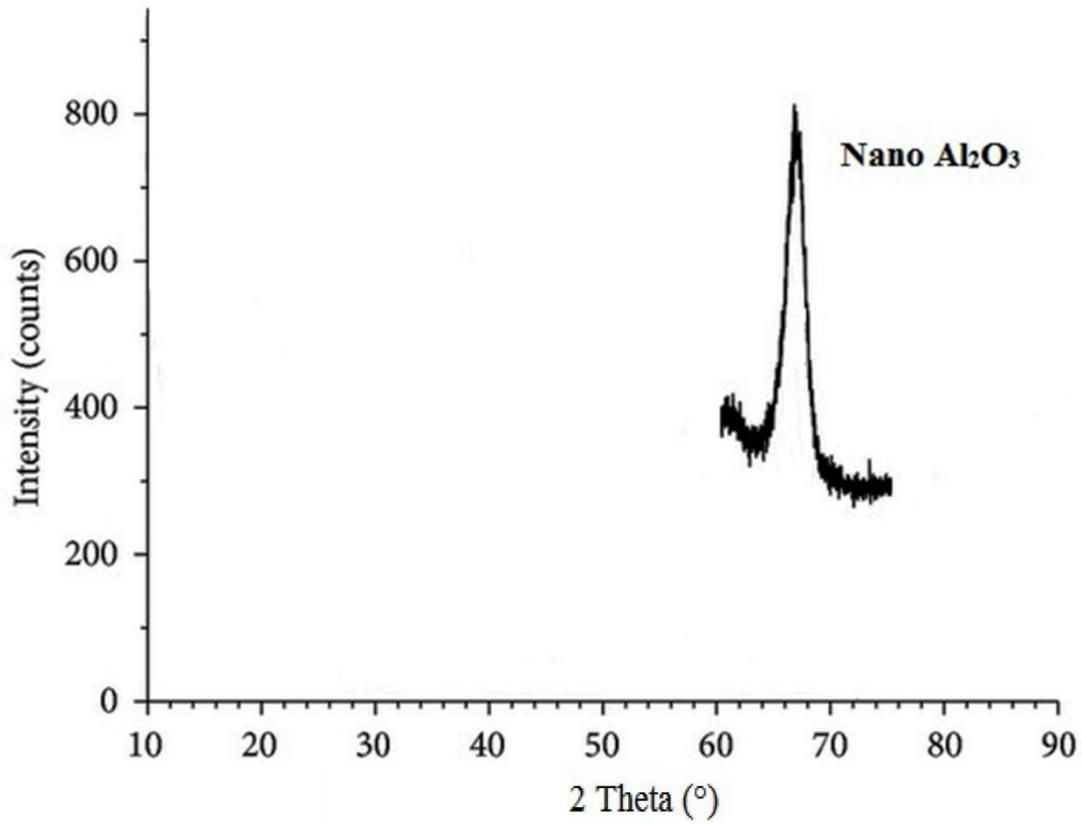


Fig. 1. Particle size distribution of RHA

626
627
628
629



630

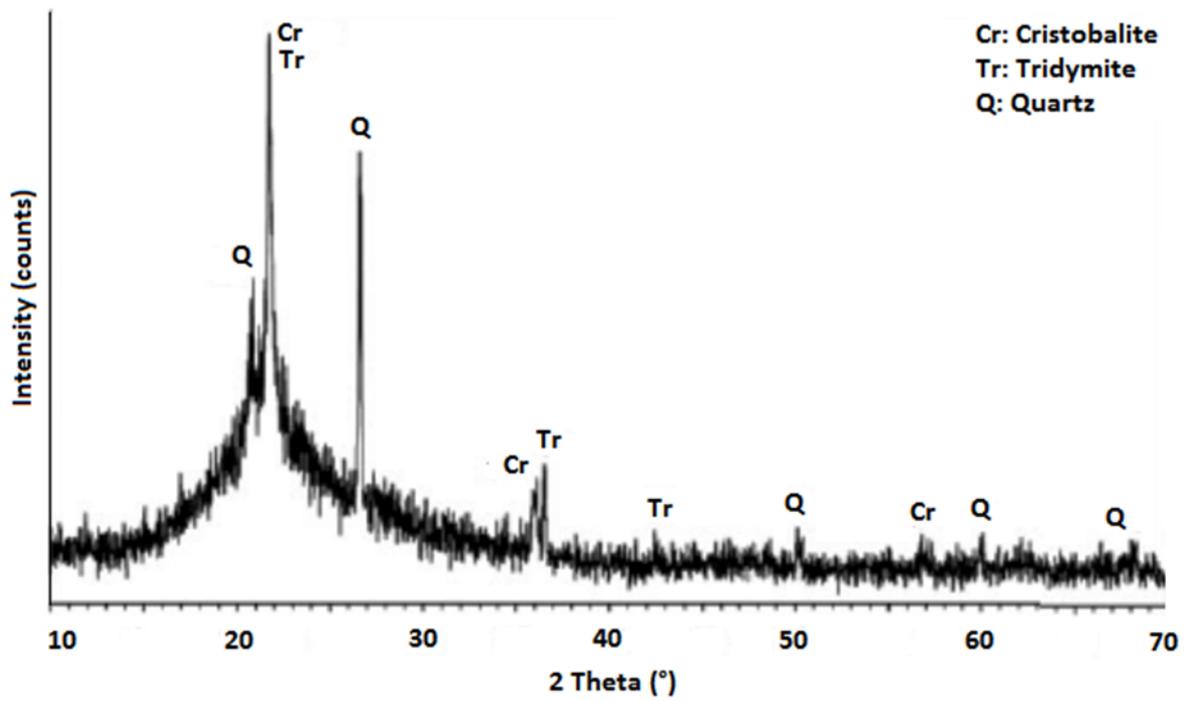
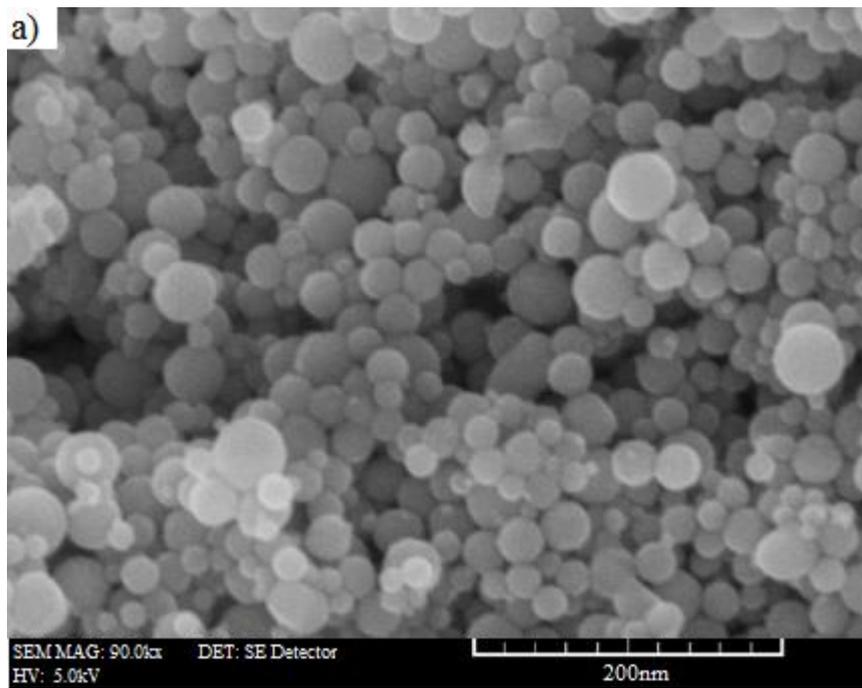


Fig. 2. XRD diagram of nano- Al_2O_3 (top) and RHA (bottom)

631

632

633



634

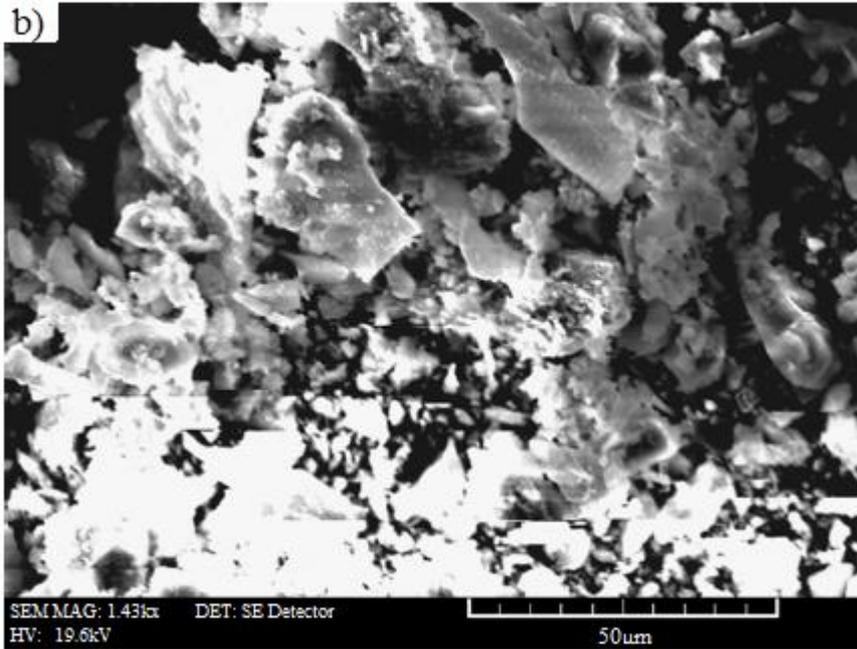


Fig. 3. SEM micrograph of the a) nano-Al₂O₃ and b) RHA



Fig. 4. Polypropylene fibers

635

636

637

638

639

640

641

642

643

644

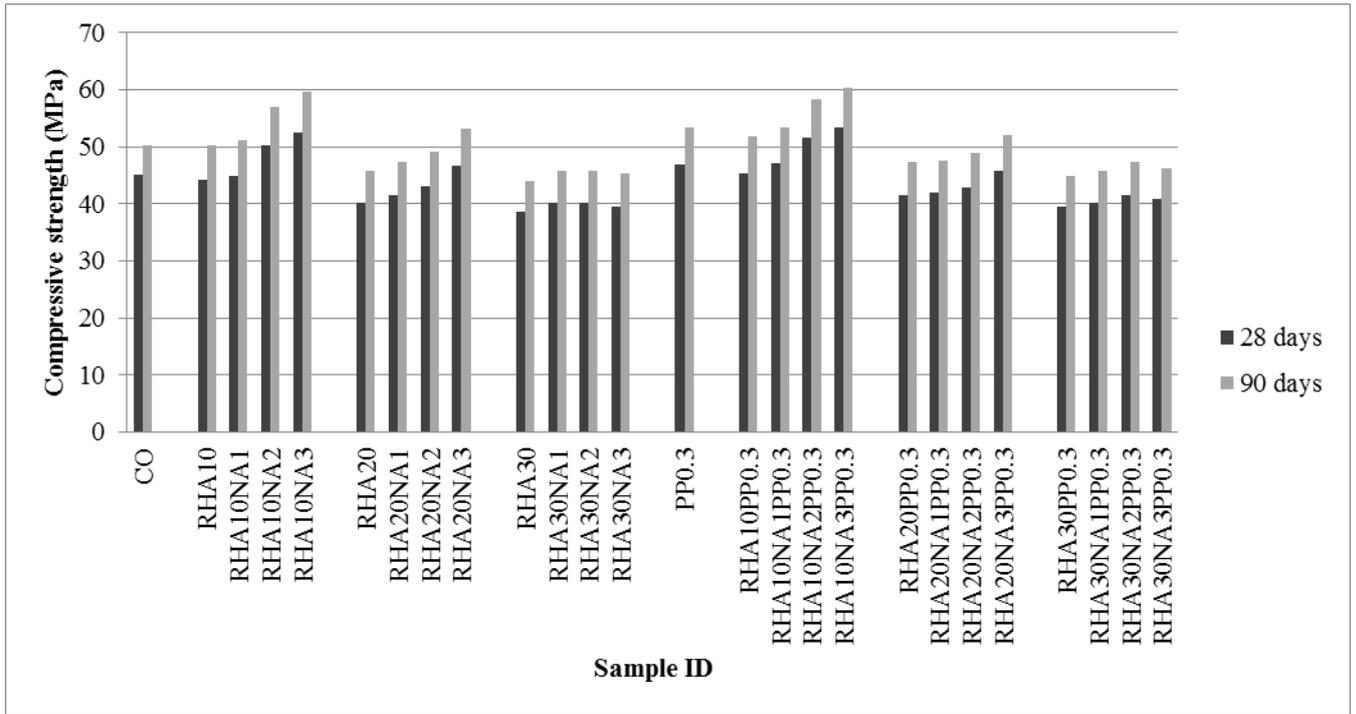
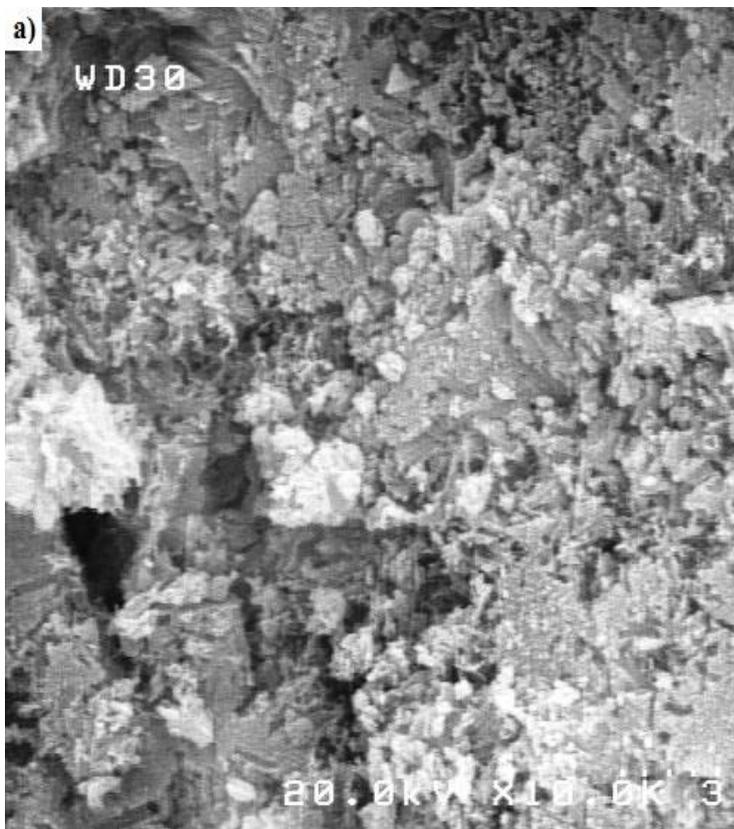


Fig. 5. Compressive strength values at 28 and 90 days of curing

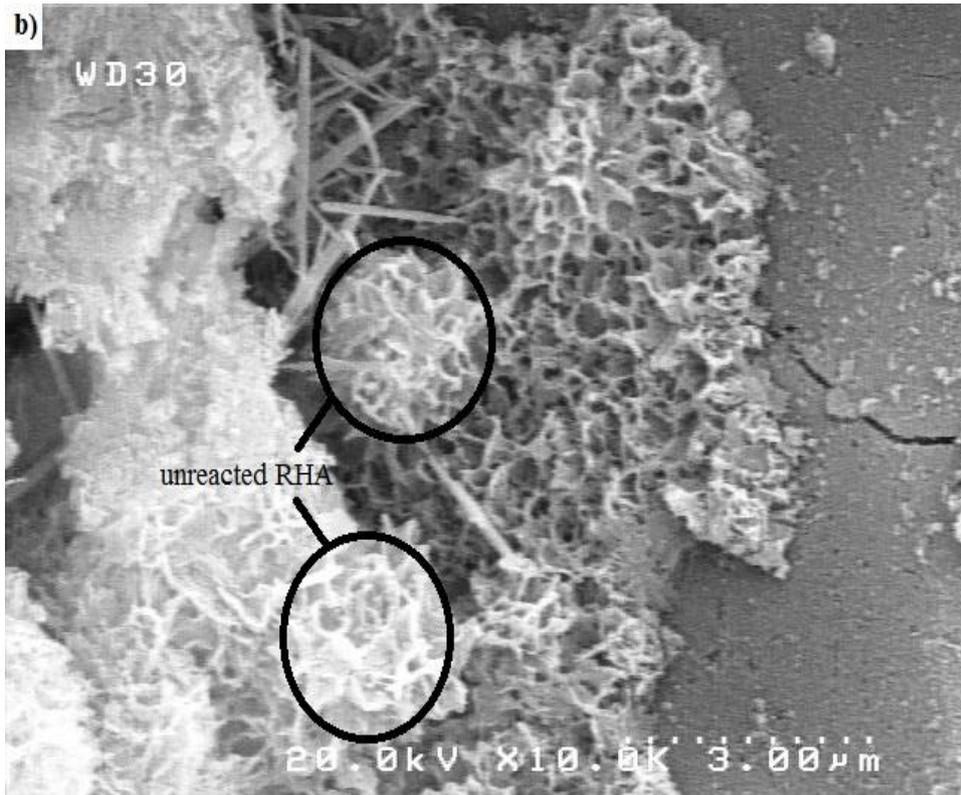
646

647

648



649



650



651

Fig. 6. SEM images of a) Control b) RHA10 and c) RHA10NA3 mixtures at 28 days of curing

652

653

654

655

656

657

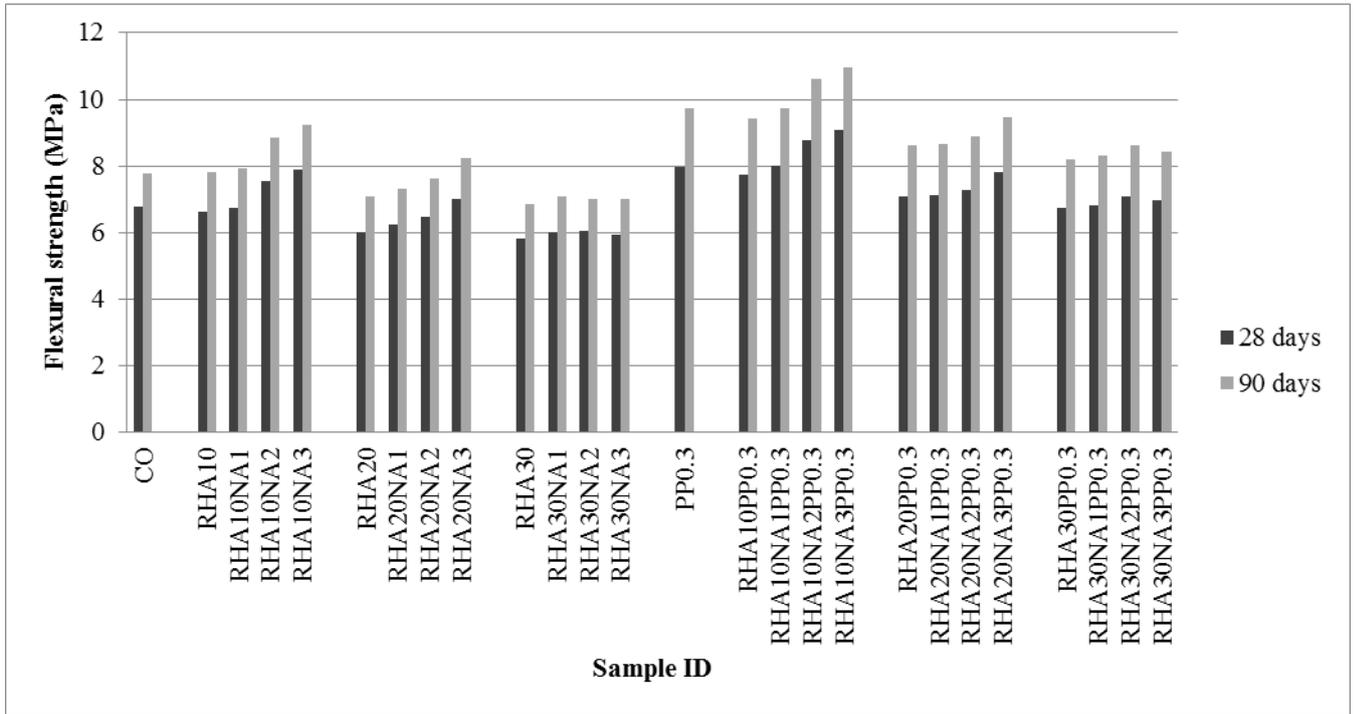
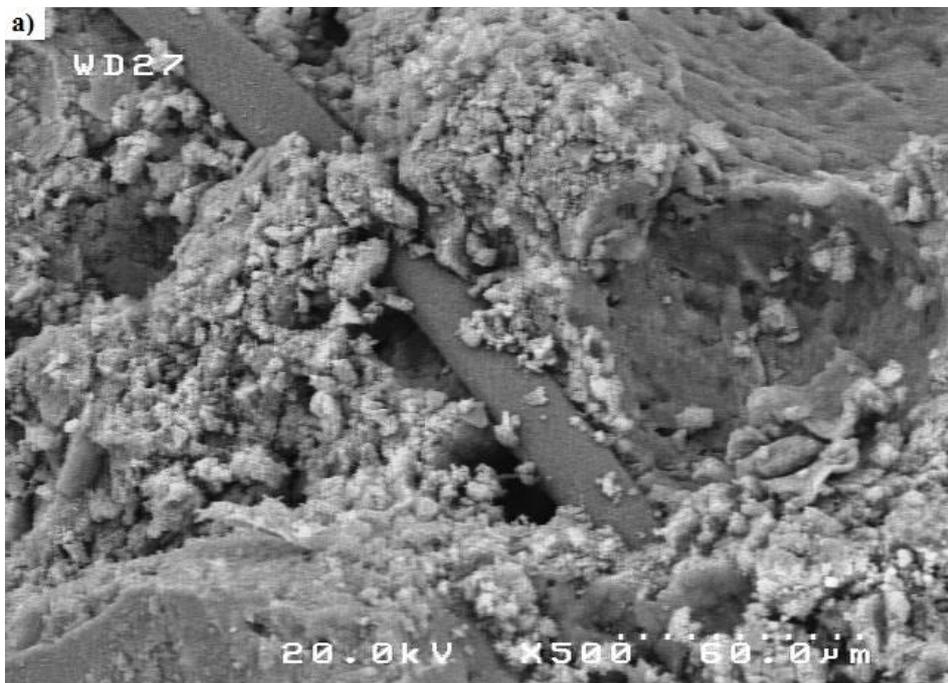


Fig. 7. Flexural strength values at 28 and 90 days of curing

659

660

661



662



663
664
665
666



667

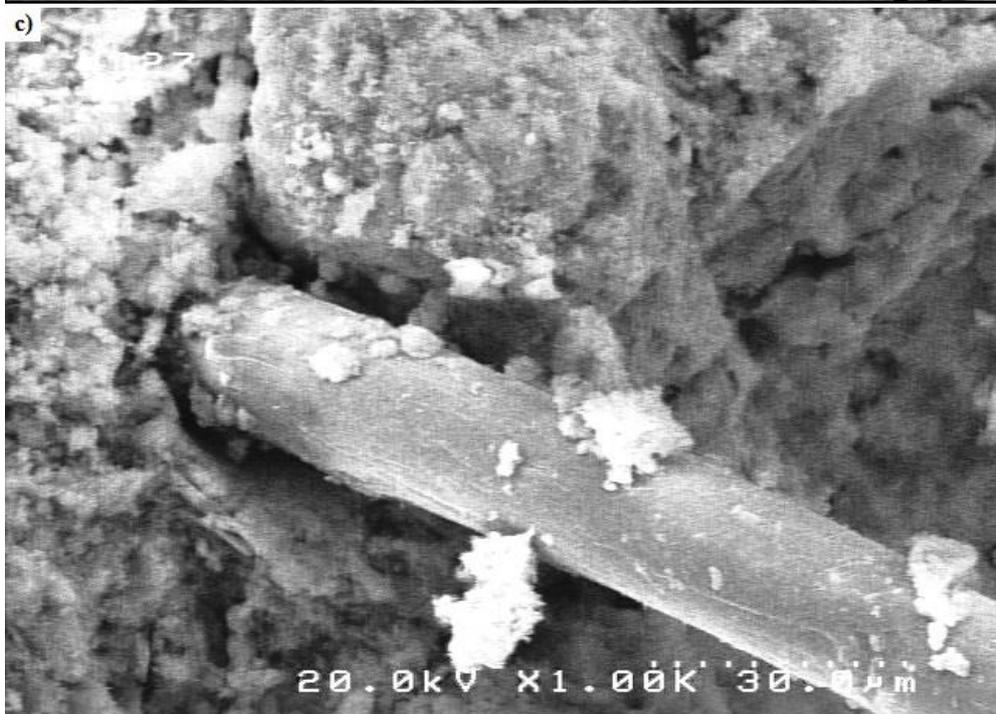
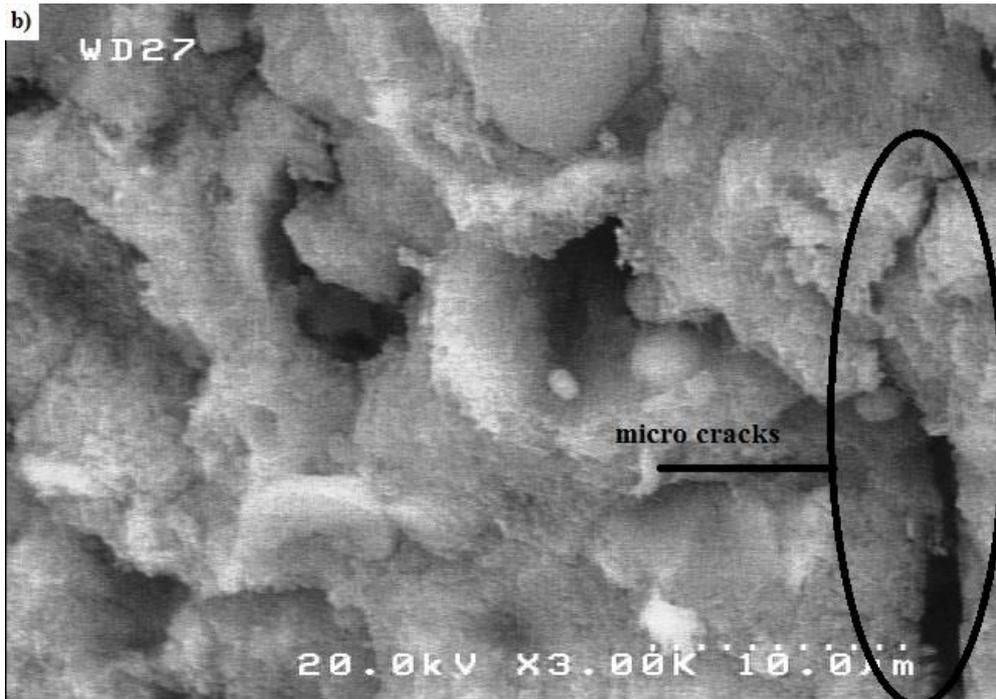


Fig. 9. SEM Micrograph of mortar fracture surface. (a) Control sample @ 15000 Res. b) Control sample @ 3000 Res. (c) Containing PPF @ 1000 Res at 90 days of curing

668

669
670
671
672
673
674
675
676

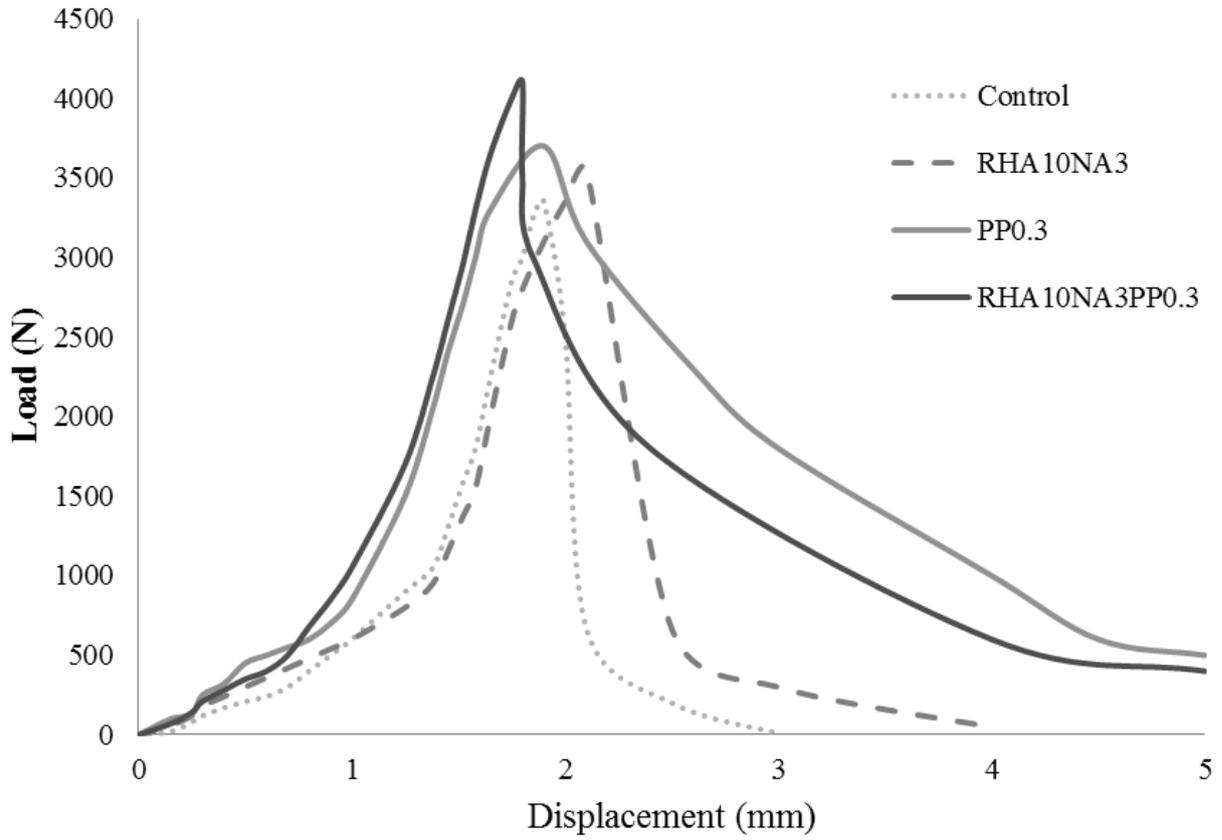


Fig. 10. Load-displacement curve for mortars reinforced with PPF at 90 days of curing.

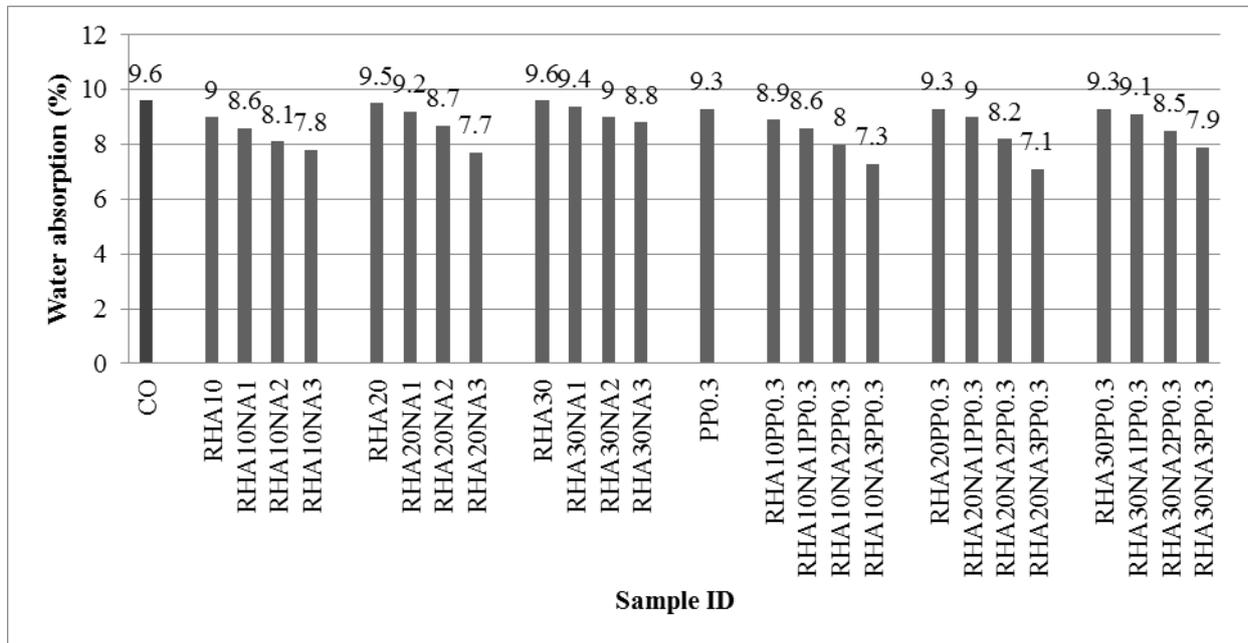


Fig. 11. Water absorption values at 28 days of curing

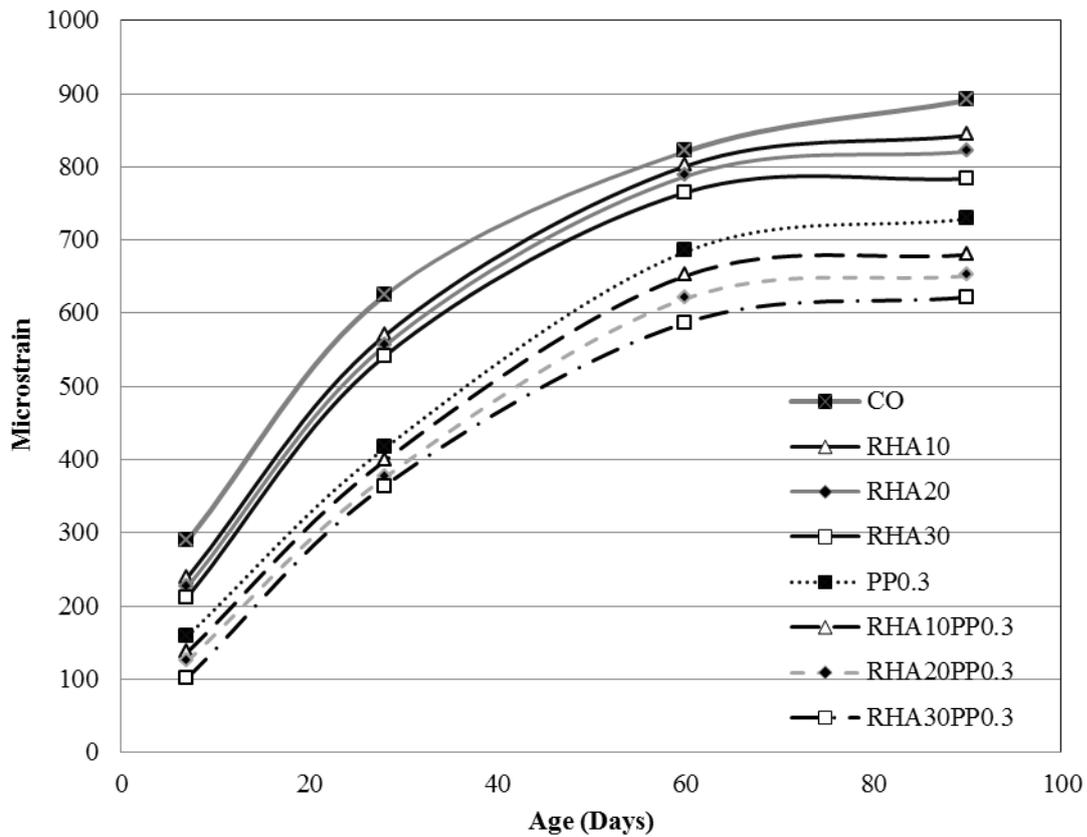


Fig. 12. Effect of RHA and polypropylene fibers on the drying shrinkage of mortars at various ages

683
684
685
686

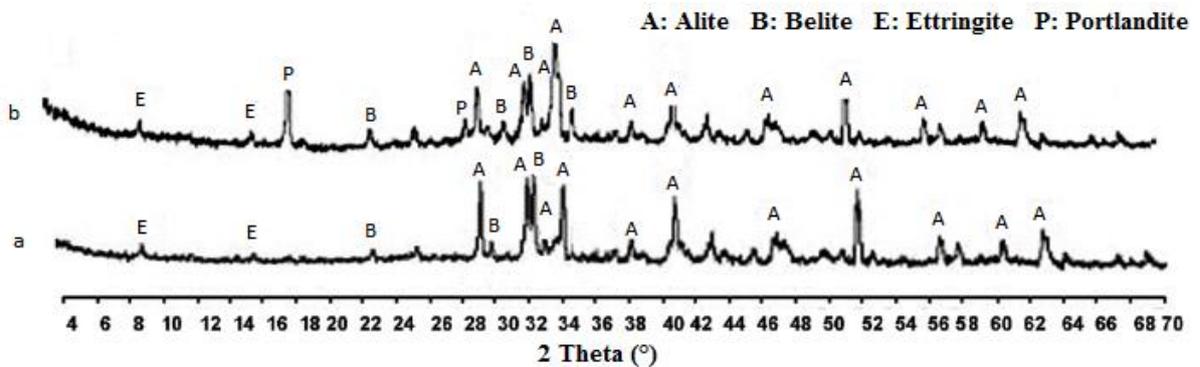


Fig. 13. XRD analysis of mortars a) without NA and b) with NA at 7 days of curing

687
688
689
690