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Microstructure and durability properties of cement mortars containing nano-TiO_2 and rice husk ash

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HIGHLIGHTS

- Cement mortar is produced with incorporation of nano-TiO_2 and rice husk ash.
- Improvement in durability of mortar is showed by addition of NT and RHA.
- More packed pore structure is observed by addition of nanoparticles.
- The permeability is reduced with an increase in the contents of RHA and NT.
- Synergic influence of nanoparticles is illustrated by XRD results.

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ABSTRACT

In the present study, Compressive strength, water absorption, electrical resistivity, Rapid Chloride Permeability Test (RCPT) and Ultrasonic Pulse Velocity (UPV) tests of the hardened composites incorporating two supplementary cementitious materials: agricultural waste ash namely as rice husk ash (RHA) and nano-TiO_2 (NT) in cement mortars were investigated. The interfacial transition zone (ITZ) and the microstructure were studied by using Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD) analysis, respectively. Compressive strength results showed a substantial improvement in samples containing NT and also a slight increase in mortar performance was observed by using up to 10 wt% of RHA as a replacement of cement. However, binary mixtures displayed the best results for strength development and durability. It is also seen that a combination of 15% RHA and 5% NT in mortar led to a positive contribution to durability properties. XRD analysis showed that intensity of Alite and Belite phases decreased and new peak of portlandite achieved with the addition of NT. The SEM micrographs illustrated the widespread distribution of mortars containing NT with packed pore structures which resulted in promoting of strength and durability of specimens. Consequently, the combined mixture of RHA and NT has led to the enhancement of strength and durability properties of mortars. In general, it seems that 15% RHA and 5% NT can be considered as a suitable replacement regarding to the economic efficiency and hardened properties.

1. Introduction

A large number of studies were conducted in order to investigate the influence of agricultural waste materials like rice husk ash (RHA) or rice hulls which is the shells produced during the de-husking operation of paddy rice, as it is available in large quantities since it is the most important crop in many countries to be used as a supplementary cementitious material. Van et al. [1] reported that usage of RHA has some positive impacts such as improving the properties of the cement concrete or mortar, reduction of the negative environmental effects, and decreasing the cost of concrete production. Therefore, these research and development in various countries have led to the conclusion that RHA is appropriate mineral admixture as partial replacement of cement because of its very high content of amorphous silica.

Nanotechnology has recently received special attention in virtue of its performance. In recent years, the number of studies related to nanotechnology for utilizing in the military strategies, technology and science of the countries has fostered remarkably. Nanotechnology is utilization and comprehension of new

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properties of materials that achieves novel physical impacts. When nano-scale particles are incorporated in cement paste, mortar or in concrete, the products with different properties will be created.

In the last two decades, some nanomaterials have been also utilized in cementitious mixtures, since the mechanical properties of concrete, such as compressive strength and flexural as well as microstructure and hydration rate of cement composites can be considerably promoted. Despite the fact that the effects of some nanoparticles, such as nano-CuO, nano-Al_2O_3, nano-TiO_2 (NT), nano-ZnO_2, nano-Fe_2O_3 on the physical properties have been investigated in some studies [2–7] most of the research on nanoparticles were done with nanosilica (SiO_2) [8–10] in cement-based materials. TiO_2 nanoparticles are well known for strong photocatalytic activity. The influence of the microstructure of cement paste on photocatalytic pollution degradation and the application of photocatalytic action of TiO_2 nanoparticles in terms of purification of air and environment, self-cleaning, and self-disinfection were investigated [11–14]. Moreover, restricted studies on the effect of nanoparticles on the microstructure and durability of cementitious materials have been directed. In this respect, Quercia et al. [15] investigated durability of self-compacting concrete (SCC) mixtures containing NS in terms of permeable porosity (following the procedure described by ASTM C 1202), freeze-thaw resistance, water penetration under pressure and rapid chloride migration. The obtained results demonstrated that nano-silica efficiently used in SCC can improve its mechanical properties and durability. The combined effects of fibers and nanosilica on the mechanical, rheological, and durability properties of SCC were measured by Beigi et al. [16]. The results showed improvement in mechanical properties and durability of SCC incorporating both nanosilica and reinforcing fibers in optimal percentages. Chloride induced corrosion durability of high volume fly ash concretes containing nano silica (NS) and nano calcium carbonate (NC) has been presented by Shaikh et al. [17]. The results indicate that the addition of NS and NC can significantly reduce the capillary pores and gel pores of concretes and also shift the pore concentration towards the medium capillary pores. Rao et al. [18] studied the mechanical properties and durability of self-compacting mortars incorporating SiO_2 and TiO_2 nanoparticles. They indicated that the use of nano materials in repair and rehabilitation mortars has significant potential but still needs to be optimized. Durability and pore size distribution of concrete with nano-silica was assessed by Du et al. [19]. The results verified the beneficial effects of nano-silica on the durability and microstructure of samples.

Although, different aspects of cement-based materials containing by-product materials and nanoparticles separately have been reported in the literature, to the authors' knowledge, the performance of such additives in conjunction with nanoparticles is not well documented. In particular, the effects of RHA as by-product materials and NT as a high surface area powder additive on the workability as well as pore structure and durability properties of SCC need to be studied in details. So, the present study is an attempt to study the durability, mechanical, and microstructure properties of mortar containing RHA and NT. In this respect, the durability properties were evaluated by water absorption, electrical resistivity, rapid chloride penetration test (RCPT) and ultrasonic pulse velocity (UPV) tests. Microstructure properties were also assessed via Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD).

2. Experimental program

2.1. Material

In this study, Natural river sand and ordinary Portland cement type I complying with the requirement of ASTM C778 [20] and ASTM C150 [21], respectively, and various ratios of RHA were used as a pozzolanic material with cement [22]. Table 1 shows the Chemical composition and physical properties of cement and RHA. Nano-TiO_2 in a form of dispersed suspension of 30 wt% in water was added to the mixture. The nanoparticles have an average particle size of 20 nm and a nearly spherical morphology with specific surface area of 200 m^2/g. Fig. 1 illustrates The X-ray diffraction (XRD) diagrams of NT and RHA. The scanning electron micrographs (SEM) of NT and RHA are also given in Fig. 2. It can be seen from these figures that the TiO_2 nanoparticles are spherical while the RHA particles are of irregular shape. Natural river sand with fineness modulus 2.25 and a specific gravity of 2.58 g/cm^3 was used as the natural fine aggregate. To accelerate the compaction process of specimens, a polycarboxylic-ether type super plasticizer (SP) of PCE with a density of 1.03 g/cm^3 conforming to ASTM C494 [23] was utilized. The content of (SP) was adjusted for each mixture to keep the same fluidity of the mortars.

2.2. Mix proportions

A total of 13 different mixtures with different amounts of RHA, NT and SP were prepared with total binder contents of 700 kg/m^3, for all mix proportions. The percentage of RHA was varied between 0 and 15% by weight of the total binder. The percentage of nanoparticles was 0, 1, 3 and 5% of the binder. The amount of SP varied between 0.6 and 1.2% by weight of the binder. The water to binder ratio (w/b) was kept constant at 0.4 for all the mixtures. Detailed mix proportions of the mortars have been given in Table 2. The mixture proportions of the ingredients were calculated by the volumetric method. Since the specific gravity of RHA and NT is lower than that of cement, use of RHA and NT in place of cement by weight percentage reduced the amount of sand to maintain the same volume. In labeling of the mixtures, the number before RHA and NT represents the percentage of rice husk ash and nano-TiO_2, respectively.

2.3. Production of specimens

The large surface area of nano-TiO_2 particles may prevent them showing a unified distribution in the mortar mixture due to their tendency to agglomerate [24]. As this can directly effect on the physical and mechanical properties of the mortars, the specimen production procedure which was used in this study was finalized after conducting some preliminary experiments and the following mixing procedure was considered: To begin, the cement and RHA were dry-mixed in the mixer for 1 min at a speed of 80 rpm. Then, nanoparticles and 90% of the water were added and mixed at a high speed for about 1 min. Afterward, the sand was gradually added in 30 s while the mixer was running at a medium speed. The superplastisizer and remaining water, then were added and mixed at high speed for 30 s. After stirring the materials, the mixture was allowed to rest for around 1.5 min and then mixing procedure was followed in order to achieve a uniform distribution of the nanoparticles in the mortar. Eventually, fresh mortar was cast into 50 * 50 * 50 mm cubes for compressive strength, water absorption and electrical resistivity tests. Cylindrical specimens of 100 * 50 mm were cast for the RCPT. After casting, the specimens were left inside the mold for 24 h. Then the specimens were de-molded and kept in water at 23 ± 3 °C until they were tested.

2.4. Test methods

2.4.1. Compressive strength

Compression tests for three 50 mm cubic mortar specimens were conducted at 3, 7, 28 and 90 days in accordance to ASTM C109 standard [25]. Compressive strength for each mixture was obtained from an average of the compressive test results of 3 cubic specimens.

2.4.2. Water absorption

Water absorption test was carried out using 50 mm cubic specimens at the age of 90 days. After measuring the initial weight, the specimens were placed in an oven at 110 °C for 3 days. Then the weight of dried samples was assessed by a digital

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

	Constituents (wt%)	Cement	RHA
Chemical composition	SiO_2	21.75	91.15
	Al_2O_3	5.15	0.41
	Fe_2O_3	3.23	0.21
	CaO	63.75	0.41
	MgO	1.15	0.45
	SO_3	1.95	0.62
	K_2O	0.56	6.25
	Na_2O	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