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Fire resistance and mechanical properties of carbon nanotubes – clay bricks wastes (Homra) composites cement

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HIGHLIGHTS

- Effect of carbon nanotubes (CNTs) on the fire resistance of Homra/OPC blends.
- Small additions of CNTs to OPC–Homra blends improve the fire resistance.
- 0.1% CNT could be considered as the optimum addition to each mix.
- Presence of CNTs does not affect the hydration reaction of OPC or Homra/OPC blends.
- Presence of CNTs does not affect the microstructure of the formed hydrates.

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ABSTRACT

This paper aims to evaluate the effect of carbon nanotubes (CNTs) on the mechanical properties and the fire resistance of Homra/OPC blends; Homra represents the solid waste generated from clay bricks industry in Egypt. The nanocomposites, thus produced, were obtained by different additions of CNTs of 0.02, 0.05, 0.1 and 0.2 mass% to Homra/OPC blends, prepared by the partial replacement of OPC by 10, 20 and 30 mass% by Homra. Fire resistance of the nanocomposite blends was studied by firing of the various blended cement pastes at 300, 600, and 800 °C for 3 h. The compressive strength values were determined for different blended cement–CNTs composites at each firing temperature, in addition, the phase composition, thermal analysis and microstructure were investigated for some selected samples. The results obtained revealed that addition of 0.1 (mass%) of CNTs showed better improvements in the thermal and mechanical properties of the hardened Homra/OPC blended cement–CNTs composites. XRD, DSC and SEM results revealed that the presence of CNTs does not affect the rate of hydration reaction of the neat OPC or Homra/OPC blends; but increases their compressive strength and fire resistance through their physical contribution; where it can further fill in the pores between the hydration products and acts as bridges between hydrates and across cracks.

1. Introduction

Cement products are premier materials in construction industry. They have excellent compression properties but are weak in tension. To increase the tensile strength, these products can be reinforced with bars, rods, and fibers or prestressing. Introduction of nanoparticles in cement based materials has gained popularity in recent years due to their excellent mechanical properties and application potential. Addition of carbon nanoparticles in the cementitious materials may provide extra-ordinary strength increase as well as controlling cracks prevention [1,2].

A great potential has been identified in the modification of mechanical properties of cement based materials using carbon nanotubes (CNTs). Many studies demonstrated that the incorporation of CNTs into cementing matrices lead to improve their mechanical properties [3–10]. CNTs occur as single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs are composed of a single graphite sheet rolled into a long hollow cylinder, whereas MWCNTs are nested arrays of SWCNTs. The average diameter of an individual SWCNT is on the order of 1 nm whereas the average diameter of an individual MWCNT is on the order of 10 nm [2]. Carbon nanotubes have desirable mechanical, show very high thermal conductivity of

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1700–3000 W/mK and very low electrical resistivity of 5×10^{-8}–2×10^{-6} Ω m. In addition, upon stress, composites containing CNTs show a 'piezoresistive response' wherein the electrical properties are changed with respect to different stress levels [11,12].

However, beside the enhancement of the mechanical and electrical properties of cement composites by addition of CNTs, several challenges must still be considered. One of these is achieving effective dispersion of CNTs at the single tube level. CNTs have high aspect ratios and strong van der Waals self-attraction between nanotubes, and tend to form CNT bundles [13,14]. Poor dispersion of CNTs leads to the formation of many defect sites in the nanocomposite and limits the efficiency of homogeneous dispersion of CNTs in the matrix. Another major challenge is to enhance the interfacial interaction between CNTs and hydration products of cement; CNTs are expected to provide mechanical reinforcement between hydration products of cement with nano-scale dimensions. However, hydration products such as calcium–silicate–hydrates (C–S–H), calcium hydroxide (CH) and ettringite have similar or larger size than CNTs, and consequently only a few CNTs could be anchored by the hydration products in studies reported to date [15]. Carbon nanotubes were found to improve strength properties of Portland cement, the reason given was that the functionalized carbon nanotubes could provide chemical bonds between the –COOH groups of the nanotubes and the calcium silicate hydrate phase (CSH) of the cement matrix, which enhanced the transfer of stresses. Furthermore, previous research has demonstrated that the addition of multi-walled carbon nanotubes of less than 1 mass % of cement can greatly improve the mechanical properties of the cement composites [16–18].

Combination of CNT in blended cement with other materials such as fly ash, nanoclay, nano Fe needles, bagasse fiber and carbon nanofibers among others has also been studied [19–23]. Homra (clay bricks waste) is a solid waste material, which is constituted mainly of silica quartz, aluminosilicate, anhydrite, and hematite. Therefore, it acts as a pozzolanic material [24]. Homra as a pozzolanic material reacts with lime liberated from the hydration of ordinary Portland cement (OPC). This pozzolanic reaction improves the microstructure of cement pastes and also increases their heat resistance [25].

The aim of this study is to identify the effect of both Homra and carbon nanotubes on the mechanical and thermal resistivity of Portland cement pastes.

2. Experimental

2.1. Materials

The cement used in this study was ordinary Portland cement (OPC), supplied from Lafarge cement company, Suez, Egypt, with Blaine surface area of 3320 cm^2/g. Blender was crushed clay bricks (Homra) of particle size ⩽0.125 mm and Blaine surface area of 3300 cm^2/g. Table 1 shows the chemical oxide composition for OPC and Homra.

The purified multi-walled carbon nanotubes (MWCNTs) with surface area of 93.81 m^2/g and purity > 90%. The outside estimated diameter and length of MWCNTs ranged from 10–40 nm to 5–10 μm respectively. The density of MWCNTs was about 2.1 g/cm^3 and their electrical conductivity was more than 100 S/cm, provided by Egyptian Petroleum Research Institute (EPRI), Cairo, Egypt, were used. Morphology and microstructure of MWCNTs are shown in Fig. 1.

Polycarboxylate surfactant (Sika Viscocrete 5230 L) with specific gravity 1.08 g/ml was supplied from Sika Company, Elobour City, Egypt, to assist the dispersion of MWCNTs.

2.2. Methodology

Different cement blends were prepared from different OPC–Homra dry mixes. Table 2 shows the percentage composition of the different cement blends and their designations. Each dry cement blend was mechanically mixed in a porcelain ball mill for 8 h to assure complete homogeneity of the dry mixture.

For the preparation of MWCNTs dispersions, the surfactant (Viscocrete), was used; suspensions were prepared by mixing MWCNTs in an aqueous solution (using the whole mixing water) containing different amounts of surfactant. The CNTs/surfactant ratio was of 1:3 and the resulting suspensions were sonicated at room temperature for 1 h.

Different cement pastes were made using a water/solid (W/S) ratio of 0.30. Each paste was prepared by mixing the dry mix with the required amount of water containing the dispersed MWCNTs for about 3 min. After complete mixing, the resultant paste was molded into cubic specimens by using 1 inch cube molds. The molds containing specimens were cured at about 100% relative humidity for 24 h to attain the final setting; then the cubic specimens were demolded and cured under tap water at room temperature for different time intervals of 3, 7, 28 and 90 days.

At each time interval, compressive strength tests were performed on the hardened blended cement pastes using three cubic specimens at each hydration time, and the average value was recorded. The resulting crushed specimens were ground, and the hydration reaction was stopped using the method described in an earlier publication [26]. The samples were then dried at 90 °C for 3 h in CO_2-free atmosphere and maintained in a desiccator containing soda lime and $CaCl_2$ until the time of testing was reached.

In addition, the specimens cured for 28 days were subjected to thermal treatment in a muffle furnace at 300, 600 and 800 °C for 3 h with a heating rate of 10 °C min^{-1}. The thermally heated specimens, after cooling in a desiccator were subjected to compressive strength test and the residual strength values were recorded. The percentage of residual strength was calculated as follows:

$$\text{Residual strength } \% = [(\text{C.S.})_t/(\text{C.S.})_0] \times 100$$

$(\text{C.S.})_t$: compressive strength after firing at temperature t °C.
$(\text{C.S.})_0$: compressive strength at room temperature.

The phase composition and microstructure of the formed hydrates were investigated by X-ray diffraction (XRD), differential scanning calorimetery (DSC) and scanning electron microscopy (SEM).

3. Results and discussion

3.1. Compressive strength

The results of compressive strength of the hardened OPC–Homra composite cement pastes blends are graphically represented as a function of hydration age in Fig. 2. For all of the pastes made of the OPC and OPC–Homra blends, the compressive strength was found to increase continuously with increasing age of hydration. This increase in compressive strength is mainly attributed to the formation and later accumulation of hydration products which act as binding centers between the remaining unhydrated parts of cement grains, (Fig. 2). The hydration products of composite blends, mainly as calcium silicate hydrates (CSH, I & II) and calcium aluminate hydrates represent the main binding centers between the remaining unhydrated parts of OPC and Homra grains. On the other hand, the pastes made of mix B0 (90% OPC + 10% Homra) possess the highest compressive strength values especially at later ages of hydration (28 and 90 days) as compared to other pastes containing 0, 20 and 30% Homra. The highest strength values of the hardened pastes made of mix B0 can be attributed to the pozzolanic reaction between the free calcium hydroxide, liberated from Portland cement hydration, with Homra to form excessive amounts of hydration products, mainly as CSH, CAH and CASH gels as well as crystalline hydrates, that serve as micro-

Table 1
Chemical oxide composition of OPC and Homra (mass%).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Cl^-	LOI
OPC	18.57	4.29	3.75	62.45	1.88	3.20	0.28	0.32	–	2.10
Homra	74.80	14.03	5.04	1.25	1.30	0.80	–	–	–	–