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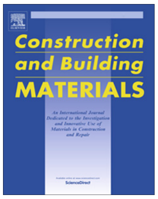

Hybrid effect of carbon nanotubes and polypropylene microfibers on fire resistance, thermal characteristics and microstructure of cementitious composites

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HIGHLIGHTS

- Fire resistance of cementitious composites with CNTs and PP fibers is investigated.
- Thermal characteristics of cementitious composites with CNTs and PP fibers is investigated.
- CNTs enhance the residual mechanical properties of PP fiber-reinforced mortar exposed to elevated temperature.
- Residual fracture energy is improved by adding CNTs and PP microfibers.
- Thermal conductivity of cement mortar is increased by adding CNTs but not the PP fibers.

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ABSTRACT

The current study experimentally investigates the hybrid effect of carbon nanotubes (CNTs) and polypropylene (PP) microfibers on fire resistance and thermal characteristics of cementitious composites. Cement mortar with small dosages of CNTs and PP fibers are prepared and heated at 150 °C, 200 °C, 450 °C, and 600 °C. The residual mechanical properties, microstructure deterioration, and thermal properties of heated mortar are reported. The results shows the ability of the CNTs to enhance the residual compressive and flexural strengths of PP fiber-reinforced mortar exposed to elevated temperature up to 600 °C. Residual fracture energy is improved by adding small dosage of PP microfibers and CNTs. The improvement was less significant in the case of exposure temperatures greater than melting point of the fibers. Thermal conductivity of cement mortar is increased by the addition of the CNTs but not the PP fibers for all heating levels. According to the DSC and TGA analysis, presence of CNTs increased heat absorption needed for decomposition of the hydration products of cement mortar whereas the presence of the fibers has minor effect. SEM images show that the CNTs filled the pores and delayed the initiation of the cracks, whereas the PP fibers bridged these cracks and mitigated their propagation.

1. Introduction

Polypropylene (PP) fibers with their lightweight, corrosion resistance, and relatively low cost are incorporated in concrete production to enhance its mechanical strengths, cracking patterns, durability, and fire resistance [1–4]. In the event of fire, the high temperatures usually causes dehydration of the portlandite and C-S-H gel, which generates water steam thus increase the pore pressure inside the concrete. The generated pore pressure causes splitting of concrete cover or structural spalling [5,6]. Spalling can be considered as one of the major concerns when dealing with concrete structures under fire [6,7]. One of the proposed methods to control and mitigate concrete spalling during fire is to incorporate polypropylene fibers within the concrete mix [2,4,5,8,9]. Once the melting point of the polypropylene fibers is exceeds, the fibers melt and create extra capillary pores in the microstructure of concrete. The additional pores allow the water steam generated due to the dehydration process to release thus reduce the pore pressure and delay the spalling. The above literature reflects that adding polypropylene fibers into concrete mix not only enhance the structural performance of concrete but also improve its fire resistance. However, other studies show that adding polypropylene fibers caused negative effect on the residual strengths of concrete when subjected to elevated temperatures [8,10]. One suggested solution

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is to use hybrid fiber-reinforcement system contains polypropylene fibers combined with other type of fibers such as steel fibers. Adding steel fibers enhances the stiffness, ductility, and energy absorption of concrete but increase the corrosion potential [10–13].

On the other hand, carbon nanotubes (CNTs) with their small size and excellent mechanical and thermal characteristics are introduced as promising additives for concrete. Many studies show that incorporating CNTs into cementitious materials enhance their mechanical strengths and durability [14–17]. Recently, the research was directed towards investigating the effect of CNTs on the behavior of cementitious composites at high temperatures. Sedaghatdoost et al. [18] showed that cement mortar contains CNTs had higher residual compressive strength than that of plain mortar for temperatures between 200 and 800 °C. Zhang et al. [19] showed that the effect of CNTs on the residual flexural and compressive strengths of cementitious composites are more obvious at temperatures below 400 °C. Lee et al. [20] showed that mixing CNTs in sand more efficiently improved the thermal characteristics of cement mortar.

The aforementioned literatures indicate that adding polypropylene fibers to the cementitious composites control structural spalling thus enhance fire resistance of concrete. Whereas CNTs addition improves the residual strengths of concrete due to elevated temperatures. The current study investigates the combined effect of polypropylene fibers and CNTs on fire resistance and thermal characteristics of cementitious composites. Cement mortar with various dosages of CNTs and PP fibers are prepared and heated at 150 °C, 200 °C, 450 °C, and 600 °C. The residual compressive and flexural properties of heated specimens are reported. The thermal behavior of cement mortar with CNTs and PP fibers is also investigated using Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA), and thermal conductivity tests. The microstructure of the heat-damaged specimens is investigated using Scanning Electron Microscopy (SEM) imaging.

2. Experimental program

2.1. Materials and mix design

Control cement mortar specimens were prepared using Portland cement, fine aggregate, and Tap water. The chemical composition of the Portland cement used in this study is summarized in Table 1. Locally available silica sand with specific gravity of 2.56, finess modulus of 2.31, and water absorption of 1.87% was used as fine aggregates. Monofilament polypropylene microfibers and carbon nanotubes aquatic solution were received from Sika® and Nanocyl®, respectively. The properties of these reinforcement materials are summarized in Table 2. Polycarboxylate ether superplasticizer namely “PC 485” provided by EPSILONE was used in all mixes to improve workability and consistency.

Table 1
Chemical compositions of cement.

Compound Name	Content Percentage
CaO	66.4%
SiO_2	18.4%
Fe_2O_3	6.1%
SO_3	3.0%
Al_2O_3	2.2%
MgO	1.4%
Na_2O	0.8%
LOI	1.5%

Table 2
Polypropylene microfibers and CNTs solution properties.

Polypropylene microfibers		CNTs solution	
Property	Values	Property	Values
Length	12 mm	CNTs Concentration by weight	3.0%
Diameter	34 μm	Average diameter (nm)	9.5
Density	910 kg/m^3	Average length (μm)	1.5
Melting point	160 °C	Carbon purity (%)	90
		Surface area (m^2/g)	250–300

Five batches of cement mortar were prepared in this study: one batch as plain mortar, two batches with different dosages of PP fibers, and two batches with CNTs and PP fibers. The dosages of CNTs and PP fibers were selected based on the optimum amount required to enhance the compression and flexural strengths of cement mortar according to previous work published by the authors. The first batch was prepared with plain cement mortar. The second batch was prepared with 0.1% PP fibers by weight of cement (equivalent to 0.08% volume proportion of the mortar), whereas the third one was prepared with 0.05% CNTs and 0.1% PP fibers by weight of cement. These two batches were used to cast compression specimens. The fourth batch was prepared with 0.05% PP fibers by weight of cement (equivalent to 0.04% volume proportion of the mortar), whereas the fifth one was prepared with 0.2% CNTs and 0.05% PP fibers by weight of cement. These two batches were used to cast flexural specimens. The water to cement (w/c) ratio and superplasticizer were used as 0.48 and 1% by weigh of cement, respectively, for all mixes. Table 3 summarizes the details of mix design.

2.2. Mortar mixing and specimens casting

The cement mortar was casted according to the ASTM C305 standard with some modifications due to presence of the fibers. The CNTs aquatic solution was firstly diluted with water to get the desired CNTs dosage. After that, water or CNTs solution and superplasticizer were added to the cement and mixed. The sand was then added and mixed to get homogenous mix. Finally, the desired amount of PP fibers were added and manually mixed to get the mortar. The fresh mortar was casted in 50 mm cube molds for compressive strength test and 40 mm × 40 mm × 160 mm prism for flexural strength test. Twenty-four hours after casting, the specimens were demolded and cured in lime-saturated water for 28 days. At the end of the curing period, the specimens were extracted from the water, dried, and then heated.

2.3. Heating procedure

Mortar specimens were exposed to the desired heating level using special electrical furnace according to the temperature–time profile shown in Fig. 1. After reaching the desired elevated temperature with a heating rate of 2 °C/min, the temperature was fixed for two hours then the furnace was turned off. When the furnace cooled to the room temperature, the specimens were removed and tested.

2.4. Test procedures

Compressive strength and flexural strength tests were performed following to the ASTM standards C109/C109M, and C348-18, respectively. The average strength values of three tested specimens from each mix was calculated and reported. After conducting the compression test, selected specimens were chosen to perform the microstructural investigation and thermal characterization. Small fragments were extracted from different locations of the selected specimens to represent the entire sample.

Table 3
Details of mix design.

Mortar batch	Cement (kg/m^3)	Sand (kg/m^3)	Water (kg/m^3)	PP Fibers (kg/m^3)	CNTs (kg)	Superplasticizer (kg/m^3)
1	706.67	1943.33	342.67	–	–	7.06
2	706.67	1943.33	342.67	0.706	–	7.06
3	706.67	1943.33	342.67	0.706	0.353	7.06
4	706.67	1943.33	342.67	0.353	–	7.06
5	706.67	1943.33	342.67	0.353	1.412	7.06

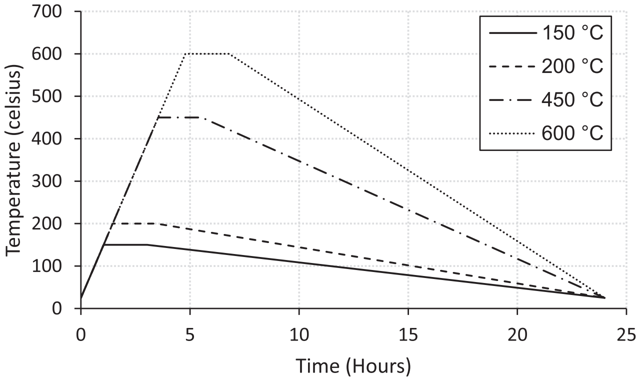


Fig. 1. Temperature-time profiles.

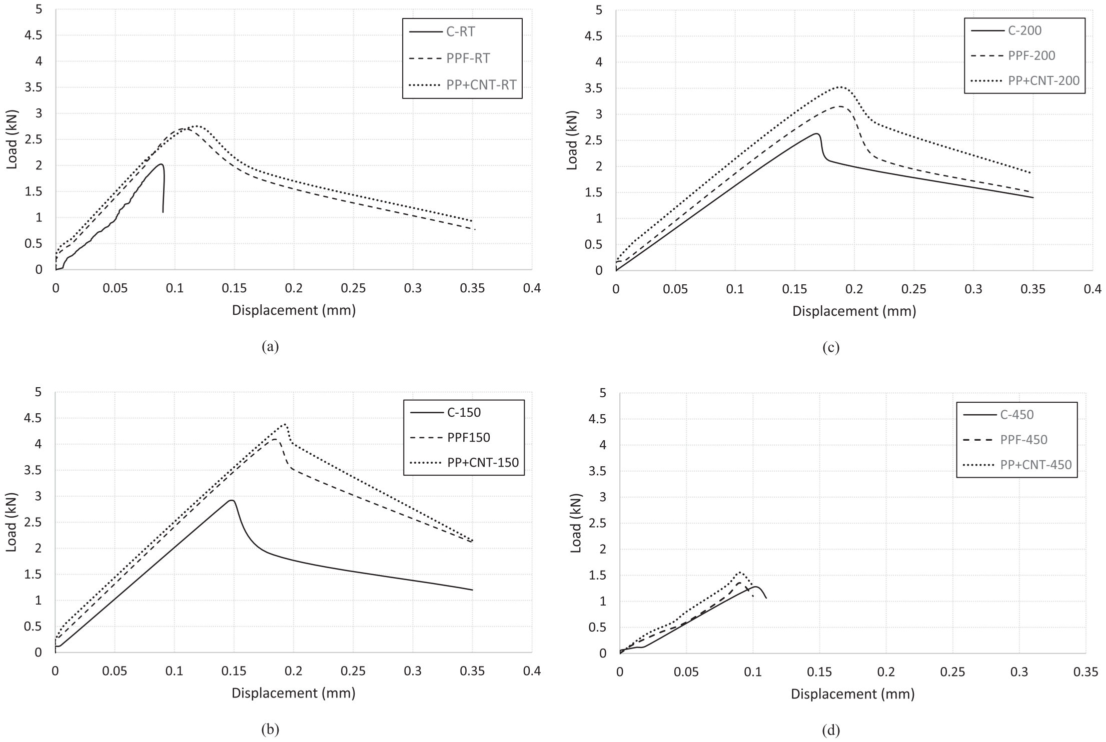
Thermal behavior of cement mortar with multi scale reinforcement was explored using Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) tests. Thermal conductivity was also investigated using a hot disk thermal constant analyzer machine. The Transient plane source method (TPS) was used to acquire the thermal conductivity data, as the sensor of the device is sandwiched between two-mortar specimens, the specimens used were taken after conducting the flexural strength test. The size of specimens was 40 mm × 40 mm × 80 mm, which was sufficient to cover the full area of the sensor. Finally, scanning electron microscopy (SEM) imaging was performed according to ASTM C1723-10 on the control and reinforced mortar at various temperatures.

3. Results and discussion

3.1. Mechanical properties degradation

3.1.1. Flexural load–deflection curves

Flexural test was conducted for mortar specimens heated at various levels up to 450 °C. For specimens heated at 600 °C, sever and wide cracks had been observed after heating exposure and hence the flexural test could not be able to perform. The load–displacement curves for plain-mortar specimens, mortar with PP fibers, and mortar with PP fibers and CNTs were plotted in Fig. 2. Plain mortar specimen owned brittle failure at room temperature as shown in Fig. 2a. It showed linear behavior until reached its maximum flexural strength then suddenly failed without post-failure performance. Incorporating PP microfibers into the mortar clearly enhanced its flexural strength and significantly improved its ductility. Adding CNTs combined with PP fibers into the mortar slightly enhanced its flexural strength but not its ductility. The main reason beyond the improvement could be attributed to the reinforcing ability of the PP fibers to mitigate crack propagation [21] as shown later in the SEM images. Adding CNTs enhanced the bond between the PP fibers and the hydration products [3] thus enhanced the bridging ability of the fibers which caused an enhancement in the flexural strength.



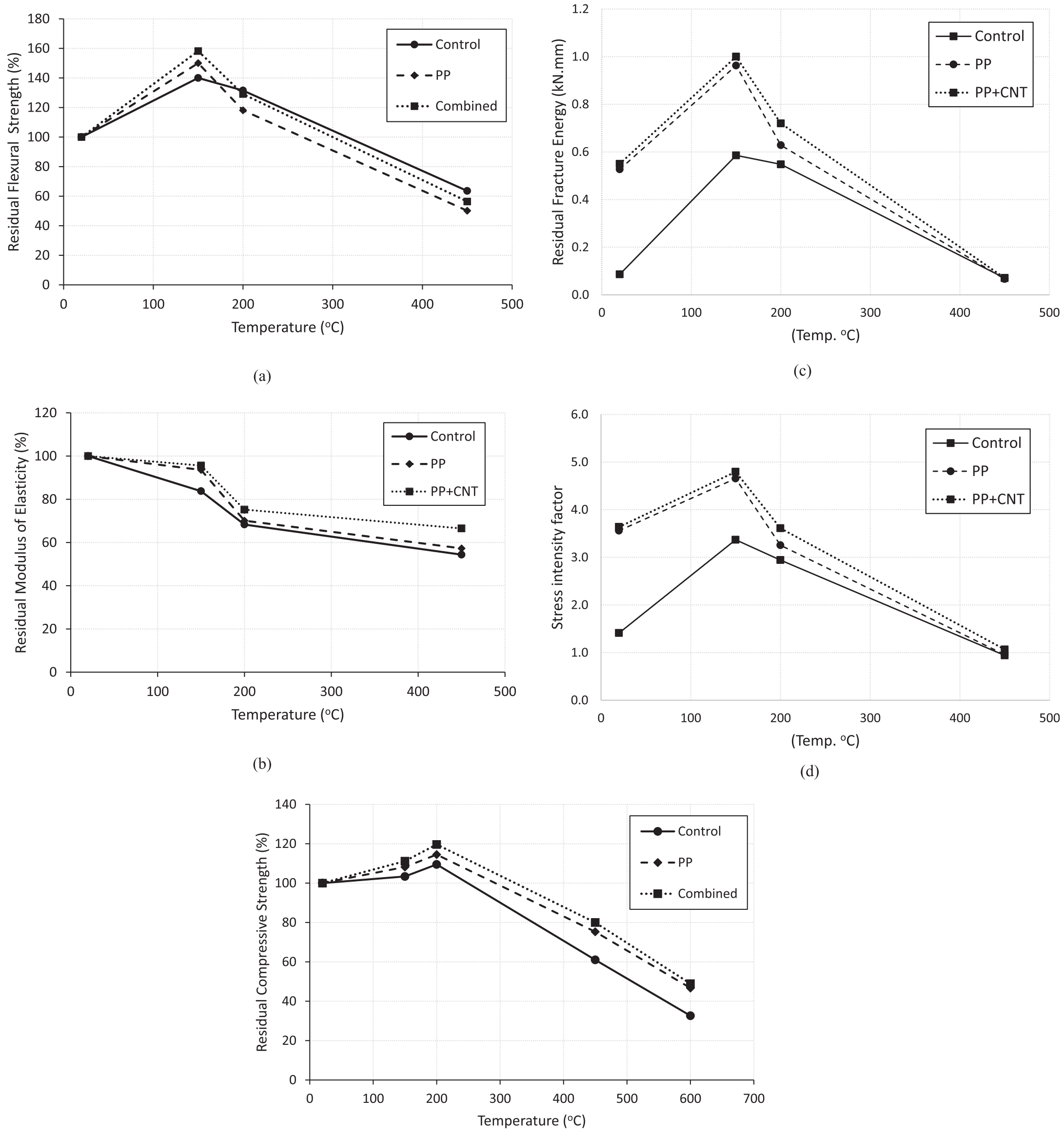
(a) (c) (b) (d)

Fig. 2. Flexural load-displacement curves for mortar specimens heated at (a) RT (b) 150 °C (c) 200 °C (d) 450 °C.

The load–deflection curves were characterized in terms of flexural strength, modulus of elasticity, and fracture energy (toughness). The results were used to calculate the stress intensity factor. All test results are summarized in Table 4 and discussed in the following sections.

Table 4
Mechanical properties of heated mortar specimens.

Specimen	Compressive strength (MPa)	Flexural strength (kN)	Elastic Modulus (GPa)	Fracture energy (N.mm)	Stress intensity factor
C-RT	30.3	2.00	23.134	86	1.41
C-150	31.3	2.80	19.38	586	3.37
C-200	33.2	2.63	15.8	548	2.94
C-450	18.5	1.27	12.58	70	0.94
C-600	9.9	0.21	NA	NA	NA
PPF-RT	38.5	2.70	24.04	527	3.56
PPF-150	41.7	4.05	22.5	963	4.65
PPF-200	44.1	3.19	16.85	628	3.25
PPF-450	29.0	1.35	13.77	66	0.96
PPF-600	18.0	NA	NA	NA	NA
Combined-RT	39.0	2.75	24.06	550	3.64
Combined-150	43.4	4.35	23	1000	4.80
Combined-200	46.7	3.55	18.1	720	3.61
Combined-450	31.2	1.55	16	71	1.07
Combined-600	19.1	NA	NA	NA	NA



(a)

(c)

(b)

(d)

(e)

Fig. 3. Residual mechanical properties of cement mortar heated at various levels (a) flexural strength (b) elastic modulus (c) fracture energy (d) stress intensity factor (e) compressive strength.

3.1.2. Residual flexural strength

To highlight the effect of heat exposure on the flexural strength of the mortar, relative residual flexural strength was calculated for all specimens as the ratio between the ultimate-load of heated specimen divided by the ultimate-load of the corresponding control specimen. The results were plotted in Fig. 3a. Heating cement mortar at 150 °C enhanced its residual flexural strength. The enhancement was more pronounced in the case of fiber-reinforced specimens and specimens with hybrid reinforcements. Further heating up to 200 °C reduced the residual flexural strength of the mortar. The reduction was more noteworthy for specimens contain PP fibers. The reason beyond that may ascribe to the exceeding of the fibers melting point (160 °C). Beyond this temperature the fiber melted and could not help in mitigating the destructive effect of micro-cracks that form at higher temperatures due to the tensile stresses created in flexural test [22]. Presence of the CNTs with their high thermal conductivity helped to scatter the thermal stresses uniformly through cementitious composites [16]. The distribution of these thermal stress that have tensile nature helped the mortar to withstand more stresses thus enhanced its flexural capacity under heating as shown in Fig. 3a. Further heating up to 450 °C significantly reduced the residual flexural strength of all specimens with almost same rate. Control specimens, fiber-reinforced specimens, and specimens with hybrid reinforcements maintained 63%, 50% and 56% of their original strengths, respectively. This reduction could be attributed to the decomposition of the hydration products and the growth of the internal cracks due to the increase in pore pressure resulted from water evaporation.

3.1.3. Residual modulus of elasticity

The residual modulus of elasticity of all specimens were calculated as the slope of the linear part of the load–deflection curves and summarized in Table 4. The relative residual modulus was then calculated as the ratio between the modulus of heated specimen divided by the modulus of corresponding control specimen. Fig. 3b shows the relative residual modulus for all specimens. It is clear that the residual modulus of elasticity decreased with increasing the heating level. For heating level of 150 °C, the reduction in the modulus of elasticity of reinforced specimens was significantly less than that of plain mortar. This trend could be attributed to the reinforcement effects of the CNTs and the PP

(a) (c)

(b) (d)

Fig. 4. Typical compressive failure mode of specimens heated up to 450oC (a) plain mortar (b) hybrid-reinforced specimen, and heated at 600oC (a) plain mortar (b) hybrid-reinforced specimen.

microfibers. Between 150 °C and 200 °C, specimens contain PP fibers showed deeper drop in the modulus than that of plain mortar specimens. This finding may be ascribed to the melting of the PP fibers when the temperature exceeded its melting point at 160 °C. Similar trend was reported in the literature [4]. Between 200 °C and 450 °C, specimens reinforced with CNTs and PP fibers showed less reduction in the modulus than that of other specimens. This behavior could be attributed to the CNTs ability to mitigate the cracks and delay their propagation. Finally, the residual modulus of reinforced mortar specimens was higher than that of plain mortar specimens for all heated levels. Plain mortar specimens, PP-fiber reinforced specimens, and specimens reinforced with CNTs and PP fibers maintain almost 54%, 57%, and 67% of their elastic modulus, respectively, when heated at 450 °C.

3.1.4. Residual fracture energy (toughness)

Fracture energy (toughness) of all specimens were calculated as the area under the load–deflection curves shown in Fig. 2. The values are summarized in Table 4 and plotted in Fig. 3c. Fracture energy or the toughness of reinforced specimens was much higher than that of plain mortar specimens at room temperature. This finding is a result to the huge enhancement in the ductility of the mortar specimens due to the CNTs and PP fibers additions as clear in Fig. 2. During the flexural test, the presence of the CNTs delayed the initiation of the cracks whereas the presence of the PP fibers bridged the cracks and mitigated their propagation. This mechanism offer an extra energy absorption thus higher fracture energy. Similar trend was reported in the literates [4,21]. Increasing the exposure temperature up to 150 °C increased the residual fracture energy of all specimens with almost same rate. Further increase in the exposure temperature up to 200 °C reduced the residual fracture energy of all specimens. The reduction was much higher for specimens contain PP fibers than plain mortar specimens. At this heating level, the polypropylene fibres start melted thus lost their ability to mitigate the cracks. Another large drop in the fracture energy of all specimens was noticed due to further heating at 450 °C.

3.1.5. Stress intensity factor

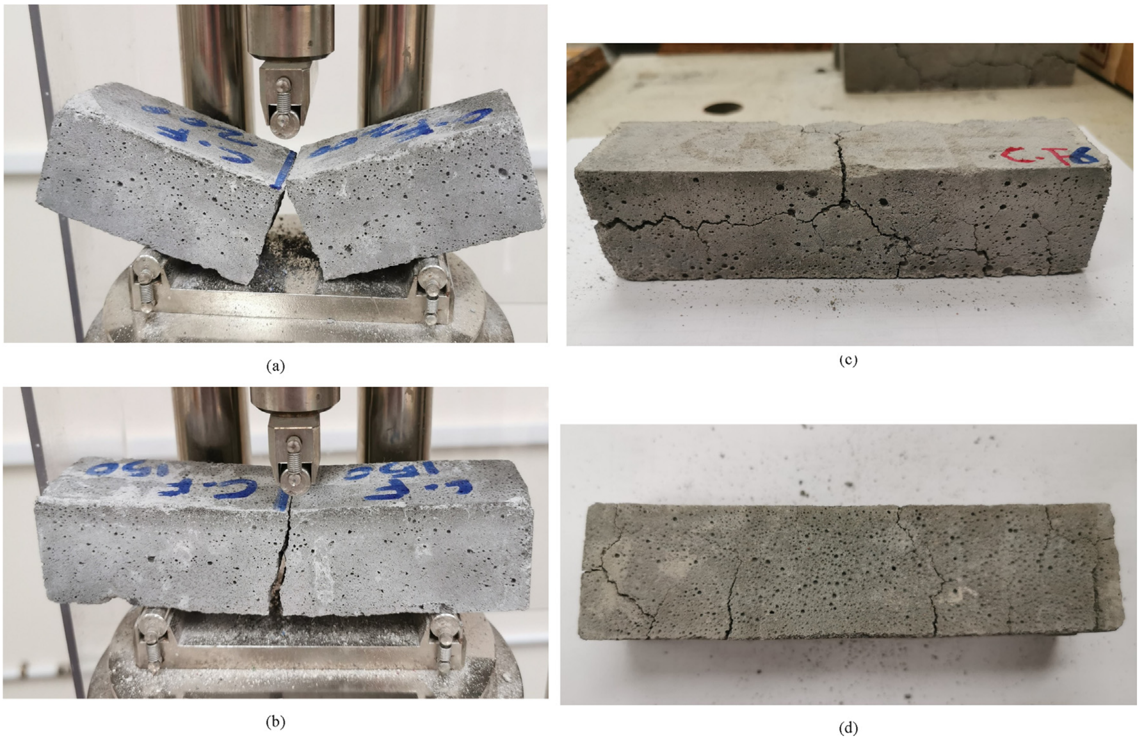
Stress intensity factor (K_I) is a representative parameter describes the overall damage behavior of fiber-reinforced mortar. It depends on the Young modulus (E) and fracture energy (E_f) of the specimen as described in Eq. (1):

$$K_I = \left(E * E_f\right)^{0.5} \tag{1}$$

Stress intensity factor of all mortar specimens subjected to various heating levels were calculated, listed in Table 4, and plotted in Fig. 3d. Presence of PP fibers and CNTs significantly increase the stress intensity factor of cement mortar for heating level below 150 °C. This trend reflect the ability of CNTs to delay cracks initiation and the ability of the PP fibers to mitigate cracks propagation through mortar specimens. At higher heating level, the difference in the stress intensity factor between plain and reinforced specimens started decreasing due to fiber melting.

3.1.6. Residual compressive strength

Compressive strength test was conducted for plain and reinforced mortar specimens heated at various temperatures ranging from RT up to 600 °C. The results are summarized in Table4. Unheated plain mortar specimen owned compressive strength of 30 MPa. Adding 0.1% PP fibers by weight of cement to the mortar significantly enhanced its compressive strength by 27%. The improvement could be ascribed to the ability of the fibers in bridging the cracks and resist their propagation [3]. Adding 0.05% CNTs combined with the 0.1% PP fibers by weight of cement enhanced the compressive strength of the mortar by almost 30%. The well distributed of the CNTs within the hydration products delayed the initiation of the cracks, whereas the presence of the PP microfibers mitigate the propagation of these cracks. In addition, CNTs



(a)

(c)

(b)

(d)

Fig. 5. Typical flexural failure mode of (a) plain mortar (b) hybrid-reinforced specimen heated up to 450oC. Thermal cracks of (c) plain mortar (d) hybrid-reinforced specimen due to heating at 600oC.

could enhance the adhesion between the PP fibers and the cement paste which improved the stress transfer thus improve the strength [23]. To investigate the behavior of cement mortar at high temperatures, relative residual compressive strength of all specimens was calculated as the ratio between strength of heated specimens and the corresponding control specimen. The results are plotted in Fig. 3e. Heated cement mortar up to 200 °C enhanced its compressive strength. The enhancement in compressive strength at this stage could be attributed to the continuation of the hydration process of cement particles as mentioned in [19]. Specimens with PP fibers, or CNTs and PP fibers showed higher residual strength than plain mortar specimen at this heating level. This finding could be ascribed to the ability of the CNTs to fill the voids and the ability of the PP fibers to bridge the cracks. Further heating of the mortar up to 450 °C significantly reduced its compressive strength. This reduction could be ascribed to the decomposition of the hydration products [12,24] and the development of the internal cracks due to the increase in pore pressure resulted from water evaporation [16]. Presence of PP fibers enhanced the residual compressive strength of the mortar. This enhancement could be ascribed to the ability of the vapour to escape throw the microscopic channels formed within the matrix by melting of PP fibers [25]. Adding CNTs combined with the PP fibers resulted in further enhancement in the residual compressive strength of the mortar at this heating level. This improvement could be ascribed to the ability of CNTs with its hollow structure to work as channels for releasing the high-pressure steam resulted from water evaporation thus reduce the damage [19], or to the nano-reinforcing action of the CNTs. Further increase in the exposure temperature up to 600 °C caused sever reduction in the compressive strength of the mortar. Control specimen, fiber-reinforced specimen, and specimen with PP fiber and CNTs maintained only 33%, 46%, and 49% of their original compressive strength. It is clear that presence of PP fiber or CNTs combined with PP fibers enhanced the residual compressive strength of the mortar at this heating level. The reduction in the strength could be ascribed to the breaking of the interfacial bond between aggregates and the surrounded paste, and the dramatic decomposition of the hydration products [19].

3.2. Visual inspection and failure modes

3.2.1. Compressive damage behavior

For plain cement mortar specimens, vertical cracks were initiated in the specimens and then propagated parallel to the direction of the load. With further load increase, explosive brittle failure was observed as shown in Fig. 4a. The failure mode did not changed with the presence of the CNTs and the PP fibers. However, more hairy cracks rather than major cracks were observed during the test. At failure, less fragments were observed showing the ability of the fibers to keep the integrity of the specimens as shown in Fig. 4b. Similar behavior was reported in the literature. Same failure modes were observed for specimens heated up to 450 °C. In the case of heating level of 600 °C, major wide cracks were visually observed during the test. Sever damage with more fragments were observed in the case of plain mortar specimens as shown in Fig. 4c. Whereas the reinforced specimens kept their integrity but owned major cracks as shown in Fig. 4d.

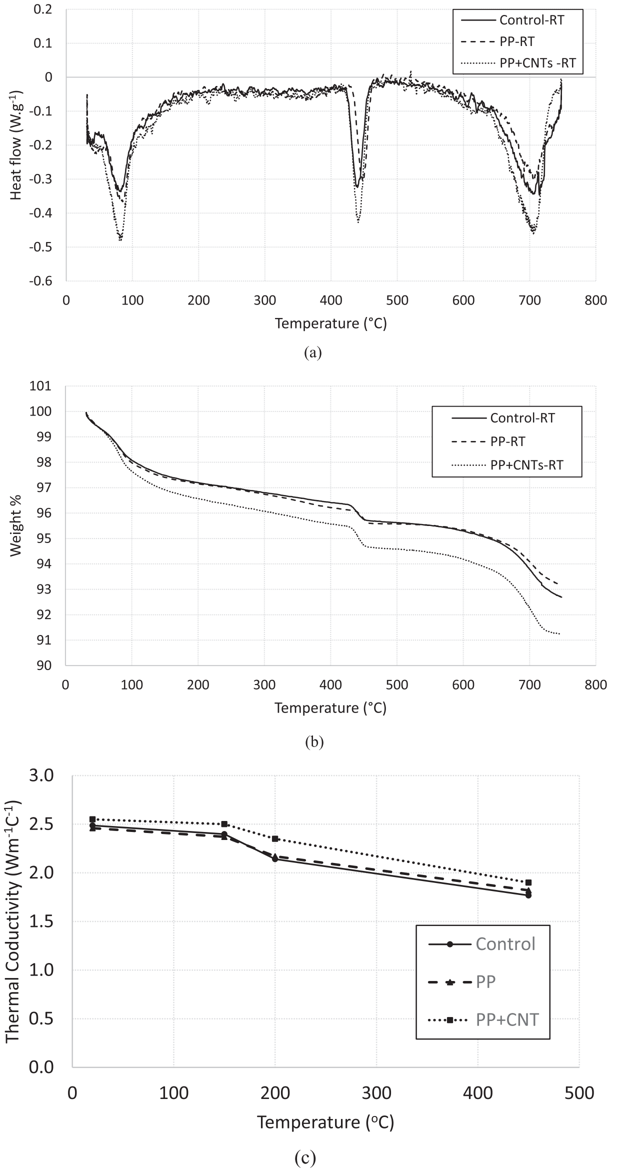
3.3. Flexural damage behavior

At room temperature, plain cement mortar specimen showed brittle failure. It reached its maximum flexural strength then suddenly failed at low deflection value without any post-failure performance. Presence of CNTs and PP fibers reduced the cracks development and mitigated their propagation thus enhanced the ductility of the specimens. Heating cement mortar specimens up to 200 °C did not change their flexural failure mode. Fig. 5 shows typical failure modes of plain and reinforced mortar specimens under flexural loading. For heating level of 600 °C, plain mortar specimens owned major and wide cracks due to heating as shown in Fig. 5c. Presence of CNTs and PP fibers reduced the intensity and the width of these cracks as shown in Fig. 5d. The flexural test could not carry out due to these cracks thus the results of specimens heated at 600 °C were omitted.

3.4. Thermal behavior characterization

3.4.1. Heat flow analysis using DSC

Heat flow analysis of cement mortar specimens was conducted using DSC technique. Three significant endothermic peaks could be observed as shown in Fig. 6a. The first peak was located in the interval of 50–120 °C which refers to the decomposition of calcium silicate hydrate (CSH) gel [26]. This peak did not affected by the presence of the PP fibers. On contrary, adding CNTs to the mortar increased the area of this peak reflecting higher heat absorption.

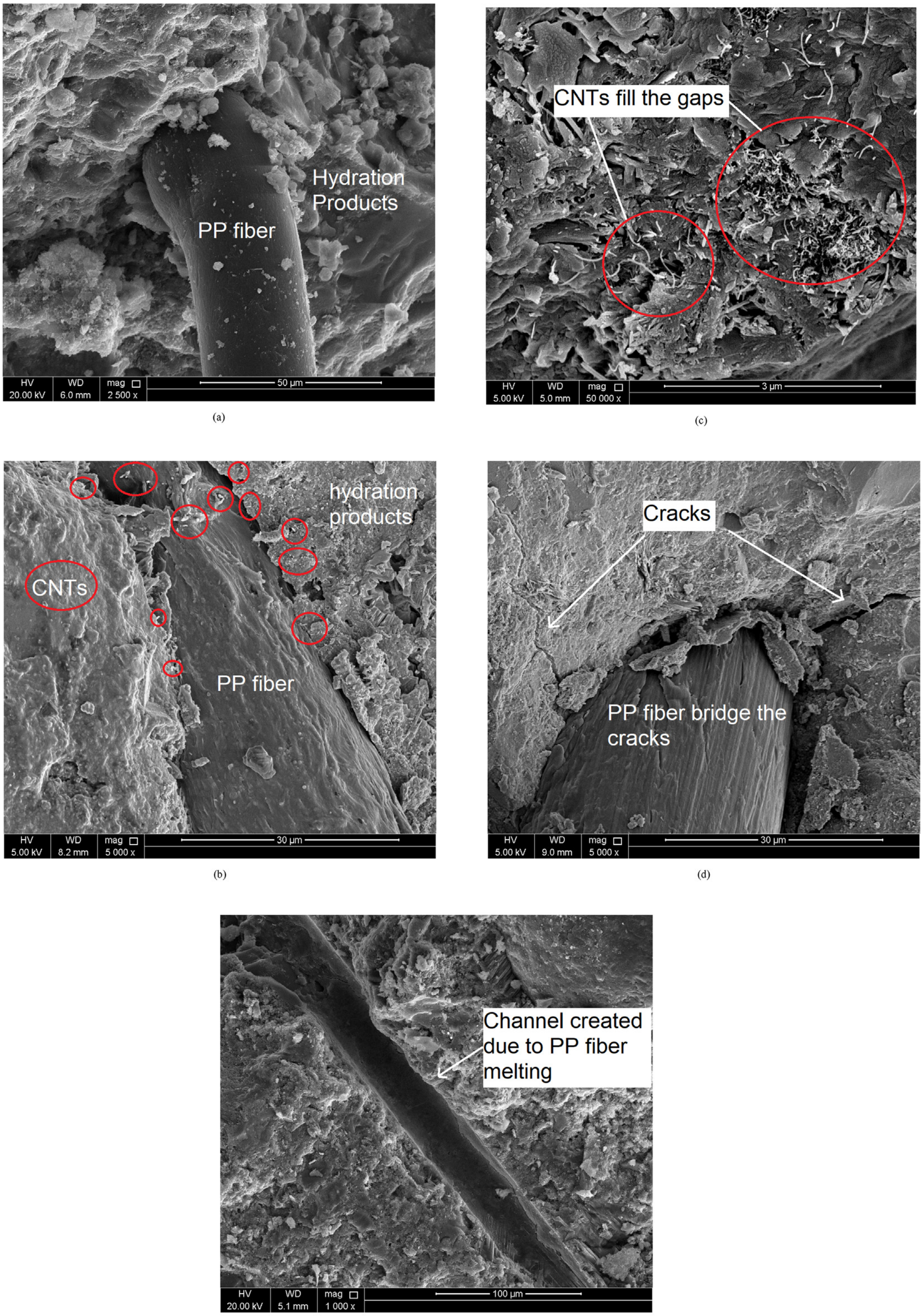


(a)

(b)

(c)

Fig. 6. Thermal characteristics of cement mortar heated at various level (a) heat flow using DSC (b) weight loss using TGA (c) thermal conductivity.



(a) (c)

(b) (d)

(e)

Fig. 7. SEM images show (a) PP fibers acted as micro reinforcements (b) CNTs enhanced the bond between PP fibers and cement paste (c) CNTs filled the pores (d) PP fibers bridged these cracks (e) original location of melted PP fibers.

The reason beyond this finding could be the fact that specimens with CNTs contain more free water due to the ability of CNTs to absorb water during mixing process [27]. The second peak was located in the interval of 420–470 °C which refers to the decomposition of calcium hydroxide (portlandite) [26]. This peak was shifted toward higher dissociation temperature in the presence of PP fibers, whereas adding CNTs increased its area. The third peak was located in the interval 640–750 °C which refers to the decomposition of calcite ($CaCO_3$) and carbonated C-S-H. This peak did not affected by the presence of the PP fibers. On contrary, adding CNTs to the mortar increased the area of this peak reflecting higher heat absorption.

3.4.2. Weight loss analysis using TGA

Weight loss analysis due to dehydration and decomposition of cement mortar were conducted using TGA technique. The Thermogravimetric profile in Fig. 6b shows three main weight loss steps, the first step located at about 85 °C which refers to the decomposition of C-S-H, the second step happened at about 440 °C which refers to the Portlandite decomposition, and the last step occurred at about 710 °C which refers to the decomposition of calcite ($CaCO_3$). In addition, a stiff slope was observed for the Thermogravimetric curve belong to specimen with CNTs below 120 °C indicating to more dehydration of pore water [28]. The first weight loss step at 85 °C did not affected by the presence of PP fibers. On contrary, this step was increased by adding CNTs indicating higher amount of calcium silicates hydrates developed in these mortar specimens. The second weight loss that observed at 440 °C did not affected by the presence of the PP fibers; however, the dissociation temperature was slightly shifted toward higher value. In case of hybrid reinforcement, this weight step slightly increased and the dissociation temperature was slightly shifted toward higher value. These results agree with the aforementioned DSC findings. Finally, the weight loss due to calcite decomposition at 710 °C decreased by adding PP fibers but increased with adding the CNTs.

3.4.3. Thermal conductivity

Thermal conductivity of cement mortar as a function of elevated temperature are shown in Fig. 6c. It is clear that the thermal conductivity of cement mortar decreased with heating regardless the presence of the reinforcements. Similar trend was reported in [13]. The reduction in the thermal conductivity could be attributed to the decomposition of hydration products thus the damage due to heating. It is clear in Fig. 6c that thermal conductivity of cement mortar did not affected by the presence of PP fibers. On contrary, adding CNTs increased the conductivity of the mortars regardless the heating level. Similar trend was reported in [29,30]. The improvement in thermal conductivity of cement mortar due to the CNTs addition could be credited to many reasons. Firstly, the high thermal conductivity of the CNTs compared to the cement particles. Secondly, the filling effect of the CNTs. The well distribution of the CNTs through the hydration products resulted in less voids and denser microstructure of cement mortar as shown in the SEM images.

3.5. Microstructure deterioration

Microstructure deterioration of cement mortar due to heating, and the role of PP fibers and CNTs in mitigating this deterioration were explored using scanning electron microscopy (SEM) analysis. For unheated mortar, typical hydration products such as Calcium Silicates Hydrates (CSH), Calcium Hydroxides (CH), and ettringite needles were captured. The PP fibers acted as micro reinforcements distributed through the hydration products as clear in Fig. 7a. In the case of hybrid reinforcement, the CNTs played a major role to enhance the bond between the PP fibers and the cement paste (Fig. 7b) which improved the stress transfer process thus enhance the mechanical properties [3]. This finding support the aforementioned mechanical properties. Heating cement mortar at 150 °C did not cause significant deterioration to the hydration products. However, thermal microcrack started to initiate and propagate through the specimen. The CNTs filled the pores and incorporated into the walls of the gaps as shown in Fig. 7c, and the PP fibers bridged these cracks and mitigated their propagation as shown in Fig. 7d. Once the melting point of the PP fibers exceeded, the fibers melted and created extra voids within the microstructure of the mortar as shown in Fig. 7e. These additional voids allow the steam generated due to the dehydration process to release thus reduce the pore pressure and could delay the spalling [30]. Generating extra voids within the cement matrix represent one of the main factors that caused reduction in the mechanical strengths of heated specimens.

4. Conclusions

The hybrid effect of polypropylene microfibers and CNTs on fire resistance and thermal characteristics of cementitious composites were experimentally investigated in this study. The following conclusions could be drawn:

1. Polypropylene microfibers improved the residual flexural strength of cement mortar heated up to the melting point of the fibers (160 °C). Beyond this temperature, the fiber-reinforced specimens showed lower residual strength than that of plain mortar.
2. Presence of CNTs enhanced the residual flexural strength of the fiber reinforced mortar exposed to elevated temperature up to 600 °C.
3. The residual modulus of elasticity of cement mortar decreased with increasing the heating level. However, it was improved by the presence of the PP fibers and the CNTs reinforcement.
4. Adding small dosage of polypropylene microfibers and CNTs enhanced the residual fracture energy and stress intensity factor of cement mortar. The enhancement was less significant in the case of exposure temperatures greater than 150 °C.
5. Adding small amount of polypropylene microfibers and CNTs enhanced the residual compressive strength of heated cement mortar. The enhancement was more visible for heating level beyond 200 °C.
6. Thermal conductivity of cement mortar decreased with heating regardless of the presence of the reinforcements. It was affected (increased) by the addition of the CNTs but not the PP fibers for all heating levels
7. According to the DSC and TGA analysis, presence of CNTs increased heat absorption needed for decomposition of the hydration products of cement mortar whereas the presence of the fibers had minor effect
8. According to the SEM images, the CNTs filled the pores and delayed the initiation of the cracks, whereas the PP fibers bridged these cracks and mitigated their propagation.

CRediT authorship contribution statement

Mohammad R. Irshidat: Conceptualization, Methodology, Formal analysis, Project administration, Resources. **Nasser Al-Nuaimi:** Conceptualization, Methodology, Resources. **Mohamed Rabie:** Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] N. Flores Medina, G. Barluenga, F. Hernández-Olivares, Enhancement of durability of concrete composites containing natural pozzolans blended cement through the use of Polypropylene fibers, Compos. B Eng. 61 (2014) 214–221.

[2] M. Szeląg, Evaluation of cracking patterns of cement paste containing polypropylene fibers, Compos. Struct. 220 (2019) 402–411.
[3] Y. Qin, X. Zhang, J. Chai, Z. Xu, S. Li, Experimental study of compressive behavior of polypropylene-fiber-reinforced and polypropylene-fiber-fabric-reinforced concrete, Constr. Build. Mater. 194 (2019) 216–225.
[4] M. Ezziane, T. Kadri, L. Molez, R. Jauberthie, A. Belhacen, High temperature behaviour of polypropylene fibres reinforced mortars, Fire Saf. J. 71 (2015) 324–331.
[5] P. Müller, J. Novák, J. Holan, Destructive and non-destructive experimental investigation of polypropylene fibre reinforced concrete subjected to high temperature, J. Build. Eng. 26 (2019) 100906.
[6] V.K.R. Kodur, B. Yu, R. Solhmirzaei, A simplified approach for predicting temperatures in insulated RC members exposed to standard fire, Fire Saf. J. 92 (2017) 80–90.
[7] C. Maluk, L. Bisby, G.P. Terrasi, Effects of polypropylene fibre type and dose on the propensity for heat-induced concrete spalling, Eng. Struct. 141 (2017) 584–595.
[8] J. Eidan, I. Rasoolan, A. Rezaeian, D. Poorveis, Residual mechanical properties of polypropylene fiber-reinforced concrete after heating, Constr. Build. Mater. 198 (2019) 195–206.
[9] D. Choumanidis, E. Badogiannis, P. Nomikos, A. Sofianos, The effect of different fibres on the flexural behaviour of concrete exposed to normal and elevated temperatures, Constr. Build. Mater. 129 (2016) 266–277.
[10] A. Jameran, I.S. Ibrahim, S.H.S. Yazan, S.N.A.A. Rahim, Mechanical Properties of Steel-polypropylene Fibre Reinforced Concrete Under Elevated Temperature, Procedia Eng. 125 (2015) 818–824.
[11] R. Serrano, A. Cobo, M.I. Prieto, M.d.L.N. González, Analysis of fire resistance of concrete with polypropylene or steel fibers, Constr. Build. Mater. 122 (2016) 302–309.
[12] F.B. Varona, F.J. Baeza, D. Bru, S. Ivorra, Influence of high temperature on the mechanical properties of hybrid fibre reinforced normal and high strength concrete, Constr. Build. Mater. 159 (2018) 73–82.
[13] N. Yermak, P. Pliya, A.-L. Beaucour, A. Simon, A. Noumowé, Influence of steel and/or polypropylene fibres on the behaviour of concrete at high temperature: Spalling, transfer and mechanical properties, Constr. Build. Mater. 132 (2017) 240–250.
[14] A.M. Rashad, Effect of carbon nanotubes (CNTs) on the properties of traditional cementitious materials, Constr. Build. Mater. 153 (2017) 81–101.
[15] K.A. Bani-Hani, M.R. Irshidat, R.K.A. Al-Rub, N.A. Al-Nuaimi, A.T. Talleh, Strength optimisation of mortar with CNTs and nanoclays, Proc. Instit. Civil Eng. – Struct. Build. 169 (5) (2016) 340–356.
[16] M.R. Irshidat, A. Al-Shannaq, Using textile reinforced mortar modified with carbon nano tubes to improve flexural performance of RC beams, Compos. Struct. 200 (2018) 127–134.
[17] S. Alrekabi, A.B. Cundy, A. Lampropoulos, R.L.D. Whitby, I. Savina, Effect of high-intensity sonication on the dispersion of carbon-based nanofilaments in cementitious composites, and its impact on mechanical performance, Mater. Des. 136 (2017) 223–237.
[18] A. Sedaghatdoost, K. Behfarnia, M. Bayati, The effect of curing period on the residual strength of Portland cement mortar containing MWCNTs at elevated temperature, Constr. Build. Mater. 196 (2019) 144–153.
[19] L.W. Zhang, M.F. Kai, K.M. Liew, Evaluation of microstructure and mechanical performance of CNT-reinforced cementitious composites at elevated temperatures, Compos. A Appl. Sci. Manuf. 95 (2017) 286–293.
[20] H. Lee, Y.M. Song, K.J. Loh, W. Chung, Thermal response characterization and comparison of carbon nanotube-enhanced cementitious composites, Compos. Struct. 202 (2018) 1042–1050.
[21] S. Aydın, H. Yazıcı, B. Baradan, High temperature resistance of normal strength and autoclaved high strength mortars incorporated polypropylene and steel fibers, Constr. Build. Mater. 22 (4) (2008) 504–512.
[22] W.L. Baloch, R.A. Khushnood, W. Khaliq, Influence of multi-walled carbon nanotubes on the residual performance of concrete exposed to high temperatures, Constr. Build. Mater. 185 (2018) 44–56.
[23] A. Sedaghatdoost, K. Behfarnia, Mechanical properties of Portland cement mortar containing multi-walled carbon nanotubes at elevated temperatures, Constr. Build. Mater. 176 (2018) 482–489.
[24] A. Bilodeau, V.K.R. Kodur, G.C. Hoff, Optimization of the type and amount of polypropylene fibres for preventing the spalling of lightweight concrete subjected to hydrocarbon fire, Cem. Concr. Compos. 26 (2) (2004) 163–174.
[25] M.R. Irshidat, M.H. Al-Saleh, Thermal performance and fire resistance of nanoclay modified cementitious materials, Constr. Build. Mater. 159 (2018) 213–219.
[26] S.-H. Jung, S. Oh, S.-W. Kim, J.-H. Moon, Effects of CNT dosages in cement composites on the mechanical properties and hydration reaction with low water-to-binder ratio, Appl. Sci. 9 (2019) 4630.
[27] Z. Pavlík, A. Trník, T. Kulovaná, L. Scheinherrová, V. Rahhal, E. Irassar, R. Černý, DSC and TG analysis of a blended binder based on waste ceramic powder and portland cement, Int. J. Thermophys. 37 (2016) 32.
[28] A. Sarı, A. Biçer, G. Hekimoğlu, Effects of carbon nanotubes additive on thermal conductivity and thermal energy storage properties of a novel composite phase change material, J. Compos. Mater. 53 (21) (2019) 2967–2980.
[29] M.K. Hassanzadeh-Aghdam, M.J. Mahmoodi, M. Safi, Effect of adding carbon nanotubes on the thermal conductivity of steel fiber-reinforced concrete, Compos. B Eng. 174 (2019) 106972.
[30] V. Kodur, Properties of concrete at elevated temperatures, ISRN Civil Eng. 2014 (2014) 1–15.