Influence of flame retardant addition on the durability of epoxy based polymer concrete after exposition to elevated temperature

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HIGHLIGHTS

- Different Polymer Concrete systems were subjected to elevated temperatures.
- The effects of addition of two types of flame-retardant were examined.
- After exposure, PC (ATH) system has the lowest decrease of mechanical properties.
- The incorporation of flame-retardants increase the rigidity of the polymer concrete.

ARTICLE INFO

ABSTRACT

The use of the resin in the civil engineering applications for repair applications, precast elements, etc., was well-developed in the last decade. Polymer concrete (PC) is strongly prescribed for applications where chemical resistance, strength and stiffness are required.

When exposed to high temperatures, PC losses significantly its strengths as a consequence of the matrix degradation mainly. Durability concern after exposure to high temperatures is investigated here. A comparison between the physical and mechanical characteristics of an optimized PC before and after adding flame retardant (FR) is undertaken in this study.

Mechanical and ultrasonic propagation waves testing were performed on polymer concrete based on epoxy resin with 6, 9, 13 and 16% of resin show that the higher performances are obtained for polymer content of 13%. Two types of FR, consisting on Ammonium Polyphosphate (APP) and aluminium hydroxide (ATH) compounds, are then introduced to this formulation and the three types of concretes were exposed to thermal cycles.

Porosity, thermal conductivity and mechanical resistance were measured and their evolution as a function thermal amplitude was studied. It appears that adding ATH improves considerably the mechanical properties of PC vs. Temperature rise. But the second has inversely influence on properties while increasing the effect of temperature.

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1. Introduction

The use of polymer concrete in civil engineering applications is becoming very common and attractive thanks to its superiority compared to other construction materials in term of good resistance to chemical aggressions, rapid hardening, good adhesion with existing material and high mechanical properties. This "new material" (PC) consists generally of aggregates and thermoset resin combined together in a mix process to form a rocklike substance strongly prescribed for applications where chemical resistance, strength and stiffness are required [1–3]. The thermoset resin is used as a substitute of water and cement binder used in Portland cement concrete (OPC).

Because of the organic nature of matrix (resin), the exposure to high temperatures is not recommended since it may lead to product deterioration. The resistance of polymer concrete structure to high temperatures depends upon the type of binder. For the epoxy and polyester concretes, the maximum service temperature is about 60 °C for exposures that occur over long periods of time and about 100 –120 °C for short exposures.

At the present time, the bad resistance to high temperatures and to flame or fire and the relatively high cost, restrains significantly the use and development of PC in civil engineering applications. Hence, the current study aims to overcome some of these limitations.

A large number of research projects have been focused on the investigation of the physico-mechanical properties of mortars or concretes based on polyester or epoxy resin and on the effect of temperatures cycles or reinforcement by adding fibres [4–9]. It was noticed that the behaviour of the PC at high temperatures and the influence of addition of flame retardant components is less investigated [10].

The optimization of the PC formulation is already investigated in previous study [11]. Higher performances are obtained for 13% of epoxy content by total weight of PC and the maximum packing density for aggregates is given for 35% of gravel and 65% of sand by the total weight of the granular skeleton. Similar results have been reported by various authors who conclude that optimum resin content lies mostly in the range of 12–16% by weight of polymer concrete [12].

To improve the thermo-mechanical behaviour of these concretes, the solution adopted was a flame retardants addition; an Ammonium Polyphosphate component (APP) and an Alumina Trihydrate (ATH) product were added at a rate of 20% by the weight of polymer.

The ATH belonging to metal hydroxides group remains by far the most widely used inorganic flame retardants system; it is a white, odorless, powdery, solid substance, not expensive and it is easy to incorporate into the polymers. Its mechanism of action is based on the heat absorption and release of water which cooled the system and dilutes the gas in the area of flames from temperatures between 180 °C and 200 °C [13].

Inorganic phosphorus products like APP act essentially in the condensed phase. But it has been shown that some can influence the reactions that take place in gas phase. Thermal decomposition of phosphorus flame retardants gives phosphoric acid and promotes the formation of an intumescent char layer that acts as a physical barrier to slow the heat and mass transfer through the surface of the material. They are particularly effective in polymers containing a lot of oxygen and are widely used in resins thermoplastics and thermosets, polyurethane foams. However, the low hydrolytic stability of APP and the low compatibility between APP and the matrix have a negative effect on the durability and physical–mechanical properties of the composites [14].

Optimized polymer concrete samples with and without considered flame retardant type have been subject to different temperatures ranging from 23 °C to 250 °C were studied.

Mechanicals strengths and thermal conductivity were measured. The Dynamic non-destructive properties of PC are predicted using ultrasonic pulse velocity (UPV) method [15].

Moreover, the total porosity was measured by mercury intrusion porosimetry (MIP).

2. Experimental investigation

2.1. Material and sample preparation

Table 1 summarizes the constituents of the optimized epoxy based PC used in this study. The binder, Eponal 371 (Bostik), has a room temperature (RT) viscosity between 5000 and 12,000 mPa·s and a density ranging from 1.42 to 1.48. The binder is mixed at a ratio of 100:60 by weight (resin/hardener) according to the manufacturer recommendations.

The inorganic aggregates used are commercially silico-calcaire aggregates (Saint-Louis quarry in France), 0/4 sand and 4/10 gravel, having a real density of 2470 and 2530 Kg/m³, respectively. The aggregates were allowed to dry for 24 h at 105 °C, before mixing with resin, to ensure a good adhesion between PC constituents .

Two formulations of PC containing two types of flame retardant were studied. The quantity of flame retardant added represents 20% of the total weight of the optimal polymer content (13% of the total mass of PC). The composition of each system is given in Table 1. The first type of flame retardant is ammonium polyphosphate (APP) and the second is aluminium hydroxide (ATH) both commercialised and recommended to be used with epoxies. The two formulations are called PC (APP) and PC(ATH).

PC constituents are mixed at a speed of 200 to 300 rev/min for 3 to 5 min. The mixture was then poured into three layers according to the standard test methods ASTM [16,17]. Each layer is compacted. The PC specimens are allowed to cure for 24 h at RT (23 ± 2 °C). They are then demoulded and kept for 6 other days before being exposed to considered environmental conditions.

2.2. Testing

The dimensions of flexural test specimens (three-point flexural) are 50 × 50 × 305 mm. For uniaxial compression studies, 50 × 100 mm compacted cylindrical specimens were prepared. The loads are applied at a constant speed of 1 mm/min and 1.25 mm/min for flexure and compression tests respectively [18–20].

The midspans deflection of the beam were measured using LVTD device (Linear Variable Displacement Transducer) attached to a L-shape angle metal fastened to samples at midheight as shown in Fig. 1.

2.3. Temperature cycles

During their service lifetime, PC can increase temperatures over long or short periods of time. Thus the knowledge of the behaviour of the PC under different temperature conditions is of crucial importance since it aims efficiency while designing and using material. In spite of this importance, only a limited number of studies were done in this context [4,8,10,21,22].

Table 1
Compositions of PC systems.

PC Systems	Polymer[*] (%)	Sand[*] (%)	Gravel[*] (%)	Flame retardant[*] (%)
PC (APP)	13	53,95	30,45	2,6
PC (ATH)				
PC13% (Optimal)	13	56,55	30,45	0

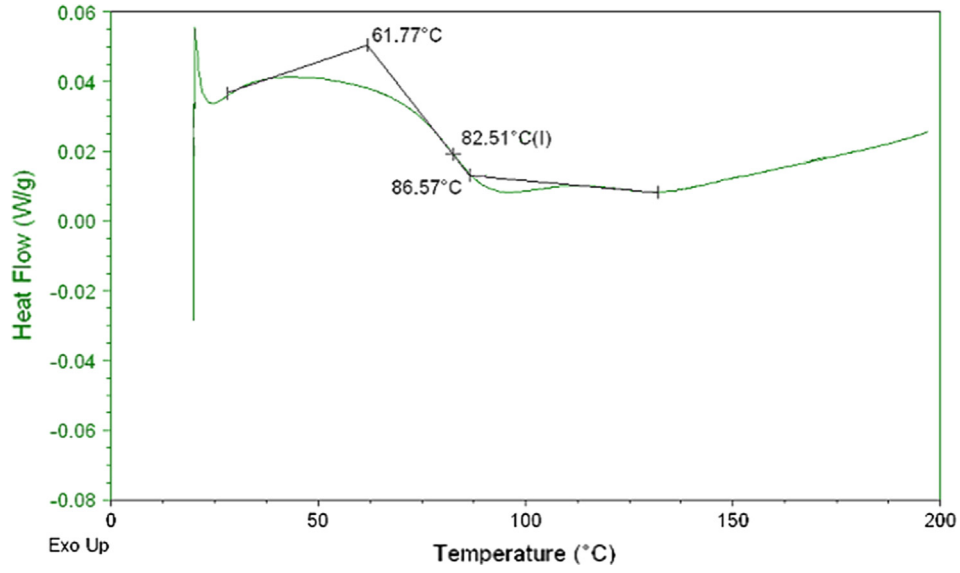[*] By weight of PC.
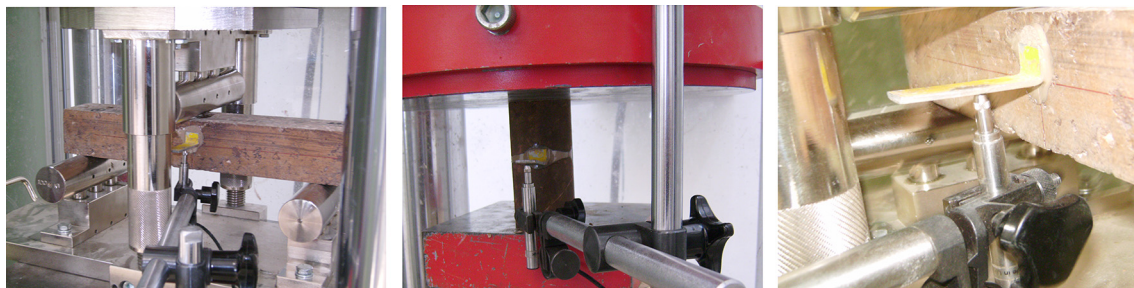
Fig. 1. Mechanical tests.
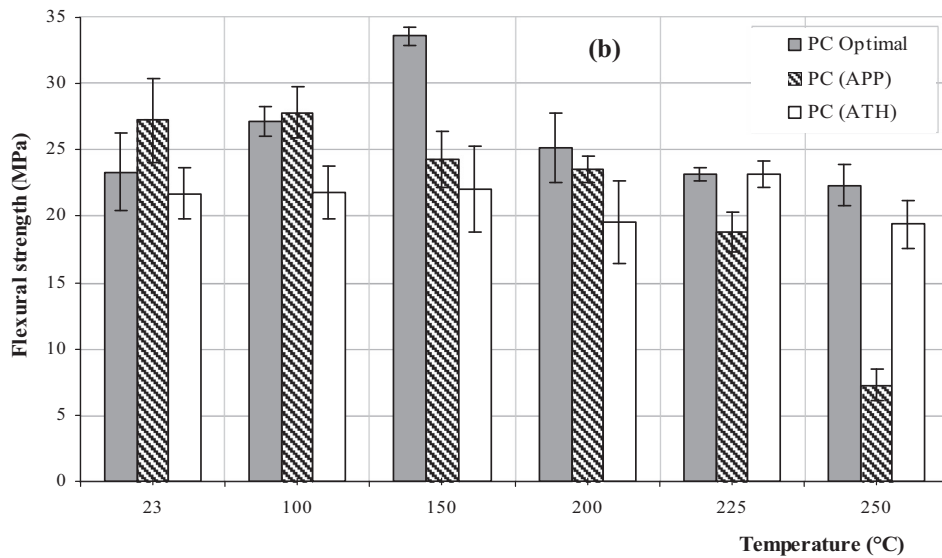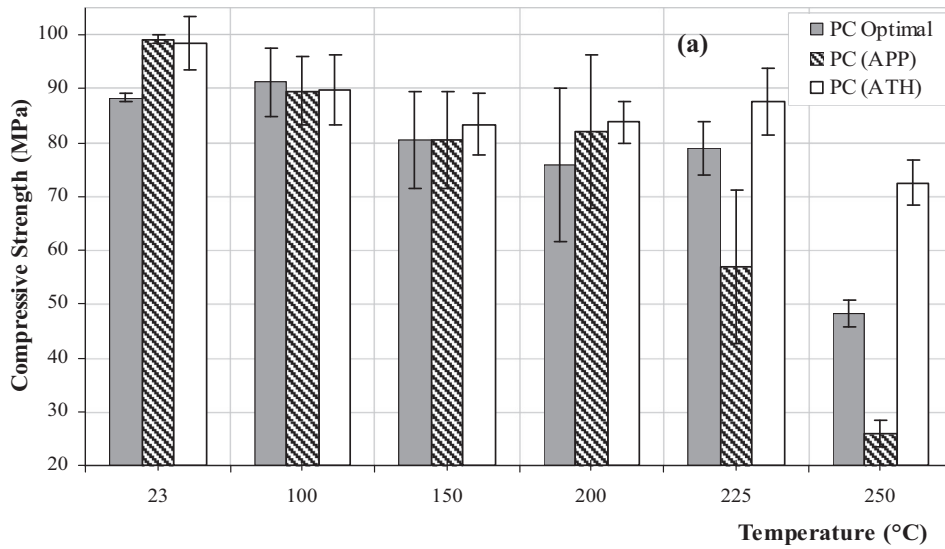
Fig. 2. DSC test.

Fig. 3. Evolution of mechanical strengths vs. temperatures.

To reproduce the real environmental conditions, 7 days old PC specimens at RT were heated at rate of 0.5 °C/min until test temperature was reached. The last temperature was maintained continually for a period of 3 h. The specimens are then cooled at the same heating rate until the temperature fall to the RT. The PC samples were kept for 24 h at the same temperature before testing.

To make sure that the setting temperature is compatible with specimen temperature, two thermocouples were connected to one side and in the middle of samples. The setting and recorded temperatures were close and the difference between them didn't exceed ±3 °C.

The test temperatures (from 100 °C to 250 °C) are selected on the basis of the polymer's glass transition temperature measuring 82.51 °C (Fig. 2). Differential scanning calorimetry test was performed using a TA Instruments Q100 DSC machine.

3. Influence of flame retardant addition

3.1. Mechanical properties

Fig. 3a and b representing compressive and flexural strengths according to the exposure temperatures. The results revealed that the addition of flame retardant hasn't a real influence on the

mechanical strengths at RT. Indeed, only a small increase in the flexural strength of APP based PC was recorded.

By increasing temperature the PC(APP) shows a significant reduction in its mechanical strengths. PC(APP) loses about 73.36% of its flexural strength and 73.92% of its compressive strength between RT and 250 °C. The APP flame retardant type did not improve the PC behaviour at high temperatures.

PC(ATH) also presents a reduction in its mechanical strengths after exposure to high temperatures. This reduction is less marked than that recorded for PC(APP) and PC without flame retardant addition. Indeed, the flexural and compressive strength of PC (ATH) record a fall of 26% and 10% after an exposure to 250 °C respectively.

The addition of APP or ATH decreased the flexural strength of the optimum PC (no flame retardants) [14].

For optimum PC, increasing the exposure temperature (Texp) improves the flexural strength for temperatures below 150 °C followed by a decrease for higher temperatures (decrease of 4.26% between RT and 250 °C).
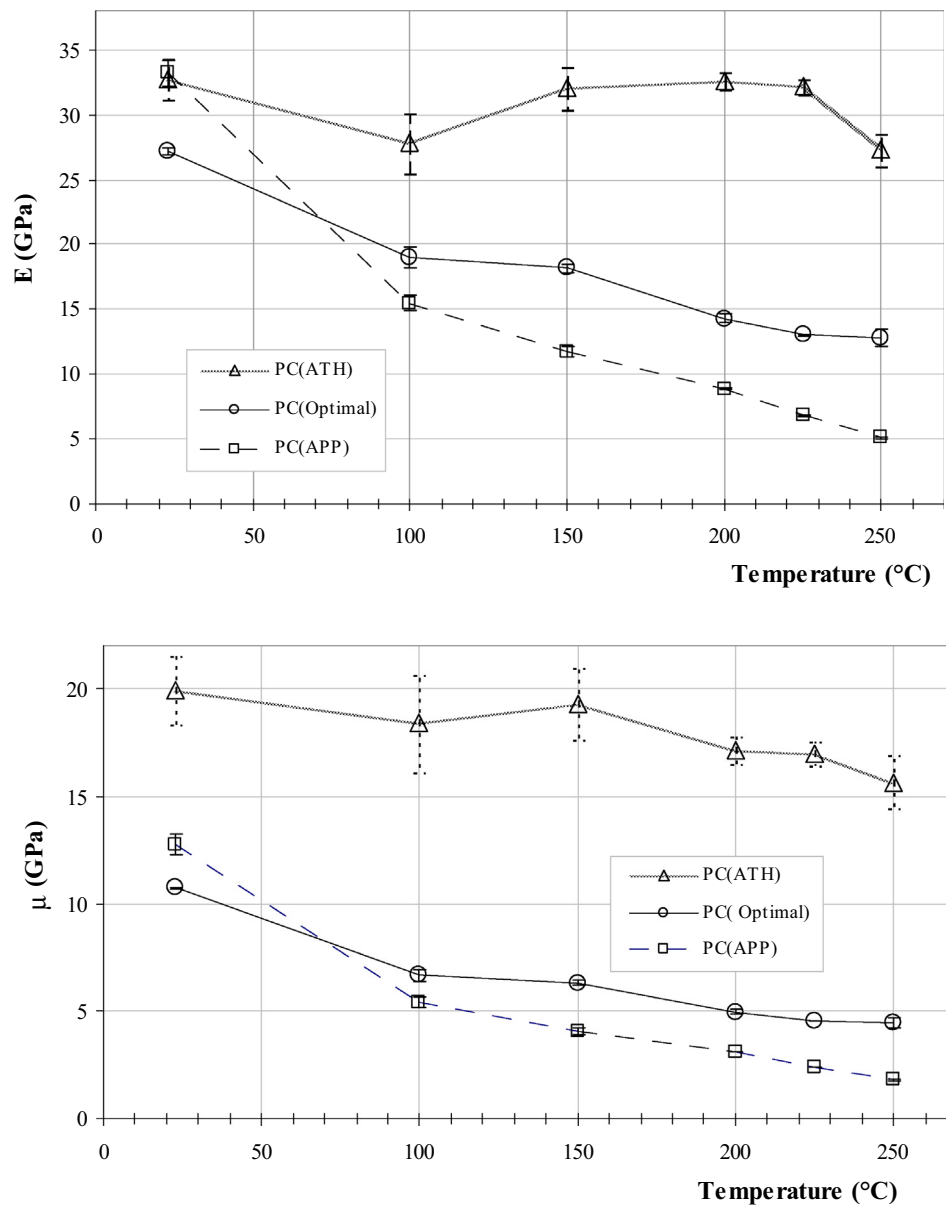

Fig. 4. Evolution of mechanical properties with temperature.

In the case of compressive strengths, records show an important decrease for temperatures ranged from 100 to 150 °C. While continuing heating for temperature around 250 °C, the compressive strength losses for instance about 45% of its original value.

3.2. Elastic properties of PC

The dynamic Young (E_d) and shear moduli (μ_d) were carried out by using the ultrasonic pulse velocity method (UPV), a non destructive test [15,23]. The two dynamic moduli are given by Eqs. (1) and (2) below:

$$E_d = \mu_d \cdot \frac{3V_L^2 - 4V_T^2}{V_L^2 - V_T^2} \tag{1}$$

$$\mu_d = \rho V_T^2 \tag{2}$$

where ρ = mass density of materials, V_L = P-wave velocity and V_T shear wave velocity.

Pulse velocities for PC systems were measured using two transducers and a wave generator. To have a good coupling between transducers and specimens a commercially silicone gel for longitudinal waves (P-waves) and a highly viscous liquid for transverse waves (shear waves) were used.

The wave's travel time was recorded using an oscilloscope under direct transmission mode.

The dynamic moduli are then transformed to static moduli (E, μ) using a model proposed by Lydon and Balendran [24]:

$$E = 0.83 \times E_d \tag{3}$$

Fig. 4a and b show the evolution of static young and shear modulus respectively with temperature for PC systems.

It is noticed that the variations of the two moduli are similar, the PC(APP) have the lowest moduli and PC(ATH) results in the most rigid PC for all exposure temperatures.

The reduction in elastic moduli can be explained by the damage of PC as a result of the loss of cohesion in the aggregates-matrix interface. This damage is due to the difference of thermal expansion of two materials and due the creation and propagation of cracks in PC (Fig. 5) controlled by the chemical degradation of the binder. Moreover the density of PCC (ATH) records a loss approximated to about 0.8% and 2.14 for the PCC(APP) for an exposure temperature equal to 250 °C. This fact explain clearly the small reduction in elastic moduli for the PCC (ATH) and optimized systems compared to PC(APP).

3.3. Total porosity

Total porosity measured using mercury intrusion porosimetry (MIP) techniques presented in Fig. 6 shows close values for all PC systems for T ≤ 150 °C. For higher exposure temperatures, PC (APP) presents the highest total porosity (i.e. 13.86% for 250 °C).

PC(Optimal) displays an increase by 2% while increasing exposure temperature from 23 °C to 250 °C. This reinforce the fact that the degradation of PC is due primarily to the chemical degradation of the matrix and the crack of PC for the high and average temperatures.

The APP based PC system presents a decrease of porosity between 150 and 225 °C. The PC(APP) have the lowest porosity for all the exposure temperatures compared to the other systems (Fig. 6).

As the temperature increased, pore populations are created especially for the PC (APP) system which includes the largest pore distribution as shown in the Fig. 7a and b.

On the other hand, The PC(ATH) records the absence of the few diameters even after exposure to the highest temperature. The highest amount of mercury introduced for the same pore diameter also corresponds to the most degraded system it means the PC (APP).

3.4. Thermal conductivity

Three cylindrical PC samples for each type of exposure, with size Ø50 × 150 mm, were conditioned according to the same process as for the other tests and then kept at RT for two days prior to testing.

The transient plane source (TPS) technique was used to measure the thermal conductivity of PC by the mean of a hot disk sensors (a Kapton sensor 8563 with a 9.868 mm of diameter) sandwiched between two specimen halves.
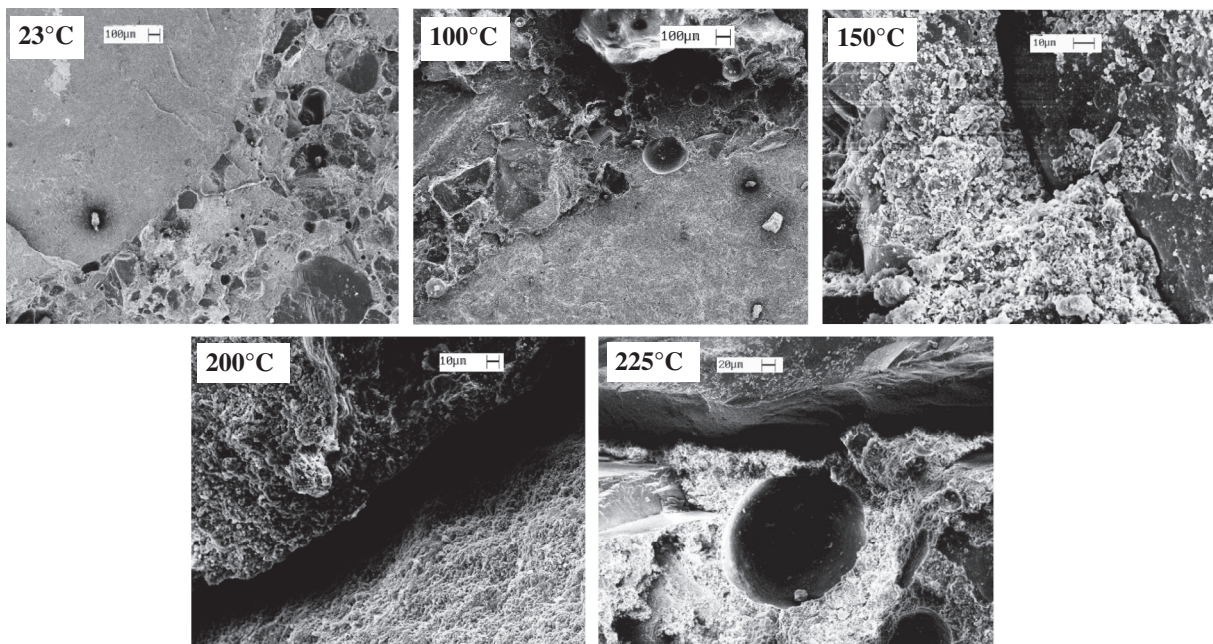

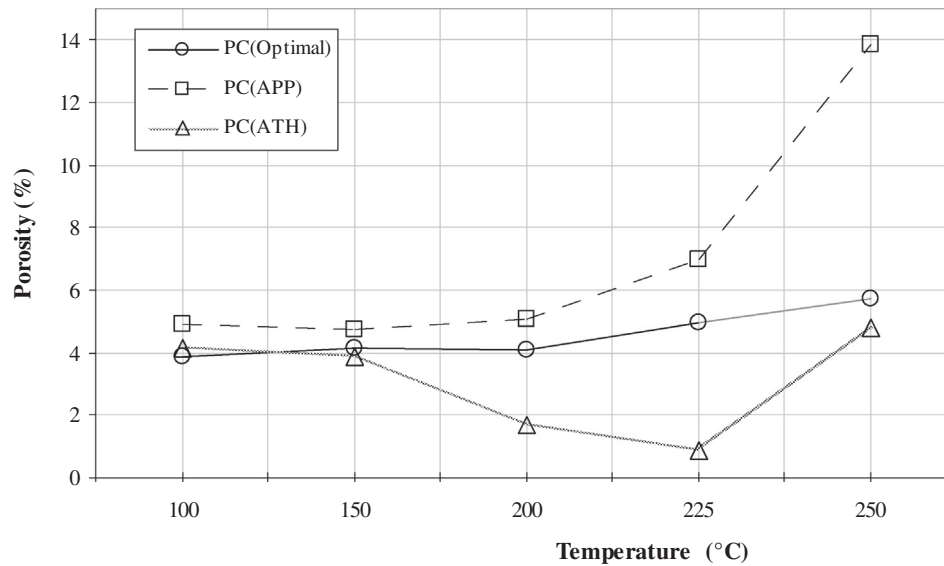**Fig. 5.** SEM Photos for matrix-inclusion interface for PC (Optimal).

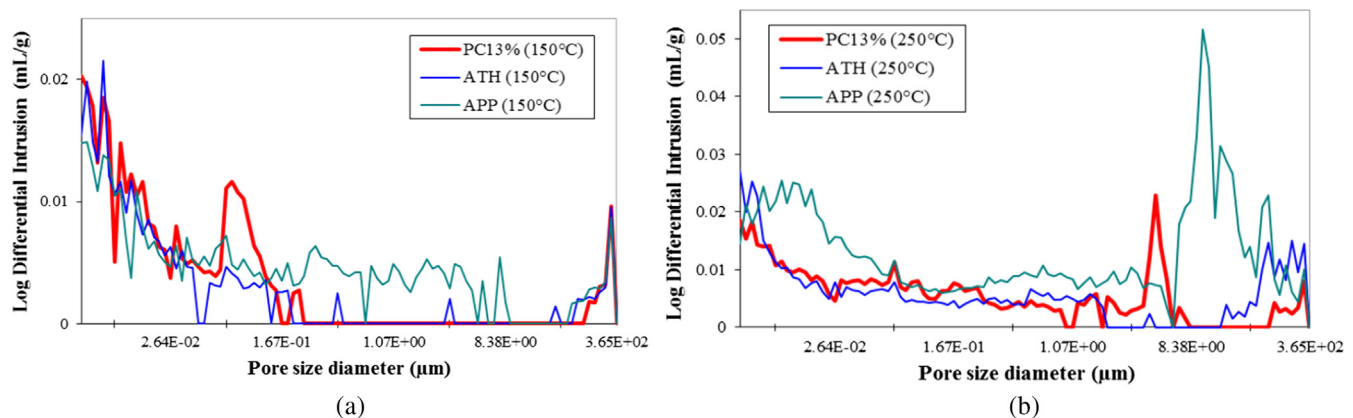Fig. 6. Mercury intrusion porosimetry for PC systems.

(a)

(b)

Fig. 7. Pore-size distribution for (a) 150 °C and (b) 250 °C exposure temperatures for different PC systems.

Table 2
Thermal conductivity for PC systems.

PC Systems	PC(Optimal)	PC(ATH)	PC(APP)
λ (W/m/K)	2.044	2.06	2.12

During the measurement the sensor works both as an emitter and receptor (heat source and a temperature sensor).

The comparison of thermal conductivities of PC systems (Table 2) showed that values for PC(ATH) and PC(Optimal) are very close. Thermal conductivity for APP based PC system is higher than those for other systems. This explains clearly that PC(APP) have the worst physical and mechanicals properties for temperatures exceeding the room temperature.

The incorporation of flame retardants leads also to an increase in thermal conductivity as a consequence of the increase in concrete density.

4. Conclusions

The mechanical and residuals properties of PC systems depend largely on temperature and they are clearly influenced by high temperatures mainly for those up to the glass transition temperature of polymer.

The decrease of the mechanical properties of PC containing ATH is less than that recorded for PC(APP) and PC with optimal polymer content.

Flame retardant ATH type addition increased the rigidity of the polymer concrete before and after its exposure to the selected temperatures.

Thermal conductivity for APP based PC system is higher than those for other systems given that it has the worst physical and mechanicals properties while increasing temperatures.

The incorporation of flame retardants results in an increase in concrete density which consequently increase the thermal conductivity.

Conflict of interest

The authors declared that there is no conflict of interest.

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