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Use of fibres in improving the mechanical properties of a multifunctional cement for structural repair purposes

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Abstract. Calcium phosphate cement (CPC) is a multifunctional cement whose potential application depends on the reactants used to synthesise it. Just like many inorganic cements, the pure CPCs synthesised in all cases are very brittle and have low toughness values under loading. In this research, the CPC material is formed from the exothermic reaction between phosphoric acid and calcium silicate at controlled room temperature. Three fibre types, namely; macro polypropylene fibres, amorphous metallic fibres and recycled carbon fibres were chosen due to their corrosion resistance in acid to enhance the mechanical performance of this cement as a repair material. 1.5% by volume of each of these fibres were added to the CPC material and autogenously cured for 14 days at room temperature. Mechanical destructive and non-destructive tests were carried out on the resulting composites. The experimental results revealed that each type of fibre contributes to increase flexural strength, compressive strength, fracture energy and dynamic elastic modulus of CPC material. However, for this purpose the recycled carbon fibres have proven to be more efficient.

1. Introduction

Calcium phosphate cement (CPC) is an inorganic multifunctional cement developed for biomedical applications due its osteoconductivity, biocompatibility, bioactivity, injectability and in-situ setting properties. They are used for stabilization of dental implants, bone substitution and reinforcement of multiple bone fractures [1]. This cementitious material could exist in several forms depending on the reacting solid and liquid components involved, the work environment and the intended application. Examples of the different variations of this type of cement include; hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), dicalcium phosphate dihydrate ($CaHPO_4.2H_2O$), monocalcium phosphate monohydrate ($Ca(H_2PO_4)_2.H_2O$) and dicalcium phosphate ($CaHPO_4$). The production of this cement in larger configurations could be cost intensive due to the presence of powdered calcium phosphate raw materials. An alternative raw material has been developed [2] to allow for the creation of larger samples at relatively lower cost. This involves an acid-base reaction between phosphoric acid and wollastonite powder ($CaSiO_3$) at room temperature to form a hard cementitious material with an almost neutral pH. This cement could also be classified as a type of chemically bonded phosphate cement (CBPC).

The property of CPC is believed to be in-between that of ordinary Portland cement (OPC) and ceramic because it hardens at room temperature as seen in OPC and still possesses mechanical properties in close range to that of ceramics, which undergo a sintering process to gain strength. In comparison with OPC, the strength/density ratio of CPC is far superior to that of OPC. A compressive strength of 100 MPa in minutes after their casting has been reported for CBPCs, unlike in OPC cement which gains strength of 20 MPa at 28 days [3]. This offers the advantage of minimised construction waiting time, which overall brings down the cost of infrastructural projects. CPC is a lightweight material with a density in the range of 1.8-2.19 g/cm^3, whereas the density of OPC is about 3.15 g/cm^3. This implies lesser burden on an existing foundation if utilised as repair cementitious materials. Furthermore, the use of wollastonite in hardened CPC is considered environment friendly because the problems of acidification of the soil and the production of greenhouse gases when manufacturing the raw materials in OPC are completely eradicated [4]. Due to these beneficial features, they are further being researched for potential applications in civil engineering infrastructural

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development and/or repair and management of low-level radioactive waste (e.g. macro-encapsulation of concrete debris used for micro-encapsulation of low-level radioactive waste). Also, other interesting benefits of CPC such as thermal stability, neutral pH, green structural cement and less generation of VOC (volatile organic compounds) during production have been given [5].

However, it has been shown that all inorganic CPC materials have low fracture energy and high brittleness, which limit their load carrying functions both as bio-material and civil engineering material. Several research works have looked at the possibility of increasing the mechanical properties and durability of CPC through the addition of fibres. Colorado et al. [3] studied the bending properties of pultruded chemically bonded phosphate cement (CBPC) having 15% by volume of fibres. They found 29 and 17 times increment of the bending strengths of carbon and glass fibre reinforced CBPC respectively when compared to the pristine material. Cuypers et al. [6] carried out an investigation on the damage mechanism of glass fibre reinforced CPC composites in both constant and variable environmental loading conditions. The research demonstrated that the presence of glass fibres prevented the detrimental effects caused by freezing-thawing. Also, an extensive review on the mechanical properties of fibre reinforced CPC has shown additional areas of improvement of this material for clinical applications. Nevertheless, more research work is required to understand the impact of fibre reinforcement on the fracture toughness and ductility of CPC for structural applications.

In this research, the fracture energies of composites made from the addition of 1.5% by volume of macro polypropylene fibres, amorphous metallic fibres and recycled carbon fibres to pure CPC matrix were studied. In addition, the effects of these fibres on other mechanical properties like compressive strengths, flexural strengths and dynamic elastic modulus were quantified.

2. Materials

The materials used in this research are classified into reactive and non-reactive. The reactive materials are phosphoric acid (liquid) and calcium silicate (solid/powder), which are provided by Sulitec Insulating Composites. The phosphoric acid has a density of 1.70 g/cm^3 and composed of metallic oxides of aluminium, boron, iron, magnesium, zinc, sodium and calcium. The concentration of the liquid is reported to be in the range of 50-75%. The calcium silicate also known as wollastonite is composed mainly of calcium oxide and silica. Its density is given as 2.90 g/cm^3.

The non-reactive materials are the fibre inclusions, which are macro polypropylene fibre, amorphous metallic fibre and recycled carbon fibre. These fibres were selected based on their stability in acidic solutions, since the fresh state of calcium phosphate cement has a pH value close to 1. The individual properties of these fibres are given in **Table 1**.

3. Methods

3.1 Mixing and curing

The liquid component (phosphoric acid) and the solid component (wollastonite) are mixed in a planetary mixer conforming to EN 196-1. They are combined at a liquid/powder (L/P) ratio of 1.00 and a high volume fibre content of 1.5% added during the mixing process. The mixing procedure adopted for all composites produced includes; i) the phosphoric acid and the wollastonite powder are added in the 5L capacity mixing bowl and mixed for 90 s at 140 RPM, ii) the individual fibres are added and the mixing is continued at 140 RPM for 30 s, iii) the mixing is finished at 285RPM for 180 s. A low revolution speed (≤ 140 RPM) is used immediately after the fibres are added to allow them to be enmeshed in the cement matrix before a higher revolution speed is adopted. This is done to avoid the problem of over-spill of the mix components from the bowl when a higher mixing speed is used on addition of the fibres. Where fibre inclusions are not used, like in the case of pure CPC, the second stage of the mixing is omitted. The composites having macro polypropylene fibre inclusions are denoted by CPC+1.5%Fpp, while those of amorphous metallic fibre and recycled carbon fibre are CPC+1.5%Fam and CPC+1.5%Fcf respectively.

The resulting freshly mixed composites are cast in a PVC mould, and covered with a plastic film to prevent loss of H_3PO_4 water from the fresh paste. All samples are de-moulded after 24 hours of placing them in the moulds. The mixing, placing and curing are done at controlled atmosphere of 20 ±2ºC and relative humidity of 65 ±5%. All samples were cured autogenously (wrapped in a plastic film) for a period of 14 days, as preliminary tests showed that at this age the strength of CPC produced in similar conditions is in quasi-stable state.

3.2 Flexural test

The flexural tests are carried out on notched and on un-notched prismatic beams of dimensions 70x70x280 mm^3 and 40x40x160 mm^3 respectively. The bending test on the notched beams aims to determine and compare the toughness parameter(s), while the un-notched beam gives the modulus of rupture of the cement composite. The use of 70x70x280 mm^3 specimens to determine the fracture energy was to avoid the problem of excessive heat of reaction associated with CPC if larger specimens were to be used.

A closed-loop servo-hydraulic MTS universal testing machine with a 100 kN capacity was utilized to carry-out the bending test on the notched beams. The arrangement of the beams between the load platens is in accordance to EN 12390-5 for a three-point load system as shown in **Fig. 1**. The notch width and depth are 2.0 mm and 7.5 mm respectively. The notch was done at the mid-span of the

Table 1. Individual properties of fibres used

Type of fibre	Length-L (mm)	Diameter /Width-W (mm)	Aspect ratio (L/W)	Tensile strength (MPa)	Elastic Modulus (GPa)	Density (g/cm^3)	Melting point (°C)	Reaction with Acid
Macro polypropylene fibres (Fpp)	17	0.5	34	360-600	5	0.92	160	Corrosion resistant
Amorphous Metallic fibres (Fam)	20	0.185	108	1400	>120	7.25	---	Corrosion resistant
Recycled Carbon fibres (Fcf)	Un-defined	0.005-0.010	---	5407	>200	1.50-2.00	>2760	Corrosion resistant

beam at a side perpendicular to the face of casting of the composites using a handheld saw. The test was controlled by the crack mouth opening displacement (CMOD). Two load rates of 5 μm/min up to a CMOD of 0.05 mm and 50μm/min from a CMOD of 0.05 mm to the end of the test were used. The load-deflection values were also recorded during the test with the aid of an LVDT attached to the specimens. Two representative samples were used to determine the load-deflection curve of each mix composition for the calculation of their respective fracture properties.

The modulus of rupture of the cementitious composites were determined following the requirements of EN 1015-11. The loading rate of the universal testing machine adopted was 0.5 kN/s. The loading arrangement of each specimen on the universal testing machine which

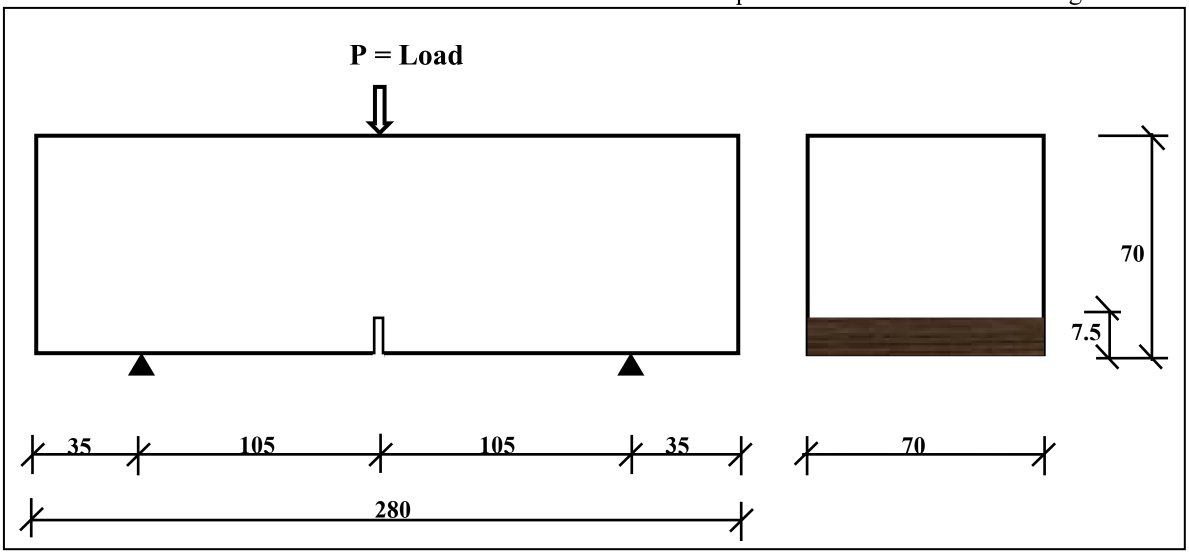

Fig. 1. Three-point bending test of notched beam (all dimensions in mm)

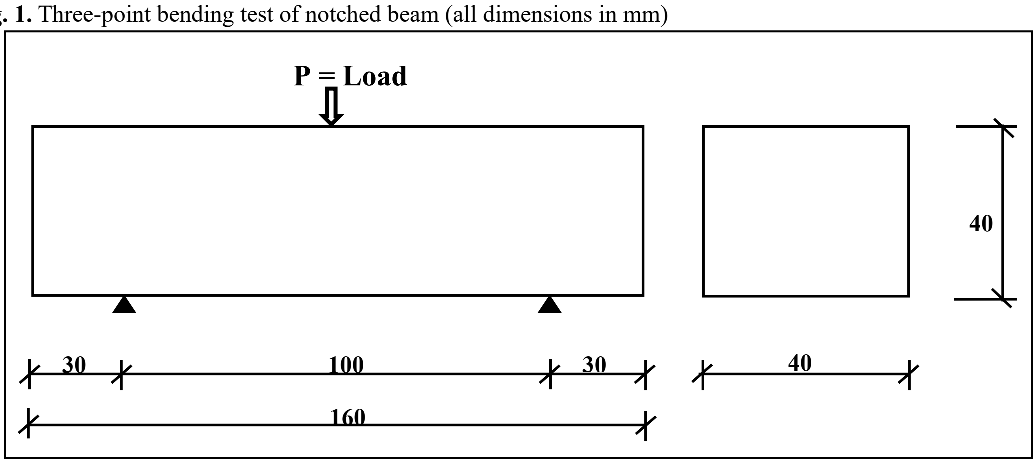

Fig.2. Loading arrangement for modulus of rupture experiment (all dimensions in mm)

has a capacity of 25 kN is as given in **Fig.2**. Three samples were used to determine the modulus of rupture of each mix composition.

3.3 Compressive tests

The compressive strengths of the pure CPC and fibre reinforced composites were determined using 40x40x40 mm^3 cube size specimens conforming to EN 1015-11. They were realised from the halves of specimens obtained after the modulus of rupture experiment was conducted. A total of six (6) representative samples were tested for each mix composition at a load rate of 0.3 MPa/s. The capacity of the universal testing machine used was 250 kN.

3.4 Dynamic elastic and shear modulus experiment

The effects of fibre inclusions on the dynamic elastic modulus, shear modulus and Poisson's ratio of CPC was determined by a non-destructive test performed in accordance to ASTM C215-02 using the GrindoSonic device. The impact resonance method was used to obtain the longitudinal and torsional frequencies from which the dynamic elastic and shear modulus are calculated using Equations 1 and 2 respectively. Equation 3 was used to determine the dynamic Poisson's ratio values. A total of six (6) frequency values (longitudinal and torsional) were recorded for each sample from which the average is obtained as the measured value. Three representative samples were used to evaluate the dynamic elastic and shear modulus of each CPC composite

$$E = DM(n^I)^2 \quad (1)$$

$$G = BM(n^{II})^2 \quad (2)$$

$$v = \left({}^{E}/_{2G}\right) - 1 \quad (3)$$

Where,

E = Dynamic elastic modulus (GPa), G = Dynamic shear modulus (GPa)

v = Dynamic Poisson's ratio, M = Mass of specimen (kg)

n^I = Fundamental longitudinal frequency (Hz), n^{II} = Fundamental torsional frequency (Hz)

D = 4(L/bt) ($N.s^2/(kg.m^2)$) = 400 $N.s^2/kg/m^2$, B = 4LR/A ($N.s^2/(kg.m^2)$) = 473.2 $N.s^2/kg/m^2$

L= length = 0.16 m, b= t = 0.04 m (b = width, t = depth), R = 1.183 (shape factor for square cross section), A = Area of cross section = 0.0016 m^2.

4. Results and discussion

Generally, the load-deflection curves of fibre reinforced CPC composites (shown in **Fig. 3**) are composed of three stages, namely; the elastic region, the crack development stage and the failure stage. At the limit of proportionality stage (elastic region), the applied load is carried mainly by the CPC matrix before the development of first crack.

In the crack development stage, the stresses acting on the composites are shared by the combined action of the fibres and the cement matrices. The fibre inclusions at this stage provide the bridging mechanism restraining further crack growth and promoting the stress transfer through the crack. This stage is also known as the strain hardening stage. It comprises of the region from the first micro-crack to the peak load on the load-deflection graph. The strain softening behaviour occurs in the failure stage, where the fibres are mainly carrying all the stresses on the cementitious composites. Depending on the type of fibre and the length of embedment in the cement matrix, the fibre can either fail by breaking or pulling-out from the cement matrix. The composite beams reinforced with macro polypropylene fibres failed by complete pull out of the fibres from the CPC matrix while the beams reinforced with recycled carbon fibres failed by complete rupture of the fibres. Those with amorphous metallic fibres failed by either total fracture or pull out of fibres at the line of crack propagation of the notched composite beams. The kind of failure experienced depends on the length of embedment and orientation of the fibres in the CPC matrix. Failure by pull-off was observed mostly in the amorphous metallic fibres which have very short embedment length from the failure surface/plane. Complete fracture is experienced by those other fibres that are sufficiently embedded at the opposing ends across the line of failure.

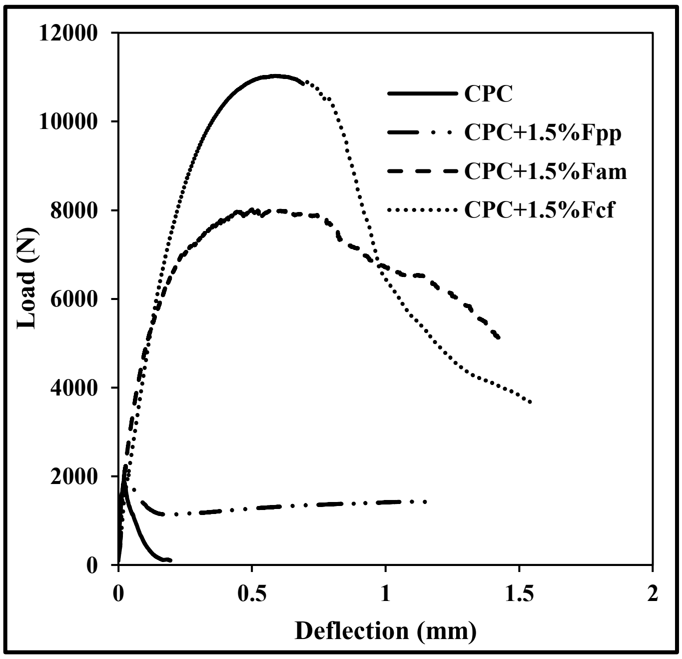

Fig. 3. Load-deflection curve of fibre reinforced CPC composites

Table 2. Fracture properties of fibre reinforced CPC composites

S/N	Mix Composition	Peak Load, P_L (N)	Peak Nominal Strength, F_L (MPa)	Deflection @ Peak Load (mm)	Energy Absorption Capacity @ 1.2mm (Nmm)	Fracture Energy @ 1.2mm (N/mm)
					(130.16)*	(0.187)*
					1528.11	2.199
3	**CPC+1.5%Fam**	8041.94	11.58	0.586	8236.35	11.860
4	**CPC+1.5%Fcf**	11030.21	15.88	0.590	9840.28	14.170

*The deflection value at the end of the test was less than 1.2mm

The load-deflection curves of the pure CPC and fibre reinforced CPC materials are used to determine the parameters given in **Table 2**. The values of the peak loads and deflections at peak loads are directly obtained from the graph (**Fig. 3**) while the nominal peak strength, energy absorption capacity and fracture energy values are calculated. Equation 4 given by Ye et al. [7] is used to estimate the nominal flexural strengths of the cementitious materials, since the fracture of the cementitious materials begin from the pre-cracks provided on the notched beams, due to stress concentration. The fracture properties of the different composites are determined and compared based on the area under the load-deflection and nominal flexural strength-deflection curves at a reference point of 1.2 mm, being the maximum deflection value of macro polypropylene fibre reinforced CPC.

$$F_L = \frac{3}{2}\frac{P_L L}{b(h-a_0)^2\left(1-{}^{a_0}/_{h}\right)^2} \qquad (4)$$

In which, P_L = Peak load, F_L = Nominal peak strength, b = width of the beam, h = depth of the beam, a_0 = notch depth.

From **Table 2**, it can be noticed that the pure CPC material has the smallest value of peak load, nominal flexural peak strength, deflection at peak load, energy absorption capacity and fracture energy. Addition of 1.5% by volume of the three different types of fibres in CPC increased these properties, however in varying proportions. The recycled carbon fibres caused the growth in the peak load and fracture energy of CPC by a factor of 5.9 and 76.1 respectively and were the most efficient if compared with the other fibres. The amorphous metallic fibre reinforced composite cement was the second best and then the macro polypropylene fibres. All these results point to the increase in toughness and ductility of CPC through fibre addition. A similar pattern was also found in the deflection values at peak load, which could also serve as the strain capacity of the composites. In ascending order, the deflection at peak load of all samples tested is as given; CPC < CPC+1.5%Fpp < CPC+1.5%Fam < CPC+1.5%Fcf. These results provide further explanation to the strain hardening behaviour as well as the effectiveness of the different fibres in restraining the crack propagation before failure. The amorphous metallic fibre and recycled carbon fibre reinforced CPCs which have high strain capacity values show higher strain hardening behaviour than the macro polypropylene reinforced cements. Nonetheless, the cementitious composites with macro polypropylene fibres have low but wide post peak plateau strain softening.

The performance of these fibres in the CPC matrix could be linked to the intrinsic properties of the fibres and the bonding strengths between the fibres and the matrix. The intrinsic properties in this case refers to their tensile strengths and elastic moduli. The recycled carbon fibres and amorphous metallic fibres which are high stiffness fibres tend to dwarf the low stiffness macro polypropylene fibres in all the fracture properties measured. This shows that there is a direct relationship in the behaviour of fibre reinforced CPCs and the individual elastic modulus and/or tensile strength of the fibres investigated. In addition, the interactions between individual fibres and the cement matrix played a contributory role.

The modulus of rupture and compressive strength values of CPC composites determined at 14 days are shown in **Fig.4** and **Fig. 5** respectively. The compressive strengths of pure CPC cured autogenously at room temperature for 14 days are well above the minimum required for structural cements (i.e. 17MPa, ACI 318). Adding 1.5% by volume of macro polypropylene fibre, amorphous metallic fibre and recycled carbon fibre resulted in the increase of the flexural strength value of

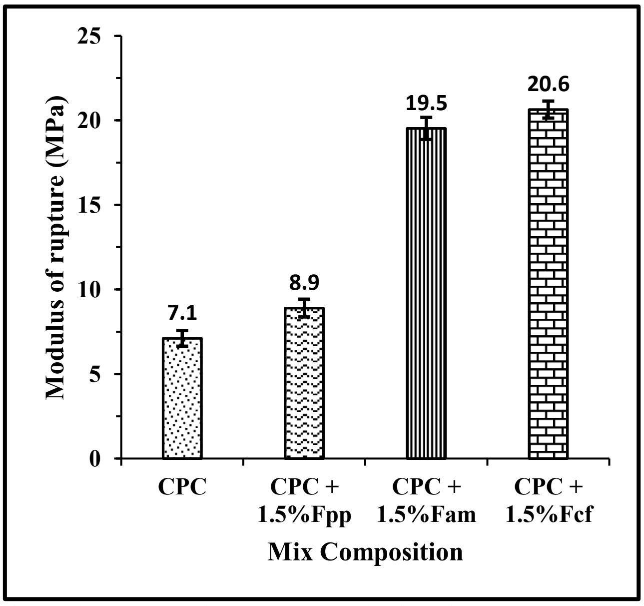

Fig.4. Modulus of rupture of CPC composites at 14 days

CPC by 25.2%, 174.6% and 190.3% respectively. Also, a slight growth of 17.9%, 10.2%, and 20.3% was observed for the compressive strengths of macro polypropylene fibre, amorphous metallic fibre and recycled carbon fibre-reinforced cementitious composites. These results show a positive contribution to the mechanical properties of CPC materials by the three distinct fibres utilised in this research. This may be likened to the beneficial interactions between the CPC matrix and the fibres. The dominance of chemical bonding (ionic/electrovalent and covalent) in CPC material, as well as the properties of the individual fibres are responsible for these noticeable enhancements in the compressive strengths and modulus of rupture values.

Table 3. Dynamic elastic moduli, shear moduli and Poisson's ratio at 14 days

S/N	Mix Composition	ρ (g/cm^3)	E (GPa)	G (GPa)	v
1	**CPC**	1.90	15.41	6.55	0.18
2	**CPC+1.5%Fpp**	1.98	16.39	6.56	0.25
3	**CPC+1.5%Fam**	1.99	16.25	6.49	0.25
4	**CPC+1.5%Fcf**	1.91	16.66	6.66	0.25

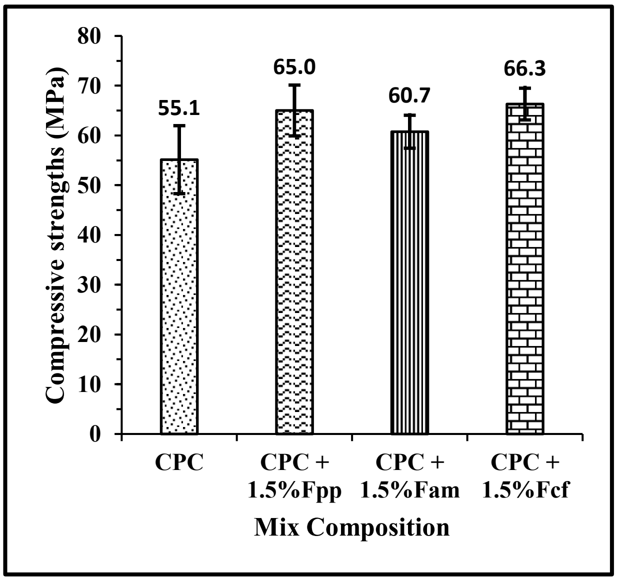

Fig. 5. Compressive strengths of CPC composites at 14 days

The dynamic elastic modulus, shear modulus and Poisson's ratio of pure CPC (shown in **Table 3**) are similar to those of inorganic cements. A rise in the dynamic elastic modulus and Poisson's ratio values was noticed for all the composites made from the three different types of fibres considered. The percentage increase recorded in dynamic elastic modulus values for CPC reinforced with 1.5% by volume of Macro polypropylene fibre, amorphous metallic fibre and recycled carbon fibre is 6.4%, 5.5% and 8.1% respectively. An overall increment of 38.9% compared to the pure CPC was obtained for the dynamic Poisson's ratio values of all the cementitious composites formulated.

5. Conclusions

The addition of macro polypropylene fibres, amorphous metallic fibres and recycled carbon fibres contribute to improve the multifunctional properties of CPC made from the exothermic reaction between phosphoric acid and wollastonite powder at room temperature. This is through the improvement in the toughness and ductility of CPC materials in addition to enhancing other properties such as compressive strength, flexural strength, and elastic modulus. Of the three types of fibres investigated, recycled carbon fibres seem to contribute more to the fracture energy of CPC. The results obtained from the research show that all designed composites are potentially suitable for repair purpose and their individual use will depend on the desired properties of the repair fibre reinforced cementitious material. For instance, where higher resistance to the action of loads in bending is expected for the repair cementitious material, CPC composites reinforced with either recycled carbon fibres or amorphous metallic fibres will be appropriate for use. This is because of the elevated values of their fracture energies and flexural strengths.

Having examined the mechanical properties of these composites, there is need to study the short and long term effects of these fibre inclusions on the bonding properties of CPC to OPC concrete substrates. There is an on-going research to address these aspects.

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Cost and environmental impact of CPC

The market cost of each of the two component materials (wollastonite and phosphoric acid) for making CPC in France is around €10.50-€18.00/kg, which is far more expensive than OPC. The reason for this might be attributed to the absence of the raw materials for producing these chemical compounds in large quantity. Therefore, they are sourced from other countries where they are present in large deposit and that inflates the cost of production. This implies that the cost of these materials is expected to be much lower in countries where they are found as natural occurring mineral deposits. For instance, the market value of wollastonite in North or South American countries or even in Asia Pacific nations and South Africa where they can be found naturally in large amount is in the range of €0.12-€1.00/kg. And this is in a close range to the price of OPC.

The environmental impact from the use of CPC material in terms of its CO_2 emission, release of VOC, energy cost, acidification and eutrophication can be estimated at two stages; i) production stage of its component materials ($CaSiO_3$ and H_3PO_4) and ii) mixing, curing and service-life stage of the CPC material. The impact analysis will be done based on the assumption that the CPC material is used in the region where they occur naturally. This will bring the energy consumed as a result of haulage to a bare minimum.

The wollastonite used to make CPC is a natural acicular material, which may contain some impurities (i.e. calcite) depending on the location where they are mined. Where these impurities are minimal, less energy is expended in the calcination (purification) process that breaks the calcite ($CaCO_3$) into CaO and CO_2. Thus, in this case, it is possible to say that the process of producing the wollastonite does not pose adverse environmental effect. For the phosphoric acid, its manufacturing process impacts negatively on the environment regardless of the grade of the phosphoric acid produced. The highly purified phosphoric acid, used directly as an acid utilises the high energy consuming thermal production process. In like manner, the commercial impure grade of the acid, used mainly for the production of phosphate fertilizers generates a hazardous compound known as phosphogypsum through the wet production process. This makes the production process of phosphoric acid unsustainable to the environment. However, with efficient practices in place, this can be mitigated.

The mixing of the two component inorganic phosphate cement, the hardening process and its behaviour in service life have very negligible environmental impact. For example, there is no release of low level ozone emissions (e.g. VOC) during the combination of the phosphoric acid and the wollastonite powder. The freshly mixed CPC hardens at room temperature (i.e. requiring less energy) to form cementitious materials with properties that are superior to those of OPC. In addition, the problem of acidification of the soil in the near future is totally eradicated due to the elemental make-up of the hardened CPC compound. Also, eutrophication due to the presence of phosphate occurs at a minimal level which poses no threat to the environment.