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Electrical and Thermal Properties of Wollastonite-based Inorganic Phosphate Cement Modified with Fibres and Recycled Rubber Aggregates

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Abstract - *The use of fibres and recycled rubber aggregates to improve the fracture properties of wollastonite-based inorganic phosphate cement would have corresponding effects on the functional properties of the material. In this research, cement composites were designed to incorporate rubber aggregates (i.e. 7.5-17.5 wt%), 1.5% volume fibre contents (i.e. macro polypropylene, amorphous metallic and carbon fibres), and a hybrid blend of both inert materials into the cement matrix. The electrical resistivity of the developed cement composites was measured using the Gamry device while their thermal conductivity was determined based on the guarded hot plate steady state method. It was found that the electrical resistivity of wollastonite-based inorganic phosphate cement increased with increasing curing age at room temperature. The incorporation of rubber aggregates into the cement matrix caused a significant increase and decrease in the electrical resistivity and thermal conductivity respectively, of cementitious composites formed. Meanwhile, as expected, the conductive fibres lowered the electrical resistivity and simultaneously increased the thermal conductivity of the inorganic cement. However, the polypropylene fibres increased both the electrical and thermal properties. Therefore, inert additives which have insulating properties (rubber aggregates and polypropylene fibre) favoured the production of cement composites with improved energy savings in buildings while the conductive (amorphous metallic and carbon) fibres can contribute to the material's smart potential.*

Keywords: Electrical and thermal properties, Fibres, Recycled rubber aggregates, Wollastonite-based inorganic phosphate cement

1. Introduction

Wollastonite-based inorganic phosphate cement also known as calcium phosphate cement (CPC) is a low carbon cement, which represents a type of chemically bonded phosphate cement (CBPC) formed at room temperature through an exothermic acid-base reaction. Other types of CBPC may include: iron phosphate cement, aluminium phosphate cement, magnesium phosphate cement and zinc phosphate cement. Of these cements, only CPC and magnesium phosphate cement are currently being explored for use as construction materials because of the technological advancements in the processing of their individual raw materials. To date, it appears that fewer research works have actually studied the behaviour of CPC as a building material than its counterpart (i.e. magnesium phosphate cement), although it has relatively cheaper raw materials **[1]**.

CPC is believed to exhibit properties that put them in-between the features of ceramics and ordinary Portland cement (OPC). This means that CPC can be formed at room temperature like OPC and yet achieve enormous strength, close to that of ceramics, which is produced by sintering processes. Other reported properties of CPC include: i) high strength/density ratio, ii) neutral pH and iii) greater stability than OPC materials in aggressive environments. However, our preliminary findings have shown that this cement tends to develop cracks at early age when prepared at room temperature. Also, it is very brittle like other inorganic cements when hardened. These negative attributes limit the potential of this material in high value civil engineering applications. In previous research works, fibres and recycled rubber aggregates have been incorporated into the matrices of other inorganic cementitious materials to improve their cracking resistance, strain capacities and fracture energies [2]. Hence, a similar concept has been applied in this research to address these problems associated with CPC. The use of recycled materials such as rubber aggregates and carbon fibres minimised the production costs of CPC composites in addition to improving the fracture properties of the material. As the inert additives come from end-of-life products, their use as building materials contributes to the circular economy and a healthy environment in the construction industry.

However, the use of fibres and rubber aggregates to enhance the mechanical performance of plain CPC would also cause some changes to its functional properties, which are equally important parameters in construction materials. This, in particular, is relevant in cases where the high strength CPC composite materials are expected to provide other functional benefits in addition to their mechanical properties. To our knowledge, there is no existing research work on electrical resistivity and thermal conductivity properties of CPC composites incorporating rubber aggregates and fibre reinforcements. Therefore, this research focuses on the electrical and thermal properties of rubberised CPC composites, fibre-reinforced CPC composites and CPC composites formed through hybrid blends of rubber aggregates and fibres.

2. Materials

The materials employed in this research are grouped into two categories, namely: reactive components and inert components. The reactive components consist of the phosphoric acid (H_3PO_4) and wollastonite powder ($CaSiO_3$). Meanwhile, the inert components consist of the recycled rubber aggregates from end-of-life tires and corrosion resistant fibres (i.e. macro polypropylene fibres-F_{pp}, amorphous metallic fibres-F_{am} and recycled carbon fibres-F_{cf}). Primarily, these inert additives were selected to improve the mechanical behaviour of the inorganic phosphate cement, but given that the pH of CPC is close to 1 in the fresh state, these additives were chosen because they are corrosion resistant.

The reactive materials were provided by Sulitec Insulating Composites. The H_3PO_4 has a density and concentration of 1.70 g/cm^3 and 50-75% respectively. It was composed of mainly phosphorus pentoxide with minor traces of metallic oxides like zinc, calcium, aluminium, boron, iron and magnesium oxides. On the other hand, the $CaSiO_3$ is made up of an approximate equivalent contribution of calcium oxide (48.8%) and silica (50.2%). The density and median particle size of the wollastonite powder were given as 2.90 g/cm^3 and 10 µm respectively. The recycled rubber aggregates were obtained from the grinding of end-of-life car tyres. They have a density and size distribution of 1.15 g/cm^3 and 0-4 mm respectively. The F_{pp} used are discrete, low strength fibres with a density and aspect ratio of 0.92 g/cm^3 and 34 respectively. They possess a circular cross-section and are hydrophobic. The F_{am} and F_{cf} are both referred to as high strength fibres. While the F_{am} are discrete, the F_{cf} are non-discrete, where a bundle of the fibre has several filaments or strands. The density and aspect ratio are 7.25 g/cm^3 and 108 respectively for F_{am} and 1.5-2.0 g/cm^3 and undefined respectively for F_{cf}.

3. Methods

3.1. Mix design, mixing, placing and curing

The H_3PO_4 and $CaSiO_3$ were combined at a liquid/powder (L/P) ratio of 1.00 to produce the plain calcium phosphate cement (CPC). Three categories of cement composites were developed with enhanced mechanical properties than the plain CPC. They are i) rubberised CPC composites ($CPC_{7.5RA}$, $CPC_{12.5RA}$ and $CPC_{17.5RA}$), ii) fibre-reinforced CPC composites ($CPC_{1.5Fpp}$, $CPC_{1.5Fam}$ and $CPC_{1.5Fcf}$) and iii) rubberised fibre-reinforced CPC composites ($CPC_{17.5RA,1.5Fpp}$, $CPC_{17.5RA,1.5Fam}$, and $CPC_{17.5RA,1.5Fcf}$). Where, $CPC_{7.5RA}$, $CPC_{12.5RA}$ and $CPC_{17.5RA}$ represent partial substitution by weight of the components of CPC with 7.5%, 12.5% and 17.5% of rubber aggregates respectively. 1.5% volume fibre content (V_f) of F_{pp}, F_{am} and F_{cf} individually added into the CPC matrix are denoted as $CPC_{1.5Fpp}$, $CPC_{1.5Fam}$ and $CPC_{1.5Fcf}$ respectively. For cement composites incorporating both fibres and rubber aggregates, $CPC_{17.5RA,1.5Fpp}$, for instance, would represent CPC material incorporating 17.5% by weight of rubber aggregates and 1.5% by volume of macro polypropylene fibres.

The mixing of the constituent materials was done in a 5L capacity planetary mixer complying with the requirements of **EN 196-1 [3]**. The steps adopted to mix the constituent materials are: i) the H_3PO_4 and $CaSiO_3$ are mixed for 90 s at a speed of 140 RPM, ii) the fibres and/or rubber aggregates are added into the fresh paste of CPC and the mixing continued for 30 s at a speed of ≤140 RPM, and iii) the mixing is finalized at a speed of 285 RPM for 180 s to form homogenous molten CPC materials. The second stage of mixing was necessary to enmesh the inert inclusions into the cement paste before the application of a higher mixing speed in order to prevent over-spill. Hence, it could be omitted when preparing the plain CPC. The fresh homogeneously mixed CPC composites were placed into the moulds and covered with plastic film to prevent loss of hydration water from the H_3PO_4. They were removed from the moulds after 24 hours. The mixing, placing and curing operations were carried out in room controlled conditions of temperature and relative humidity of 20±2 ºC and 65±5% respectively.

3.2. Electrical resistivity

This experiment was performed to evaluate the response of each cement composite to the flow of current in order to assess their potential for use as smart cementitious materials. The results from the experiment will also showcase the influence of the recycled rubber aggregates and the three fibre types on the electrical property of CPC. The electrical resistivity was conducted with the Gamry device, which was programmed to run at the Galvanostat mode. To measure the electrical resistance, a small amount of direct current (say, I = 0.001A) was passed through the electrodes connected to the top and bottom of each specimen as demonstrated in **Fig. 1.** The potential difference (E) between the electrodes was recorded and the electrical resistance was obtained as the ratio of the potential difference to the current passed (i.e. R = E/I). First, the resistivity of the plain CPC was studied over a 28-day period at room temperature to determine the influence of curing age on the electrical resistivity of CPC. After, the electrical resistivity of the different mix compositions of the cement composites were measured at 14 days of being cured in a protective plastic covering at room temperature. Here it seems necessary to specify that it has been preliminarily established that the properties of CPC exhibit quasi-stability after 14 days at room temperature **[4]**. Three (3) specimens (measuring 40x40x160 mm^3) were examined for each mix design. The resistivity of all the samples tested was determined using **Eq. 1**.

$$Electrical\ resistivity, \rho = \frac{RA}{L} \tag{1}$$

where, R = electrical resistance (Ω), A = cross sectional area = 0.0016 m^2, L = length of the specimen = 0.16 m.

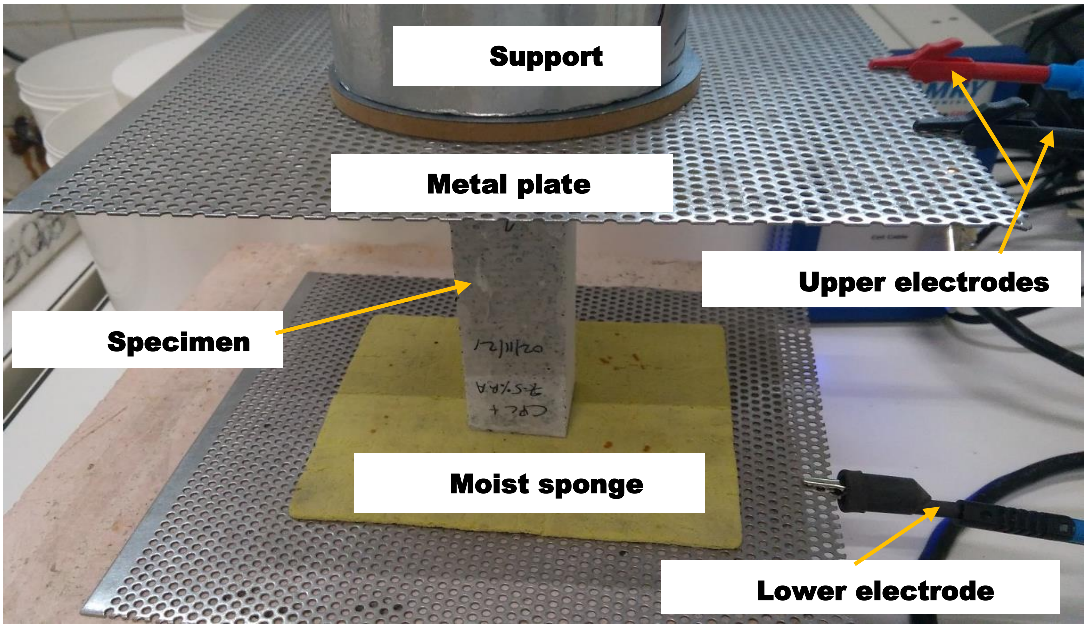

Fig. 1. Set-up for electrical resistivity experiment

3.3. Thermal conductivity

The thermal conductivity was investigated in order to measure the impact of the recycled rubber aggregates and fibre inclusions on the thermal property of CPC. The property measured would give an insight of the thermal insulation and energy saving potentials of the different cement composites. The thermal conductivity of the composite materials was determined following **EN 12667 [5]** standard. Equipment used for this experiment was the thermal conductivity lambda (λ) meter EP500, which operates according to the steady state guarded hot plate method. The temperature of measurement of the CPC composites were chosen to reflect the ideal material behaviour at room temperature. The size of each specimen prepared for this experiment was 150x150x50 mm^3 based on the design of the thermal guarding insulation frame. The specimens were further pre-conditioned (i.e. dried) after they were initially cured and protected in a plastic film at room temperature for 14 days. This procedure was essential to accurately obtain the thermal conductivity of the cement composites. The pre-conditioning of the specimens involved drying the composites first at 20 ºC and 50% RH and then at 40 ºC and 50% RH until the difference in mass within 24 hours of two consecutive measurements was less than 0.05%. The dried specimens were preserved in a desiccator maintained at 20 ºC and 0% RH until they were tested. This was done to prevent free transfer of moisture into the specimens while they were being preserved for testing. The choice of lower temperature for the preconditioning of the samples was to ensure that the pore diameter of the materials was not adversely affected during the drying process. The specimens were positioned in the EP500 device and the thermal conductivity values were obtained directly from the equipment. In addition, separate samples of CPC composites measuring 40x40x160 mm^3 were prepared and dried at room temperature until a constant mass was obtained. The density of each mix composition was estimated as the ratio of its mass to bulk volume.

4. Results and discussion

As the plain CPC material cured in plastic bags continued to age, its electrical resistivity increased from 48 Ωm at 1 day to 480 Ωm at 28 days (**Fig. 2a**). This rise was due to the continuous hydration of the reacting components (H_3PO_4 and $CaSiO_3$), which led to the formation of a more compact structure with reduced water content. Thus, the longer the curing age of plain CPC at controlled room temperature, the higher its resistivity value. Also, it appeared like a quasi-stability in its electrical resistivity was attained at 7-14 days curing age.

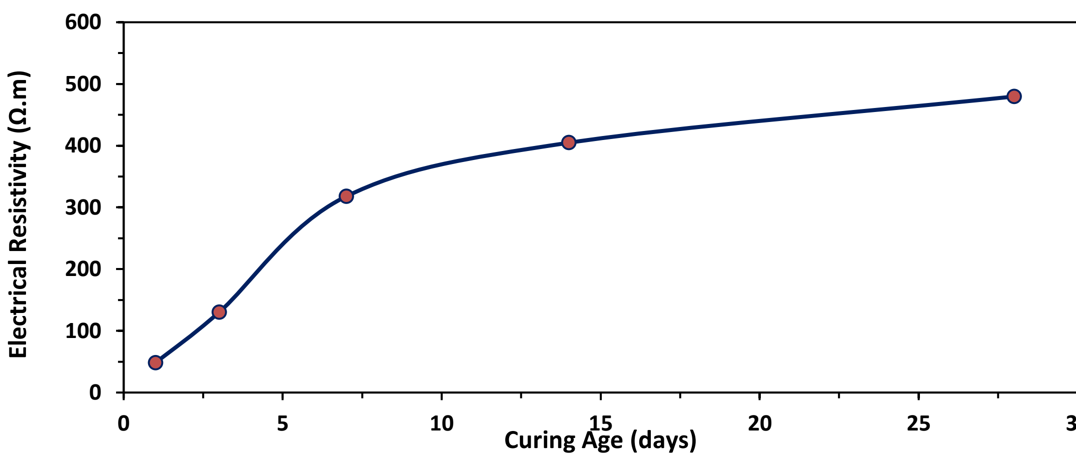

Fig. 2a. Electrical resistivity of pure CPC over 28-day period

The effects of recycled rubber aggregates and fibres on the electrical resistivity of CPC were determined as presented in **Fig. 2b**. It was clear that the addition of rubber aggregates led to increment in the electrical resistivity of the inorganic cement. For example, the percentage increase in the electrical resistivity of CPC was recorded as 15.1%, 23.8% and 39.0% for $CPC_{7.5RA}$, $CPC_{12.5RA}$ and $CPC_{17.5RA}$ respectively. Rubber aggregates are di-electric materials and/or poor electric conductors, and so would raise the electrical resistivity of any cementitious material they are incorporated into **[6]**. Meanwhile, the effects of the fibre reinforcements on the electrical resistivity depend on the content, length and type of fibres used. Results available in the literature also indicate that the orientation and distribution of the fibres have significant influence on the electrical resistivity of the composite **[7]**. It was evident from **Fig. 2b** that while the macro polypropylene fibres slightly increased the resistivity of CPC materials, both the amorphous metallic fibres and recycled carbon fibres greatly reduced the electrical resistivity of the material. This is because the amorphous metallic and recycled carbon fibres are both conductive materials while the synthetic (polypropylene) fibres are insulating materials. The fibre content of 1.5% V_f of macro polypropylene fibres somewhat raised the resistivity of the plain cement by 1.6%. By adding 1.5% V_f of amorphous metallic and carbon fibres to CPC matrices, its resistivity was significantly lowered by 67.4% and 95.4% respectively. The carbon fibre-reinforced composites yielded a smaller resistivity value than the amorphous metallic fibre-reinforced ones. This could result from its higher electrical conductivity compared to the one of the metallic fibre. In addition, their orientation and distribution within the inner structure of the cement after mixing could be another factor. By visual inspection of the cross section of cement composites cut with diamond blade, the carbon fibres appear to be more uniformly distributed in the matrices of CPC than the amorphous metallic fibres. Also, at the same volume content, the number of carbon fibres in the cement matrix seemed higher than the metallic fibres. The hybrid blends of recycled rubber aggregates and fibres in CPC gave rise to hardened cement composites that were less conductive if compared to their individual fibre-reinforced cement composites. It is believed that the insulating property of the rubber aggregates was responsible for raising the electrical resistivity of the composite materials, which have both rubber aggregates and fibre inclusions. For example, the incorporation of 17.5 wt% rubber aggregates and 1.5% V_f fibre reinforcement increased the electrical resistivity for $CPC_{1.5Fpp}$, $CPC_{1.5Fam}$, and $CPC_{1.5Fcf}$ by 37.2%, 11.4% and 398.9% respectively. While the electrical resistivity of $CPC_{17.5RA,1.5Fpp}$ was 39.3% higher than the one of plain CPC, those of $CPC_{17.5RA,1.5Fam}$ and $CPC_{17.5RA,1.5Fcf}$ were 63.7% and 77.1% respectively lower than the one of plain CPC. Both the macro polypropylene and rubber aggregates impeded the flow of current in the cement composites leading to high resistivity values. However, amorphous metallic and carbon fibres are poor electrical insulators and thus, they lowered the resistivity values in their individual cement composites.

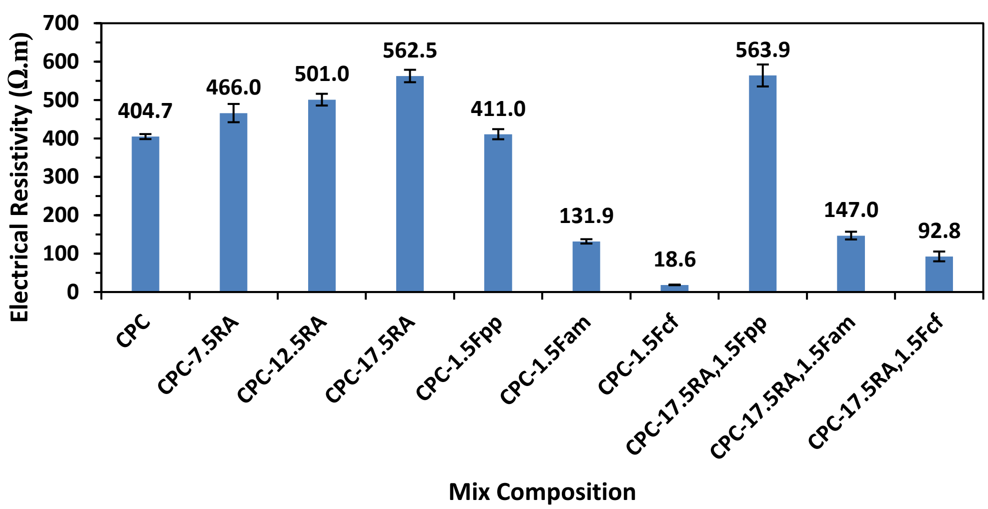

Fig. 2b. Electrical resistivity of CPC composites

The thermal conductivity of CPC composites produced in this research incorporating rubber aggregates and fibres are in the range of 0.345-0.437 W/(m.K). The thermal conductivity values measured at varied temperature intervals of 15 ºK, 25 ºK and 35 ºK showed that the thermal property of the cementitious composites rose as the temperature of measurement was increased. It appears that the presence of rubber aggregates in CPC matrix lowered the thermal conductivity. Also, it could be observed that the thermal properties measured continued to decrease as the percentage incorporation of rubber aggregates was raised from 7.5 wt% to 17.5 wt%. The drop in thermal conductivity of the rubberised cement composites is because the rubber aggregates are better heat insulators than the inorganic cement. Thus, when both materials are combined, the resulting cement composite will have partly the insulating property of the rubber aggregates, and hence, its thermal conductivity will be lower than that of the plain cement. However, it is clear from **Fig. 3** that 1.5% volume fibre content of the macro polypropylene fibres and the amorphous metallic fibres both increased the thermal conductivity of the plain CPC material. Polypropylene fibres used are high density synthetic fibres (i.e. 0.92 g/cm^3), which marginally have higher thermal conductivity than the plain CPC. Hence, they would increase the thermal conductivity of the pure cement when they are combined with the raw materials of the cement. The impacts of the amorphous metallic fibres were more significant than the

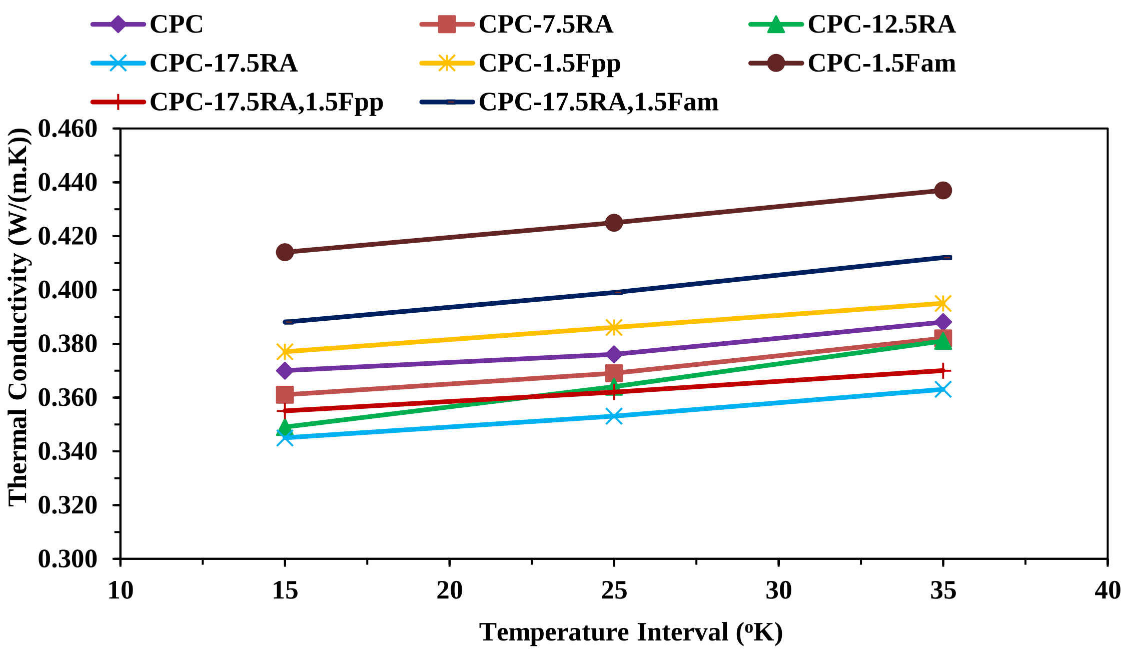

Fig. 3. Thermal conductivity of CPC composites at different temperature values

macro polypropylene fibres. This is because they possess better heat conducting property and would have greater effect on the thermal property of CPC than the polypropylene fibres when both are separately introduced in any cementitious material. The CPC materials with hybrid combination of the rubber aggregates and fibres have thermal properties that were lower than their respective individual fibre reinforced composites. Overall, the changes in thermal conductivity due to the incorporation of rubber aggregates and fibres were around 21%-27%. Comparing the thermal conductivity with the estimated densities of each of the mix compositions examined, a positive correlation was found, as represented in **Fig. 4a**. That is, the higher the density of the cement composite, the greater its thermal conductivity **[8]**. $CPC_{1.5Fam}$ gave the optimum thermal conductivity value of 0.414-0.437 W/(m.K) because it was denser than other cement composites. On the other hand, an inverse correlation (relationship) does exist between the thermal conductivity and electrical resistivity values obtained in this research (**Fig. 4b**). That is, the fibre-reinforced CPC composites, which yielded low electrical resistivity values produced the highest thermal conductivity values ($CPC_{1.5Fam}$) while the rubberised CPC composites with high electrical resistivity values have the lowest thermal conductivity values ($CPC_{17.5RA}$). The range of values for thermal conductivity from this research are akin to the ones obtained for lightweight inorganic cements **[9]**. In comparison to the polystyrene (heat insulating) materials and normal weight concrete, the CPC composites are in-between these two categories of materials. This implies that their thermal conductivity values are higher than the one for heat insulating materials **[10]**, but less than the values given for normal weight concrete and ceramics **[11]**. In summary, CPC composites have moderately low thermal conductivity, which make them potentially useful in the construction industry as energy efficient materials. The significance of this is that wherever they are used as structural repair materials or part of a structural element, they could provide additional functional benefits by reducing heat transfer and energy consumption in a building or other infrastructures. The rubberised CPC composites will yield higher energy savings than the fibre reinforced CPC composites.

5. Conclusions

The CPC material is a low-carbon, lightweight structural cement and when it is used as a repair material or in the construction of structural elements, contributes not just to its superior strength properties, but also other functional benefits (i.e. low thermal conductivity), which are attractive for energy savings in the building sector. Fibre and recycled rubber aggregate inclusions could be used to lower or enhance these functional properties of CPC. While the incorporation of recycled rubber aggregates caused a decrease in the thermal conductivity of CPC, conductive fibres (metallic and carbon fibres) were used to lower the electrical resistivity of the cementitious material. Like in other inorganic cements, an inverse relationship was also found between thermal conductivity and electrical resistivity of CPC composites developed in this research. Finally, the use of end-of-life inert additives (e.g. rubber aggregates and carbon fibres) is a positive contribution to the circular economy and the general ecology of the built environment.

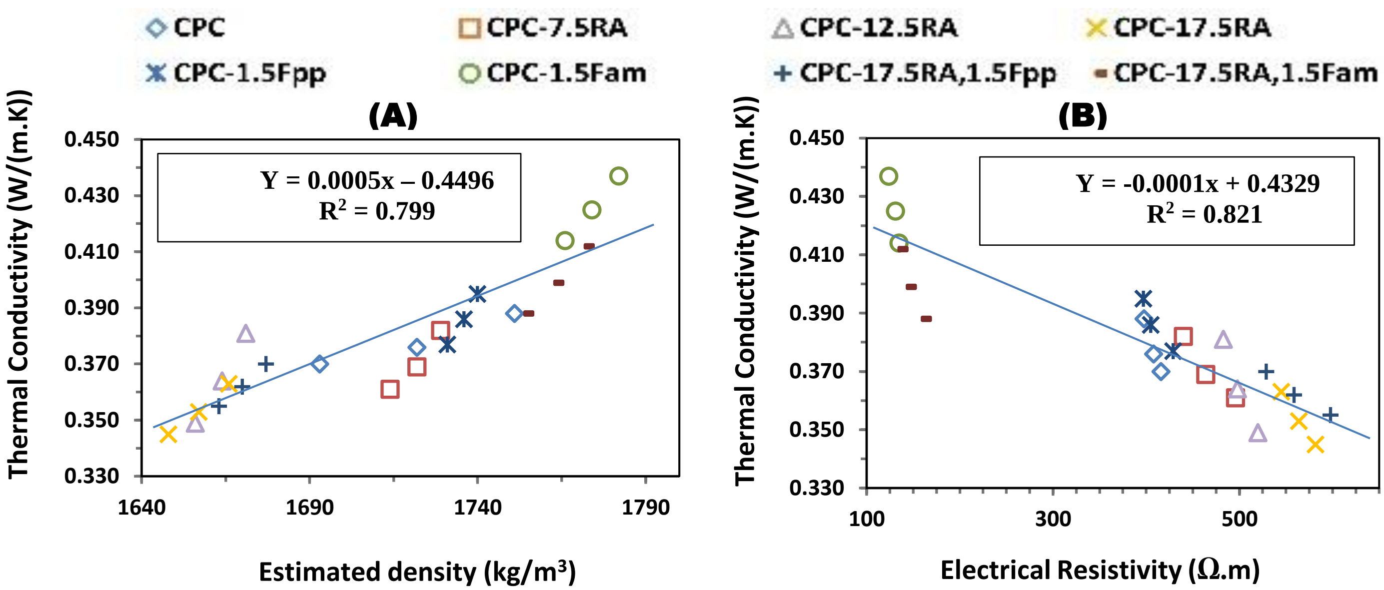

Fig. 4. Relationship between; a) thermal conductivity and density, b) thermal conductivity and electrical resistivity of CPC composites

Acknowledgements

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