Chapter

Incorporation of Phase Change Materials and Application of 3D Printing Technology in the Geopolymer Development

Ahmed Nmiri

Abstract

The building sector accounted for the largest share of both global final energy use and energy-related CO_2 emissions. Despite the efforts made during the last decade to reduce energy consumption and greenhouse gas emissions, the demand for energy is increasing steadily. Thus, development of novel strategies to reduce energy costs and save the environment through a new building regulation has critical importance. Several new technologies are emerging to help achieve the aim of reducing energy usage in building sectors, eliminating greenhouse gas emissions, and recycling waste. Some of these technologies are: (1) the development of geopolymer binder that may be used as an alternative to ordinary Portland cement, (2) the adoption of three-dimensional (3D) printing technology in the civil engineering, and (3) the integration of phase change materials (PCM) in cementitious materials to increase energy efficiency of buildings. In this chapter we review some research about phase change materials-based geopolymer cement, and the adoption of the additive manufacturing technology in geopolymer applications, as well as, point to further areas of study required for wide-scale industry adoption.

Keywords: Aluminosilicate materials, Alkaline activator, Geopolymer, Phase change material, 3D printing

1. Introduction

Due to some advantageous properties of thermal conductivity, high density, and high mechanical strength of Portland cement concrete (PCC), it is a frequently used concrete for applications utilizing PCMs in especially microencapsulated form [1–3]. However, carbon dioxide emission during the production of PCC causes a negative effect on the environment. Compared to PCC, geopolymer concrete (GPC) has several beneficial properties as PCC, but also higher initial strength [4], superior acid resistance [5], high fire resistance [6], and shorter setting time [7, 8]. These features of GPC make it an alternative binder for preparation of PCM containing cementitious materials to be considered for improving building energy efficiency.

Phase change material (PCM), the thermal energy storage (TES), is one of the promising methods used to reduce the environmental impact and to increase energy efficiency of buildings. Phase change materials (PCM) are latent heat storage materials, which can store and release large amounts of energy during a phase change that can occur according to one of many matter transitions (solid–liquid or solid–gas or liquid–gas or solid–solid). However, the most commercially viable transition is between the liquid and solid phases. When the temperature rises above melting point of PCM, this last one melts and absorbs heat, when the temperature drops below melting point; the PCM solidifies and release heat. Heat can also come from other sources such as non-air-conditioned buildings and industrial machinery. There are three main types of PCM: organic, inorganic and eutectic. The most commercially viable PCM is organic since it is chemically stable, safe and nonreactive, does not loss its effectiveness with cycling, can be microencapsulated and has a wide temperature range [9]. The addition of PCM into building materials leads to store the excess of the outdoor environment heat (During the day) and reduce heat transfer to the indoor side of the concrete wall. While, during the cold periods (or at night) the PCM release the stored heat into the building if the inside temperature is too low, and thus causing an increase comfort level in building through providing heating in the winter and providing cooling in the summer without the use of an air-conditioning system. Thereby reduce the fossil fuels-based energy consumption.

Most of the investigations were focused on the addition of microencapsulated PCM (MPCM) to the standard concrete recipes. The literature survey indicated that the combination of MPCM with cementitious material resulted in low composition fraction due to the fact that more loading is resulted in the final product with low TES capacity and low mechanical strength. Another problem is the leakage of PCM caused by breaking some parts of capsules during mixing and compression processes. Moreover, the combination of MPCM with GP is not cost effective because of the high cost and complex synthesis nature of MPCM.

Moreover, microencapsulated or encapsulated phase change materials are particles consisting of a core material the (PCM) and an outer wall (shell). The shell is an inert, stable polymer or plastic or metallic [10]. It does not melt under normal processing and use conditions. The shell acts as a barrier between the core material and the surrounding matrix and controls the volume change of the PCM during its phase change. Due to the very high cost of PCM metal-based encapsulations other method has been adopted to avoid the high cost of the encapsulation of PCM. This method consists in direct incorporation of non-encapsulated PCM into concrete materials. However, this method leads to the leakage of PCM during its liquid state, as well as the corrosion of the concrete matrix due to the corrosive nature of some PCMs. Not to mention the corrosion of the exposed surfaces of the concrete matrix and the reinforcement bar embedded in concrete causing by the environment (air, humidity, salt water, or other hostile environment), which enhances the porosity and permeability of the materials, thereby reducing its mechanical and structural properties.

Because of its cost-effective and eco-friendly, 3D printing is an excellent method to create a building with an efficient thermal regulation and make the integration of PCM in building more efficient, less expensive and more environment friendly [11]. However, among the obstacles for application of 3D printing in geopolymer-based construction are the low mechanical strength, long setting time, and low tensile strength [12, 13].

2. Geopolymers

Geopolymer cement (GP) has several beneficial properties as Portland cement (PC), but also it is much more ecological. It is known as green material [14], because of its low energy consumption, and low emission of polluting gases during manufacture, which makes it an alternative binder for cementitious materials. Geopolymer is produced from the activation of aluminosilicate materials such as metakaolin [15], blast furnace slag [16], fly ash [17] and so on, by a homogenous solution of alkali hydroxide and alkaline silicate, at ambient conditions [14, 18]. The mechanism consists of (1) the dissolution of the aluminosilicate structure under the effect of the alkali hydroxide to form oligomers of silicate $[SiO(OH)_3]^-$ and aluminate $[Al(OH)_4]^-$, and (2) the condensation of these free oligomers under the effect of the alkaline silicate to form another amorphous three-dimensional network [14, 18, 19]. The role of Na^+ and K^+ ions consists in balancing the electrical charge of Al^{3+} in IV-fold coordination [20, 21]. Geopolymer materials can be used for encapsulating heavy metals. In fact, the charge-balancing-alkali ions in the geopolymer network can be partially replaced, by ion exchange, with radioactive elements, and reducing them migration into the environment.

Alkali silicate solutions, also called water glass, such as sodium silicate, potassium silicate, lithium silicate etc. are consolidating agents for the material, they increase the formation rate of tetrahedrally coordinated aluminum [22] and improve the mechanical and physical properties of the final materials. Alkali silicate solutions have many applications, such as the production of silica gel and formulation of refractory ceramics and cements. The use of a highly reactive alkaline silicate solution and a highly amorphous aluminosilicate material enhances the formation of the geopolymer network [22]. The reactivity of alkaline silicate solutions was found to be dependent on the SiO_2/Al_2O_3 and SiO_2/Na_2O ratios. According to some literatures [15, 23–25], the highest mechanical properties of geopolymers is obtained when SiO_2/Al_2O_3 molar ratio is between 3.0 and 3.8, Na_2O/Al_2O_3 molar ratio is about 1 and the NaOH solution concentration is approximately 10 M. The SiO_2/Al_2O_3 ratio may change with the type of raw material used as source of alumino-silicate [17] and then impacts on geopolymers properties [26]. The physical properties of geopolymers are improved when SiO_2 are added to the mixture [14, 27]. Kong and Sanjayan [28] stated that alkaline solution selection and SiO_2/Al_2O_3 ratio are critical parameters necessary to optimize the performance of geopolymer (at ambient or at elevated temperature).

Recent studies show that use waste can offer an alternative to alkaline silicate with potential advantage of lower cost and lower environmental impact. Torres-Carrasco and Puertas [21] have studied the feasibility of using industrial waste glass as a source of silica to replace sodium silicate in the alkaline activation of fly ash. They found, according to the analysis of the mechanical properties, degree of reaction and microstructure of alkali-activated fly ash, that the dissolved waste glass silicate by the NaOH solution had a substantial impact on the composition of the geopolymerisation reaction. Other studies demonstrated that usage of waste glass in concrete enhances its acid resistance as well as its physical and mechanical properties [29, 30]. In contrast the addition of waste glass reduces the plasticity of the fresh paste, thereby reduce its workability, thus a super-plasticizer is needed [31].

Tong et al. [32] investigated the production of sodium silicate solution from Rice Husk Ash (RHA). A hydrothermal process for the dissolution of RHA in sodium hydroxide solution was developed. Optimized procedure parameters were found to be: NaOH concentration 3 M, heating temperature 80°C and heating duration 3 h. The obtained solution was used for the production of alkali-activated binder made with a blend of fly ash and ground granulated blast furnace slag. Obtained compressive strength of mortar was in the range of 60 MPa at 28 days, which confirmed the equivalence between the solution produced with the optimized method and commercially available options. Cost analysis indicated that the proposed method could allow a reduction of almost 55% of the cost for the activation of alkali-activated binder.

Silica fume has been used as activator in metakaolin-geopolymer preparation [24], the Mk-based geopolymer with a silica fume content of 6 wt% (compared with those with 2% and 10%), corresponding to a SiO_2/Al_2O_3 molar ratio of 3.84, resulted in the highest compressive strength, which was explained based on its high compactness with the smallest porosity. Silica fume improved the compressive strength by filling interstitial voids of the microstructure because of its fine particle size.

Geopolymer materials are differentiated by their SiO_2/Al_2O_3 ratio that affects their structure and application. Aluminosilicate-based GPs are designated by the term "poly (sialate)," which is an abbreviation of poly (silico-oxo-aluminate) or $(-Si-O-Al-O)_n$. The various types of poly (sialate), according to Davidovits [14], are polysialate or (-Si-O-Al-O-) or (PS) (with $SiO_2/Al_2O_3 = 2$), poly (sialate-siloxo) or (-Si-O-Al-O-Si-O-) or (PSS) (with $SiO_2/Al_2O_3 = 4$) and poly (sialate-disiloxo) (-Si-O-Al-O-Si-O-Si-O-) or (PSDS) (with $SiO_2/Al_2O_3 = 6$). Each type of GP cement possesses special features: good thermal insulation for PS, high strength and good solidification in presence of toxic waste for PSS, excellent fire resistance and high adhesion for PSDS [14, 33].

Silva et al. [15] revealed that the properties of GP systems can be drastically affected by minor changes in the available SiO_2 and Al_2O_3 concentrations during synthesis. The best resistance of metakaolin-based GPs was obtained when the SiO_2/Al_2O_3 molar ratio is between 3.0 and 3.8. These ratios could however change according to the type of raw material used as a source of aluminosilicate. Yunsheng et al. [34] found for example the highest compressive strength (34.9 MPa) for metakaolin-based GPs with a higher SiO_2/Al_2O_3 ratio (equal to 5.5).

Burciaga-Diaz et al. [35] investigated the compressive strength evolution as a function of the curing temperature at 20 and 80°C, and using the molar ratios of SiO_2/Al_2O_3 (2.64–4.04) and Na_2O/Al_2O_3 (0.62–1.54). The results revealed that the optimal ratios that yielded the greatest compressive strength were $SiO_2/Al_2O_3 = 2.96$ and $Na_2O/Al_2O_3 = 0.62, 0.93$. For greater SiO_2/Al_2O_3 ratios, good final compressive strengths were registered, but the setting time was very long. Curing at 80°C for 24 h was favorable for a rapid strength gain only at early ages, however, at later ages, the highest compressive strengths were obtained after curing at 20°C (this temperature makes it possible to avoid any thermal degradation of the geopolymer). Catauro et al. [36] investigated the structure and the mechanical behavior of the organic–inorganic hybrid materials consisting of an inorganic matrix of a metakaolin-based GP in which the polyethylene glycol (PEG) was added as a plasticizer. The results revealed that the elastic strain increased for a fixed value of stress with the percentage of PEG increases but a decrease of flexural and compressive strengths due to the increasing of porosity. PEG-free samples can reach final mechanical resistance faster than hybrid systems.

3. PCM and construction materials

Numerous studies have investigated the integration of PCM to improve the building energy efficiency. Shadnia et al. [37] studied the mechanical and thermal properties of fly ash-based GP mortar containing different amount of PCM in the form of micro-encapsulated powder. They found that the unit weight and compressive strength of the GP mortar decreased when more PCM was incorporated due to lightweight, small shear strength and stiffness of PCM. In the meantime, the effect of the melting of PCM on the strength of GP mortar is negligible. Cao et al. [7] investigated the effect of microencapsulated PCM (paraffin Rubitherm) on the thermal performance and compressive strength of PC concrete and GP concrete. The results revealed that the increasing of the amount of micro-encapsulated PCM (MPCM) improved the latent heat, lowered the thermal conductivity, which could improve the thermal performance of building materials, and decreased the compressive strength in GP concrete compared to PC concrete due to the enhancement of porosity. The results also revealed that GP concrete exhibited better energy saving properties than PC concrete at the same conditions.

In another investigation, Duy Cao et al. [38] conducted a more detailed study on the effect of the polymer shell on the microstructure, thermal, and mechanical properties of GP concrete by using different kinds of MPCMs. They have found that the integration of PCM with a polymer shell containing polar functional groups into GP concrete at 5.2% by weight shows the best thermal performance but the lowest compressive strength due to the largest increase of GP concrete porosity and better interface bonds between microcapsules and the concrete matrix.

In order to know and examine the cause of low compressive strength after adding PCM, Pilehvar et al. [39] investigated the effect of incorporation of MPCM in solid and liquid states on the mechanical properties and microstructure of both GP and PC concretes. The results revealed that the compressive strength of both GP concrete and PC concrete decreased with increasing amount of MPCM. This decrease might be caused by the lower stiffness and strength of MPCM compared to sand, causing MPCM to be deformed or broken during the compression test [37]. It is also possible that air gaps, low adhesion and weak bonds between MPCM and the surrounding matrix may contribute to the strength reduction. The results also revealed that whether the PCM was in solid (Temperature below melting point) or liquid (temperature above melting point) state did not significantly affect the mechanical properties of GPC, while melting the PCM was found to reduce the strength of PC concrete. This was due to the fact that GP concrete has higher compression strength than PC concrete.

GP has been considered as an alternative carrier matrix to hold PCM in macro or micro encapsulated form as well as their being of more environmentally friendly material. Jacob et al. [33] fabricated encapsulated phase change materials EPCM (10 mm) consisting of molten chloride salt as a core encapsulated by fly ash geopolymer-based shells. They employed tow methods (dip-coating and pre-formed shells) to fabricate the geopolymer capsules. They found that the dip-coated capsules resulted in non-uniform shell thickness and shape, which promotes uneven heat transfer and high stress areas during phase change. However, the preformed capsules method allowed a greater control over size, shape and shell thickness.

Frattini et al. [40] synthesized GP mortar containing an expanded clay aggregate (supporting-shape) incorporated paraffine PCM. The results showed that with the paraffin content up to about 30–40% by weight, the matrix exhibited good mechanical properties and very high fire resistance.

Sukontasukkul et al. [41] studied the mechanical properties and heat insulation of wall panels made of fly ash-GPC containing porous lightweight aerated block (9.5–19 mm) impregnated with paraffin PCM. The results showed that the incorporation of PCM aggregate improved both thermal storage and heat insulation of GP panel. The results also showed that the density of GP increased with the increase in paraffin content in aggregate. Nonetheless, since lightweight aggregate was much weaker than GP paste, the increase in lightweight aggregate content caused the strength reduction.

Wang et al. [42] studied the influence of PCM on mechanical and thermal properties of clay GP mortar, PCM has been prepared by vacuum method using paraffin as the heat-absorbing material, expanded perlite as the supportive material, and two encapsulation methods were developed by using $CaSiO_3$ and Na_2SiO_3 as the capsules, and the corresponding PCMs were incorporated with clay GP mortar. They found that the incorporated PCM in clay GP mortar effectively reduced the transport heat. In addition to this, expanded perlite plays good package effect on paraffin during the process of solid–liquid phase change, which can guarantee the composite PCM in solid conditions during the solid–liquid phase change in the macro. By using $CaSiO_3$ and Na_2SiO_3 as the capsules, the PCM building materials can effectively avoid the leakage of paraffin.

In order to obtain effective composite PCMs for thermal energy storage purpose in buildings, Sarı et al. [3] developed a form-stable composite PCM composed of the cement impregnated with the eutectic mixture of capric acid(CA)-myristic acid(MA) as PCM through vacuum impregnation method. And then they investigated its chemical structure. The FTIR spectra/XRD patterns not showed any new band/peak. This result confirms the fact that any chemical reaction is not carried out between the cement matrix and form-stable composite PCMs.

Kastiukas et al. [43] performed an investigation to determine the most efficient coating method and material regarding its ability at retaining the PCM. They produced macro-encapsulated aggregates using expanded clay lightweight aggregates (in the 2–10 mm size range + numerous small and large pores) as supportive shape impregnated with paraffin PCM. The different coating materials used were: Sika Latex, Weber dry-lastic and polyester resin adhesive (Palatal). The macro-encapsulated aggregates were then used as aggregates in GP binders made from a combination of aluminosilicate rich mud and waste glass. The results revealed that PCM vacuum impregnation was very successful for expanded clay lightweight aggregate. The polyester resin was determined to be the most suitable choice of coating material for the PCM impregnated lightweight aggregates. Polyester resin coating was also chemically stable and neutral, and improving thermal conductivity.

As conclusion several methods have been proposed to incorporate PCM in buildings:

1. The first method is direct incorporation of PCM into concrete materials at the time of mixing [44]. In this case, PCM is distributed freely in concrete. However, this method leads to the leakage of PCM during their liquefaction. This causes contamination of the host material, PCM loss and a reduction of the thermal energy storage capacity and mechanical properties of the building materials.

2. The second method consists in microencapsulation of PCM into small closed sphere capsules called microencapsulated phase change materials MPCM to mixing them later with the fresh concrete [7]. This method prevents leakage. MPCM improve thermal energy storage. However, this method is very expensive and the deterioration of MPCM during the mixing process may cause leakage of PCM into the building materials. In addition, a poor compatibility between MPCM and the concrete matrix, and the tendency of MPCM to agglomerate may be the main causes of increased porosity, and therefore a decrease in compressive strength of the building materials [45].

3. The third method consists in direct immersion of the cementitious powder in liquid PCM until obtain a form-stable PCM material [46]. This method is simple and low cost and allows for better dispersion of PCM. However, the stress of the volume expansion during phase change process leads to enhance

the porosity in buildings, and crack the concrete matrix, thereby causing the concrete matrix to crack and reduce mechanical strength.

4. Another method is the impregnation of PCMs in porous supportive shape materials through vacuum impregnation to obtain a macro-encapsulated PCMs and then mixing them with fresh concrete [33]. This method controls the volume expansion during phase change process. However, the solidification of PCM only around the edges during the time of heat regaining from liquid state prevents effective heat transfer. Overall, encapsulated PCM may be spherical, rectangular, cylindrical or irregular. It was found that spherical capsules resulted in the highest heat transfer rate. Also, the small size of encapsulated PCM leads to an increase in the heat transfer rate [33]. Moreover, the small encapsulated PCM can fill the cavities between aggregates and sand, thereby reducing the concrete porosity [7].

Therefore, there is strongly needed to develop geopolymer material with thermal energy storage TES ability besides without including these difficulties. In order to make this product more efficient, cheaper, and more environmentally friendly, the 3D printing technology could be used [11, 13].

4. Additive manufacturing

Additive manufacturing technology, also called 3D printing technology, is also one of the promising methods used to reduce the energy demand and to reduce greenhouse gas emissions, in fact the application of this method takes less time than conventional manufacturing, and it uses the precise amount of material needed for the construction, which reduces the material costs, waste and negative impact on the environment [47, 48]. The digitally controlled construction process is done by a 3D printer. It consists in placing the fresh paste inside the loading container. Then, this last one is installed on the construction robot to start the printing process. The movable extrusion head is controlled by software to move in x, y, and z directions. The printer nozzle, on the extrusion head, traces the desired shape, layer by layer, until the final structure is achieved. The printing conditions could be optimized by modifying the nozzle diameter, the extrusion speed, layer heights, and the time gap between each layer [47–49].

The development of building materials adapted to the construction-based 3D printing technology has become of great importance in the world since the beginning of the second decade of the 21st century [11, 50].

3D printing process depends on two main factors, namely flowability and buildability [51]. The flowability is the fresh concrete extrusion capacity through the nozzle of the printer. The buildability is the ability of fresh concrete to retain the desired shape and hold layer overlays without collapsing. The buildability depends on the setting time and the mechanical property of the fresh material. Flowability and buildability can be considered as against each other, indeed if flow is increased, buildability decreases, and vice versa. Which is the main obstacle to applying the 3D printing method in the building construction [11, 52].

The mechanical activation of raw materials is one of many solutions used to overcome these obstacles. The mechanical activation reduces the setting time and improves the mechanical performance of the resulting material [53]. For example, the increasing of grinding time of the raw materials breaks the crystalline structure of the inert material and increases its reactivity which improves the mechanical

properties of the hardened product. However, overgrinding leads to a decrease in fresh material flowability, which causes further demand of water to reincrease the flowability [54]. Then the evaporation of water during curing process increases shrinkage and cracks in the resulting material which causes a decrease in its mechanical properties. If water does not added, the interaction between activators and aluminosilicate material remains low, thereby the unreacted materials causes cracks and affects the mechanical properties of the resulting material [55].
To increase the flowability and workability of fresh past while maintaining its mechanical performance, plasticizers should be used [56].

To reinforce the geopolymer material, Ma et al. [57] entrained a continuous micro steel cable during filaments deposition process, which demonstrated significant improvement of mechanical strength, toughness and post-cracking deformation of geopolymer composite. Shakor et al. [58] added lithium carbonate to reduce the setting time for the cement mixture.

5. Wall coating material with anti-corrosion and anti-leakage properties

Wall coatings are decorative or protective layer that are applied to the interior or exterior surfaces of walls. Coating is applied to the surface of the wall via different methods depending on the nature of that wall and the nature of the coating itself. Among these methods are plastering [59], paint brush [60], roller [61], air spray [62] and etc. Coating designed for thermal energy storage and thermoregulating should be corrosion resistance, anti-leakage and anti-heat [63–65].

Corrosion is the gradual destruction of the concrete matrix by chemical reaction with the environment [66, 21]. This reaction enhances the porosity and permeability in the concrete matrix. Moisture, CO_2, chloride, and other harmful ions could reach the surface of reinforcement bars, thereby causing corrosion of the bars and reducing the mechanical and structural properties of the concrete.

To reduce the water absorption and chloride diffusion coefficient, Zheng et al. [67] coated the concrete with Epoxy resin nanocomposites containing 0.3 wt% of graphene oxide. The chloride ion penetration resistance is due to the formation of crosslinking in the composite coating, improvement of hydrophobicity and shielding effects of graphene oxide.

To prevent penetration of hostile elements, and early crack of concrete, epoxy resin nanocomposites modified with graphene oxides (GOs) were prepared using a solution blending process and then sprayed onto testing blocks of concrete [68].

Waterborne silicate coating is an anticorrosive coating used to protect steel bar in the concrete, it consists of alkali metal silicate, rust-proof pigment, and modification material (to modify the alkali metal silicate solutions) such as acid modification, silicone acrylic emulsion, styrene acrylic emulsion… [69, 70]. The waterborne silicate coating has excellent corrosion resistance, good acid-alkali resistance and high heat resistance [71]. The zinc silicate works with the alkali metal silicate, forming a dense and stable film on the metal surface, and reducing the penetration rate of water and other ions. Coatings for reinforcement bars are widely available. In addition, the reinforcement bars are embedded in the concrete matrix and they do not expose to the hostile environment. Moreover, geopolymer materials have high corrosion resistance. The coating of the reinforcement bars may be not necessary The interaction between geopolymer-based coating material and the superficial elements of reinforcement bar or mild steel leads to formation of passive layer which prevent reinforcement bar and mild steel from corrosion [66]. Fly ash-slag geopolymer has good corrosion resistance and low corrosion rate compared to fly ash geopolymer [72].

Afshar et al. [73] reported that the zinc-rich epoxy primer as a coating on mild steel rebar has the best performance when used in combination with concrete containing 25% fly ash, 10% silica fume and 3% inhibitor by cementitious material weight.

Zhao et al. [74] believed that adding ultrafine silica powders dispersed by hexamethyldisilazane (HMDS) and polyacrylic acid PA emulsion improved the water, acid, alkali, heat and aging resistance of the polymer modified cementitious coatings PCCs. The appropriate amount of the modified ultrafine silica powders is about 5% of the mass of the PA emulsion, because higher water absorption and decreased tensile properties happened when the amount is too large (10%). Hexamethyldisilazane (HMDS) disperses the ultrafine silica SiO_2 powders and reduces their agglomeration. SiO_2 chemically interacts with the polyacrylic acid PA emulsion to form a cross-linked network structure. It was found the PCCs with 4 wt% HMDS modified SiO_2 powders had fewer micro-defects and more compactness, thus the tensile properties and durability under different conditions, such as water, acid, alkali, heat and artificial aging, were significantly improved. The water absorption and chloride ion permeability coefficient of concrete coated by the PCCs with 4 wt% well-dispersed SiO_2 powders were also decreased.

Xu et al. [75] developed a colorful and robust superhydrophobic concrete (CSC) coating composed of cement, sand, water-based stone protector, and dyes, and meets both performance and esthetic requirements. And they reported that this coating exhibits excellent chemical durability and weather resistance, and has promising application prospects on the outside wall of concrete.

Several studies demonstrated that usage of glass waste in concrete enhances its acid resistance as well as its physical and mechanical properties. Bisht et al. [29] have used waste of glassy materials made of soda lime to produce acid resistance concrete. They have shown that the best optimized performance in terms of compressive strength and acid resistance can be obtained by substituting up to 21% of sand by glass waste. The overadding of glass waste above to 21%, although it increases the acid resistance, it enhances the porosity which decreases mechanical strength of the concrete. Glass waste can also be used as aggregate or as source of silicate in the manufacturing of geopolymer concrete [30]. In contrast the addition of glass waste reduces the plasticity of the fresh paste, thereby reduce its workability, thus a super-plasticizer is needed [31].

Morefield el al. [76] have developed a novel coating that is based on hydraulically reactive silicate cement blended with a glass enameling frit and fused onto the steel reinforcement: If the enamel coating is cracked the freshly exposed calcium silicate cement grains will react with any humidity in contact with them to produces a cement paste in the crack.

6. Discussion and conclusion

As can be seen from the literature, the PCMs were incorporated by building materials in two ways: (i) addition of MPCM to building materials (ii) the addition of non-encapsulated PCM to building materials by impregnation (directly or by vacuum) method. Despite numerous studies carried out to make fresh materials suitable for 3D printing, no study has developed geopolymer-based PCM for 3D printing construction.

- Although the vermiculite and perlite clay minerals have been used to prepare FSCPCMs with leakproof property until now [77, 78], vermiculite and perlite based FSCPCMs has not been yet integrated with fly ash based-GP to prepare novel kinds of GP-FSCPCM concretes which can be used to decrease temperature fluctuations of building inside.

- Literature survey indicated that paraffin as PCMs were commonly used with geopolymers. However, bio-based fatty acid eutectic mixtures are rarely used. When compared to the paraffins, the fatty acid has better TES characteristics in terms of especially subcooling degree, volume change, latent heat energy storage capacity, phase change reversibility and low-cost due to their produce ability from the vegetable and animal fats [79, 80].

Therefore, based on these considerations, we think that the most proper way to achieve GP-FSCPCM concrete with the most effective is incorporation of non-encapsulated PCM with proper material by vacuum infiltration method and then addition to the GP mortar.

To prepare form-stable composite phase change materials (FSCPCMs), PCMs may be impregnated separately with vermiculite and perlite using vacuum impregnation technique (**Figure 1**) [78, 81].

To achieve the form-stable composition, the mass fraction of PCM could be changed. Then, each of the vermiculite/PCM and perlite/PCM composite samples could be subjected to leakage test by heating them above melting temperature of regarded PCM. After this test, the composite with free of leakage will be defined as FSCPCM.

Different clays such as diatomite, perlite, kaolinite, bentonite, vermiculite etc. as porous, lightweight supporting materials have been used to produce form-stable composite PCMs (FSCPCMs) [82, 83]. Among these clay minerals, vermiculite (VMT) and perlite (PER) are good supporting materials for absorbing organic PCMs. VMT is a lightweight material with porous, inexpensive, ecologically harmless, non-toxic and expandable as much as 8–30 times its original size, when heated to about 800°C. Therefore, VMT is used for construction and insulation in buildings. Perlite (PER) is glassy volcanic rhyolitic rock. PER can be expanded up to 10–20 times its original volume when heated rapidly at 850–1150°C. The resulting expanded perlite (EPER) particles are spherical in shape, usually fluffy, highly porous due to a foam-like cellular internal structure. EPER has low sound transmission, high fire resistance, a large surface area, low moisture retention and a very low density. Besides it is classified as environmentally safe ultra-lightweight

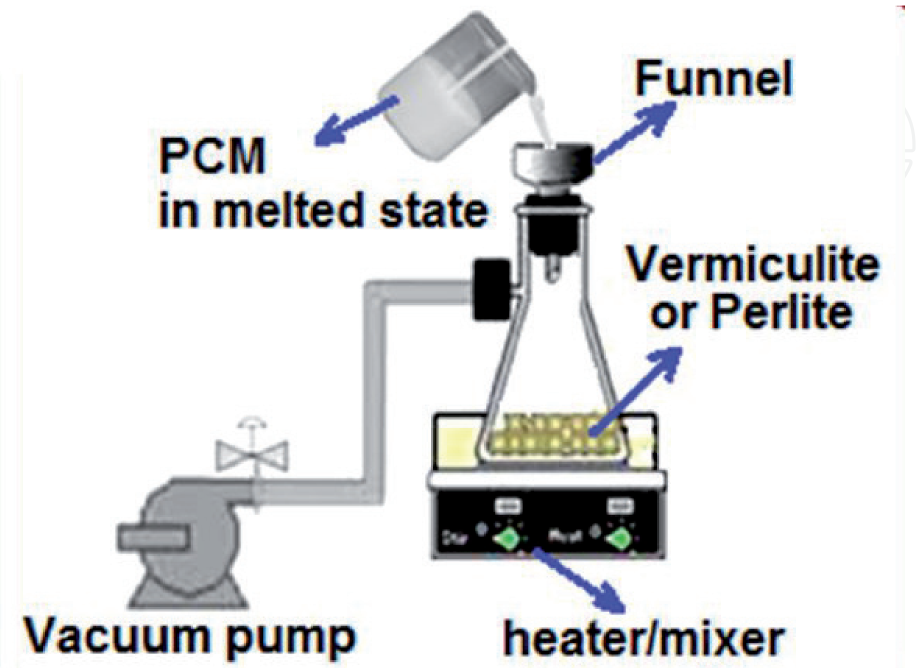

Figure 1.
Vacuum impregnation technique used for preparation of FSCPCMs.

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building material. In the buildings, VMT and PER are used as lightweight aggregate for plaster, concrete compounds, firestop mortar, and component of interior fill for walls. Moreover, they have good chemical compatibility with organic PCMs such as fatty acids and their binary mixtures. Therefore, both clay minerals are promising candidates as building material to prepare FSCPCMs for TES applications in buildings [78, 81].

By using, 3D printing technology, GP, PCMs and charging storage facilities with energy generated from renewable sources, we can reduce the greenhouse gas emissions and the dependence on fossil fuels, preserve the environment, attenuate the overheating or excessive cooling of the room and maintain a desirable temperate without the use of the air-conditioning system, allow to positively influencing indoor room temperature by storing direct solar radiation.

Author details

Ahmed Nmiri
Department of Chemistry, Faculty of Sciences of Tunis, University of Tunis El-Manar, Tunis, Tunisia

*Address all correspondence to: nmiriahmed@gmail.com

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