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Graphene geopolymer hybrid: A review on mechanical properties and piezoelectric effect

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Abstract. A review on graphene geopolymers hybrid is presented, focusing on the mechanical properties and piezoelectric effect. The method and way of mixing graphene with geopolymers are discussed, including form of graphene that frequently being used by researchers which is graphene oxide (GO) and reduced graphene oxide (rGO). Type of geopolymers being focused in this paper is fly ash and kaolin. The flexural and compressive strength, fracture toughness and stiffness are highlighted in terms of mechanical properties after mixing with geopolymers. The piezoelectric effects on geopolymer is emphasized as graphene acted as conductive filler. Research findings revealed that graphene geopolymer hybrid displayed improvement in mechanical properties despite agglomeration and some defects that need to be rectified. Geopolymers such as metakaolin exhibited piezoelectric effect after being compressed cyclically with the migration of ions and by incorporating graphene nanoplatelets.

1. Introduction

Graphene has grabbed enormous attention in this new era of technology and development of materials. Materials are growing its capability and potential by adding another material, incorporating micro or nano sized fillers or changing its dimension. When it comes to dimension, graphene is a two-dimensional flat monolayer of sp^2 bonded carbon atoms, arranged in honeycomb lattice with high aspect ratio layer geometry and high specific surface area. Altering the dimension of carbon material will result in modification to its name obviously, structure, properties and ability. Carbon can be wrapped into 0-dimensional fullerenes, rolled into 1-dimensional carbon nanotubes (CNT), stretched into 2-D graphene and stacked into 3-dimensional graphite [1] as summarized in Figure 1.

The tremendous interest of graphene is due to its excellent mechanical and chemical properties, such as high surface area ($2630 \text{ m}^2 \text{ g}^{-1}$) [2], excellent thermal conductivity ($5000 \text{ W m}^{-1} \text{ K}^{-1}$) [1], high electron mobility at room temperature around $250,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at electron densities of $2 \times 10^{11} \text{ cm}^{-2}$ [3], high Young's modulus [3], very high light transmittance $\sim 98\%$ [4], excellent gas impermeability, chemical stability and exceptional quantum hall [5–11]. Graphene has been established in matrixes to gain new properties and achieve exceptional capabilities. Materials from polymer and ceramics has shown great improvement in properties as it hybrid with graphene, such as the elastic modulus, tensile strength, electrical conductivity and thermal stability [2], [12–14].



However, the challenge of using graphene is to fulfil its homogenous dispersion in composites without using hazardous or costly solvents before being espoused for broad application [15]. On the other hand, graphene oxide (GO) was composed of multiple oxygen-functional groups, promote easier dispersion in aqueous solvent. It is highly hydrophilic and can form steady aqueous colloids to ease the fabrication of macroscopic structures cheap and simple solution processes, which are vital to the huge-scale uses of graphene. GO is the exfoliated sheets of graphite oxide, containing only one or few layers of carbon atom like graphene. The most tempting property of GO is it can be reduced, removing the oxygen-containing groups with the retrieval of conjugated structure, becoming reduced graphene oxide (rGO) [16].

Geopolymers is an “inorganic polymers” which composed of amorphous alkali aluminosilicate. It essentially consists of repeating chain of silicate monomer (-Si-O-Al-O-) [17]. The prefix “geo” refers to inorganic aluminosilicate based on geological materials which reacted with alkaline solution forming binder via polycondensation reaction [18]. There are variety of aluminosilicate materials such as kaolinite, feldspar, industrial solid remainders such as fly ash, slag and mining wastes. These materials are refer as solid raw materials. To undergo geopolymerization process, geopolymer need to be mixed with alkaline activator such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium silicate (Na_2SiO_3) and potassium silicate (K_2SiO_3). After mixing, curing process will take place at room temperature or slightly higher temperature in the range of 20-100 °C [19, 20]. This procedure is summarized in Figure 2.

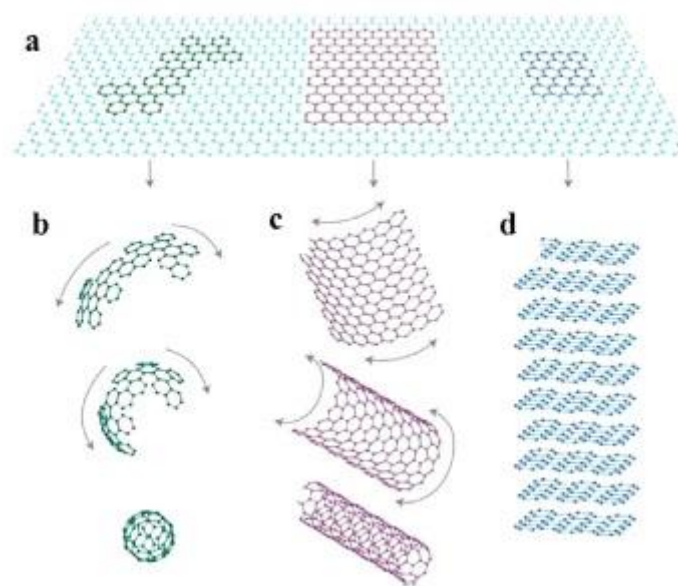


Figure 1. Allotropes of carbon: a) 2-D graphene b) 0-D fullerene, c) 1-D carbon nanotube d) 3-D graphite [21].

Geopolymers provides alternative for ordinary Portland cement (OPC) for greener concrete and cement industry. Geopolymer is considered as the third generation cement after lime and ordinary portlant cement [21-23]. OPC emits more green-house gases, promoting pollution and unhealthy environment. Geopolymers despite environmentally friendly nature, are low cost, low density and simple to be processed [25–30]. The properties of geopolymers can be developed by choosing specific raw materials, proper mix and processing route to achieve a particular application [30]. Besides that, hybridizing geopolymer with reinforcing materials such as carbon fibers, polymeric materials, natural fibers and steel fibers can improve the mechanical properties of the geopolymer [31–35].

Despite the advantages and excellent properties of geopolymers compared to OPC, geopolymers properties are hugely dependent on the origin materials such as fly ashes and kaolin which differ from

source to source like physical properties, chemical compositions and amorphous proportion. For example, the difference in properties of fly ash is based on vary in burning the coal procedures and type of coal used. The end properties will significantly affect the materials. Thus no standard method exists to anticipate the properties of geopolymers based on their mix design [36]. Another setback of geopolymers is they are brittle and possessed low tensile strength and fracture toughness, similar to OPC [37]. Thus, reinforcing geopolymers with micro and nanofibers are one of the solution to overcome this problem.

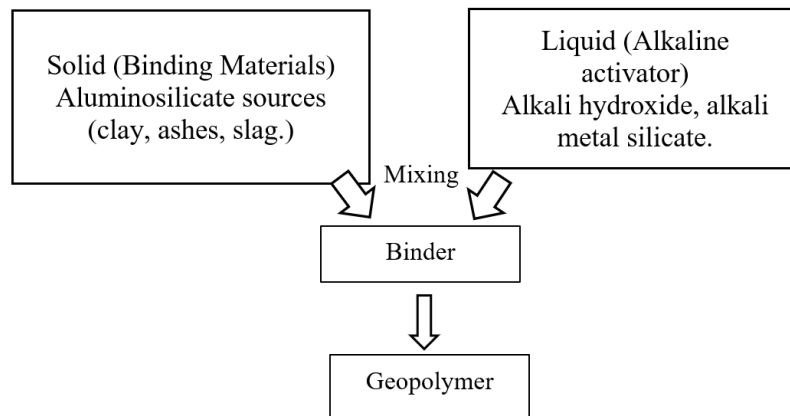


Figure 2. Schematic diagram of geopolymer process [18].

This paper focused on reviewing graphene as carbon material used as reinforcing agent in geopolymers material, specifically fly ash and kaolin to characterize the mechanical and electrical properties.

2. Geopolymers: fly ash and kaolin

Fly ash (FA) is the product of coal combustion composed of fine particles with huge amount of production, estimated around 780 million tons annually [38,39]. The ash is derived from electric power generation plants, collected using mechanical and electrostatic separators from the fuel gases of the power plants [40]. This ash is called fly ash because the fine particles are flown together with flue gases released to the air using a series of mechanical separators, followed by a highly competent electrostatic precipitator. If the particle sizes is larger and fall down to the bottom furnace, it is called bottom ash [41]. Fly ash is made from amorphous silica and alumina with exceptional size and shape, promoting its ease of processing and workability for geopolymer production. Based on the total element of Si, Fe and Al, FA can be categorized into two types. FA is categorized as class C if the entire element content is more than 50% and class F if more than 70%. In addition to that, FA can be classified as low calcium content (low Ca) if the Ca level is in the range of 8-20%. If the range is more than 20%, the FA is classified as high calcium content (high Ca) [42].

Kaolin is an earth mineral with the shape of chalk-like sedimentary rock, lightweight and soft. It is the most abundant mineral found in the earth [43] and one of the most versatile industrial materials [44]. It composed of silica, alumina, and water with changeable combinations. Kaolinite is formed by rock weathering, mainly by decomposition of feldspar (potassium feldspars), granite and aluminium silicates. "Kaolinite" term is referring to kaolin clays. It composed of alumina octahedral sheets and silica tetrahedral sheets arranged alternately [45]. Besides that, kaolin can be transformed into metakaolin upon heating to certain degree. Metakaolin is an anhydrous aluminosilicate that is fabricated after undergoing thermal decomposition of kaolin at temperature 550 °C or above [45]. The activation of metakaolin by alkaline activator render a path in producing high-strength cementitious materials. Generally, kaolin is chemically inert over a broad pH range, non-abrasive and has low

conductivity of heat and electricity. It is widely used in industrial applications and other applications like paper, paint, rubber, plastics and ceramics industries [46].

3. Graphene hybrid with geopolymer composite

Even though graphene is an exceptional reinforcing material to be incorporated in the geopolymer composite, most researchers utilized GO or rGO in their preparation of the geopolymer composites due to their properties is comparable with graphene and easier to be produced and dispersed in solution. Additionally, to produce graphene single-handedly is very difficult, time consuming and require expensive equipments and devices. To purchase graphene occasionally is quite costly. Thus it is not surprising for GO or rGO are most desired in most research. For geopolymer, mostly fly ash and kaolin are used, and the kaolin will be treated with heat in thermal decomposition process, converting into metakaolin. The preparation procedure for rGO/geopolymer composites are shown in Figure 3.

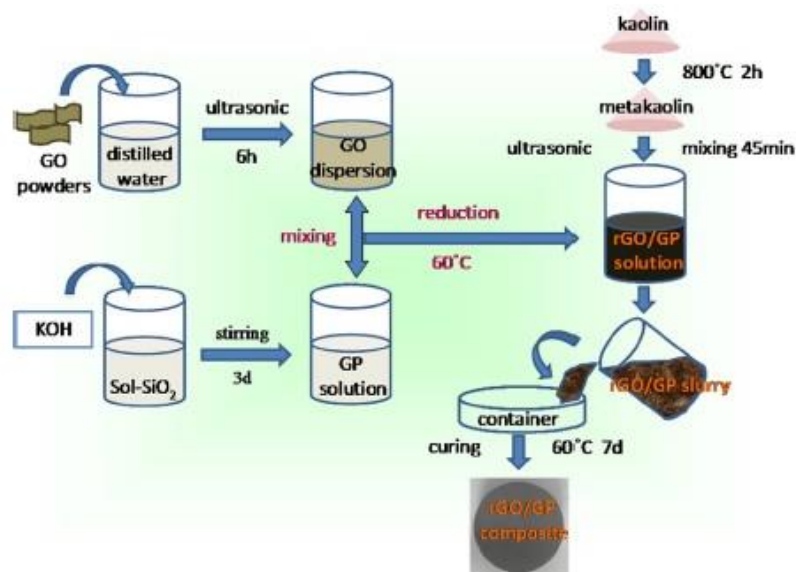


Figure 3. Schematic illustration of preparation procedure for rGO/geopolymer composite [15].

Most of the researcher hybrid geopolymers composites with GO/rGO to improve its mechanical properties. According to Yan et al. [47], GO powders was used and transformed into GO dispersion solution by ultrasonic dispersion process in distilled water. Metakaolin is used as the geopolymer, mixed with GO dispersion solution in a prepared potassium silicate solution. The rGO/KGP slurry was casted in a plastic container and cured. The research characterized the flexural strength and fracture toughness of the composites comparing rGO/KGP with pure KGP. It can be concluded that introducing rGO in the composites enhanced flexural strength and fracture toughness approximately 7% and 30% respectively. Also, increasing soaking time will deteriorate the mechanical properties since it degenerates the rGO sheets due to higher number of defects formed.

Yan et al, [48] has reported a number of properties of graphene/geopolymer composites on the effect of temperature on the reduction of GO during graphene/geopolymer preparation. It shows that the reduction degree of rGO increased with increasing temperatures and the C/O ratio increased from 2.48 (GO) to 3.36 (rGO, 80 °C) with the elevated temperatures. The rGO sheets also dispersed homogenously and attached well with geopolymer matrix [48]. He also reported on the fracture toughness and flexural strength of the composites which increase remarkably with the addition of rGO. However, increasing volume fraction (0.5 wt%) made the rGO hardly dispersed due to their large specific surface area and strong attractive van der Waals force, leading to agglomeration of the

rGO sheets. This will cause poor interfacial compatibility and formation of defects like pores and voids, leading to low flexural strength of the hybrid composites [49].

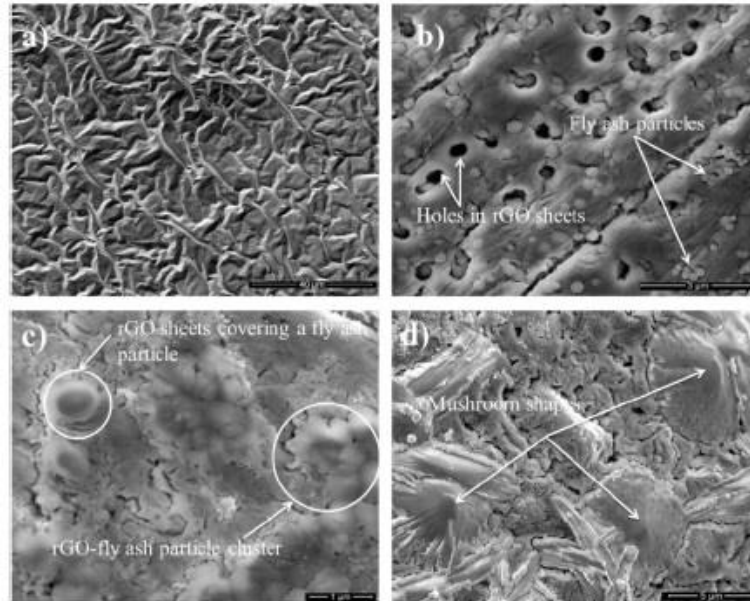


Figure 4. SEM micrographs of (a) rGO sheets, (b) GO sheet interaction with submicron fly ash, (c) GO sheets covering submicron fly ash particles and (d) GO sheet interaction with larger fly ash particles [37].

Yan et al, [15] also studies on the fabrication and characterization of graphene/geopolymer composites [15]. Apart from that, graphene also being employed in cubic-leucite composite through graphene oxide/kaolin combination [50]. The rGO/cubic-leucite composites were fabricated by in situ reduction of rGO/geopolymer and proper post high temperature treatment. The purification of leucite grains and rGO pulling-out have improved the flexural strength and fracture toughness of the composites.

Besides kaolin, fly ash was also being used in incorporating with graphene to produce a hybrid. A couple of research has been made thoroughly in fabricating graphene/geopolymer composite using fly ash. Saafi et al. has used class F fly ash, with sodium silicate and sodium hydroxide as the alkaline activator and pristine GO sheets utilized in the composites. The samples are prepared in the form of geopolymeric beams with different concentrations of rGO. It can be concluded that the flexural strength, stiffness and flexural toughness of the geopolymers composites improved with the increasing rGO contents. In addition to that, the rGO sheets moved by the fly ash particles filled the voids and hollow spaces in the matrix as shown in Figure 4 [37].

This promotes good chemical bonding thus improving mechanical properties of the composites. Fly ash (low calcium FA) also being used by Ranjbar et al. [51] in their research. The different was they utilized graphene in nanoplatelet form (GNP). The incorporation of GNP displayed an improvement of the compressive and flexural strength, toughness and stiffness of the composites are increased due to toughening enhancer mechanisms and uniform stress distribution by increasing GNP content. However, the existence of overlapped GNPs caused defects, resulted in canceling out the extra resistance from the drag by GNP sheets and stress concentration respectively.

For piezoelectric effect characterization of graphene/geopolymer composites, Candamano et al. [52] in their research reported an electro-mechanical behaviour in geopolymer which is metakaolin after being incorporated with graphene nanoplateletes (GNPs). The composites displayed value of

11.99 pC/N for charge coefficient d_{33} when 1% wt of GNPs is used. This phenomenon developed promising potential to pave the way in not just civil application, but also advanced materials as self-sensing or energy harvesting technology. Another research by Saafi et al. [53] reported the existence of piezoresistive effect of rGO-geopolymeric composites under mechanical tension and compression using four-point bending and axial compression tests. The report also characterized the electrical conductivity and found out the rGO increased the electrical conductivity of fly ash-based rGO composites from 0.77 S m^{-1} at 0.0 wt% to 2.38 S m^{-1} at 0.35 wt%. The report suggests the composites could had potential as self-sensing materials for civil applications.

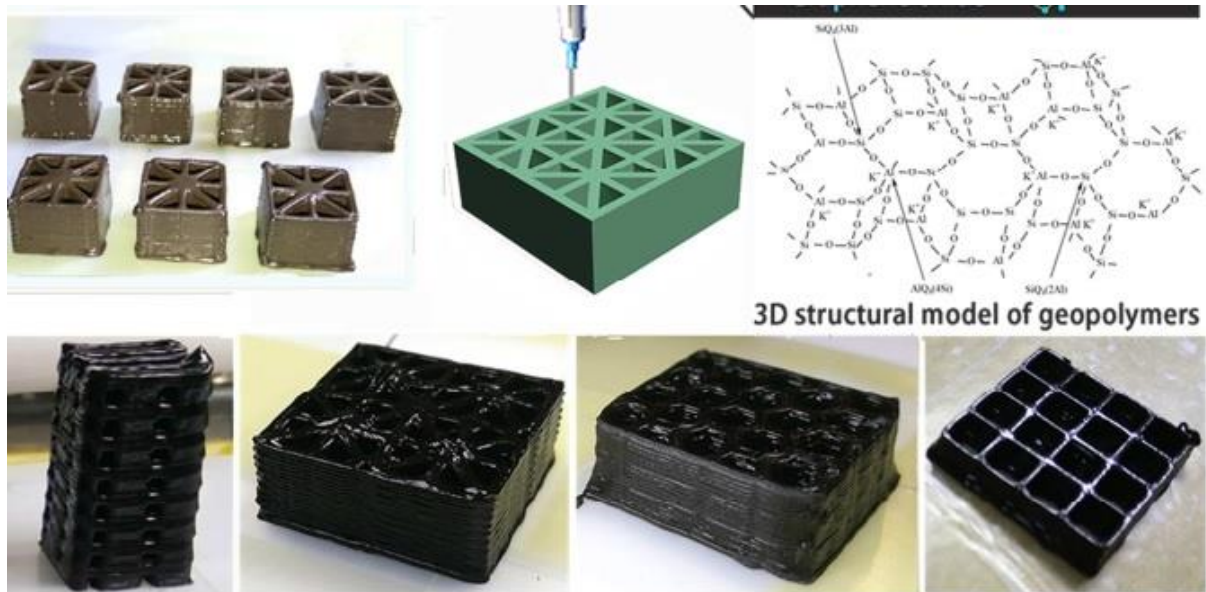


Figure 5. Some 3D printed structures and model. The colors of the printed samples turn from brownish to blackish when the GO loading increased [54].

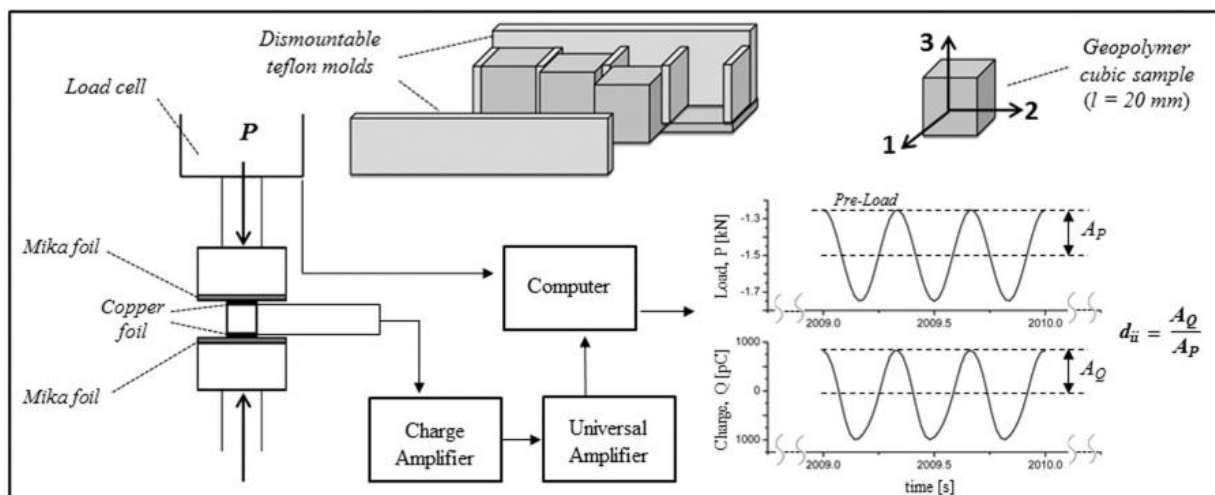


Figure 6. Schematic representation of the setup realized for the direct piezoelectric characterization with the adopted reference system [55].

Another paper reporting on piezoelectric effect on geopolymer samples is from Lamuta et al. [55]. The research used metakaolin as the geopolymeric material. The piezoelectric effect was measured by

means of electro-mechanical instron biaxial testing machine. The samples were tested under cycling compression with electrodes were put on the surface of the samples and connected with charge amplifier. The setup is shown in Figure 6. The samples were also being characterized by converse piezoelectric where electric was excited to the samples via AC voltage of 10 V. The result stipulates that quartz state could possibly contribute to electrical dipoles creation during mechanical stress, thus to piezoelectric activity. Another key finding is the presence of Na^+ in charge balancing disposition that leads to piezoelectric effect. The model of the chemical-physical structure of the geopolymer for piezoelectric effect is shown in Figure 7. The existence of charge imbalance due to hydration and local dipoles generated from compressive stress have led to piezoelectric activity within the geopolymers. However, it was found that a completely dried samples did not exhibit any direct piezoelectric effect, thus prevent any other source of piezoelectric effect and the author convinced the model proposed in Figure 7 is a reliable one.

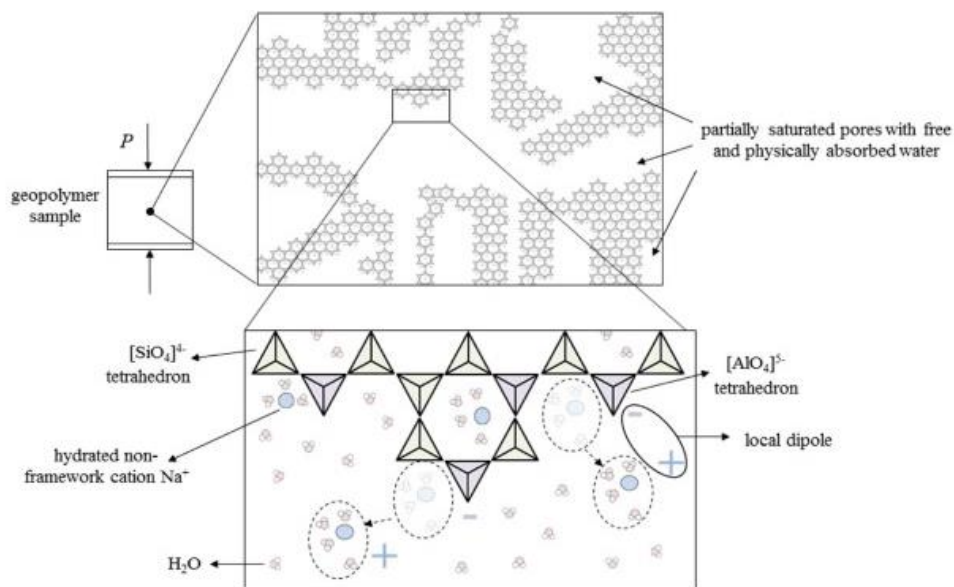


Figure 7. Schematic representation of the chemical-physical model proposed for the explanation of the direct piezoelectric effect detected in geopolymers [55].

Other papers mainly characterizing the electrical properties of geopolymer. For example, Zhong et al. [54] reported a paper where extrusion based 3D printing GO/geopolymer (GOGP) was used for the first time. The preparation of GOGP initially was almost the same as the previous papers from Yan et al. method, except there are specific ratio for alkaline-source particles and aluminosilicates particles (ASOPs), GO suspensions and deionized water (DI water). The GOGP was 3D-printed with suitable pressure to extrude the ink through the nozzle. GOGP nanocomposites were converted into graphene/geopolymer (GrGP) composites by sintering process. The prepared 3D-printed composites are shown in figure 5. After sintering, all the composites displayed very high electrical conductivity of the order 10^2 S/m, indicating the formation of electrically conductive network. Apart from that, addition of GO has altered the rheology of geopolymer precursors, enabling the 3D-printing of geopolymer and improve the mechanical performance of the composites. However, this paper did not characterize the piezoelectric effect properties.

4. Conclusion

This paper reviews graphene hybrid with geopolymers composites, the methodology and the properties achieved after being hybrid. It can be concluded that incorporating graphene with geopolymers has exceptionally improved the mechanical properties, regardless of the graphene

configuration or form and what type of geopolymers being used. Most of the researchers utilized graphene in the form of GO or rGO for easier processing and better workability. Geopolymers are non-conductive materials [56], but may increase its conductivity when graphene is employed, thus improving the electrical properties. Besides that, the existence of piezoelectric effect on geopolymer such as metakaolin has broadened the research scope of geopolymer in electrical area, despite the reported findings and research still not at large and minor. This respective piezoelectric effect on geopolymers show great potential and significant outcome for future applications and technology in civil area and design [57]. Based on the review, graphene and geopolymers hybrid may unleash promising properties to be applied in various fields and new applications are yet to be discovered in future.

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