Engineering Science & Technology
http://ojs.wiserpub.com/index.php/EST/

UNIVERSAL WISER
PUBLISHER

Research Article

Use of Commercial Starch, Starches Derived from Cassava, Potato, and Yam as Additives for Synthesising Metakaolin-Based Geopolymer Composites

Cedric Mbiakop Dieuhou[1], **Amadou Oumarou Amadou**[2], **Hervé Kouamo Tchakouté**[1, 3*], **Charles Peguy Nanseu-Njiki**[1], **Claus Henning Rüscher**[3], **Pengkun Hou**[4]

[1]Laboratory of Electrochemistry Analytic and Materials Engineering, Department of Inorganic Chemistry, Faculty of Science, University of Yaounde I, P.O. Box 812, Yaounde, Cameroon
[2]Department of Applied Chemistry, National Advanced School of Agro-Industrial Sciences, Ngaoundere, P.O. Box 455, Ngaoundere, Cameroon
[3]Institute of Mineralogy, Leibniz University Hanover, Callinstrasse 3, D-30167 Hanover, Germany
[4]Shandong Provincial Key Laboratory for preparation and measurement of building materials, University of Jinan, Jinan, Shandong, China
Email: htchak@yahoo.fr

Received: 25 February 2024; **Revised:** 28 April 2024; **Accepted:** 14 May 2024

Abstract: The main objective of this work is to investigate the use of different starch sources (yam, sweet potato, cassava, and commercial starch) as additives for the production of metakaolin-based geopolymer composites. Geopolymer composites were prepared by replacing metakaolin with 0 and 15 wt% of each type of starch. The different powders obtained were separately mixed with a hardener containing a molar ratio of SiO_2/Na_2O of 1.6. X-ray diffraction and Fourier transform infrared spectroscopy analysis were used to determine the structural properties. The compressive strength and morphology of the prepared geopolymer composites were investigated. Results show that the reference geopolymer compressive strength is 36.25 MPa. These are 64.66, 48.49, 46.03, and 44.71 MPa when commercial starch, yam starch, cassava starch, and sweet potato starch, respectively have been used as additives. It can be seen that the compressive strength values of the geopolymers containing starches are higher than those of the reference geopolymer. The compressive strength of the geopolymer composite made by replacing metakaolin with commercial starch is higher than those made with yam starch, cassava starch, and sweet potato starch. The X-ray patterns of all the geopolymers show the same mineral and the infrared spectra show the same absorption bands, except for the one at 2,935 cm^{-1} which appears on the spectra of the geopolymers containing starch. The geopolymer composite containing commercial starch has a more compact and dense microstructure. Those containing starches from yam, cassava, sweet potato, and the reference geopolymer material have a coarser microstructure. Compressive strength is consistent with the more compact and dense microstructure of geopolymer composite containing commercial starch. The incorporation of 15 wt% of starches derived from yam, cassava, sweet potato, and commercial starch was found to increase compressive strength. It was found that starches from various crops could be used as additives in the synthesis of geopolymer composites.

***Keywords*:** yam starch, sweet potato starch, cassava starch, metakaolin, geopolymer composites, compressive strengths

DOI: https://doi.org/10.37256/est.5220244500

1. Introduction

Starches are semi-crystalline organic polymers whose crystal structures allow them to be classified into three types, A, B, and C, based on X-ray powder diffraction analysis [1]. The C-type pattern is a mixture of A- and B-type polymorphs according to Zobel [2] and Xie et al. [3]. He and Wei [4] and Guo et al. [5] claimed that the A-type polymorphic starch is found in cereals or rhizomes, such as maize, wheat, and rice, etc. Some tubers, such as potatoes and sweet potatoes, and rhizomes contain type B crystals. The latter is the type that is rich in amylose. According to Dome et al. [6], Sarko and Wu [7], Frost et al. [8], and Alay and Meireles [9], crystalline consists of amylopectin while amorphous consists of amylose chains. Starch consists of the A-type, which is mainly derived from cereal starches such as maize, wheat, and rice, according to Zakaria et al. [10]. The B-type is derived from tubers such as potatoes, cassava, and sago. The C-type contains both the polymorphic A and B crystallinity generally found in beans and other root starches. The amylopectin under sodium silicate forms C--O-O-SiO_2Na units. This was reported by Rashid et al. [11]. The compressive strength may be affected by the formation of C--O-O-SiO_2Na units in the structure of geopolymer materials. Geopolymer materials are inorganic polymers made by mixing a semi-crystalline source of aluminosilicate with sodium water glass. They are cured at room temperature for 24 hours before demoulding. Geopolymers are chains or networks of mineral molecules that can be linked together by covalent bonds. They include the following molecular entities [12]-[14]:

-Si-O-Si-O-siloxo, poly (siloxo)
-Si-O-Al-O-sialate, poly (sialate)
-Si-O-Al-O-Si-O-sialate-siloxo, poly (sialate-siloxo)
-Si-O-Al-O-Si-O-Si-O-sialate-disiloxo, poly (sialate-disiloxo)
-P-O-P-O-phosphate, poly (phosphate)
-P-O-Si-O-P-O-phospho-siloxo, poly (phospho-siloxo)
-P-O-Si-O-Al-O-P-O-phospho-sialate, poly (phospho-sialate)
-(R)-Si-O-Si-O-(R) organo-siloxo, poly-silicone
-Fe-O-Si-O-Al-O-Ferro-sialate, poly (ferro-sialate)

The properties of these inorganic materials could be improved by the incorporation of additives. For example, Chub-uppakarn et al. [15] investigated the influence of partial substitution of metakaolin by palm oil fuel ash (POFA) and alumina waste ash on compressive strength and microstructure in metakaolin-based geopolymer mortar. The partial substitution of metakaolin by POFA results in a decrease in the polymerisation reaction rate. On the other hand, calcium carbide residues and fly ash were evaluated as sustainable binders for the environmentally friendly stabilisation of loess soils by Julphunthong et al. [16]. It was reported that carefully designed blends based on the chemical interactions between calcium carbide residuals and coal fly ash can provide a sustainable, efficient approach to soil stabilisation, potentially revolutionising construction practices. [17] and [18] reported that geopolymer materials could be used for the production of asphalt pavement with a high volume. Dieuhou et al. [19] used commercial starch as an additive for the synthesis of geopolymer composites; these authors investigated the partial substitution of metakaolin by commercial starch. They concluded that suitable starch content for the synthesis of geopolymer composites is around 15% by weight. The work of Dieuhou et al. [19] reported that C--O-O-SiO_2Na units can be incorporated into the structure of geopolymer materials and therefore play a very important role in the properties of geopolymer materials. Hence, the formation of C--O-O-SiO_2Na in the structure of geopolymers when starch has been used as an additive could be responsible for the increased compressive strength. Zakaria et al. [10] reported that the content of amylose and amylopectin in the starch was dependent on the source of the plant. This suggests that the amylopectin content of the starch may be responsible for the properties of the geopolymer materials. This may indicate that due to the variation in amylopectin content of the starch sources, the starch source can influence the structure of the geopolymer materials [20].

This work investigates the compressive strengths and microstructural properties of geopolymer composites using starch from yam, sweet potato, cassava, and commercial starch as additives. 0 and 15 wt% of each starch was used to replace metakaolin. A hardener was added to each formulation to obtain geopolymer materials. The influence of different starch on the compressive strengths and microstructural properties of geopolymer materials have been studied by measuring compressive strengths. Scanning electron microscopy was used to observe the morphologies of the geopolymer materials. The functional groups were studied by Fourier transform infrared spectroscopy and the crystalline phases were monitored by X-ray diffraction analysis.

2. Materials and experimental procedures

2.1 *Materials*

The kaolin used in this work came from the Mayouom site in the western region of Cameroon. The sample that was collected was broken up into small pieces by hand. The pieces were air-dried for 12 hours. A mass of the sample obtained was pulverised in a ball mill (MGS Srl) for 30 minutes and the powder obtained is referred to as MY3. In order to obtain metakaolin, called MK-MY3, the MY3 powder was calcined in an electrically programmable furnace (MGS, Srl) at 700 °C for 4 hours. The heating and cooling rate was 5 °C/min. This metakaolin has been used by several researchers to produce geopolymer materials [21]-[22]. The hardener used was a commercially available sodium silicate with a molar ratio of SiO_2 to Na_2O equal to 1.6. It was supplied by Ingessil of Verona, Italy. Commercial starch called AC containing 0.5% by weight of sulfated ash and 0.04% by weight of chloride was provided by Kermel. The starch powders were made from yam, sweet potato, and cassava. They were harvested in Yaounde, the centre region of Cameroon.

2.2 *Experimental procedures*

2.2.1 *Extraction of starches from yam, potato and cassava*

Yam starch, sweet potato starch, and cassava starch are white substance starches that are extracted from yam, sweet potato, and cassava, respectively. The processes for obtaining starches from yam, sweet potato, and cassava are as follows: The tubers are cut up with a grater, water is added and the mixture is left to macerate for a period of 10 to 20 minutes. The liquid phase is separated from the crushed tuber residue by filtration through a cotton cloth. The solid residue is macerated again in water and filtered in the same way as before. The process is repeated 5 times and the collected liquid is decanted for an average of 24 hours. The clear supernatant is removed. The sediment is air-dried for 72 hours. The dried samples were sifted through a sieve with a mesh size of 100 µm and placed in a polyethylene bag for storage. Starches from yam, sweet potato, and cassava are described as AI, AP, and AM, respectively.

2.2.2 *Synthesis of metakaolin-based geopolymer composites*

The metakaolin powder was replaced separately by 0 and 15 wt% of commercial starch (AC), yam starch (AI), sweet potato starch (AP), and cassava starch (AM). The reference geopolymer material was prepared by adding metakaolin to the hardener and mixing it for approximately 5 minutes. This resulted in a fresh geopolymer paste. Metakaolin was substituted with AC, AI, AP, and AM at 15 wt% to produce four formulations of geopolymer composites. To obtain a homogeneous powder, each formulation was mixed for approximately 5 minutes. In accordance with the findings of Dieuhou et al. [19], the substitution of metakaolin with 15 wt% of different starches was chosen. Each formulation was added to the hardener and mixed for approximately 5 minutes. The mass ratio of liquid to solid is 0.83 for the reference geopolymer material and 1.24 for the geopolymer composites containing 15 wt% of each starch. Fresh geopolymer mixes of each formulation were vibrated for 5 minutes on a vibrating table and poured into the $40 \times 40 \times 40\ mm^3$ cubic moulds and allowed to cure for 24 hours at room temperature in the laboratory before demoulding. The freshly cast geopolymers are covered with a polystyrene bag during the curing process. Table 1 summarises the mix proportions of the various geopolymer composites and Figure 1 shows the mixing steps of the geopolymer composites. The reference geopolymer material without added starch is called GB0, those replacing metakaolin with 15 wt% of AC, AI, AM, and AP are called GBC, GBI, GBM, and GBP, respectively. After removal from the mould, each sample was sealed in a plastic bag and left to stand at room temperature for 28 days before the compression test.

Table 1. Mix proportions of the various geopolymer composites

Metakaolin (g)	GB0 (g)	GBC (g)	GBI (g)	GBM (g)	GBP (g)	Hardener (g)	Liquid/solid mass ratio (g)	Geopolymer composites
300	-	-	-	-	-	249	0.83	GB0
255	-	45	-	-	-	372	1.24	GBC
255	-	-	45	-	-	372	1.24	GBI
255	-	-	-	45	-	372	1.24	GBM
255	-	-	-	-	45	372	1.24	GBP


Metakaolin + starch
Mixing metakaolin + starch
Geopolymer paste

Poured geopolymer paste vibrated
Geopolymer composites
Geopolymer composites

Figure 1. Mixing steps of the geopolymer composites

2.2.3 *Characterization methods of different starches and geopolymer composites*

The compressive strength values of the geopolymer materials were determined after 28 days on samples sealed in plastic bags and stored at room temperature in the laboratory in accordance with DIN 1164. The rate of loading was kept constant at a rate of 0.500 MPa/s. They were measured using an automatic hydraulic press with a capacity of 250 kN (Impact Test Equipment Limited, UK KA20 3LR, Stevenston, United Kingdom). Fragments of all specimens were collected and some were finely crushed in porcelain mortar after compressive strength testing. X-ray diffractograms and infrared spectra were recorded from the powders obtained. The morphologies of the samples were observed using other fragments.

A Bruker D8 Advance equipped with a LynXeye XE T detector was used to record the X-ray patterns of various starches and geopolymer composites. The detector detects CuKα1,2 in Bragg-Brentano geometry. The 2θ range is between 3 and 100° for 2 h with 0.05 2θ steps. X'Pert HighScore Plus software was used to identify the crystalline phases.

The infrared spectra of various starches and geopolymer composites were recorded using the KBr method with the Bruker Vertex 80 v. Pellets were prepared by addition of approximately 1 mg of each sample to approximately 200 mg of KBr. This was mixed in an agate mortar. It was then hydraulically pressed at 100 kN (ENERPAC P392, USA). Each spectrum was recorded using the pellet obtained from each sample with a resolution of 2 cm^{-1} and 16 scans. OPUS software was used to collect the data.

The morphology of the metakaolin-based geopolymer composites was determined from the fragments obtained from the compressive strength measurements. The morphology was characterized by scanning electron microscopy (SEM) using a ZEISS GEMINI 500 microscope coupled to an X-max detector from Oxford Instruments, with an acceleration voltage of 1. The microstructure was characterised by scanning electron microscopy and elemental analysis using a ZEISS Gemini 500 microscope coupled to an Oxford Instruments X-max detector. 1 kV acceleration voltage was used for imaging. Without any additional conductive sputter layer, the samples were mounted on an aluminum stub. Carbon tape was used to secure the stub.

3. Results and discussion

3.1 *Characterization of different starches*

3.1.1 *X-ray patterns*

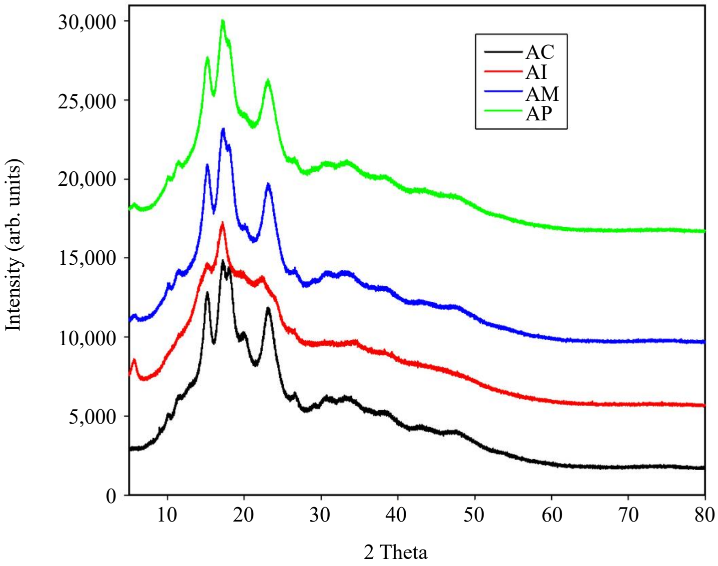

Figure 2. X-ray patterns of different starches (AC: commercial starch, AI: starch from yam, AM: starch from cassava, and AP: starch from sweet potato)

The X-ray patterns of starches AC, AI, AM, and AP are depicted in Figure 2. On the X-ray pattern of commercial starch (AC) peaks at 15.03, 19.82, and 23.02° (2θ), and a doublet peak at 17.24 and 17.97° (2θ) are observed. These peaks correspond to the A-type crystal structure according to Singh et al. [23] and Munoz et al. [24]. Yam starch (AI) shows peaks at 5.72, 15.16, 17.13, 22.52, and 26.20° (2θ). They have a B crystal structure [25]-[26]. On the X-ray pattern of starch from manioc (AM) and sweet potato (AP), peaks at 5.47, 10.13, 11.36, 17.13, 17.97, 20.07, 23.01, and 26.69° (2θ) were observed. All others, except for peaks such as 10.13 and 11.36° (2θ), are mixtures of the two crystal types A and B. The mixture of the two crystal types A and B belongs to the C-type crystal structure according to Zobel et al. [2]. Therefore, starches AM and AP have a C-type crystalline structure [2], [26]-[28]. These crystalline peaks are associated with the amylopectin compounds, according to Todica et al. [28]. These diffractograms show the broad hump structure between 8 and 60° (2*θ*) in addition to these peaks. This is consistent with the presence of amylose compounds.

3.1.2 *Infrared spectra*

Figure 3 displays the infrared spectra of starches AC, AI, AM, and AP. It is observed that these spectra have the same absorption bands. They show absorption bands at 3,393 cm^{-1} that correspond to the stretching vibration modes of the O-H bonds. The stretching vibrations of the C-H bonds are assigned to the doublet bands at 2,913 and 2,872 cm^{-1} [29]. The H-O-H bending vibration at 1,644 cm^{-1} belongs to absorbed water molecules. According to Garrido et al. [30], this region is assigned to the amorphous region. The absorption bands at 1,410 and 1,346 cm^{-1} are assigned to the bending vibrations of the -CH bonds [31]. The stretching and bending modes of the C-O, C-C, and C-O-H bonds are assigned to those at 1,147 and 1,071 cm^{-1}, respectively [30]. The bending vibrations of the C-O-H and C-O-C bonds are responsible for the bands at around 1,001-995 and 907 cm^{-1}, respectively [32]. The one at 849 cm^{-1} belongs to the vibration of the CH_2 bond, while those at 749-696, 568, and 509 cm^{-1} correspond to the vibration modes of the glucose-pyranose ring [32].

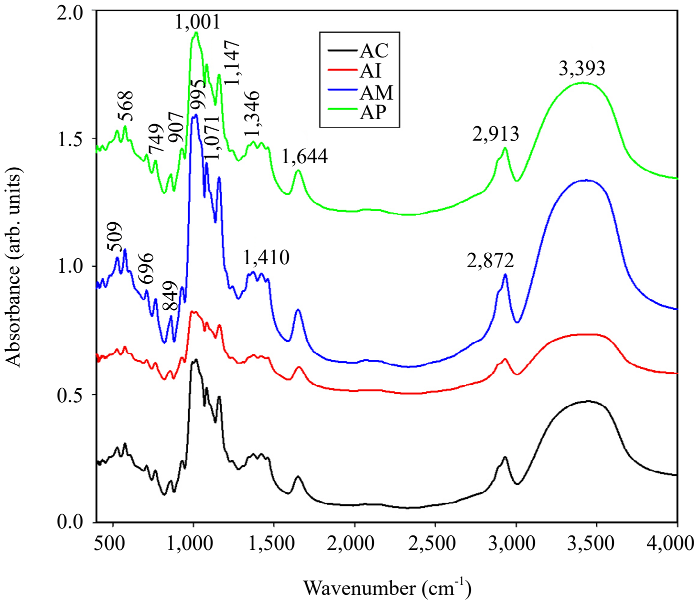

Figure 3. Infrared spectra of different starches (AC: commercial starch, AI: starch from yam, AM: starch from cassava, and AP: starch from sweet potato)

3.2 *Characterization of geopolymer composites*

3.2.1 *X-ray patterns*

Figure 4 shows the X-ray patterns of the geopolymer composites GB0, GBI, GBM, GBP, and GBC. The crystalline peaks of muscovite, illite, quartz, and anatase are clearly visible in these diffractograms. The X-ray pattern of metakaolin also shows these crystalline minerals (Figure 5). This suggests that they did not participate in the geopolymerisation process, or that only a small proportion of crystalline minerals such as quartz could have reacted during geopolymerisation, as suggested by Bewa et al. [33]. These authors reported that the reaction of some quartz particles contributes to the formation of long chains of siloxane (Si-O-Si) groups in the structure of geopolymer materials. This increases the compressive strength. Some of these minerals act as fillers, such as quartz [34]-[35], anatase or titanium oxide [36]-[39], and illite [40], and therefore positively influence the mechanical properties of geopolymer materials. Besides these crystalline phases, the X-ray patterns of geopolymer composites show the broad hump structure between 18 and 40° (2*θ*) belonging to the binder in the geopolymer structure. This is attributed to the binder. The broad hump structure is observed between 15 and 38° (2θ) on the X-ray pattern of metakaolin (Figure 5). This suggests that the geopolymerisation reaction changes the microstructure of the metakaolin.

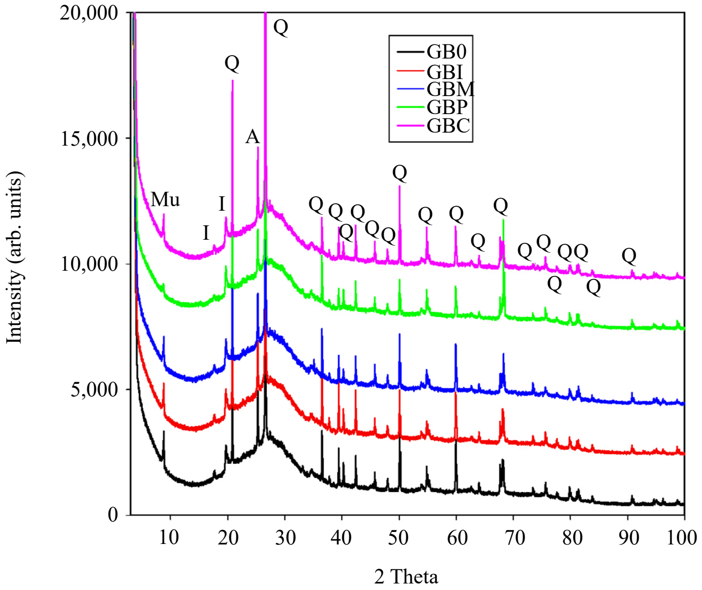

Figure 4. X-ray patterns of geopolymer composites (GB0, GBI, GBM, GBP, and GBC). Mu, I, Q, and A denote peaks of muscovite, illite, quartz, and anatase, respectively

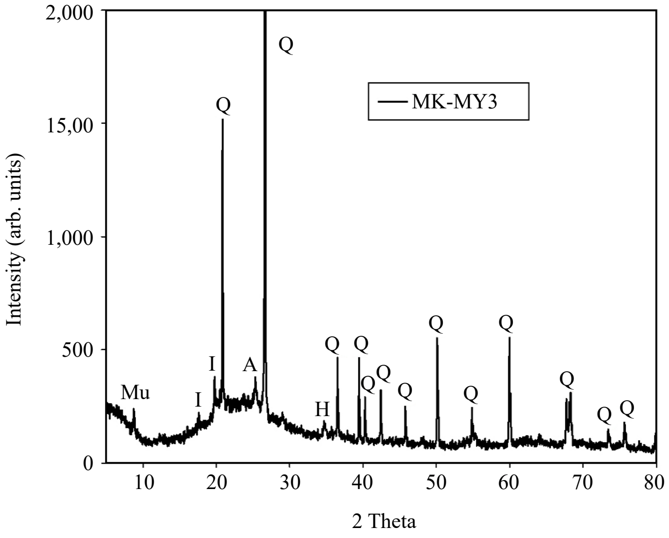

Figure 5. X-ray pattern of metakaolin (MK-MY3). Mu, I, Q, and A denote peaks of muscovite, illite, quartz, and anatase, respectively

3.2.2 *Infrared spectra*

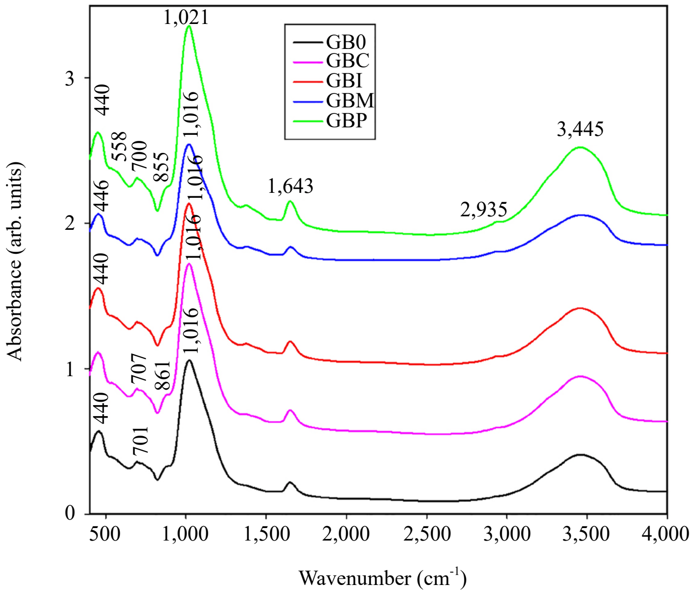

Figure 6. Infrared spectra of geopolymer materials GB0, GBI, GBM, GBP, and GBC

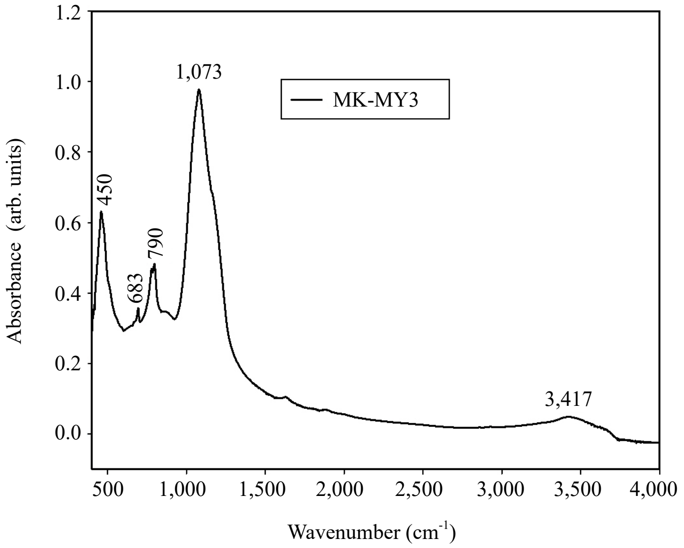

Figure7. Infrared spectrum of metakaolin (MK-MY3)

Figure 6 shows the infrared spectra of the geopolymer composites GB0, GBC, GBI, GBM, and GPB. The bands corresponding to the bending vibrations of Si-O-Si bonds are seen at 446-440 cm^{-1} in these spectra. According to Fernandez-Jimenez et al. [41] the presence of a more significant siloxane band in the structure of geopolymers contributes to the formation of the long chain that helps to densify the microstructure of geopolymers. They also indicate the broad ones, located at 707-700 cm^{-1}, which belong to the stretching vibrations of the sialate (Si-O-Al) bonds with Al in the IV-fold coordination [42]. This broad band could also be attributed to the stretching vibrations of Si-O-C bonds [43], indicating the overlapping bonds of Si-O-Al and Si-O-C [19]. The absorbing band of Si-O-C could act as an adhesive and could help densify the geopolymer composites. The bending and stretching modes of H-O-H and OH are 1,643 and 3,445 cm^{-1}, respectively. The stretching band of C-H with the lowest intensity is observed at 2,935 cm^{-1}. This suggests the presence of starches in the structure of geopolymer composites. The stretching modes of Si-OH and CH_2 bonds are responsible for the absorption band at 861-855 cm^{-1}. The broad one at 558 cm^{-1} is assigned to the Si-O-AlVI in the muscovite and the illite. The main bands of geopolymer composites appearing at 1,016 cm^{-1} for GB0, GBC, GBI, and GBM, and 1,021 cm^{-1} for GBP are attributed to the symmetric and asymmetric vibrational modes of Si-O-Si and Si-O-Al bonds. This absorption band appears at 1,073 cm^{-1} on the infrared spectrum of metakaolin (Figure 7). This observation has been made by other researchers [15], [44]-[45]. The shift towards lower wavenumbers on the infrared spectra of the final products corresponds to the depolymerisation of metakaolin and/or the mixture of metakaolin and starch leading to the formation of geopolymer composites [46].

3.2.3 *Compressive strengths*

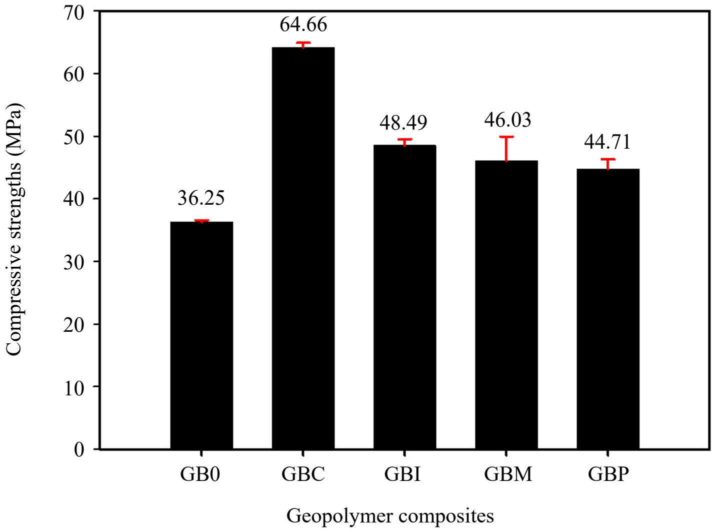

Figure 8. Compressive strengths of geopolymer materials (GB0, GBI, GBM, GBP, and GBC)

Figure 8 shows the compressive strengths of the geopolymer composites. It can be seen that the compressive strength values of GB0, GBC, GBI, GBM, and GBP are 36.25, 64.66, 48.49, 46.03, and 44.71 MPa, respectively. The compressive strength of the geopolymer material without starch addition is lower (36.25 MPa) compared to those obtained by incorporation of 15 wt% starch (from 44.71 to 64.12 MPa). This suggests that through the formation of Si-O-C, known as the adhesive, the incorporation of starches into the structure of geopolymer materials has a positive effect on their compressive strength [44], [47]-[48] and therefore densifies the geopolymer matrix. This could be related to the formation of Si-O-C bond in the structure of geopolymer composites which reinforces the structure of geopolymer composites. The formation of Si-O-C bonds in the structure of geopolymer composites is related to the reaction between starch and sodium water glass (hardener) due to gelatinisation [11], [49]. It can be seen that the compressive strength of the geopolymer composites made by adding commercial starch (AC) is much higher compared to the others. The high compressive strength of GBC geopolymer composites in comparison to GBI, GBM, and GBP may be due to the dense packing of this starch [6] which fills in the pores present in the structure of the GBC geopolymer composite, thereby increasing the compressive strength of the composite. Compressive strength values of 48.49, 46.03, and 44.71 MPa were obtained for the GBI, GBM, and GBP geopolymer composites, respectively. Compressive strength for GBI is slightly higher than that for GBM, which is slightly higher than that for GBP. In fact, it could be said that these compressive strengths are almost identical in terms of value. The fact that yam starch has a higher degree of short-range ordered structure than cassava starch may explain the slight difference observed in these compressive strengths. In addition, the amorphous structure of cassava starch had a greater degree of disorder [48]. On the other hand, Zou et al. [49] concluded that yam starch has a higher requirement during gelatinisation and can retain a higher viscosity, resulting in starch gels with a higher hardness and gel strength. The starch gels are fluid and spongy, whereas the cassava starches are more soluble. The mechanism by which amylose is leached out during the gelatinisation process may explain the difference in compressive strength between geopolymer composites made from sweet potato starch and yam starch. For example, Valetudie et al. [50] reported that amylose is released through micropores formed in sweet potato starch granules during the expanding phase, whereas this amorphous phase escaped only through pinholes formed in yam starch granules.

3.2.4 *Micrograph images*

Figure 9 depicts the micrographs of geopolymer composites GB0, GBC, GBI, GBM, and GBP geopolymer composites have a more compact and dense microstructure, consistent with their higher compressive strength (64.66 MPa). GB0, GBI, GBM, and GBP geopolymer composites have coarse microstructures. These are consistent with their compressive strength values (Figure 8). The micrographs of the geopolymer composites show that those of GBI, GBM, and GBP are denser than those one of GB0. This could be related to the reaction between the starch and the sodium silicate solution, known as gelatinisation, which facilitates the dissolution of the metakaolin and leads to the incorporation of carbon into the siloxo chains due to the formation of Si-O-C bonds. Therefore, the incorporation of Si-O-C, the so-called adhesive, into the structure of the geopolymers could be responsible for the higher compressive strength values of the geopolymer composites compared to the reference geopolymer material.

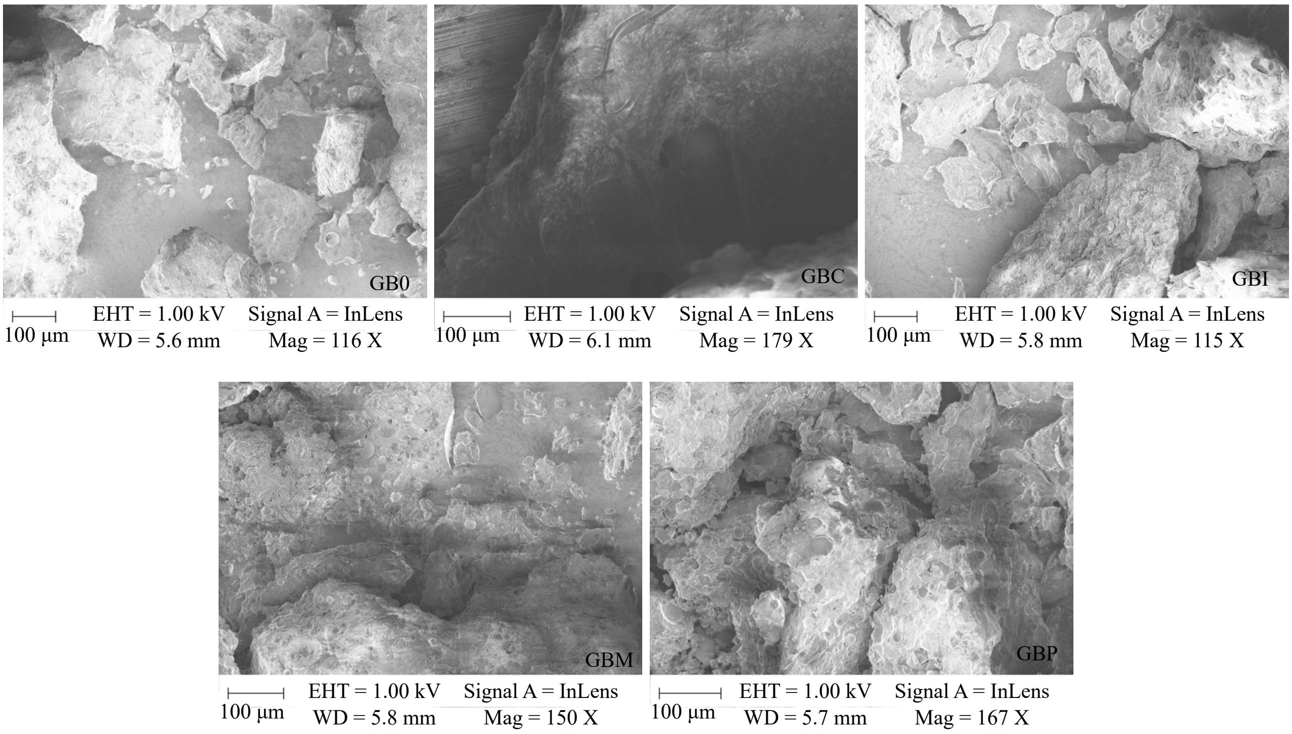

Figure 9. Micrograph images of geopolymer composites GB0, GBC, GBI, GBM, and GBP

4. Conclusions

Geopolymer composites were synthesised using metakaolin as aluminosilicate source and sodium water glass as a hardener. 0 and 15% by weight of different types of starch, such as commercial starch, starch from yam, starch from potato, and starch from cassava, were used as additives. The aim was to investigate their influence on the compressive strength and structural properties of geopolymer composites. The following conclusions are drawn from the available results:

The X-ray patterns of commercial starch, yam starch, sweet potato starch, and cassava starch show that commercial starch and yam starch belong to the A and B-type crystal structures, respectively. C-type crystals are found in cassava and sweet potato starches.

The Si-O-C bonds can be seen at around 700 cm^{-1} on the infrared spectra of geopolymer composites. The formation of Si-O-C bonds in the structure of geopolymer composites could strengthen the structure of geopolymer composites and therefore increase their compressive strength.

The compressive strength of the geopolymer material without the addition of starch is 36.25 MPa. These are 64.66, 48.49, 46.03, and 44.71 MPa for commercial starch, yam starch, cassava starch, and sweet potato starch, respectively. The compressive strength of the geopolymer composite using commercial starch (A-type crystal form) as an additive is found to have the highest compressive strength compared to the rest. Therefore, the most convenient starch to use as an additive for geopolymer synthesis may be starch with an A-type crystal structure.

The micrographs of the geopolymer composites from the addition of starches from yam, cassava, and sweet potato are denser than the ones without the addition of starch. The addition of starch induces the incorporation of Si-O-C into the structure of the geopolymer composites. This could contribute to densification and therefore increase the compressive strength values. It can be concluded that adding starch to metakaolin increases the compressive strength of metakaolin-based geopolymer composites.

Ethical approval

This article does not contain any studies with human participants performed by any of the authors.

Conflict of interest

The authors declare no competing financial interest.

References

[1] S. Hizukuri, “Relationship between the distribution of the chain length of amylopectin and the crystalling structure of starch granules,” *Carbohydrate Research*, vol. 14, pp. 295-306, 1985.

[2] H. F. Zobel, “Starch crystal transformations and their industrial importance,” *Starch-Stärke*, vol. 40, pp. 1-7, 1988.

[3] Z. Xie, J. Guan, L. Chen, Z. Jin, and Y. Tian, “Effect of drying processes on the fine structure of A-, B-, and C-type starches,” *Starch-Stärke*, vol. 70, pp. 1700218, 2017.

[4] W. He, and C. Wei, “Progress in C-type starches from different plant sources,” *Food Hydrocolloids*, vol. 73, pp. 162-175, 2017.

[5] K. Guo, L. Zhang, X. Bian, Q. Cao, and C. Wei, “A-, B- and C-type starch granules coexist in root tuber of sweet potato,” *Food Hydrocolloids*, vol. 98, pp. 105279, 2020.

[6] K. Dome, E. Podgorbunskikh, A. Bychkov, and O. Lomovsky, “Changes in the crystallinity degree of starch having different types of crystal structure after mechanical pre-treatment,” *Polymers*, vol. 12, pp. 641, 2020.

[7] A. Sarko, and C. H. Wu, “The crystal structure of A-, B- and C-Polymorphs of amylose and starch,” *Starch*, vol. 30, pp. 73-78, 1978.

[8] K. Frost, D. Kaminski, G. Kirwan, E. Lascaris, and R. Shanks, “Crystallinity and structure of starch using wide angle X-ray scattering,” *Carbohydrate Polymers*, vol. 78, pp. 543-548, 2009.

[9] S. C. A. Alay, and M. A. A. Meireles, “Physicochemical properties, modifications and applications of starches from different botanical sources,” *Food Science Technology (Campinas)*, vol. 35, pp. 215-236, 2015.

[10] N. H. Zakaria, N. Muhammad, and M. M. A. B. Abdullah, “Potential of starch nanocomposites for biomedical applications,” *International Conference on Innovative Research IOP Conference Series: Materials Science and Engineering*, vol. 209, no. 1, pp. 012087, 2017.

[11] I. Rashid, M. H. Al Omari, S. A. Leharne, B. Z. Chowdhry, and A. Badwan, “Starch gelatinization using sodium silicate: FTIR, DSC, XRPD, and NMR studies,” *Starch-Stärke*, vol. 64, no. 9, pp. 713-728, 2012.

[12] P. Duxson, A. Fernández-Jiménez, J. L. Provis, G. C. Lukey, A. Palomo, and J. S. J. van Deventer, “Geopolymer

technology: The current state of the art," *Journal of Materials Science*, vol. 42, pp. 2917-2933, 2007.

[13] J. G. Sanjayan, A. Nazari, L. Chen, and G. H. Nguyen, "Physical and mechanical properties of lightweight aerated geopolymer," *Construction and Building Materials*, vol. 79, pp. 236-244, 2015.

[14] J. Davidovits, *Geopolymer: Chemistry and Applications*, 4th ed. Geopolymer Institute, 2015.

[15] T. Chub-uppakarn, T. Chompoorat, T. Thepumong, W. Sae-Long, A. Khamplod, and S. Chaiprapat, "Influence of partial substitution of metakaolin by palm oil fuel ash and alumina waste ash on compressive strength and microstructure in metakaolin-based geopolymer mortar," *Case Studies in Construction Materials*, vol. 19, pp. e02519, 2023.

[16] P. Julphunthong, P. Joyklad, P. Manprom, T. Chompoorat, M. T. Palou, and T. Suriwong, "Evaluation of calcium carbide residue and fly ash as sustainable binders for environmentally friendly loess soil stabilization," *Scientific Report*, vol. 14, pp. 671, 2024.

[17] T. Chompoorat, S. Likitlersuang, and P. Jongvivatsakul, "The performance of controlled low-strength material base supporting a high-volume asphalt pavement," *KSCE Journal of Civil Engineering*, vol. 22, pp. 2055-2063, 2018.

[18] T. Chompoorat, T. Thepumong, P. Nuaklong, P. Jongvivatsakul, and S. Likitlersuang, "Alkali-activated controlled low-strength material utilizing high-calcium fly ash and steel slag for use as pavement materials," *Journal of Materials in Civil Engineering*, vol. 33, no. 8, pp. 01775136, 2021.

[19] C. M. Dieuhou, H. K. Tchakouté, A. N. Kamlo, C. P. Nanseu-Njiki, and C. H. Rüscher, "Influence of starch powder on the compressive strength and microstructural properties of geopolymer composite materials based on metakaolin," *Engineering Science and Technology*, vol. 5, no. 2, pp. 180-194, 2024.

[20] N. L. Garc, L. Fam, N. B. D. Accorso, and S. Goyanes, "Biodegradable starch nanocomposites," in *Eco-Friendly Polymer Nanocomposites*, V. K. Thakur, M. K. Thakur, Eds. New Delhi, India: Springer, 2015, pp. 17-77.

[21] F. K. Tazune, L. D. D. Nzangue, A. N. Kamlo, H. K. Tchakouté, and C. H. Rüscher, "Investigation of the properties of metakaolin-based geopolymer materials using ferrisilicates as additives synthesised in sodium hydroxide solution or distilled water," *Engineering Science and Technology*, vol. 5, no. 1, pp. 136-157, 2024.

[22] F. K. Tazune, H. K. Tchakouté, C. H. Rüscher, J. J. Kouadjo Tchekwagep, and P. Hou, "Effects of Fe_2O_3/SiO_2 molar ratios in the Fe-silica on the compressive strengths and microstructural properties of geopolymer materials derived from waste fired clay brick and metakaolin," *Journal of Inorganic and Organometallic Polymers and Materials*, vol. 34, no. 4, pp. 1-13, 2023.

[23] V. Singh, S. Z. Ali, R. Somashekar, and P. S. Mukherjee, "Nature of crystallinity in native and acid modified starches," *International Journal of Food Properties*, vol. 9, no. 4, pp. 845-854, 2006.

[24] L. A. Munoz, F. Pedreschi, A. Leiva, and J. M. Aguilera, "Loss of birefringence and swelling behavior in native starch granules: Microstructural and thermal properties," *Journal of Food Engineering*, vol. 152, pp. 65-71, 2015.

[25] D. J. Gallant, M. Bewa, Q. H. Buy, B. Bouchet, Q. Szylit, and L. Sealy, "On ultrastructural nutritional aspects of some tropical tuber starches," *Starch-Stärke*, vol. 34, no. 8, pp. 255-262, 1982.

[26] R. D. Lauzon, K. Shiraish, M. Yamazaki, S. Sawayama, N. Wugiyama, and A. Kawbata, "Physicochemical properties of cocoyam starch," *Food Hydrocolloids*, vol. 9, pp. 77-81, 1995.

[27] A. E. McPherson, and J. Jane, "Comparison of waxy potato with other root and tuber starches," *Carbohydrate Polymers*, vol. 40, pp. 57-70, 1999.

[28] M. Todica, E. M. Nagy, C. Niculaescu, O. Stan, N. Cioica, and C. V. Pop, "XRD investigation of some thermal degraded starch based materials," *Journal of Spectroscopy*, vol. 2016, pp. 1-7, 2016.

[29] S. Weng, *Fuliye Bianhuan Hongwai Guangpu Fenxi*, 2nd ed. China, Chemical Industry Press: Beijing, 2010, pp. 291-362.

[30] L. H. Garrido, E. Schnitzler, M. E. B. Zortéa, T. S. Rocha, and I. M. Demiate, "Physicochemical properties of cassava starch oxidized by sodium hypochlorite," *Journal of Food Science and Technology*, vol. 51, pp. 2640-2647, 2014.

[31] R. Kizil, J. Irudayaraj, and K. Seetharaman, "Characterization of irradiated starches by using FT-Raman and FTIR spectroscopy," *Journal of Agricultural and Food Chemistry*, vol. 50, pp. 3912-3918, 2002.

[32] J. J. G. Van Soest, H. Tournois, D. De Wit, and J. F. G. Vliegenthart, "Short-range structure in (partially) crystalline potato starch determined with attenuated total reflectance Fourier-transform IR spectroscopy," *Carbohydrate Research*, vol. 279, pp. 201-214, 1995.

[33] C. N. Bewa, H. K. Tchakouté, C. Banenzoué, L. Cakanou, T. T. Mbakop, E. Kamseu, and C. H. Rüscher, "Acid-based geopolymers using waste fired brick and different metakaolins as raw materials," *Applied Clay Science*, vol. 198, pp. 105813, 2020.

[34] C. H. Rüscher, A. Schulz, M. H. Gougazeh, and A. Ritzmann, "Mechanical strength development of geopolymer

binder and the effect of quartz content," in *Developments in Strategic Materials and Computational Design IV*, W. M. Kriven, J. Wang, Y. Zhou, A. L. Gyekenyesi, S. Kirihara, S. Widjaja, Eds. Hoboken, NJ, USA: John Wiley & Sons, 2013.

[35] H. K. Tchakouté, C. H. Rüscher, J. N. Y. Djobo, B. B. D. Kenne, and D. Njopwouo, "Influence of gibbsite and quartz in kaolin on the properties of metakaolin-based geopolymer cements," *Applied Clay Science*, vol. 107, pp. 188-194, 2015.

[36] L. Y. Yang, Z. J. Jia, Y. M. Zhang, and J. G. Dai, "Effects of nano-TiO_2 on strength, shrinkage and microstructure of alkali activated slag pastes," *Cement and Concrete Composites*, vol. 57, pp. 1-7, 2015.

[37] Z. Li, B. Han, X. Yu, S. Dong, L. Zhang, X. Dong, and J. Ou, "Effect of nano-titanium dioxide on mechanical and electrical properties and microstructure of reactive powder concrete," *Materials Research Express*, vol. 4, pp. 095008, 2017.

[38] S. Jiang, D. Zhou, L. Zhang, J. Ouyang, X. Yu, X. Cui, and B. Han, "Comparison of compressive strength and electrical resistivity of cementitious composites with different nano- and micro-fillers," *Archives Civil and Mechanical Engineering*, vol. 18, pp. 60-68, 2018.

[39] R. S. Raj, G. P. Arulraj, N. Anand, B. Kanagaraj, E. Lubloy, and M. Z. Naser, "Nanomaterials in geopolymer composites: A review," *Development in Built Environment*, vol. 13, pp. 100114, 2023.

[40] F. Zibouche, H. Kerdjoudj, J. B. D. E. de Lacaillerie, and H. Van Damme, "Geopolymers from Algerian metakaolin. Influence of secondary minerals," *Applied Clay Science*, vol. 43, no. 3-4, pp. 453-458, 2009.

[41] A. Fernández-Jiménez, A. Palomo, I. Sobrados, and J. Sanz, "The role played by the reactive alumina content in the alkaline activation of fly ashes," *Microporous Mesoporous Materials*, vol. 91, pp. 111-119, 2018.

[42] A. Tironi, M. A. Trezza, E. F. Irassar, and A. N. Scian, "Thermal treatment of kaolin: effect on the pozzolanic activity," *Procedia Materials Science*, vol. 1, pp. 343-350, 2012.

[43] T. Oh, and C. K. Choi, "Comparison between Si-O-C thin films fabricated by using plasma enhance chemical vapor deposition and SiO_2 thin films by using fourier transform infrared spectroscopy," *Journal of the Korean Physical Society*, vol. 56, no. 4, pp. 1150-1155, 2010.

[44] R. Bajpai, A. Shrivastava, and M. Singh, "Properties of fly ash geopolymer modified with red mud and silica fume: a comparative study," *SN Applied Sciences*, vol. 2, pp. 1846, 2020.

[45] E. L. Hseumou, A. M. N. Moudio, H. K. Tchakouté, and C. H. Rüscher, "Investigation of the compressive strength, ultrasonic pulse velocity, calorimetric, microstructural and rheological properties of the calcined laterite-based geopolymer materials," *Journal of Inorganic and Organometallic Polymer Materials*, vol. 34, pp. 979-998, 2023.

[46] R. Kaze, L. Beleuk à Moungam, M. F. Djouka, A. Nana, E. Kamseu, U. C. Melo, and C. Leonelli, "The corrosion of kaolinite by iron minerals and the effects on geopolymerization," *Applied Clay Science*, vol. 138, pp. 48-62, 2017.

[47] Y. Ohkubo, K. Endo, and K. Yamamura, "Adhesive-free adhesion between heat-assisted plasma-treated fluoropolymers (PTFE, PFA) and plasma-jet-treated polydimethylsiloxane (PDMS) and its application," *Scientific Reports*, vol. 8, no. 1, pp. 18058, 2018.

[48] J. J. Swinkels, "Composition and properties of commercial native starches," *Starch-Stärke*, vol. 37, no. 1, pp. 1-5, 1985.

[49] J. Zou, Y. Li, F. Wang, X. Su, and Q. Li, "Relationship between structure and functional properties of starch from different cassava (Manihot esculenta Crantz) and yam (Dioscorea opposita Thunb) cultivars used for food and industrial processing," *LWT -Food Science and Technology*, vol. 173, pp. 114261, 2023.

[50] J. C. Valetudie, L. Guadeloupe, P. Colonna, B. Bouchet, and D. J. Gallant, "Gelatinization of sweet potato, tania and yam tuber starches," *Starch-Stärke*, vol. 47, no. 8, pp. 298-306, 1995.