SYNTHESES AND CHARACTERISTICS OF CALCIUM-BASED GEOPOLYMER FROM SOLAR-CELL PANEL-GLASS WASTE BY HYDROTHERMAL METHOD

SINTEZE IN ZNAČILNOSTI GEOPOLIMERJA NA OSNOVI KALCIJA IZ STEKLENIH ODPADKOV SOLARNIH CELIC S HIDROTERMALNO METODO

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A calcium-based geopolymer was synthesized using a blend of recycled glass powder from solar panels (PV glass waste), limestone, and a sodium silicate solution, which underwent hydrothermal autoclaving at 180 °C for varying durations. This material is regarded as environmentally friendly and has garnered research attention worldwide. In this investigation, limestone served as the calcium source, while recycled glass from solar panels provided the SiO₂ necessary for producing calcium-based geopolymer materials. Currently, solar-panel waste poses a significant environmental challenge that requires attention. The objective of this research was to develop a sustainable and high-performance calcium-based geopolymer using waste materials, specifically recycled glass from solar panels and limestone. The study aimed to evaluate the effects of hydrothermal autoclaving on the compressive strength, volume weight, porosity, and water absorption of the synthesized geopolymer, as well as to understand the microstructural transformations involved. The results revealed a remarkable 430 % increase in the compressive strength of the specimens following hydrothermal autoclaving for 24 to 96 hours compared to the unautoclaved samples. Concurrently, the volumetric weight had a substantial rise from 1.54 % to 2.31 g/cm³, with corresponding decreases in the porosity and water absorption from 38.1 % to 16.9 % and 10.26 % to 5.08 %, respectively. An X-ray diffraction (XRD) analysis of the mineral composition and a scanning electron microscope (SEM) examination of the microstructure demonstrated a transformation of all samples from an amorphous gel structure to needle- or spike-shaped fibrous, and then sheet-like CSH structures. These new structures exhibited dimensions of less than 10 μ m in length, less than 2 μ m in width, and less than 400 nm in thickness. The resulting CSH products constitute calcium silicate hydrate minerals, characteristic of calcium silicate materials, which are synthetic products arising from

Keywords: calcium-based geopolymer, solar photovoltaic panel, glass waste, hydrothermal method, calcium silicate

Avtorji so geopolimere sintetizirali z uporabo recikliranega odpadnega steklenega prahu iz sončnih fotovoltaičnih panelov, apnenca in raztopine natrijevega silikata. Mešanico so izpostavili v avtoklavih hidrotermalni obdelavi pri 180°C. Te vrste stekla mnogi raziskovalci smatrajo kot okoljsko prijazen material in zato ga po svetu tudi načrtno zbirajo. V raziskavi, ki jo opisuje ta članek so avtorji uporabili apnenec kot vir kalcija, medtem ko je reciklirano steklo iz sončnih panelov služilo kot vir SiO₂, ki se potrebuje za izdelavo geopolimernih materialov. V tem trenutku odpadni sončni paneli predstavljajo določen okoljski izziv glede njihove nadaljne uporabe oziroma reckliranja. Predmet te raziskave je torej bil: razviti trajen in visoko kakovosten geopolimer na osnovi kalcija (Ca) iz recikliranega odpadnega stekla solarnih panelov in apnenca (CaCO₃). Študija je bila osredotočena na učinek hidrotermalne obdelave v avtoklavu na tlačno trdnost, masni volumen, poroznost in absorpcijo vode sintetiziranih geopolimerov, kakor tudi razumeti in pojasniti mikrostrukturne transformacije, ki potekajo med hidrotermalno obdelavo v avtoklavu. Rezultati analiz so pokazali, da je prišlo do znatnega, postopoma tudi do 430 %-nega povečanja tlačne trdnosti biopolimernih vzorcev, ki so bili avtoklavirani od 2,4 do 96 ur v primerjavi z neavtoklaviranimi vzorci. Nadalje se je tudi masni volumen vzorcev izrazito povečal z 1,54 g/cm³ na 2,31 g/cm³. Skladno s tem sta se zmanjšali poroznost vzorcev z 38,1% na 16,9% in absorpcija vode z 10,26% na 5,08%. Rentgenska strukturna analiza (XRD; angl.: X-ray diffraction) mineralne sestave in morfološke preiskave z vrstičnim elektronskim mikroskopom (SEM) so pokazale transformacijo amorfne gelne strukture vseh vzorcev v igličasto ali koničasto vlaknasto oblikovano in nato ploščičasto C-S-H strukturo. Te nove strukture so izredno majhne, dolžine pod 10 µm, širine manj kot 2 µm in debeline manj kot 400 nm. Rezultirajoči C-S-H produkti so izvirajo iz kemičnih reakcij med SiO₂, CaO, in H

Ključne besede: geopolimer na osnovi kalcija, solarni fotovoltaični paneli, stekleni odpadki, hidrotermalna obdelava, kalcijev silikat

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1 INTRODUCTION

The solar panels available on the market, commonly referred to as photovoltaic (PV) panels, are crafted from crystalline silicon (c-Si), constituting more than 95 % of the total production as of 2023 and holding nearly 90 % of the market share over the past two decades. At the end of their operational lifespan, c-Si photovoltaic panels are anticipated to become a significant source of photovoltaic waste.^{1,2} These PV panels typically have a lifespan estimated at 25-30 years.³ Projections suggest that by 2030, the waste generated by PV panels may amount to approximately 1.7-8.0 million tons, with an anticipated escalation to 60-78 million tons by 2050.4 According to reports, each solar panel weighs approximately 21,036 kg, with the tempered glass panel constituting 13.2 kg, equivalent to 62.75 % of the total weight. Consequently, the projected glass waste from solar panels by 2030 range from 1.07-5.02 million tons, with a global increase to 37.65-48.95 million tons by 2050. This substantial waste output poses significant environmental and economic challenges worldwide, prompting researchers to devise technology systems aimed at efficiently recycling photovoltaic panels.5 The studies on glass recycling showed that the tempered glass waste in solar panels contains amorphous SiO₂, exceeding 70 %, presenting a promising avenue for research into recycling this type of waste glass as a raw material for producing products such as geopolymer or calcium silicate for applications in construction materials.6

Presently, there are alarming concerns regarding the environmental pollution stemming from waste, emissions, and global warming induced by the greenhouse effect.⁷ One significant contributor to the elevated levels of CO_2 in the atmosphere is the conventional cement production industry.⁸ The combustion of fossil fuels such as coal, oil, or natural gas for the calcination of limestone and other raw materials results in the emission of CO_2 , as depicted in the following chemical reactions.^{7–9}:

Burning coal: $C + O_2 \Rightarrow CO_2$ (1)

Burning petroleum and gas:

 $2C_{x}H_{y}O_{z}N_{t} + (2x+y/2-z)O_{2} \Longrightarrow 2xCO_{2} + yH_{2}O + tN_{2} (2)$

Limestone calcination: $CaCO_3 \Rightarrow CaO + CO_2$ (3)

The amount of CO₂ discharged into the atmosphere has surged in recent decades, exacerbating global warming. Consequently, the imperative to mitigate CO₂ emissions as a response to environmental challenges has intensified.¹⁰ A primary source of CO₂ emissions within the construction materials sector, particularly in cement production, stems from the high-temperature sintering of limestone to synthesize CaO and others, as outlined earlier.¹¹ In efforts to curtail CO₂ emissions within the construction materials industry, numerous studies have explored the geopolymerization method.^{12,13} This technique involves utilizing alumino-silicate or calcium silicate in an alkaline environment to solidify raw powder at lower temperatures.^{12,14} Furthermore, some studies have demonstrated the feasibility of effectively curing calcium carbonate powder through hydrothermal autoclaving.¹⁵

Geopolymer is an environmentally friendly material with many superior properties to replace cement-based materials. These properties include high mechanical strength, excellent heat resistance, chemical durability, and the capacity to immobilize heavy metal ions.14,16,17 Moreover, geopolymer offers the advantage of utilizing recycled raw materials sourced from inorganic waste rich in SiO₂, Al₂O₃, and CaO, facilitating a straightforward manufacturing process with minimal energy consumption and negligible CO2 emissions.18 Various studies have explored hydrothermal autoclaving at temperatures below 200 degrees Celsius and the curing properties within the xCaO·ySiO₂·nH₂O system.^{19,20} This process instigates the formation of new phases, such as tobermorite gel and calcium silicate hydrate (CxSy·nH gel), which augment the durability of hydrothermally cured materials during the formation of xCaO·ySiO₂·nH₂O.^{21,22} The hydrothermal reaction process, conducted at relatively low temperatures, proves to be an effective method for curing calcite powder without triggering a decomposition into CO₂ at this temperature.23

This research conducted geopolymerization of a mixture of PV glass waste from solar panels and limestone, with the addition of sodium silicate binders. Then, specimens were cured under hydrothermal autoclaving conditions for different reaction times. Notably, there have been no other studies testing the production of construction materials from limestone combined with PV glass waste from solar panels using both the geopolymerization method and hydrothermal method during the curing of specimens.

2 EXPERIMENTAL PART

Tempered glass was separated from solar panels from Solar Power Vietnam Technology Joint Stock Company, Ho Chi Minh City, Vietnam. Initially, a heat gun was employed to heat the solar panel surface, facilitating the manual separation of glass from the EVA adhesive layer. The separated materials encompassed fragments of PV glass waste, solar cells, wires, and aluminum frames. Subsequently, the glass waste fragments were being ground in a ball mill for 6 hours. After grinding, the PV glass waste was sieved through a 90 µm mesh to ensure a uniform particle size of the PV glass waste powder while eliminating EVA glue residue as shown in **Figure 1** (on the left).

Limestone was from FICO Tay Tinh Cement Joint Stock Company (Tay Ninh province, Vietnam) and was preliminarily crushed to a size of less than 5 mm, then dried at 110 °C for 24 h. Finally, limestone powder was obtained via grinding in a ball mill for 5 h and passing through a 90 μ m sieve as shown in **Figure 1** (at the centre).

N. H. THANG et al.: SYNTHESES AND CHARACTERISTICS OF CALCIUM-BASED GEOPOLYMER FROM SOLAR-CELL ...



Figure 1: Raw materials including PV glass waste (a) and limestone (b), and calcium-based geopolymer (c)

Sodium silicate solution or water glass solution is an inorganic binder, which was used to increase the shaping ability. It had a silica modulus of 2.41, and a density of 1.47 g/cm³, and was provided by New Ha Viet Silicate Joint Stock Company (Binh Duong province, Vietnam).

The powders of limestone and PV glass waste were tested for physico-chemical properties such as density, volumetric weight, moisture, loss on ignition (L.O.I), chemical composition, and mineral composition. The raw materials were mixed dry in a 1:1 ratio (in weight) of limestone and PV glass waste for 10 min and then this mixture was mixed with a 10 % water glass solution for 15 min; 30 % water was added and mixed for 15 min to get a paste. The paste mixture was cast into a mold measuring $(20 \times 20 \times 20)$ mm, kept there for 24 h to harden and dry before removing the mold as shown in Figure 1 (on the right). After de-molding, the samples were classified in two groups, including non-autoclaved specimens (sample M0) and autoclaved specimens. The autoclaved samples were autoclaved in a hydrothermal reactor at a temperature of 180 °C for periods of 24 h (sample M24), 48 h (sample M48), 72 h (sample M72) and 96 h (sample 96). After the process in hydrothermal conditions, all the specimens (samples M0, M24, M48, M72, and M96) were tested for engineering properties such as compressive strength, volumetric weight, water absorption, porosity and characterized microstructural properties using XRD (Brucker D2 Phaser X-ray diffractometer) and



Figure 2: XRD patterns of limestone and PV glass waste

Materiali in tehnologije / Materials and technology 58 (2024) 4, 467-475

SEM (JEOL JSM-IT200 Instrument). The D2 Phaser X-ray diffractometer was set at the analytical conditions as follows: an operating temperature of 25 °C, a measurement time per step of 38.4 s, a diffraction angel of 2-Theta of 5–80 degrees, using a copper (Cu) anode material with λK_{α} of 0.15406 nm and others. The JEOL JSM-IT200 scanning electron microscope operated at a beam voltage of 10 kV, using a secondary electron detector.

3 RESULTS

3.1 Physico-chemical properties of raw materials

Raw materials including PV glass waste and limestone were tested for physical and chemical properties such as density, volumetric weight, moisture content, loss in ignition (L.O.I), chemical composition, and mineral composition, and the results are shown in **Table 1**, **Table 2**, and **Figure 2**. The chemical composition of the materials was analyzed by X-ray fluorescence (XRF) using a Brucker S2 PUMA device, while the mineral composition was characterized by X-ray diffraction (XRD) using a D2 Phaser device from Brucker. Limestone had a moisture content of 2.73 %, volume weight and density of 1.84 g/cm³ and 2.72 g/cm³, respectively. Meanwhile, PV glass waste had a moisture content of 1.2 %, volumetric weight of 1.58 g/cm³, and density of 2.83 g/cm³ as shown in **Table 1**.

Table 1: Engineering properties of limestone and PV glass waste

No.	Engineering properties	Limestone	PV glass waste
01	Density (g/cm ³)	2.72	2.83
02	Volumetric weight (g/cm ³)	1.84	1.58
03	Moisture content (%)	2.73	1.21
04	Mean particle size (µm)	36.1	52.8

In **Table 2**, the results of the chemical composition analysis by X-ray fluorescence show that the PV glass waste powder included 70.1 % SiO₂, 11.3 % Na₂O, 11.4 % CaO, 3.2 % MgO, 1.9 % Fe₂O₃, 1.6 % Al₂O₃ and

Deres en eterriele	Chemical composition of oxides (<i>w</i> /%)								
Raw materials	SiO ₂	Na ₂ O	CaO	Al ₂ O ₃	MgO	Fe ₂ O ₃	Other	L.O.I	
PV glass waste	70.1	11.3	11.4	1.6	3.2	1.9	0.2	0.3	
Limestone	_	_	55.6	_	0.3	_	0.2	43.9	
Sodium silicate solution	31.8	12.6	-	_	_	_	55.6(*)	-	

Table 2: Chemical compositions of limestone, PV glass waste, and sodium silicate solution

(*) This value is the amount of water added to sodium silicate to get a solution.

a small amount of about 0.3 % loss on ignition (LOI). The LOI test was performed at a temperature of 1000 °C and maintained for 2 h. The heating rate from room temperature to 1000 °C was 5 °C/min, with the cooling process occurring naturally in accordance with the furnace's normal temperature decrease. The LOI value of the recycled PV glass was 0.3 %, attributable to the residual glue left over from pre-processing and grinding of the solar panels. Additionally, the recycled PV glass contained up to 11.3 % Na₂O alkalinity. When calcined at 1000 °C, a portion of this alkalinity also partially evaporated. Meanwhile, limestone exhibited a CaO content of 55.6 % and loss on ignition of up to 43.9 % due to carbonate decomposition, emitting CO₂. The results of this analysis show that both PV glass waste and limestone had a high calcium silicate content, thus meeting the conditions for the formation of calcium silicate hydrate phases during the geopolymerization process combined with hydrothermal reactions in an autoclave. When limestone and PV glass waste powder were mixed in a ratio of 1:1 and 10 % sodium silicate solution was added, the mixture included 33.5 % CaO and 38.2 % SiO₂, which was almost equivalent to the 1:1 ratio of CaO and SiO₂. This is the ideal condition for synthesizing the wollastonite mineral (CaSiO₃) according to the CaO-SiO₂ phase diagram system.7,24

XRD patterns show that the PV glass waste powder contained mainly an amorphous phase with a noise spectrum and a broadened peak at the bottom in a diffraction angle range of 10–30 degrees. Meanwhile, limestone contained the main crystal mineral of calcite (CaCO₃) with diffraction peaks at 23.5°, 30.0°, 36.4°, 40.0°, 43.7°, 48.0°, 49.0° and other positions as shown in **Fig**-

ure 2. The analytical results of the raw materials are consistent with the previous reports related to PV glass waste and limestone.^{3,4,6,8}

3.2 Engineering properties of the calcium-based geopolymer

The calcium-based geopolymer samples were tested for compressive strength, water absorption, volumetric weight and porosity before and after hydrothermal autoclaving, and the results are shown in Figures 3 and 4. Based on Figure 3, the compressive strength of the specimens increased intensely after the hydrothermal reaction at 180 °C. The non-autoclaved sample (M0) had a compressive strength of 16.2 MPa. The compressive strength of the sample exposed to the hydrothermal reaction for 24 h (M24) increased 2.2 times, to 35.8 MPa. The hydrothermal reaction sample after 48 h (M48) exhibited a compressive strength that was up to 4 times higher, 65.4 MPa. The compressive strength of the samples exposed to steaming for 72 h (M72) and 96 h (M96) increased slightly compared to the sample steamed for 48 h, i.e., the compressive strength of sample M72 was 68.5 MPa, and the compressive strength of sample M96 was 69.7 MPa. The values of the compressive strength in this study are higher than those in the previous investigations. 7,12,14,17,22

This proves that when autoclaved in the hydrothermal reactor, the geopolymer-based materials continued reacting to form a new structure causing their compressive strength to become higher than that of the non-autoclaved sample. However, when autoclaved for too long, these structures were relatively saturated so their strength



Figure 3: Changes in the compressive strength and water absorption after various hydrothermal reaction times for calcium-based geopolymer synthesized from limestone and PV glass waste



Figure 4: Changes in the volumetric weight and porosity after various hydrothermal reaction times for calcium-based geopolymer synthesized from limestone and PV glass waste

did not increase as significantly as before. This is also shown through the density of the samples, with an increase in the volumetric weight from 1.54 g/cm³ up to 2.31 g/cm³, and a decrease in the porosity from 38.1 %(M0) to only 16.9 % (M72). The water absorption of the specimens also improved from 10.26 % (M0) to 5.08 % (M72). This shows the reasonableness of the results. It is noted that when increasing the hydrothermal reaction time from 72 h to 96 h, there was a slight increase in the porosity from 16.9 % to 17.4 % and water absorption also increased from 5.08 % to 5.22 %. These results are explained in detail through a microstructural analysis using imaging results of SEM and X-ray diffraction (XRD). The porosity of calcium-based geopolymer in this research changed similarly to what was mentioned in the study by Maeda et al. (2011).²⁵

3.3 Microstructural characteristics of calcium-based geopolymer

3.3.1 Effect of hydrothermal reaction times on the structure formation of the products observed with scanning electron microscopy (SEM)

Figure 5 shows SEM images of sample M0 (the non-autoclaved sample) with a geopolymeric matrix

made of particles of PV glass waste powder and limestone. There is very tight adhesion between them, with no clear boundaries between the particles. Simultaneously, there are very small and short spike- or needle-shaped structures with a width of about 50–100 nm and a length of about 1 μ m. This is the result of the dissolution and reaction between the powders of PV glass and limestone in the sodium silicate solution.

Figure 6 shows SEM images of sample M24 (the sample was reacted in hydrothermal conditions at 180 °C for 24 h) with a difference in the structure of the calcium-based geopolymer after hydrothermal autoclaving at 180 °C for 24 h compared to the same sample without the hydrothermal reaction (sample M0). The spike- or needle-shaped structures grew in size very quickly with a width of about 200-400 nm and a length greater than 3 µm (the structural size increased 3 times compared to that of sample M0). These structures changed into a fiber-like shape with length and width but they are relatively thin (their thickness is really small and difficult to observe). This explains why sample M24 had a 2.2 times higher compressive strength compared to that of sample M0. However, the fiber-like shape structures were still distributed sparsely and unevenly as shown in Figure 6.



Figure 5: Needle-shaped structures of calcium-based geopolymer (sample M0) at magnifications of: a) 5000× and b) 10000×





Figure 6: Fiber-like shaped structures of calcium-based geopolymer (sample M24) at magnifications of: a) 5000× and b) 10000×

Figure 7 shows SEM images of sample M48 (the specimen was reacted in hydrothermal conditions at 180 °C for 48 h) with a fibrous structure. It developed a denser and more uniform structure than that of sample M24. The width of this structure increased to 500–700 nm and its length increased to about 5–6 μ m. Thus, when increasing the hydrothermal reaction time, the dissolution and reaction processes were more vigorous. Many structures allowing an increase in the mechanical strength were formed and stabilized. Therefore, specimen M48 became denser (reduced porosity) and its compressive strength was 65.4 MPa, much higher than that of samples (M0) or (M24).

Figure 8 shows SEM images of sample M72 (the specimen was autoclaved in hydrothermal conditions at 180 °C for 72 h) with a growth of fibrous structures. These became sheet- or plate-like structures with a length of about 8 μ m, a width of about 1–2 μ m, and a thickness of about 100–200 nm. They are more numerous, dense, and uniform, occupying most of the structural space of the sample (it is difficult to recognize where the original matrix of material particles are). Thus, when increasing the hydrothermal reaction time, the dissolution and reaction processes were more vigorous. The

plate-like structures play a role in stabilizing the mechanical strength, and also show the void space that appears among them. Therefore, the specimen exhibited a slight increase in the volume weight and a slight decrease in the porosity compared to sample M48, but these values did not change much in comparison with the change among samples M0, M24 and M48. The compressive strength of sample M72, which was 68.5 MPa, increased slightly compared to that of sample M48, which was 65.4 MPa.

Figure 9 shows SEM images of sample M96 (the sample was autoclaved in hydrothermal conditions at 180 °C for 96 h) with sheet-like or plate-like structures that developed very quickly, overlapping and alternating into layers. The sheets became more uniform with a length of about 10 μ m, a width of about 1–2 μ m, and a thickness of about 300–400 nm. Some structures have a triangular spike at the tip indicating the direction of their growth. These structures also occupy most of the structural space of the sample (it is difficult to recognize the original matrix of material particles). It is easy to see that the sheet-like or plate-like structures became stable after autoclaving at 180 °C for 96 h. This is also evidence for the research group to stop the hydrothermal reaction time



Figure 7: Growth of fiber-like shaped structures of calcium-based geopolymeric matrix (sample M48) at magnifications of: a) 5000× and b) 10000×



Figure 8: Growth of plate-like structures of calcium-based geopolymeric matrix (sample M72) at magnifications of: a) $5000 \times$ and b) $10000 \times$



Figure 9: Overlapping of the plate-like structures in calcium-based geopolymeric matrix (sample M96) at magnifications of: (a) $5000 \times$ and (b) $10000 \times$

from exceeding 96 h without further investigation. The plate-like structures play a role in stabilizing the mechanical strength, and also show the void space that appears among them. Therefore, the specimen exhibited a slight increase in the volume weight and a slight increase in the porosity compared to sample M72. The compressive strength of sample M96, which was 69.7 MPa, increased slightly compared to that of sample M72, which was 68.5 MPa.

3.3.2 Formation of calcium silicate hydrate (CSH) structures and an amorphous phase in the calciumbased geopolymer detected with XRD

Figure 10 shows XRD patterns of calcium-based geopolymer specimens (M0, M24, M48, M72, and M96). Compared to the XRD patterns of the raw materials (limestone and PV glass waste) from Figure 2, the diffraction intensity of calcite crystal peaks of sample M0 sharply decreased from nearly 5000 cps (limestone material) to about 2500 cps at a diffraction angle (2-Theta) of around 30 degrees. This reduction is attributed to the addition of 50 % PV glass waste (in weight), which contains a predominantly amorphous phase as shown in Figure 2. Furthermore, dissolution and reaction processes between the limestone powder and PV glass powder resulted in the formation of a new gel phase in the shape of needles or spikes, as indicated in the SEM images in Figure 5. These new gel phases are also amorphous, as no diffraction peaks of any new crystal appear on the XRD pattern.

On the XRD pattern of sample M24, under hydrothermal conditions, the calcite crystals grew stronger, increasing the diffraction intensity to about 2800 cps



Figure 10: XRD patterns of the calcium-based geopolymer specimens before and after their reaction in hydrothermal conditions

(higher than that of sample M0 of about 2500 cps) at 2θ of around 30°. Additionally, a new diffraction peak appeared at 2θ of 14° on the XRD pattern of sample M24, corresponding to the formation of a new crystalline phase of calcium silicate hydrate (CSH). Although the diffraction intensity of this peak is low, it indicates the structural transformation of the spike-shaped amorphous gel to a fibrous form, as observed in the SEM images from **Figure 6**.

When the hydrothermal reaction time increased to 48 h, the dissolution and reaction processes became more effective. The XRD pattern of sample M48 shows a gradual decrease in the diffraction intensity to 1700 cps at 2θ of around 30° (similar to calcite crystals). Simultaneously, the XRD pattern of sample M48 still exhibits the diffraction peak at 2θ of 14°, corresponding to the new crystal phase of CSH, similar to that of sample M24.

For the samples with the hydrothermal reaction time of up to 72 h, the diffraction peak of calcite at 2θ of around 30° had a diffraction intensity of less than 1000 cps, much less than those of samples M0, M24, and M48. Concurrently, CSH crystals became more pronounced at 2θ of 14 degrees, with new diffraction peaks appearing at 2θ of 8°, 15°, 16°, 19°, 25°, and 31°. This is the results of the hydrothermal reaction and transformation of the amorphous gel structure into crystals, evolving from spikes to fibers and then into sheets with denser structures, as observed in the SEM images in **Figure 8**.

For the sample subjected to the hydrothermal reaction for up to 96 h, the diffraction peak of calcite at 2θ of around 30° had an intensity of less than 200 cps, the lowest among all the samples, including the initial raw materials. The intensity of the CSH phase peaks increased at diffraction angles (2θ) of 8° and 31°, with additional diffraction peaks appearing at 2θ of 32° and 32.5°. This indicates the development of sheet-like or plate-like structures that grew rapidly, overlapping and alternating into layers, as observed in the SEM images in **Figure 9**.

The remainder of a sample consists of an amorphous phase, easily identifiable through the XRD patterns of samples M96 and M72. These patterns display broad diffraction peak widths, heavily disturbed or noisy spectrum lines, and very low diffraction intensities (200 cps for sample M96 and less than 1000 cps for sample M72). The CSH structures were reported in the previous studies by Maeda et al. (2011),²⁵ Ji et al. (2024),²⁶ and others.^{7,27}

4 CONCLUSIONS

This research successfully recycled glass waste from solar panels to produce calcium-based geopolymer materials using geopolymerization and hydrothermal method. The hydrothermal reaction process demonstrated that limestone and PV glass waste dissolved and reacted to form an amorphous gel structure. As the hydrothermal reaction time increased from 24 h to 96 h, the amorphous gel structures progressively transformed from needle or spike shapes to fibrous shapes and eventually to sheet- or plate-like shapes of calcium silicate hydrate. This structural development was observed via a scanning electron microscope, while the amorphous and crystalline structures of CSH were identified through X-ray diffraction patterns.

The calcium-based geopolymer samples were evaluated in terms of compressive strength, volumetric weight, porosity, and water absorption. It was found that with longer hydrothermal reaction times, the volumetric weight of the materials increased, while their porosity and water absorption decreased, resulting in a significant increase in the mechanical strength. However, an excessively long hydrothermal reaction time did not necessarily enhance the properties of the materials substantially. This study recommends an optimal hydrothermal reaction time of approximately 48 h at 180 °C. Future research should explore different temperature conditions in controlled alkaline solutions and test other raw materials besides limestone. Additionally, application properties such as heat resistance, chemical resistance, and other relevant characteristics should be investigated.

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N. H. THANG et al.: SYNTHESES AND CHARACTERISTICS OF CALCIUM-BASED GEOPOLYMER FROM SOLAR-CELL ...

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