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Optimization of mechanical properties and microstructure of shell powder-modified geopolymer for sustainable construction



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Highlights:

- A shell powder-modified geopolymer is developed for sustainable construction.
- Shell powder enhances early-age and standard curing-period mechanical properties.
- The evolution of pore structure with varying shell powder content is revealed.
- A viable replacement range of up to 70% shell powder content is established.

Abstract: This study develops an innovative geopolymer material by incorporating shell powder (SP) as partial replacement for metakaolin. Eight mixtures with SP replacement levels from 0% to 90% were designed and systematically evaluated through density testing, P-wave velocity measurement, uniaxial compressive strength testing, and low-field nuclear magnetic resonance (LF-NMR) tests. The effects of SP content on the physical properties, mechanical properties and microstructure of modified geopolymer were discussed. An optimal replaceable region of SP to metakaolin was recommended. The results demonstrate that as SP content increases, the geopolymer exhibits initial improvement followed by deterioration in density, P-wave velocity, and compressive strength, while porosity shows an initial decrease before increasing. The comprehensive mechanical testing at 7 and 28 days revealed that, while mechanical properties generally decline with high SP content, SP can still replace up to 80% of metakaolin by mass while maintaining acceptable compressive strength, and up to 70% while maintaining acceptable elastic modulus. Furthermore, based on the mechanical characteristics relative to the plain geopolymer, the research establishes a practical classification system. This system divides the range of SP content into three distinct performance regions: (1) the reinforced region, where mechanical properties exceed those of the plain geopolymer; (2) the replaceable region, where properties are comparable to or only slightly below the reference; and (3) the rapidly decreasing region, where a significant deterioration in performance occurs. This classification provides valuable guidance for material design optimization under various engineering conditions. The findings confirm that SP can be successfully transformed into a functional component of geopolymer materials, offering a sustainable solution for solid waste utilization in construction applications.

Keywords: shell powder; geopolymer; metakaolin; mechanical properties; microstructure; solid waste utilization



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1. Introduction

The rapid expansion of mariculture has led to a substantial increase in waste shellfish shells, the majority of which are discarded without effective treatment [1–4]. This results in severe environmental issues, including land occupation and pollution of surrounding ecosystems [5,6]. Fortunately, the main component of shells is calcium carbonate (CaCO_3), which is also the primary raw material derived from limestone for cement production [7–9]. Therefore, developing waste shells into building materials represents a highly promising strategy for the sustainable recycling of this abundant solid waste.

In recent years, geopolymer has emerged as a promising sustainable alternative to conventional cement, characterized by significantly reduced carbon emissions during production [10,11]. While cement remains dominant in the construction industry due to well-established applications [12], geopolymers offer a range of compelling advantages. As inorganic aluminosilicate polymers, these materials are synthesized through the reaction of aluminosilicate sources with an alkaline activator [13]. A wide variety of industrial by-products and natural materials serve as precursors, including metakaolin, slag, fly ash, and red mud [14–17]. Beyond environmental benefits, geopolymers are recognized for high early strength, excellent durability in aggressive environments, superior fire resistance, and a proven capacity to immobilize heavy metal ions [18–22]. These properties make geopolymers suitable for a broad spectrum of civil engineering applications, from waste encapsulation to high-performance construction materials [23,24].

Research on the integration of shell-derived calcium in geopolymer systems has primarily focused on calcined shell powder (SP), where calcium oxide (CaO) represents the reactive phase. The introduction of Ca^{2+} ions from calcined shells participates in the geopolymerization process, accelerating the formation of calcium aluminosilicate hydrate (C-A-S-H) gels alongside the primary sodium aluminosilicate hydrate (N-A-S-H) gel matrix [25]. This co-existing gel system contributes to a denser microstructure, leading to reduced setting time and enhanced mechanical properties [26]. In comparison with calcined SP, research into the direct utilisation of uncalcined SP remains in its infancy and is predominantly concentrated within ordinary Portland cement systems. It is evident from extant research that, within the domain of cementitious materials, uncalcined shell flour predominantly operates as a micro-aggregate filler. A ternary system concrete admixture containing oyster SP was proposed by Liu *et al.* [27]. The SP was found to be an effective cement-assisted cementing material, exhibiting a satisfactory filling effect. However, systematic research on uncalcined SP within geopolymer systems remains particularly scarce. The inherently high alkalinity environment of geopolymers may provide more favourable conditions for the dissolution of CaCO_3 and its participation in reactions. Only a limited number of studies have indirectly addressed this field, for example Ortega-Zavala *et al.* [28], who observed in an alkali-activated limestone system that CaCO_3 could partially dissolve in strongly alkaline solutions and contribute to gel phase formation, including calcium silicate hydrate (C-S-H), sodium-calcium silicate hydrate (N-C-S-H), and other reaction products. However, it should be noted that this research did not directly utilise biogenic SP. It is evident that further investigation is required to elucidate the precise mechanism by which uncalcined SP functions within geopolymers, along with its synergistic effects with aluminosilicate precursors such as mekaolinite. Furthermore, from the perspective of sustainability and energy consumption, the direct utilisation of uncalcined SP offers significant advantages. The calcination process is an energy-intensive stage accompanied by substantial CO_2 emissions.

Conversely, uncalcined SP necessitates only basic crushing, grinding, and screening procedures, with its processing energy consumption amounting to less than one-tenth of that of the calcination process [29,30]. This analogous behavior suggests that uncalcined SP may not act as an inert filler but could play a more active role in the geopolymerization process, thereby supporting the scientific premise and practical feasibility of using this material as a sustainable and low-cost component in geopolymer design.

This study aims to address the paucity of systematic research concerning the application of uncalcined SP within geopolymers, thereby providing direct theoretical and empirical support for its large-scale, high-performance utilisation in sustainable construction engineering. In order to investigate the effects of uncalcined SP content on the mechanical properties and microstructure of metakaolin-based geopolymer. Eight groups of specimens with SP substitution levels from 0% to 90% were prepared. A series of tests were conducted, including density measurement, P-wave velocity detection, uniaxial compressive strength evaluation, and low-field nuclear magnetic resonance (LF-NMR) relaxometry. The variations in density, wave velocity, compressive strength, and porosity with increasing SP content were systematically discussed. Three characteristic regions of SP content were identified, and the appropriate substitution ranges for different curing ages were determined.

2. Materials and experimental methods

2.1. Materials

The raw materials used in this study, metakaolin and SP, are shown in Figure 1. Metakaolin exhibits a brick-red color, while the SP is beige. The metakaolin was produced by calcining kaolin from Henan, China, at 850 °C for 4 hours. The SP was supplied by Juxin Oyster Shell Factory (Yangxi County, Guangdong, China). The raw shells were first rinsed with tap water to remove salt and organic residues, then dried at 105 °C for 24 h. The cleaned and dried shells were crushed using a jaw crusher and subsequently ground in a planetary ball mill for 2 hours. The resulting powder was passed through a 200-mesh sieve. The mineralogical composition, confirmed by XRD, is predominantly calcite. The alkaline activator was prepared by first dissolving analytical-grade flake NaOH (purity exceed 99.0%) in deionized water to obtain an 8.0 M NaOH solution. This solution was then mixed with a commercial sodium silicate solution (Na_2SiO_3 , $\text{SiO}_2 / \text{Na}_2\text{O} = 3.24$) at a mass ratio of NaOH solution : Na_2SiO_3 solution = 1 : 6.05 to achieve a final activator with a molarity of 1.3 M and a $\text{SiO}_2 / \text{Na}_2\text{O}$ ratio of 1.3. The activator was allowed to cool to room temperature before use.

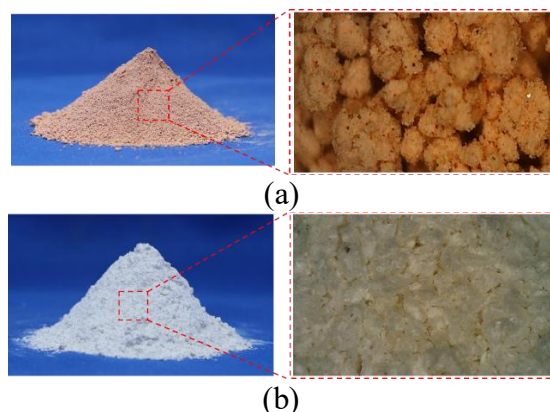


Figure 1. Metakaolin and SP samples. (a) Metakaolin; (b) Shell powder.

Figure 2 shows the X-ray diffraction (XRD) patterns of the two materials. The test employed a SmartLab X-ray diffractometer, with samples consisting of 200-mesh powder. The scanning angle range is 2.6–45 °, with an angular increment of 0.02 °. The scanning rate is 4 °/min, and the scanning mode is step scanning. The metakaolin pattern shows a broad hump, indicating an amorphous structure typical of reactive aluminosilicate materials. In contrast, the SP shows sharp crystalline peaks, with a distinct characteristic peak located at a 2 θ angle of around 30 degrees, consistent with the structure of calcium carbonate.

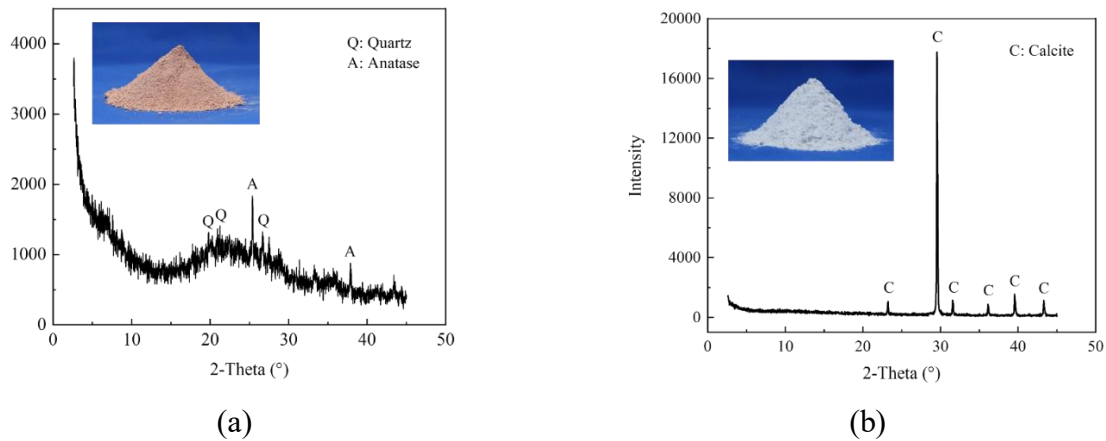


Figure 2. XRD patterns of metakaolin and SP. **(a)** Metakaolin; **(b)** Shell powder.

2.2. Specimen preparation

The test specimens were fabricated according to the mixing ratios specified in Table 1. A total of eight groups were prepared with SP contents of 0%, 10%, 20%, 30%, 40%, 60%, 80% and 90%. This study builds upon prior research into CaCO_3 within alkaline activation systems [31]. Experiments were designed with step intervals of 10 % and 20 % to more precisely identify the optimal replacement ratio and investigate the system's feasibility limits and failure thresholds. The preparation process followed these steps. First, an 8.0 M sodium hydroxide solution was prepared by dissolving solid NaOH in water. This solution was then used to adjust the Na_2SiO_3 solution to a molarity of 1.3. The resulting alkaline activator was thoroughly stirred and allowed to cool to room temperature. Subsequently, metakaolin and SP were combined in predetermined proportions and mixed thoroughly. The geopolymer mortar was produced by gradually adding the alkaline activator and mixing for approximately 180 seconds. The fresh mortar was then poured into molds and vibrated for 60 seconds. After one day of curing at 20 °C and 95% relative humidity, the specimens were demolded and continued curing under the same conditions until reaching the testing age according to GB/T 2019 [32].

Table 1. Mix proportions of geopolymer with SP content.

R	Cementitious materials (kg/m^3)		Alkaline activator solution (kg/m^3)		
	Metakaolin	Shell powder	NaOH	Na_2SiO_3	Water
0%	1320.53	0	82.55	499.47	257.98
10%	1188.48	132.05	82.55	499.47	257.98
20%	1056.42	264.11	82.55	499.47	257.98
30%	924.37	396.16	82.55	499.47	257.98
40%	792.32	528.21	82.55	499.47	257.98
60%	528.21	792.32	82.55	499.47	257.98
80%	264.11	1056.42	82.55	499.47	257.98
90%	132.05	1188.48	82.55	499.47	257.98

Two specimen sizes were employed in this study. Cubic specimens measuring 70.7 mm $\times$ 70.7 mm $\times$ 70.7 mm were used for uniaxial compressive testing and P-wave velocity testing at 7 and 28 days of curing. Cylindrical specimens with a diameter of 50 mm and height of 25 mm were used for LF-NMR relaxometry testing at 28 days of curing. Figure 3 shows the geopolymer specimens with varying SP contents. As visible in Figure 3a, the specimen color transitions from dark red to light red with increasing SP content. All specimen surfaces were polished using emery paper to minimize dimensional errors. To ensure reliability, three replicate specimens were prepared and tested for each mixture proportion.

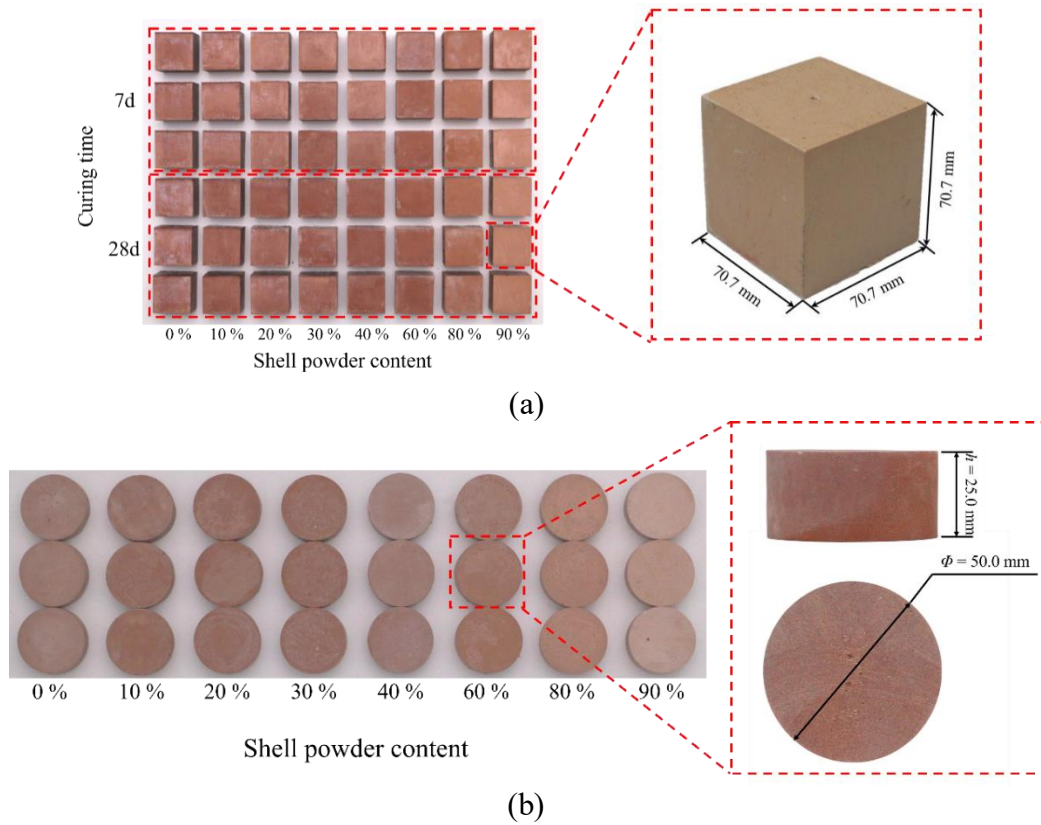


Figure 3. Geopolymer specimens with varying SP contents. **(a)** Specimens used for compressive strength tests; **(b)** Specimens used for NMR tests.

2.3. Experimental methodology

2.3.1. Physical property measurements

The density of geopolymer specimens with different SP contents was measured after 7 and 28 days of curing. Before testing, the specimens were removed from the curing chamber, and surface moisture was carefully wiped off. The mass of each specimen was weighed using an electronic balance with an accuracy of 0.01 g. The dimensions were measured with a vernier caliper with a precision of 0.01 mm, and the volume was calculated accordingly. Density was determined as the ratio of mass to volume. The influence of SP content on the density of the geopolymer was analyzed based on the measured results.

In accordance with ASTM (2016) [33], ultrasonic pulse velocity testing was performed using an HS-YS4A acoustic wave detector equipped with 50 kHz dominant frequency. A direct transmission method was employed. Prior to testing, the opposite faces of the cubic specimen were coated with a thin layer of ultrasonic couplant to ensure good acoustic contact. The transit time of the P-wave through the

specimen was recorded. The P-wave velocity was calculated as the ratio of the specimen length to the transit time. Three measurements were taken for each specimen, and the average value was reported.

2.3.2. Uniaxial compressive strength test

Uniaxial compression tests were performed on cubic specimens after 7 and 28 days of curing using a microcomputer-controlled electro-hydraulic servo universal testing machine (MTS), in accordance with GB/T 2019 [32]. A constant loading rate of 0.5 MPa/s was applied throughout the tests. Displacement during compression was measured and recorded using two micrometers. For each mix proportion, three specimens were tested, and the average value of the three measurements was reported as the final result to ensure reliability.

2.3.3. LF-NMR relaxometry

LF-NMR provides a rapid and non-destructive method for characterizing the pore structure of materials. The LF-NMR test provided the transverse relaxation time (T_2) distribution. The relationship between T_2 and pore size is governed by the fast diffusion regime equation:

$$\frac{1}{T_2} = \rho \left(\frac{S}{V} \right)$$

where ρ is the transverse relaxation strength, $\mu\text{m/ms}$; S/V is the ratio of the pore surface area to the fluid volume, in which S is the pore surface area, μm^2 , and V is the pore volume, μm^3 .

Information about the pores can be obtained by analysing the T_2 spectrum. The position of the T_2 spectrum represents the relaxation times of fluids with different pore sizes. The T_2 spectrum curve can be used to determine the number and size of mesopores. The T_2 value is positively related to pore size. The larger the T_2 value, the larger the pores. There is a positive correlation between the area of the T_2 spectrum and the number of pores. The larger the spectral area, the greater the pore number [34].

In this study, cylindrical specimens with different SP contents were prepared for LF-NMR analysis. Prior to testing, the specimens were placed in a vacuum chamber at -0.10 MPa for 6.0 h to remove air. The chamber was then filled with water and pressurized to 5.0 MPa, allowing the specimens to saturate under water for 24 h. After removal, the specimen surfaces were gently dried and wrapped in plastic film to prevent moisture loss during measurement. LF-NMR tests were carried out using a Macro-MR12-025V instrument (Niumag Corporation, Suzhou, China) maintained at 32 ± 0.02 °C, following the procedure described by Liu *et al.* [35]. The radiofrequency coil of the device has an inner diameter of 60 mm. Following comprehensive consideration of the instrument's limitations, the testing principle requirements (full saturation), and material representativeness, this study selected cylindrical specimens with a diameter of 50 mm and a height of 25 mm for LF-NMR testing [36].

3. Results and discussion

3.1. Physical properties of shell powder-modified geopolymer

Figure 4 and Table 2 show the variation in geopolymer density with SP content at different curing ages. At 7 days, density first increases and then decreases as the SP content rises. Using the baseline density

of specimens without SP as a reference, the maximum density occurs at 20% SP content, representing a 1.6% increase over the baseline. The minimum density, observed at 90% SP content, is 3.6% lower than the baseline. At 28 days, the density of specimens with the same SP content generally decreases compared to that at 7 days, although the overall trend of variation with SP content remains consistent.

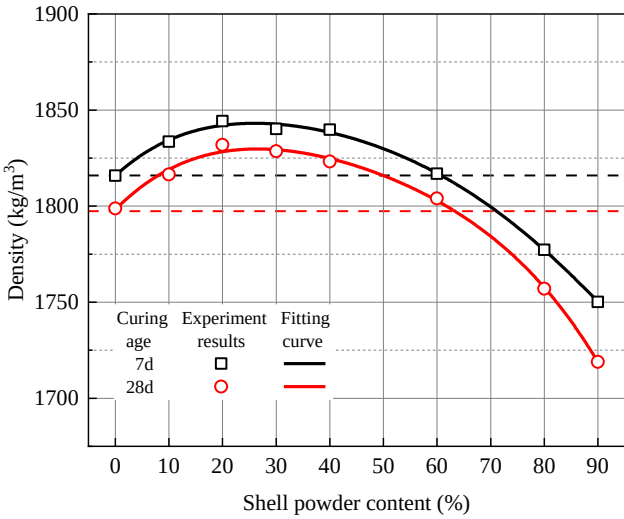


Figure 4. Density of geopolymer *versus* SP content.

Table 2. Experimental results of density.

Shell powder content (%)	7d density (kg/m ³)					28d density (kg/m ³)				
	Experimental results			Average value	Standard deviation	Experimental results			Average value	Standard deviation
0	1825.34	1820.61	1801.72	1815.89	12.49	1808.73	1802.72	1784.71	1798.72	12.49
10	1809.68	1842.28	1848.51	1833.49	20.85	1836.78	1824.62	1788.16	1816.52	25.30
20	1832.45	1851.97	1848.15	1844.19	10.34	1846.80	1837.82	1810.87	1831.83	18.69
30	1814.43	1856.03	1850.02	1840.13	22.48	1862.30	1842.07	1781.40	1828.59	42.10
40	1825.86	1845.59	1847.82	1839.76	12.08	1852.67	1834.99	1781.96	1823.21	36.79
60	1812.84	1826.12	1811.64	1816.8	8.03	1816.21	1808.91	1787.00	1804.04	15.20
80	1751.43	1790.73	1789.56	1777.24	22.35	1783.70	1767.66	1719.52	1756.96	33.40
90	1722.35	1768.52	1759.52	1750.13	24.47	1757.28	1734.27	1665.24	1718.93	47.89

Figure 5 and Table 3 illustrate the influence of SP content on P-wave velocity. After 7 days of curing, P-wave velocity initially increases and then decreases with increasing SP content. Relative to the baseline P-wave velocity of specimens with 0% SP, the highest value occurs at 20% SP, showing a 5.1% improvement. As the SP content increases to 90%, P-wave velocity drops to its lowest point, 21.5% below the baseline, with a particularly sharp decline observed beyond 80% SP. At 28 days, P-wave velocities increase for all specimens compared to the 7-day results. Since P-waves propagate faster through solid materials than through porous media, the observed trend suggests that the porosity of the geopolymer first decreases and then increases with the addition of SP [37].

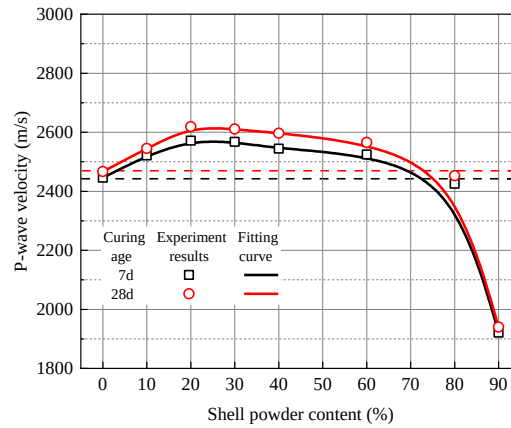


Figure 5. P-wave velocity of geopolymer *versus* SP content.

It is noteworthy that, according to elastic wave propagation theory, the P-wave velocity in solid media depends not only on the porosity of the medium but is also directly related to the material's dynamic elastic modulus and density. The theoretical relationship can be expressed as follows:

$$V_p = \sqrt{\frac{E_d}{\rho}}$$

where V_p , E_d and ρ are the P-wave velocity, elastic modulus and density. Consequently, variations in P-wave velocity are the result of the combined effects of both elastic modulus and density.

Table 3. Experimental results of P-wave velocity.

Shell powder content (%)	7d P-wave velocity (m/s)					28d P-wave velocity (m/s)				
	Experimental results			Average value	Standard deviation	Experimental results			Average value	Standard deviation
0	2456.01	2450.00	2431.99	2446.00	12.49	2494.38	2477.95	2428.67	2467.00	34.19
10	2549.18	2532.27	2481.55	2521.00	35.19	2592.01	2563.80	2479.19	2545.00	58.71
20	2610.32	2586.83	2516.36	2571.17	48.89	2653.2	2632.78	2571.53	2619.17	42.50
30	2585.34	2574.44	2541.72	2567.17	22.70	2664.25	2632.40	2536.86	2611.17	66.29
40	2589.41	2562.36	2481.23	2544.33	56.29	2628.69	2609.58	2552.22	2596.83	39.79
60	2538.75	2530.20	2504.55	2524.50	17.79	2608.01	2582.50	2505.98	2565.49	53.09
80	2458.47	2438.49	2378.54	2425.17	41.59	2491.65	2468.16	2397.69	2452.50	48.89
90	1944.21	1930.09	1887.72	1920.67	29.39	1988.91	1959.36	1870.74	1939.67	61.49

A thorough examination of the data illustrated in Figures 4 and 5 reveals a synchronous increase in both the density and P-wave velocity of the geopolymer when the SP content is below 20%. This finding suggests that the incorporation of SP within this range enhances the material's density and significantly improves its elastic modulus by refining the microstructure. This positive effect is predominantly responsible for the observed rise in P-wave velocity. However, when the SP content exceeds 20%, although the material density remains at a relatively high level or even decreases slightly before reaching 40% or 60% content, the P-wave velocity begins to decrease significantly. This phenomenon suggests that, at this stage, the introduction of excessive SP has a detrimental effect on the material's internal

structure. Consequently, the decline in elastic modulus becomes the dominant factor, with its negative impact outweighing any limited positive contribution that density changes might offer. This results in the attenuation of P-wave velocity. It is notable that when the addition exceeds 80%, both density and P-wave velocity undergo a precipitous decline, which is indicative of a tendency towards high porosity and low strength.

3.2. Mechanical properties of shell powder-modified geopolymer

Figure 6 presents the compressive stress-strain curves of geopolymer specimens with different SP contents after 7 and 28 days of curing. Taking the specimen with 60% SP content from Figure 6a as an example, the stress-strain behavior can be divided into four distinct stages according to Fan *et al.* [38]. The initial compacting stage (AB) is characterized by the closure of microcracks, resulting in nonlinear deformation. This is followed by the elasticity stage (BC), where stress increases linearly with strain, indicating elastic deformation. In the subsequent plastic stage (CD), the curve deviates from linearity as microcracks develop and surface spalling initiates, continuing until peak stress is reached. The final failure stage (DE) shows a sharp stress drop accompanied by significant spalling and transverse cracking, ultimately leading to specimen failure.

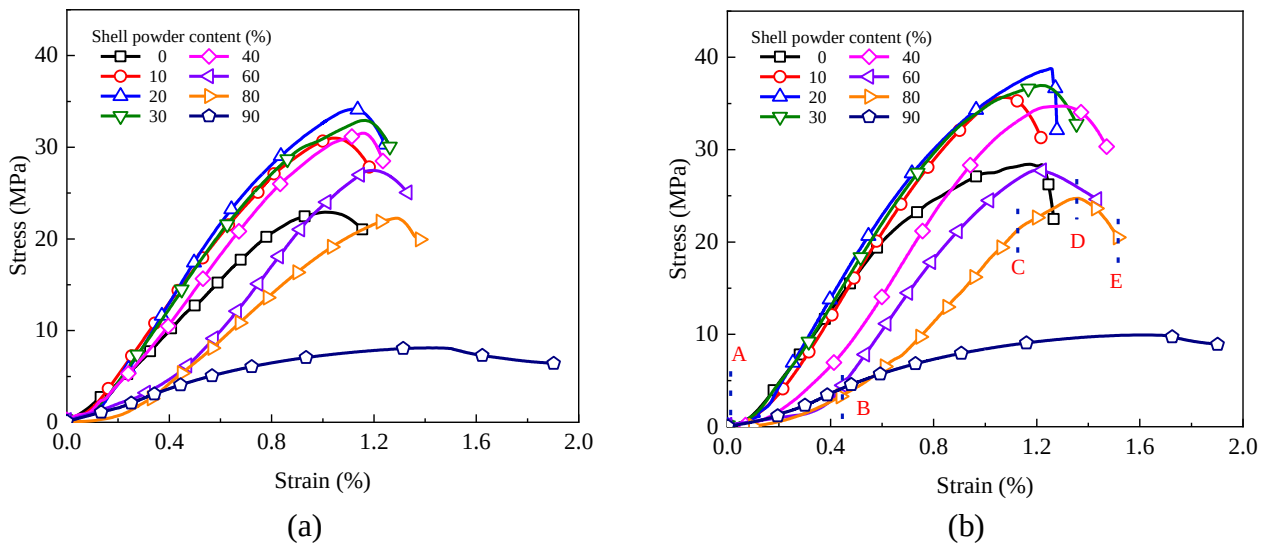


Figure 6. Stress-strain relationship of geopolymer *versus* SP content. **(a)** 7 days; **(b)** 28 days.

Figure 7 and Table 4 display the variation in compressive strength with SP content after 7 and 28 days of curing. The strength initially increases, reaches a maximum, then gradually declines before dropping rapidly with further increase in SP content. The maximum compressive strength occurs at 20% SP content, showing a 48.9% improvement over the plain geopolymer. In contrast, the 90% SP content results in a 64.6% reduction in strength. As shown in Figure 7b, the 28-day compressive strengths are generally higher than the 7-day values, while maintaining the same trend with increasing SP content. This behavior can be explained by the similarity between SP and limestone, both being primarily composed of calcium carbonate. Previous studies indicate that partial replacement of metakaolin with limestone enhances the dissolution of silicon and aluminum ions from metakaolin [39], promoting the formation of additional calcium-aluminosilicate hydrate gels that improve strength [40].

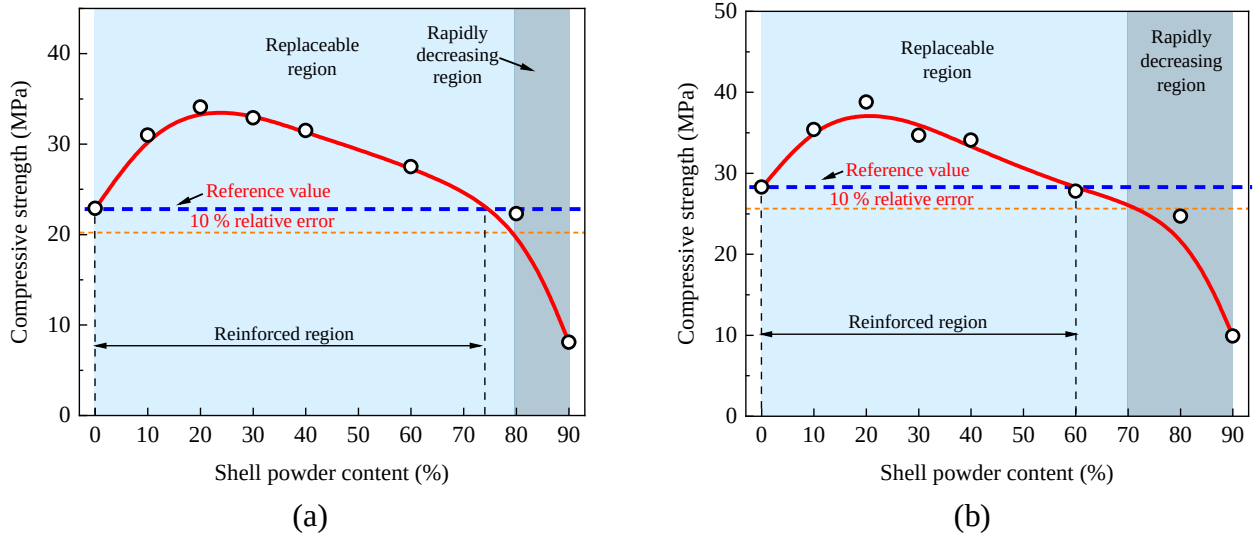


Figure 7. Compressive strength of geopolymer *versus* SP content. **(a)** 7 days; **(b)** 28 days.

Table 4. Experimental results of compressive strength.

Shell powder content (%)	7d compressive strength (MPa)					28d compressive strength (MPa)				
	Experimental results			Average value	Standard deviation	Experimental results			Average value	Standard deviation
0	22.33	24.51	26.66	24.50	2.15	27.66	28.81	29.93	28.80	1.12
10	29.88	31.31	32.71	31.30	1.43	33.84	36.22	38.56	36.20	2.34
20	30.50	34.12	37.68	34.10	3.62	34.47	37.51	40.52	37.50	3.01
30	30.37	33.32	36.21	33.30	2.89	34.51	35.41	36.28	35.40	0.87
40	29.23	32.40	35.57	32.40	3.17	32.16	35.03	37.81	35.00	2.78
60	25.76	27.48	29.26	27.50	1.78	26.22	27.81	29.37	27.80	1.56
80	20.25	24.20	28.15	24.20	3.95	23.18	26.52	29.80	26.50	3.28
90	7.00	8.12	9.18	8.10	1.06	8.49	9.12	9.69	9.10	0.63

Figure 8 and Table 5 show the evolution of elastic modulus with SP content at different curing ages. At 7 days (Figure 8a), the elastic modulus first increases, then gradually decreases, and finally drops rapidly with increasing SP content. The maximum elastic modulus occurs at 20% SP, representing a 42.5% enhancement compared to the reference mixture, while 90 % SP causes a 72.7% reduction. The 28-day curing results (Figure 8b) show higher modulus values but follow the same trend as observed at 7 days. These results confirm that moderate SP substitution enhances the mechanical properties of geopolymer, while excessive replacement adversely affects performance.

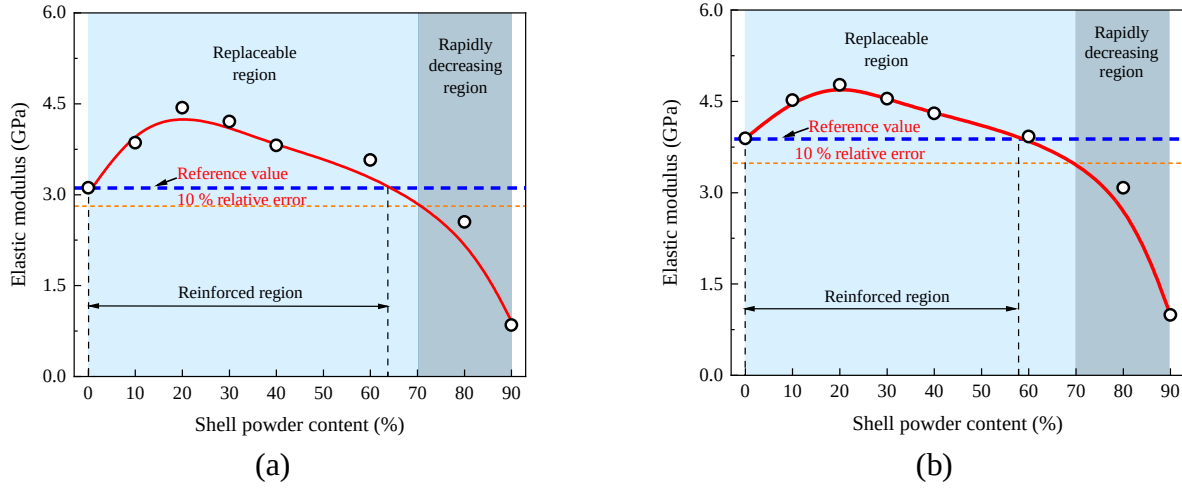


Figure 8. Elastic modulus of geopolymer *versus* SP content. (a) 7 days; (b) 28 days.

Table 5. Experimental results of elastic modulus.

Shell powder content (%)	7d elastic modulus (GPa)					28d elastic modulus (GPa)				
	Experimental results			Average value	Standard deviation	Experimental results			Average value	Standard deviation
0	3.31	3.19	2.84	3.11	0.24	4.05	3.95	3.64	3.88	0.21
10	4.17	3.98	3.42	3.85	0.38	4.82	4.64	4.10	4.51	0.37
20	4.39	4.24	3.79	4.14	0.31	5.01	4.87	4.44	4.77	0.29
30	4.27	4.05	3.39	3.89	0.45	5.02	4.80	4.13	4.65	0.46
40	4.02	3.88	3.49	3.79	0.27	4.57	4.41	3.93	4.30	0.32
60	3.20	3.00	2.39	2.86	0.42	3.65	3.45	2.85	3.31	0.41
80	2.78	2.62	2.14	2.51	0.33	3.44	3.32	2.95	3.23	0.25
90	1.08	0.94	0.52	0.84	0.29	1.31	1.12	0.54	0.99	0.40

3.3. Microstructural characteristics of shell powder-modified geopolymer

The signal intensity in LF-NMR tests is directly proportional to the number of hydrogen protons in the sample [41,42]. Since water-saturated specimens were used, the NMR signal intensity reflects the water content within the pore network. Changes in the pore structure characteristics can be interpreted from the T_2 distribution [43]. Figure 9 presents the relationship between signal amplitude and transverse relaxation time for geopolymers with different SP contents. The T_2 spectra show two distinct peaks, with the first peak located between 10^{-1} and 10^1 ms and the second peak between 10^2 and 10^3 ms.

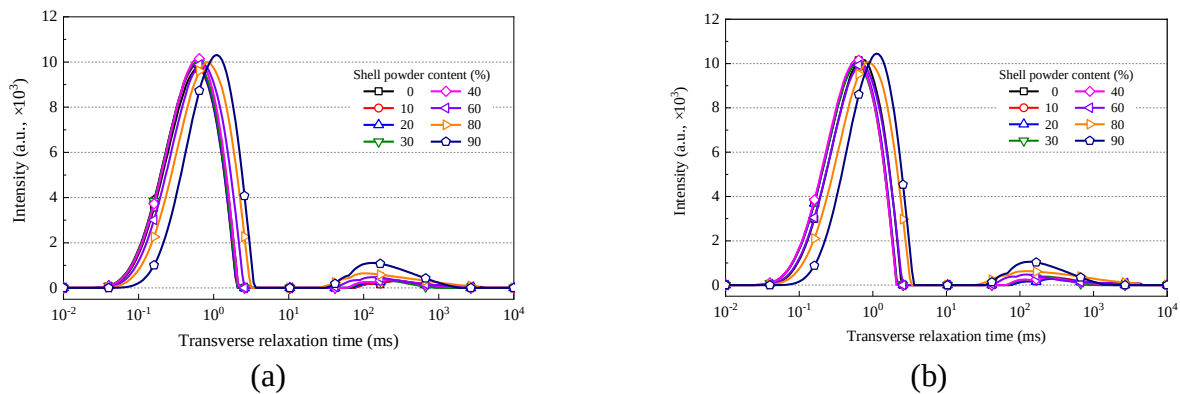


Figure 9. Transverse relaxation time distribution of geopolymer with varying SP contents. (a) 7 days; (b) 28 days.

Based on the LF-NMR results, the pore size distribution of geopolymers with varying SP content was determined, as shown in Figure 10. The distribution exhibits two predominant pore concentration ranges. The first concentration falls within 10^{-3} to 10^{-1} μm , and the second within 10^0 to 10^1 μm . Pores were classified into three categories according to size gel pores (< 0.01 μm), transition pores (0.01–0.1 μm), and capillary pores (exceed 0.1 μm) [44].

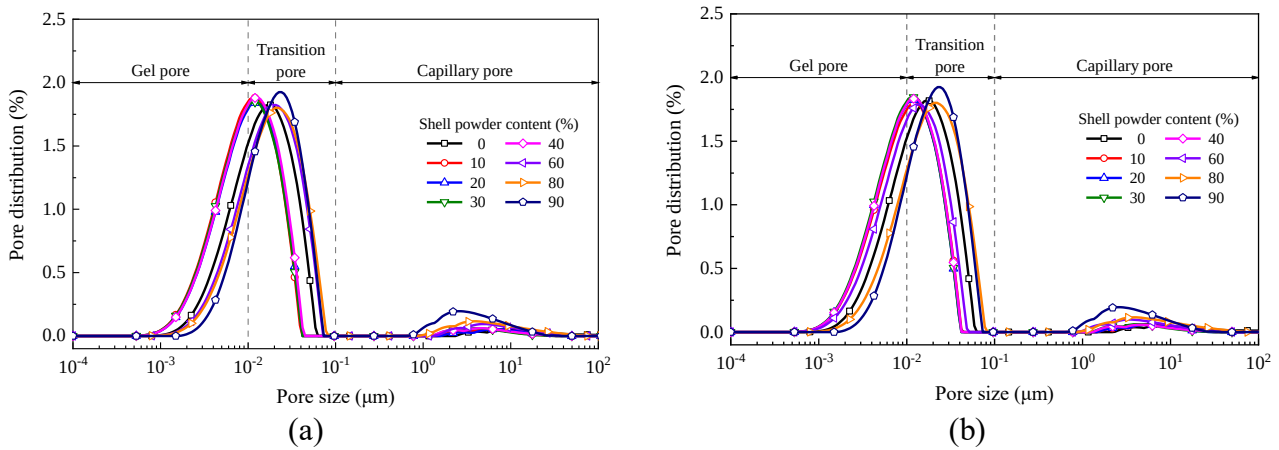


Figure 10. Pore size distribution of geopolymer with varying SP contents. **(a)** 7 days; **(b)** 28 days.

Figure 11 illustrates the influence of SP content on the volumetric proportion of each pore type, defined as the ratio of the volume of a specific pore category to the total pore volume. After 7 days of curing (Figure 11a), transition pores constitute the largest proportion, followed by gel pores, with capillary pores accounting for the smallest share. As SP content increases, the proportion of gel pores initially decreases gradually, with a sharp reduction observed beyond 60% SP. In contrast, the proportion of transition pores increases gradually and rises rapidly after exceeding 60% SP. The proportion of capillary pores decreases gradually when SP content is below 20%, beyond which it begins to increase. After 28 days of curing (Figure 11b), the proportion of transition pores decreases, while that of gel pores increases compared to the 7-day results. The proportion of capillary pores remains relatively stable.

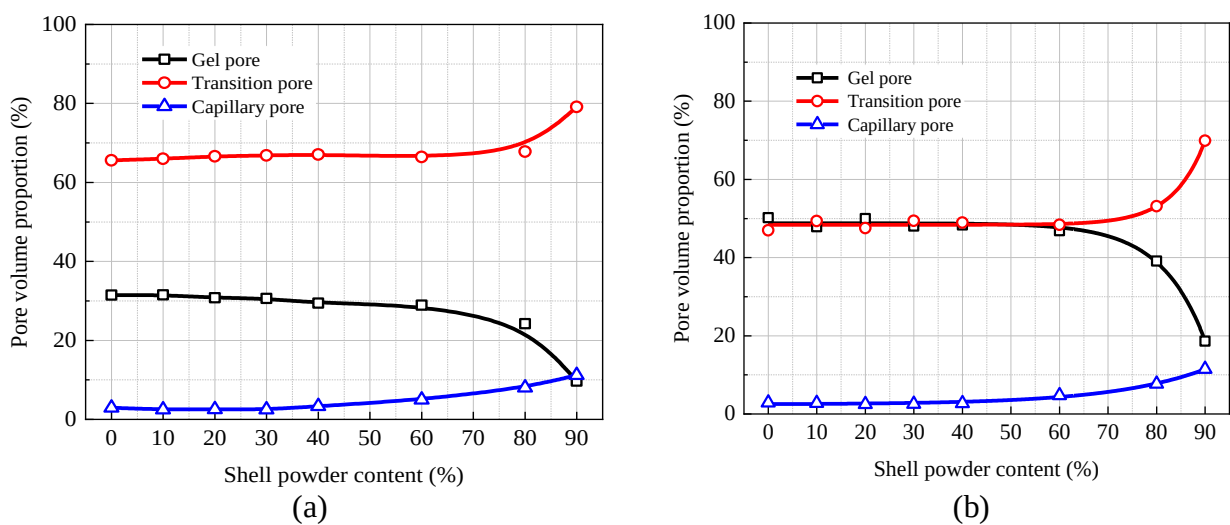


Figure 11. Pore volume distribution of geopolymer *versus* SP content. **(a)** 7 days; **(b)** 28 days.

As shown in Figure 12 and Table 6, SP content significantly affects the overall porosity of the geopolymer. The porosity first decreases and then increases with increasing SP content (Figure 12a). The

minimum porosity of 53.36% occurs at 20% SP, while the maximum porosity of 56.55% is observed at 90% SP. At 28 days of curing (Figure 12b), the porosity values are generally lower than those at 7 days, though the overall trend remains consistent. These results indicate that a moderate amount of SP reduces porosity and enhances matrix density, whereas excessive SP increases porosity and compromises compactness.

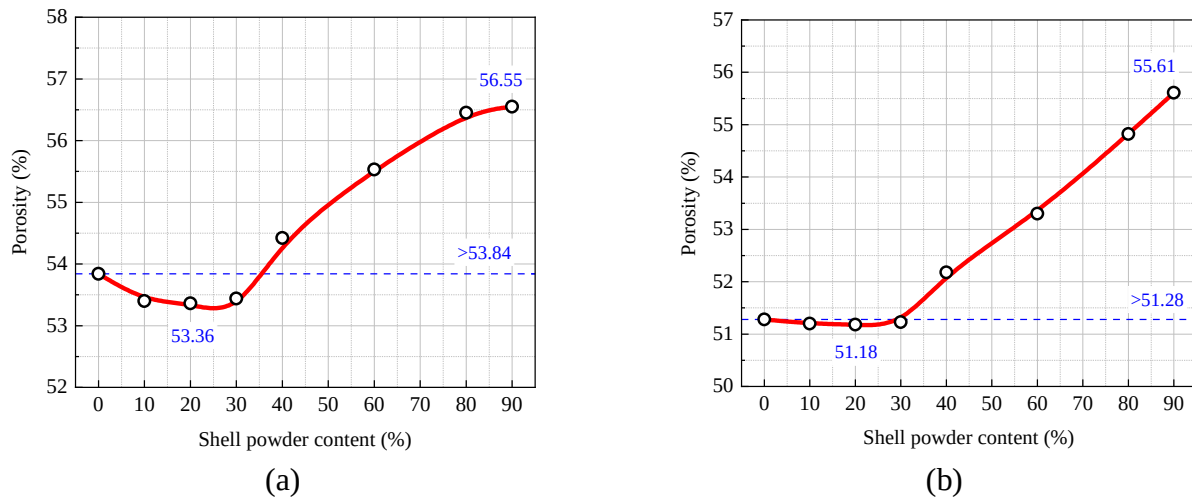


Figure 11. Porosity of geopolymer *versus* SP content. (a) 7 days; (b) 28 days.

Table 6. Experimental results of porosity.

Shell powder content (%)	7d porosity (%)					28d porosity (%)				
	Experimental results			Average value	Standard deviation	Experimental results			Average value	Standard deviation
0	53.94	53.88	53.70	53.83	0.12	51.48	51.36	51.01	51.28	0.24
10	53.63	53.49	53.08	53.40	0.28	51.51	51.32	50.77	51.20	0.38
20	53.52	53.42	53.14	53.36	0.19	51.43	51.28	50.83	51.18	0.31
30	53.69	53.54	53.09	53.44	0.31	51.60	51.38	50.72	51.23	0.45
40	54.63	54.51	54.12	54.42	0.26	52.40	52.27	51.87	52.18	0.27
60	55.67	55.59	55.33	55.52	0.17	53.64	53.44	52.83	53.30	0.42
80	56.73	56.56	56.05	56.44	0.35	55.09	54.93	54.45	54.82	0.33
90	56.73	56.62	56.30	56.55	0.22	55.85	55.70	55.28	55.60	0.29

3.4. Recommended shell powder content ranges

Based on the compressive strength and elastic modulus results obtained at 7 and 28 days, the SP content was classified into three characteristic regions: the reinforced region, the replaceable region, and the rapidly decreasing region. The mechanical properties of the plain geopolymer (without SP) were used as the reference. The reinforced region is defined as the range where both compressive strength and elastic modulus exceed the baseline values. The replaceable region is defined as the range where compressive strength and elastic modulus are no less than 90% of the baseline values. This region satisfies the performance requirements for a wide range of non-structural and semi-structural applications while maximising the utilisation of SP resources. The rapidly decreasing region commences at the point where either indicator falls below the threshold, signifying a marked and accelerated deterioration in performance. Table 7 summarizes the specific ranges of the reinforced and replaceable

regions under different reference conditions. As illustrated in Figure 13, a SP content ranging from 0% to 70% satisfies the criteria for the replaceable region across all test conditions. In the context of large-scale disposal of shell solid waste, a minor compromise in material strength is deemed acceptable. Across a broad substitution range of 0%–70%, material performance remains comparable to or only marginally reduced from the benchmark geopolymer. This provides a clear engineering window for maximising the utilisation rate of waste SP while ensuring fundamental structural functionality.

Table 7. Ranges of reinforced and replaceable regions under different reference conditions.

	Reinforced region	Replaceable region
7d compressive strength	0%–73%	0%–80%
7d elastic modulus	0%–63%	0%–70%
28d compressive strength	0%–60%	0%–70%
28d elastic modulus	0 %–58%	0%–70%

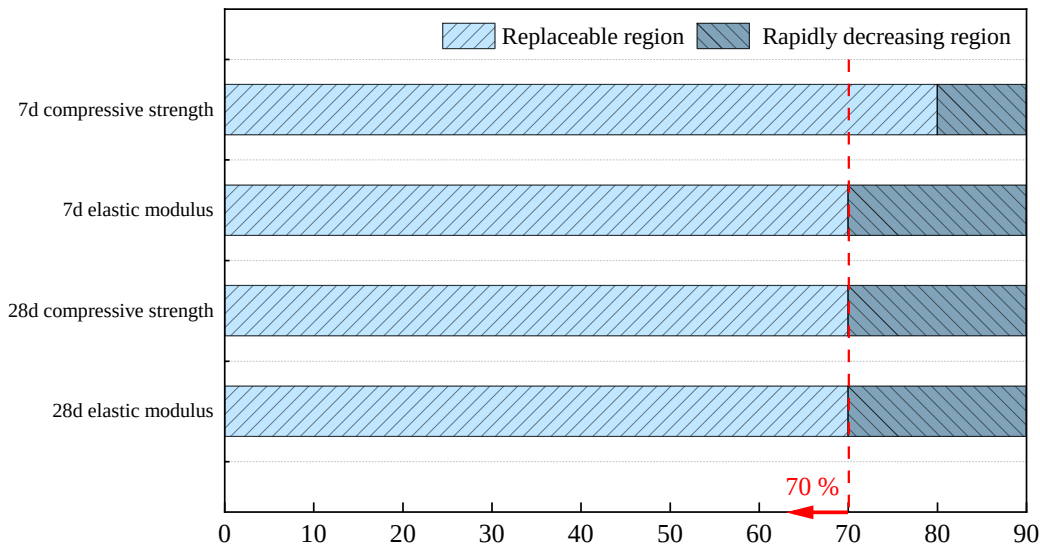


Figure 12. Recommended SP content ranges for different application scenarios.

By reference to GB 175-2023 [45], the proposed 0%–70% SP replacement range in this study provides practical guidance for the following engineering applications: medium-to-low strength structural or non-structural materials (compressive strength 15–25 MPa), such as lightweight partition panels, road base courses, and low-rise building masonry. In practical implementation, it is recommended to optimise the mix design in accordance with the target structure's strength grade to ensure material performance meets relevant specification requirements.

4. Conclusions

This study systematically evaluated the effect of SP content on metakaolin-based geopolymer through density, P-wave velocity, uniaxial compression, and LF-NMR tests at 7 and 28 days of curing. The present study transcends the prevailing research paradigm of optimising low-dose applications of uncalcined CaCO_3 fillers in geopolymers. The study delineates the performance boundaries and micro-mechanisms for high-dose utilisation, proposing a quantitative design framework based on performance zoning.

Based on the comprehensive experimental study presented in this paper, the following conclusions can be drawn:

(1) The incorporation of SP significantly influences the geopolymer's properties in a non-monotonic manner. The peak comprehensive performance was achieved at approximately 20% SP content. At this optimal level, the 28-day uniaxial compressive strength and elastic modulus increased by 48.9% and 42.5%, respectively, compared to the plain geopolymer, while the porosity reached a minimum of 53.36%.

(2) The study establishes a broad practical replacement range of 0%–70% SP. Beyond the upper limit of this range, the material enters a rapidly decreasing region where mechanical properties deteriorate significantly. For instance, at 90% SP content, the 28-day compressive strength and elastic modulus plummet by 64.6% and 72.7%, respectively, compared to the reference, accompanied by a notable increase in porosity to 56.55% and a pronounced coarsening of the pore structure (dominance of transition and capillary pores).

(3) Based on the mechanical characteristics relative to the plain geopolymer, the SP content can be categorized into three distinct regions: a reinforced region (0%–58%), a replaceable region (0%–70%), and a rapidly decreasing region (beyond 70%). The classification system provides a quantitative and flexible framework for material selection, enabling a balance between mechanical properties and solid waste utilisation rates according to specific application requirements.

The present study is chiefly concerned with the investigation of the fundamental physical, mechanical and microstructural properties of the material under standard curing conditions. Subsequent research will focus on addressing long-term performance and durability under actual environmental exposure conditions, such as freeze-thaw cycles, sulphate attack and carbonation. The aim is to advance the transformation of SP-modified geopolymers from laboratory innovations into reliable, field-applicable, sustainable building materials.

Data availability statement

The data or datasets that support the findings of this study are available from the corresponding author upon reasonable request.

Declaration of generative AI and AI-assisted technologies

The authors did not use generative AI or AI-assisted technologies in the writing of this manuscript. During the preparation of this manuscript, the authors used generative AI tools only to improve language and readability. The authors take full responsibility for the content of the manuscript.

Authors' contribution

Conceptualization, Lifeng Fan; methodology, Lifeng Fan; validation, Lifeng Fan, Zhen Li and Yunhan Zhang; formal analysis, Lifeng Fan and Zhen Li; investigation, Zhen Li; resources, Lifeng Fan; data curation, Zhen Li; writing—original draft preparation, Lifeng Fan and Zhen Li; writing—review and editing, Lifeng Fan, Zhen Li and Yunhan Zhang ; visualization, Lifeng Fan and Zhen Li; supervision, Lifeng Fan; project administration, Lifeng Fan. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

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