EFFECT OF CARBON BLACK CONTENT ON MORPHOLOGICAL, CRYSTALLINE PHASE, AND MECHANICAL CHARACTERISTICS OF POROUS CERAMIC LAYERS

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Abstract. Porous ceramic materials are important components in many technical applications due to their unique combinations of characteristics. The problem statement comes from the requirement to increase the mechanical performance of porous ceramic materials while maintaining their desirable characteristics. The objective of this study is to investigate how carbon black (CB) content affects the morphology, crystalline phase, and mechanical characteristics of porous ceramic layers. The methodology involves synthesizing ceramic mixtures and conducting comprehensive material characterizations. To accomplish this objective, porous ceramic samples with varied CB content were created utilising the double pressing method. The surface morphology and microstructure of the porous ceramic layers were investigated using field emission scanning electron microscopy (FESEM). Among the tested compositions, it was found that the addition of 3 wt% of CB yielded the most favourable outcome, characterized by uniform grain size and a porous structure. The sintered samples exhibited an average increase in flexural strength from 36.36 to 49.72 MPa in the presence of CB (1 wt% to 3 wt%) then decrease from 37.32 to 33.02 MPa (4 wt% to 5 wt%), a phenomenon commonly associated with reduced mechanical properties in highly porous materials. X-ray diffraction (XRD) was utilised to detect changes in crystalline phases caused by the presence of carbon black, and it was identified as orthoclase ($KAlSi_3O_8$). In conclusion, porous ceramic layers present a promising solution for the application in the construction industry.

Keywords: Porous ceramic layers, carbon black, pores structures

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1. INTRODUCTION

The modern industry and construction sectors are witnessing a growing need for high-performance thermal insulation materials. Traditional insulation materials, with their drawbacks of excessive weight and elevated thermal conductivity, fall short in meeting the demands of applications in high-temperature conditions [1]. Due to their favourable characteristics, including low density, low thermal conductivity, high specific surface area, stable chemical properties, and resistance to heat and corrosion, porous ceramics find extensive applications in various fields such as filtration, adsorption, thermal insulation, and catalyst support [2-4]. Various methods for manufacturing porous ceramics have been documented [5-7]. Specifically, agents designed for pore formation have demonstrated the capability to generate substantial levels of porosity. The underlying principle involves heating organic particles to their combustion temperature, resulting in voids within the ceramic structure as the particles are burned away. The structure of these voids is contingent upon the chosen pore-forming agent, and it can be regulated by adjusting the incorporation content and particle size distribution appropriately.

Several pore-forming agents have been studied, including starch [8], graphite [9], fly ash [10], poly(methyl methacrylate) [11] and carbon black [12]. Carbon black is widely used due to its outstanding engineering qualities. It is commonly employed as a filter or strengthening agent in rubber, plastic, and other polymeric materials. Carbon black may be utilised as a porous material in a variety of applications, including ceramics. While starch is commonly employed as a pore-forming agent, likely attributed to its biological origin and accessibility, challenges arise in preserving the pore structure formed through starch combustion. Additionally, the restricted size range of commercially available starch types, typically falling between 5 and 50 μm, imposes limitations on its use, especially when larger pores are required. In theory, the incorporation of spherical micropores and nanopores has the potential to enhance the mechanical properties and diminish the thermal conductivity of porous ceramics [13-14]. In contrast to traditional pore-forming agents, carbon black is distinguished by its small particle size in the nanoscale and spherical morphology. Moreover, these agents do not leave behind impurities upon combustion at elevated temperatures.

Porcelain stoneware tiles exhibit considerable promise as a material for ventilated facades. They possess notable flexural strength, nearly negligible water permeability (<0.5 %), outstanding resistance to frost and chemicals, and optimal abrasion resistance [15]. The exceptional characteristics of porcelain stoneware render it especially well-suited as a material for floor and wall tiles in challenging environments, including hospitals, shopping centres, and industrial settings. A prevalent method for decreasing product weight involves introducing porosity, a modification that concurrently enhances the thermal insulation properties of the product. Achieving this can be done through partial sintering or by utilizing templates such as polymer foam, ceramic hollow spheres, or sacrificial pore-forming agents [12,16]. The mechanical strength of the product is influenced by this porosity, and it is essential to strike a balance among all the required properties. At the same time, surfaces with porosity tend to be aesthetically unappealing, and the process of glazing becomes more challenging. To tackle these challenges, a viable approach is to manufacture a bi-layered ceramic structure by combining a compact top layer with a porous bottom layer. The preparation of bi-layered ceramic using polypropylene (PP) and poly(methyl methacrylate) (PMMA) as pore forming agents was reported by [17]. Nevertheless, current manufacturing techniques for multilayer ceramics are unsuitable for industrial applications due to their typically high solvent consumption and the involvement of multiple, time-consuming, and costly fabrication steps.

The objective of this study is to investigate how CB content affects the morphology, crystalline phase, and mechanical characteristics of porous ceramic layers. Porous ceramic layers consist of both dense and porous layers, each with adjustable thickness. The technique involves a dual pressing action, which is straightforward to execute and guarantees the establishment of a flawless interface bond between the two layers. The straightforward nature of this processing method enables mass production at a low cost. Ceramic tiles exhibit an upper layer with a density comparable to conventional floor covering materials and a lower layer with porosity. The induction of porosity in the lower layer is accomplished through the inclusion of pore-forming agents, commonly referred to as porogens. CB was chosen as a pore-forming agent because of its extensive size range of carbon black, spanning from a few nanometers to hundreds of micrometers, makes it the primary candidate material for serving as a pore-forming agent in alumina ceramics. Alongside its favourable morphological characteristics, the high purity of carbon black powder enables the production of porous ceramics without generating waste [18].

2. MATERIALS AND METHODS

2.1 Materials

Ceramic samples were produced by blending clay (kaolinite) obtained from Anji Runxing New Materials Co., Ltd., silica (silicon dioxide) obtained from CABOT Corporation, and feldspar obtained from Multifilla^{TM}, which included microcline, with the chemical formula $Al_2Si_2O_5(OH)_4$ + SiO_2 + $KAlSi_3O_8$. The overall mixture weighed 100 g, and the individual component weights can be calculated using chemical equations. Specifically, the amounts of clay, silica, and feldspar were 43.28 grams, 10.07 grams, and 46.65 grams, respectively. $2Al_2Si_2O_7 + 4H_2O$+ $KAlSi_3O$

2.2 Sample Preparation

Ceramic discs and bar shapes with two layers are manufactured using a two-step pressing method at room temperature, without the addition of binders or plasticizers. Discs with a diameter of 13 mm and a thickness of 4 mm are accessible. Five distinct ceramic combines were created, with proportions of 0, 1, 2, 3, 4, and 5 wt%, using a total material weight of 100 g. The clay and feldspar components, both in solid form, are ground using a mortar and pestle, whereas silica is in powder form. In the initial step, a 1g mass of dry ceramic powder was introduced into a stainless-steel die with a diameter of 13 mm and subsequently subjected to uniaxial pressing at 20 MPa for 60 s to create the initial compact, constituting the top layer of the green disc. Subsequently, 1 g of a blend of ceramic powder and the pore-forming agent was introduced into the mould and then subjected to pressing at 20 MPa for 60 s, shaping the bottom layer of the disc.

As previously mentioned, ceramic samples are crafted in the shape of bars and discs. The choice of the bar shape is based on its capacity to uniformly compress the powder through uniaxial loading, with average dimensions measuring 75 mm in length, 10 mm in width, and 5 mm in height. Unlike the square tile configuration, this shape requires a minimal amount of material. In the initial step, a 2 g mass of dry ceramic powder was introduced into a bar shape mould and subsequently subjected to uniaxial pressing at 20 MPa for 60 s to create the initial compact, constituting the top layer of the green disc. Subsequently, a blend of ceramic powder

and the pore-forming agent was introduced into the mould and then subjected to pressing at 20 MPa for 60 s, shaping the bottom layer of the bar shaped.

The pore-forming agent content in the bottom layer of the disc or bar shape ranges from 1 wt% to 5 wt%. Before pressing, the powder (ceramic powder) and the pore forming agent are mixed mechanically until a homogeneous layer is formed. Sintering is a process used to create durable and robust ceramic samples. The sample was dried in an oven at 100 °C for 12 hours before being sintered in the furnace. In this work, the powder combination was partly sintered by heating it to 1175 °C using a ramp-up temperature curve. The temperature is steadily raised at a rate of 5 °C/min until the appropriate sintering temperature is obtained. After then, the material is allowed to cool naturally to room temperature, which is normally approximately 25-28 °C.

2.3 Material Characterization

Sintered samples containing varying CB contents were analyzed using an X-ray diffraction (XRD) instrument, specifically the PANalytical X'Pert PRO. XRD analysis is employed to ascertain the crystalline phases within a material, thereby unveiling details about its chemical composition. XRD is a technique for determining a material's crystal structure by analysing the diffraction patterns generated when X-rays encounter its crystalline lattice. While XRD cannot directly determine a material's chemical composition, it can indirectly infer the existence of distinct crystalline phases that may correlate to specific chemical compounds or components.

Field Emission Scanning Electron Microscopy (FESEM) is an advanced technique used to capture images that depict the microstructure of materials, usually carried out in a vacuum environment. The analysis involved capturing microstructure images of the samples in this study using a Schottky FE-SEM SU5000 instrument. The investigation of the interfacial bonding between the dense (top) and porous (bottom) layers of the sintered sample was conducted using FESEM. The present research studied materials that required many preparation procedures, such as grinding, polishing, and thermal etching, before FESEM examination. Each sample was ground using abrasive sheets of grit sizes 1000, 1500, and 2000. To ensure that the surface of the sample was scratch-free, the grinding technique was carried out in accordance with the grain size of the abrasive paper. The samples were ground briefly, then polished with a micro pad and 0.05 μm Al_2O_3. After grinding and polishing, the samples were quickly oven-dried at 60 °C for less than 1 min. After drying, all samples were subjected to thermal etching, which involved submerging them in an 1100 °C atmosphere for 1 min. Before scanning, the sample must be well-cleaned and dried. The sample was mounted using an adhesive tab on the aluminium stub. The vacuum chamber was ventilated to allow air to be removed. The sample was then placed in the sample container, and the chamber door was shut. The vacuum pump worked till it reached the maximum vacuum level. Once this was done, the sample was ready for testing. The present research used FESEM to investigate the microstructure of porous ceramic samples, including pore shape and size distribution. FESEM produces high-resolution pictures of the sample surface but does not directly quantify pore size. Instead, image processing techniques were used to determine the pore size from FESEM pictures.

The mechanical strength was assessed using the three-point flexural strength measurement standard (ISO 10545/4). Experiments were conducted on bar-shaped sintered samples (75 x 10 x 5 mm) using a Shimadzu Autograph AG 25TA instrument, with a

displacement speed set at 1.0 mm/min. The specimens are positioned with the porous layer oriented downward.

3. RESULTS AND DISCUSSION

3.1 Examining the Crystal Structure and Phase Composition Through XRD

Figure 1 represents the crystal structure and phase composition of the ceramic material at different levels of CB content. The XRD pattern displayed clear peaks corresponding to the crystalline structure of the ceramic layers, along with distinctive characteristics indicative of the presence of CB. Silicon dioxide, mullite, and orthoclase were discovered to be the three principal basic elements utilised to produce ceramic [17]. The primary orthoclase peaks, observed at 2θ = 21.25, 27.36, 37.47, and 42.05°, align with the diffraction planes of (201), (202), (151), and (060), respectively. The XRD analysis of the orthoclase phase indicated that the material under examination possesses a monoclinic crystal structure. The amorphous peak typically observed around 2θ=20° for 1 wt% of CB disappeared when the CB content increases from 3 wt% to 5 wt% because at lower CB concentrations (1 wt%), amorphous patches in the ceramic matrix may become more visible due to partial crystallisation or persistent glassy phase. However, as the CB level rises to 3 wt% or 5 wt%, the nucleation impact of CB particles can encourage increased crystallisation of the ceramic matrix, reducing or removing amorphous regions. This enhanced crystallinity may lead to the disappearance of the amorphous peak seen in the XRD pattern.

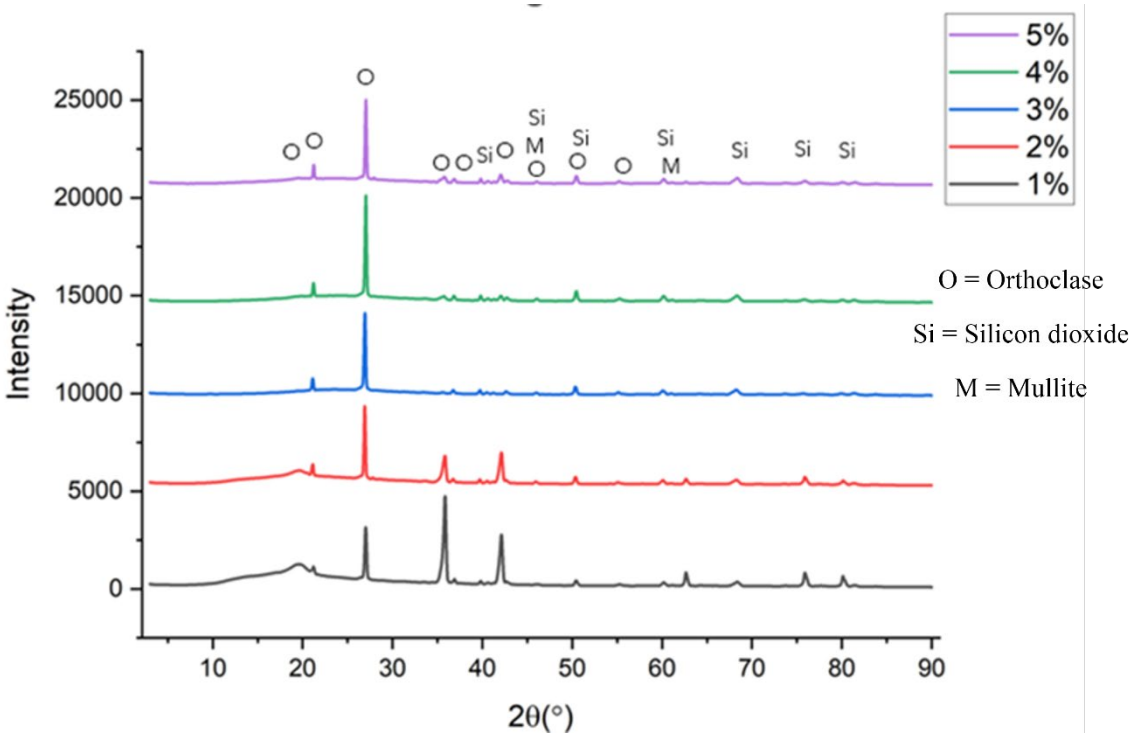

Figure 1: XRD analysis of structural variations in porous ceramic layers with varying carbon black contents

In addition, the lack of crystalline peaks for carbon black confirmed its position as a sacrificial pore-forming agent. CB most likely preserved its amorphous form during the sintering process, causing pores in the secondary layer. The distinctive XRD signature verified

the effective integration of CB as a pore-forming agent in the porous ceramic layers, resulting in the desired porous structure without causing substantial changes to the crystalline phases of the dense ceramic layer [18]. As shown in Figure 1 the peaks in the porous ceramic layers with CB as the pore-forming agent were less defined as the percentage of CB increased, indicating that the CB is amorphous or disorganised [19]. The peak related to orthoclase is the most apparent in comparison to the others, implying that orthoclase is the most dominating presence in porous ceramic layers.

3.2 The Morphological Features of the Porous Structure in Porous Ceramic Layers

Figure 2 displays a representative photograph of the prepared porous ceramic layers. As depicted, the porous ceramic layers comprise a compact upper layer, 2 mm in thickness, and a lower porous layer of equal thickness. It is worth mentioning that the method of production described in this report results in a unified structure featuring two distinct layers separated by an interface region. For all compositions, FESEM characterization was conducted to verify the macroscopic observations and assess the interfacial bonding between the dense and porous layers. To enhance clarity, will present FESEM micrographs for only two distinct compositions.

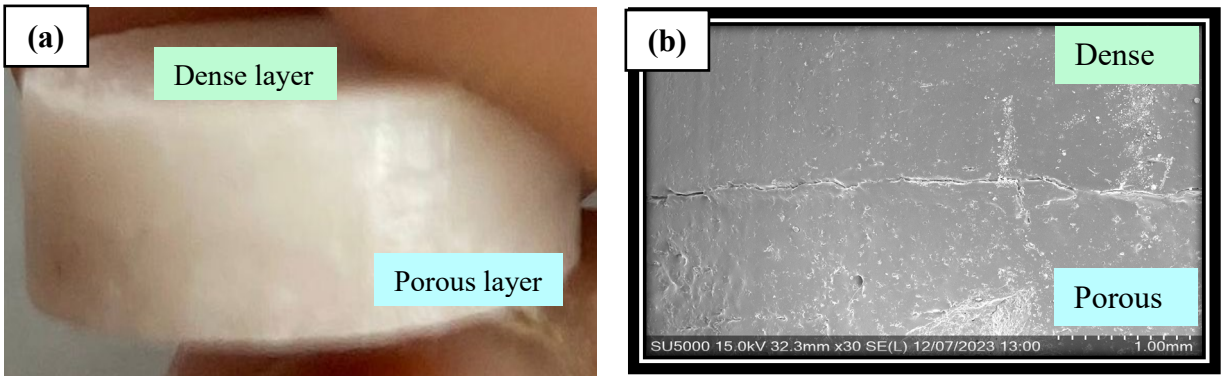

Figure 2: (a) Photograph of the prepared porous ceramic layers and (b) FESEM micrograph of porous ceramic layers

Besides, Figure 3 shows the open and closed pores of porous ceramic layers at various concentrations of CB (1, 2, 3, 4 and 5 wt%) whereas Figure 4 shows the graph plots of the average pore size (open and closed pore). During the ceramic material's sintering, gases trapped inside the pores escape, creating gaps or holes in the structure. In addition, closed pores are mainly accidental and can occur because of insufficient densification during sintering. If the ceramic material is not entirely densified after fire, isolated pores may stay trapped inside the structure.

The pore size of the closed pore decreases as the concentration of CB increases until 3 wt% then the pore size of the closed pore increases gradually at 4 wt% and 5 wt%. This because the 3 wt% of CB does not fully densify during firing, isolated pores may remain trapped within the structure. The distribution of porosity between open and closed pores at 3 wt% of CB shows the nearly compared to others.

Figure 4 shows the average pore size for both open and closed pores. Based on Figure 4, the size of open pores increases between 1 wt% and 2 wt% of CB, but then decreases at 3 wt% of CB. This was because at 3 wt% of CB can help to increase the density of the ceramic

matrix during processing. As the ceramic matrix densifies, the amount of accessible pore space shrinks, restricting the expansion of open pores. This density impact can be more significant at greater CB concentrations, resulting in smaller pores with the presence of continuous CB particles.

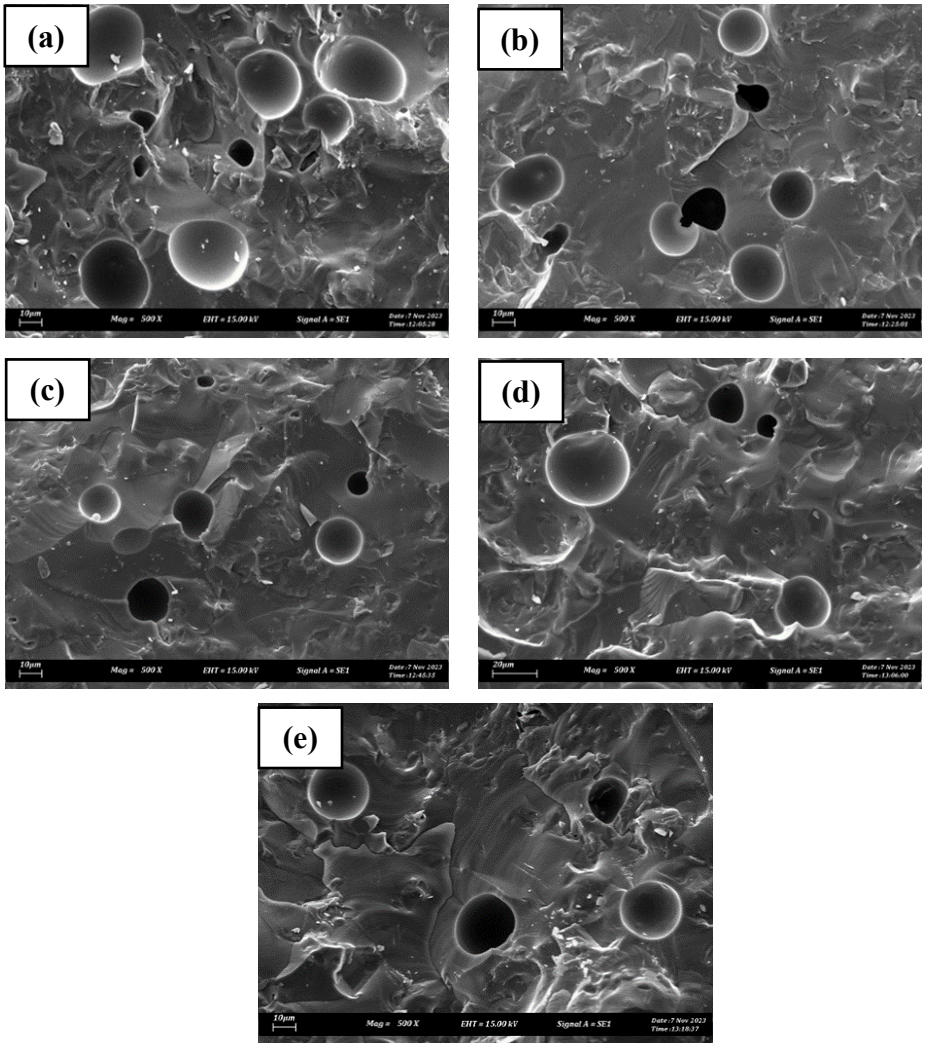

Figure 3: Open and closed pore of porous ceramic layers at various concentration of CB (a) 1 wt%, (b) 2 wt%, (c) 3 wt%, (d) 4 wt% and (e) 5 wt%

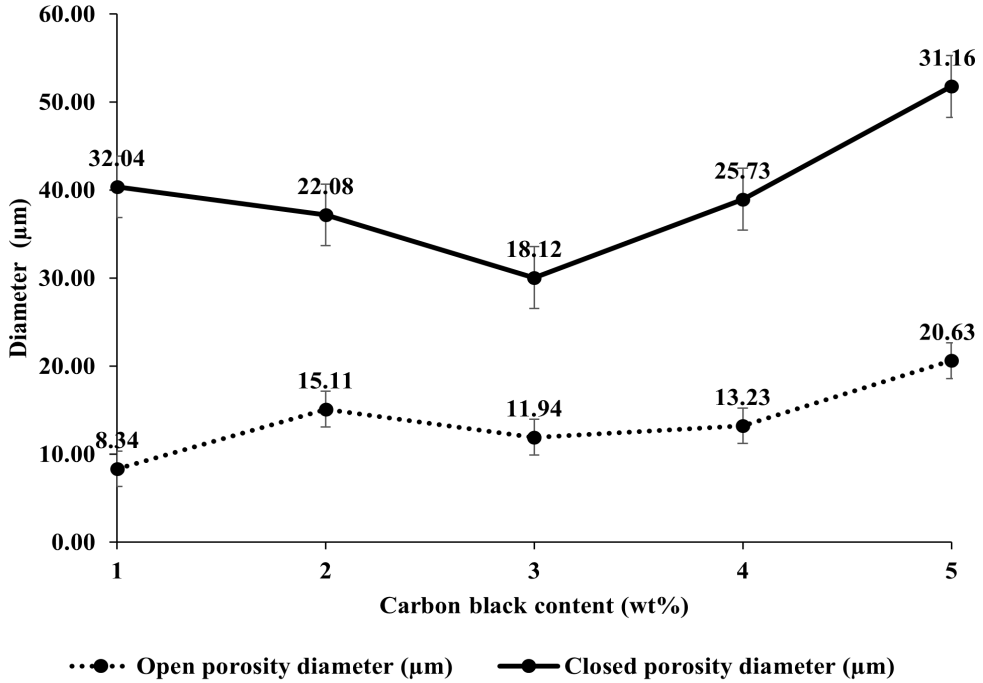

Figure 4: The average pore size for both open and closed pores

3.3 The Mechanical Characteristics of a Porous Ceramic Layer

In Figure 5, the flexural strength of the fired specimen is illustrated. In accordance with the standard (ISO 10545/4), porcelain stoneware tiles must possess a flexural strength exceeding 35 MPa. In this study, the mechanical strength of a sintered porous ceramic disc is regulated by adjusting the level of porosity in the lower layer of the disc. The findings indicate that as the concentration of CB, acting as the pore-forming agent, rises from 1wt% of CB (36.36 MPa) to 3 wt% of CB (49.72 MPa), there is a corresponding increase in flexural strength. Concerning the additional standard properties demanded for porcelain stoneware tiles, they are secured by a compact top layer.

Moreover, there is a decrease in flexural strength at concentrations of 4 wt% of CB (37.32 MPa) and 5 wt% of CB (33.03 MPa). This is because increased porosity is associated with a greater presence of microcracks and enhanced stress absorption, as observed by [6]. Hence, the strength of the composition is closely linked to the quantity and dimensions of pores, influenced by the size of individual carbon black particles or agglomerates [12].

Among the different concentrations, 3 wt% of CB exhibits the highest flexural strength, attributed to its smaller closed pores. Conversely, the trend of strength reduction does not persist with a subsequent increase in the specific surface area of CB particles, owing to substantial agglomeration within the microstructure. Hence, the strength of the composition relies significantly on both the quantity and dimensions of pores, factors influenced by the size of individual carbon black particles or their agglomerates. In accordance with [20], porcelain stoneware tiles were fabricated utilizing SiC particles as a foaming agent. The authors noted that the mechanical strength remains unaffected by the size of SiC particles, attributing this consistency to an equal level of porosity, aligning with our findings.

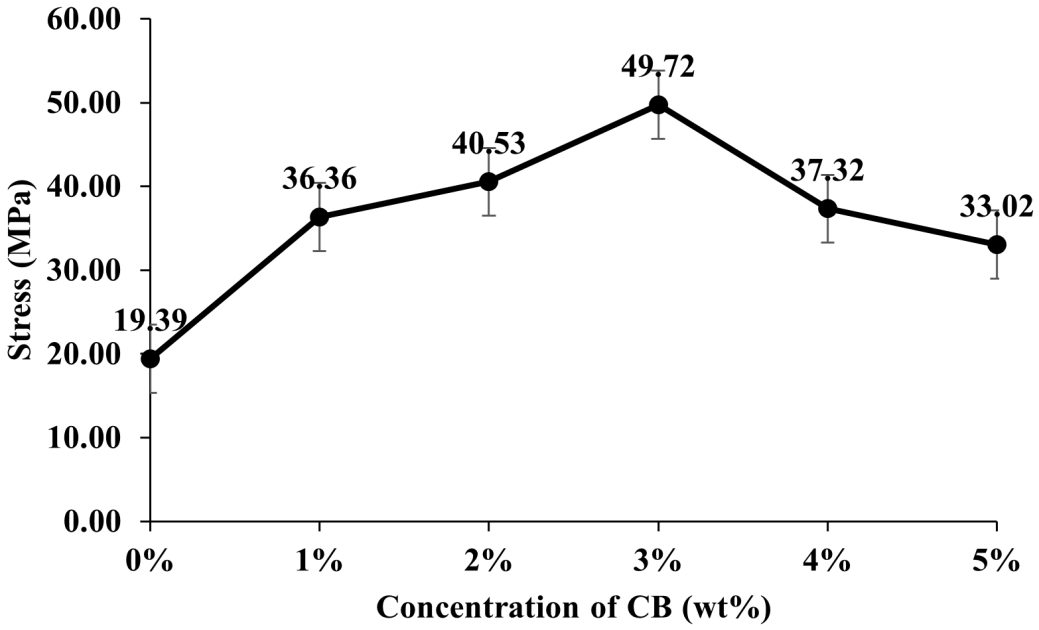

Figure 5: Flexural strength of porous ceramic layers with different concentration of CB as pore forming agent.

4. CONCLUSIONS

In conclusion, this research has provided information on how CB concentration affects the morphology, crystalline phase, and mechanical properties of porous ceramic layers. A lightweight porous ceramic layer structure with favourable mechanical properties was successfully produced, demonstrating the promising application of carbon black as a pore-forming agent in the rapid firing of ceramic products. A well-formed bonding interface between the dense and porous layers was noted, resulting from the comparable shrinkage values exhibited by both layers. The 3 wt% of CB shows the suitable concentration as pore forming agent in porous ceramic layers. 3wt% of CB exhibits the highest compressive strength (49.72 MPa), attributed to its smaller closed pores. The XRD analysis of the orthoclase phase indicated that the material under examination possesses a monoclinic crystal structure. This novel and intriguing characteristic has the potential to broaden the spectrum of porous ceramic layers applications while also contributing to sustainable building.

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Author Contributions

All authors contributed toward data analysis, drafting, and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors declare that they have no conflict of interest.

Compliance with Ethical Standards

The work is compliant with ethical standards.

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