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The effect of metakaolin and hybrid polymers on the microstructure of concrete

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ABSTRACT

It has been established that metakaolin (MK) can be applied as a supplementary cementitious material and that some polymers can enhance substantial properties of concrete. Previous studies showed that, when used in combination, MK and polymers can complement each other, and enhance further the mechanical and durability properties of concrete, which were not improved by one another separately. To have a deep observation and understanding of the mechanism of concretes modified with various combinations of MK and polymers, this study investigates the changes in the microstructures based on SEM combined with CT scan analysis scan technologies. The findings show that the microstructure of the pore of hardened concrete modified with combined MK and hybrid polymers is significantly improved compared to samples with MK or polymers alone. This indicates that this approach can be effectively used to provide additional proof on the strength and porosity properties of high-performance concrete.

Keywords: CT-Scan, metakaolin, hybrid polymers, porosity, microstructure, durable concrete

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1. Introduction

The microstructure of concrete has an important impact on the physical properties and durability characteristics [1]. The pore system, which defines the microstructure, is the key factor to control the regulation of different mechanical and chemical properties behaviours [2]. The pore systems in concrete are formed due to chemical reaction of the concrete components, changes in materials (resulting from the cement hydration) and methods of placing the concrete. Moreover, the pore system varies due to the ongoing and continuous hydration process of concrete with respect to time [3]. It is understood that the variation in the microstructure of the concrete, due to its porosity, has a significant role in effecting the long-term performance [4,5]. The porosity and the potential migration of water and gases through the material is significantly influenced by the interconnectivity, volume and surface area of the voids [6,7]. In addition, the chemical interaction with harmful solutions, such as Cl-1 ions and CO2, further alter the physical and chemical microstructures of concrete. Therefore, the main aim of creating high strength and durable concrete is to produce hardened concrete with impermeable or small pore size distributions, so it would lower the inherent flow.

Distribution of pore size, volume of pores, number of pores, surface areas of pores, sphericity of pores and connectivity of pores are required to predict the permeability of concrete. However, physical properties of solid phase of concrete and their interconnection are required for prediction of strength and deformation [8,9]. To this end, various measurement techniques of the microstructure such as Scanning Electron Microscopy (SEM) and Computed Tomography (CT) were developed over the years to understand the microstructure of concrete [10].

Previous studies have found an improved strength and durability properties of concrete by the substitution of a percentage of cement by metakaolin. On other hand, some polymers have been used mainly to improve the durability properties [11,12]. Thus, the addition of polymers and metakaolin in combination has the exciting potential to increase the properties of concrete further.

The main aim of this study is to understand the changes in concrete microstructure due to the application of metakaolin and hybrid polymers used in combination. At first, therefore, metakaolin and polymers in concrete were investigated alone and compared against a conventional concrete using SEM and CT-scanning technologies. This approach would provide a datum understanding of the microstructure of concrete, which would enable a further investigation on transport phenomena of porous concrete using numerical modelling. Furthermore, these results would provide an opportunity to validate the microscopy and similar techniques of microstructure measurement methods used in this study. Investigation also should be directed to understand changes in microstructures with time as the hydration of cement continues with time. To this end, a few samples were tested at different ages.

2. Experimental investigation

The materials used were a Portland limestone cement conforming to the requirement of British specification, natural sand of 4.75 mm maximum size and crushed limestone with a maximum size of 14 mm was used for the coarse aggregate. The cement was partly substituted with metakaolin and modified together with hybrid polymers of Styrene butadiene resin (SBR) and polyvinyl acetate (PVA). The chemical composition of the cement and metakaolin is presented in Table 1.

Table 1. Chemical composition of the cement and metakaolin

Material	Chemical composition, %								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	L.O.I
Cement	16.19	4.19	2.75	65.00	0.86	0.14	0.51	3.19	1.9
Metakaolin	59.50	34.00	0.70	0.6	0.6	0.00	2.0	1.1	0.8

Four different mixtures as shown in Table 2 were used in this investigation. The mix proportion by weight of cement, fine and coarse aggregate for all mixtures were kept constant throughout the work at 1:1.5:3. It should be noted that the metakaolin was used as partial replacement to cement, and SBR and PVA were used as additive to the concrete mixtures. These mix combinations were used to study the effect of metakaolin and hybrid polymers (SBR and PVA) separately (using mixture 2 and 4 respectively) and then compare the combined effect of metakaolin and hybrid polymers (mixture 3). These mixtures have been selected based on a previous study [13] in which it was shown that mixture 3 improved concrete strength and durability in compatibility with other mixtures. The main objective of this work is to understand the microstructural changes in concrete in the presence of metakaolin and hybrid polymers.

Table 2. Mixtures studied in this paper

Mixtures	MK %*	Polymer %*	Water cement ratio W/C
1	0	0	0.45
2	15	0	0.45
3	15	5 (4% SBR+1%PVA)	0.45
4	0	5 (4% SBR+1%PVA)	0.45

* % by the weight of cementitious binder (cement + MK)

2.1 Scanning electron microscopy

Scanning electron microscopy was used to give an in-depth understanding of the microstructure of concrete compare to optical microscopy. System magnification of 5000x was used to obtain SEM images on samples of (20 × 10 × 5 mm) at four different ages.

2.2 Computed tomography scan technology

In this investigation, the method of image segmentation was adopted for detecting volume, surface area and distribution of voids. It gives 2-dimensional (2D) and 3-dimensional (3D) data for materials. Specimens with the dimensions of 100 x 100 x 100 mm3 were prepared in this investigation. The images were generated using Phoenix device with the setting of 120 kV for the tube voltage and 200 µA for the current [10], and then analysed using VGStudio Max software to classify the voids defects and displayed in 2D and 3D dimensioning.

3. Results and discussions

3.1 Changes in microstructure due to MK and hybrid polymers

Cement continues hydrating with time, and depends upon the availability of free and capillary water. To observe this behaviour, SEM was employed at four ages of 7, 28, 56 and 270 days to gain a time related perspective. Figure 1 shows the SEM images captured at magnification 5000-fold with a scale bar of 30 µm. The results illustrate that the amount and size of voids decreased with increase of hydration time up to 270 days for all the mixtures. The SEM images of mixture 1 displays that micro and macro pores exist together at the age of 7 days. The presence of macro and micro voids in mixture 1 are significantly reduced between 7 and 28 days, and gradually reduced after 28 days until 270 days. This can be attributed to the development of the hydration process between cement and water early stage. Conventional concrete is expected to reach a significant amount of its compressive strength at 28 days [14,15] and a gradual increase in strength after 28 days. This can be justified using the microstructure of mixture 1 as shown in Figure 1.

In the SEM image of mixture 2 when cement was replaced with MK at 15%, the texture of the concrete was dense with few macro voids and cracks compared to mixture 1 at age of 28 days. This is possibly due to the metakaolin reaction as a pozzolanic material with the calcium hydroxide, which causes an increase in the formation of C-S-H gel inside the capillary pores. A denser morphological structure continues to grow with time in mixture 2. This observation can be used to justify that the MK increases the mechanical and durability properties of concrete with time as concluded by Al Menhosh et al. [13], Shekarchi et al. [16] and Al-Akhras [17].

Mixture 4 demonstrates a large area of a polymer film covering the concrete particles making the mix smoother with few micro voids. It should be noted that the SBR moderately reacts with cement while PVA is a typical water soluble polymer [18]. It can be seen that the voids are reduced when incorporating polymers, as observed by Konar at al. [19] and Wang et al. [20], while the morphology of hydrated pastes in mixture 1 and mixture 4 appeared to be the same. However, the porosity of mixture 4 texture is less that the mixture 2. It should be noted that a stronger solid phase was developed in mixture 2 compared to weaker film in mixture 4.

The results in Figure 1 clearly show that mixture 3 possesses less macroscopic voids with less connectivity than the other mixtures at any stage. Also, mixture 3 revealed a smoother structure with less pores and the constituents appear more coherent during the hydration time from 7 to 270 days as the cement hydration progressed. This is due to the high reactivity of metakaolin and the polymers contributed to refinement of the pore size by formation of a polymer film during the hydration time which fills most of the pores system in cement paste and/or covers some of hydrated particles.

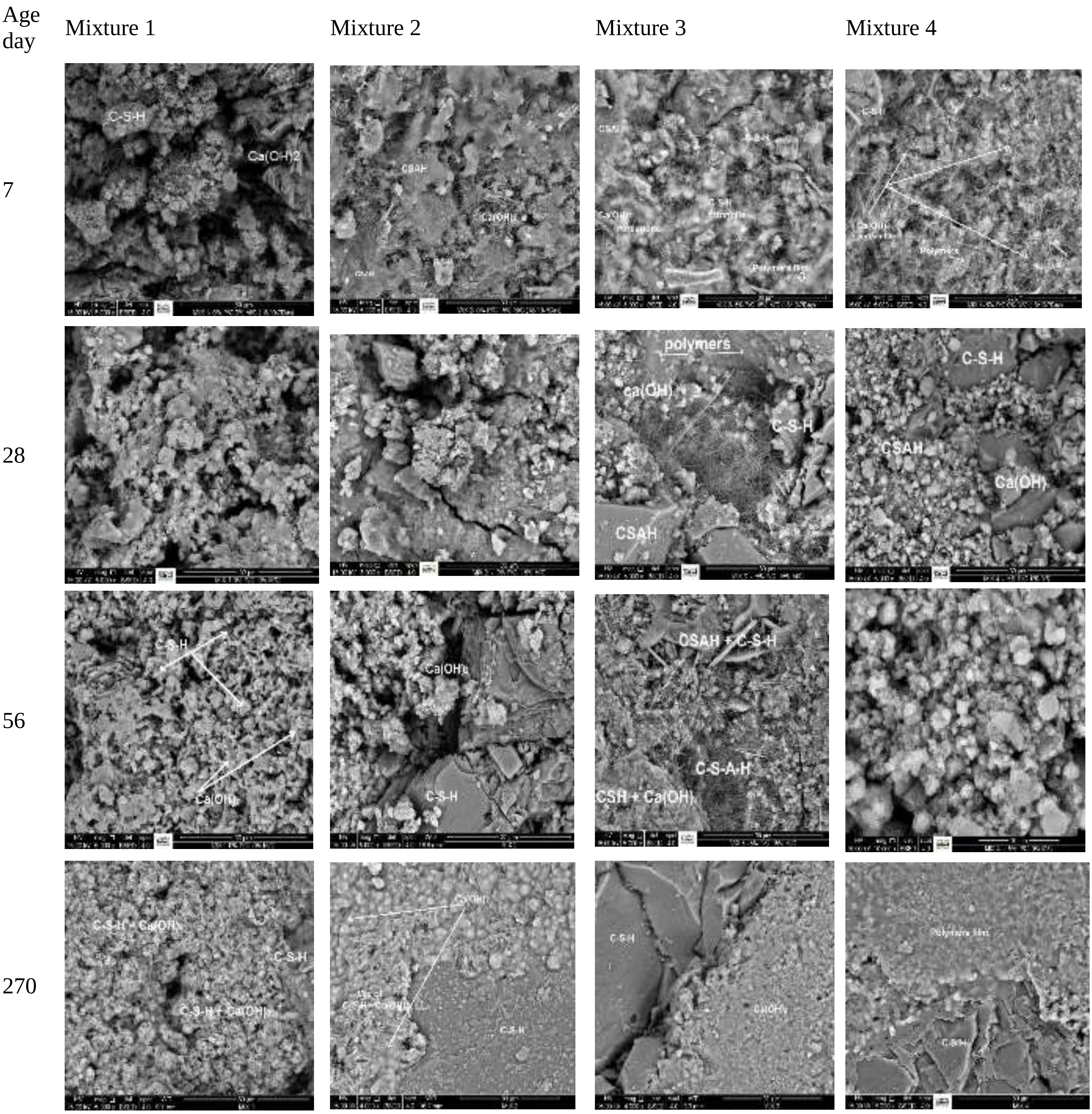


Figure 1. SEM for the four mixtures at different ages at 5000x magnifications

3.2 Porosity analysis using 2D SEM micrographs

The MATLAB image processing toolbox was used to analyse the SEM micrographs to study the interconnectivity of voids in the concrete samples. Greyscale analysis was implemented in this study. The SEM images were converted by thresholding the initial greyscale in to binary images, where pixel intensity greater than the threshold value were set to 1 (white) and all other pixels were set to 0 (black) [21,22]. The voids on the specimens are displaced in the SEM image in white and the solid phase in black. It should be noted that this method of quantitative analysis would only work when the SEM images are taken using the same power intensity and magnification, and location of SEM micrograph in the cement paste.

Sahu et al. [23] reported that "the image can be segmented into void and solid by setting the threshold intensity. Using the image processing software with setting an appropriate threshold of the greyscale, the voids area of the concrete can be quantified, and the white void space is clearly distinguished from the black solid". This was adopted in determining and comparing the percentage of void area between the modified concrete and reference mixture. SEM micrographs from all four mixtures were subjected to this image processing analysis to provide a qualitative discussion rather than quantitative information [24].

Figure 2 shows the image processing analysis of the metakaolin-modified concrete (mixture 3) in comparison with the reference mixture (mixture 1) at 7 and 28 days ages at 5000x magnification. The left aligned images are the SEM images, while the images on the right are the corresponding binary images. Greyscale of 0.5 was adopted in the analysis of the image processing mechanism. A similar study on the SEM micrographs, where the differing greyscale was used as a threshold intensity was conducted by Sahu et al. [23] and Badger et al. [25]. Visual inspection clearly shows that mixture 1 has almost 200% more pore spaces than the modified concrete, mixture 3 at the age of 7 days at 5000x magnification (see Figure 2-a). In addition, the solid phase in mixture 1 almost grows twice at the age of 28 days compared to 7 days. This results due to the process of cement hydration over time. However, the void spaces in the mixture 3 at the age of 28 days slightly higher compared to concrete at the of 7 days (see Figures 2-a and 2-b). As mentioned, this quantitative study is subjected to the location of SEM micrograph were taken. The results show lower area of pores in the modified concrete (mixture 3) compared to the reference mixture 1.

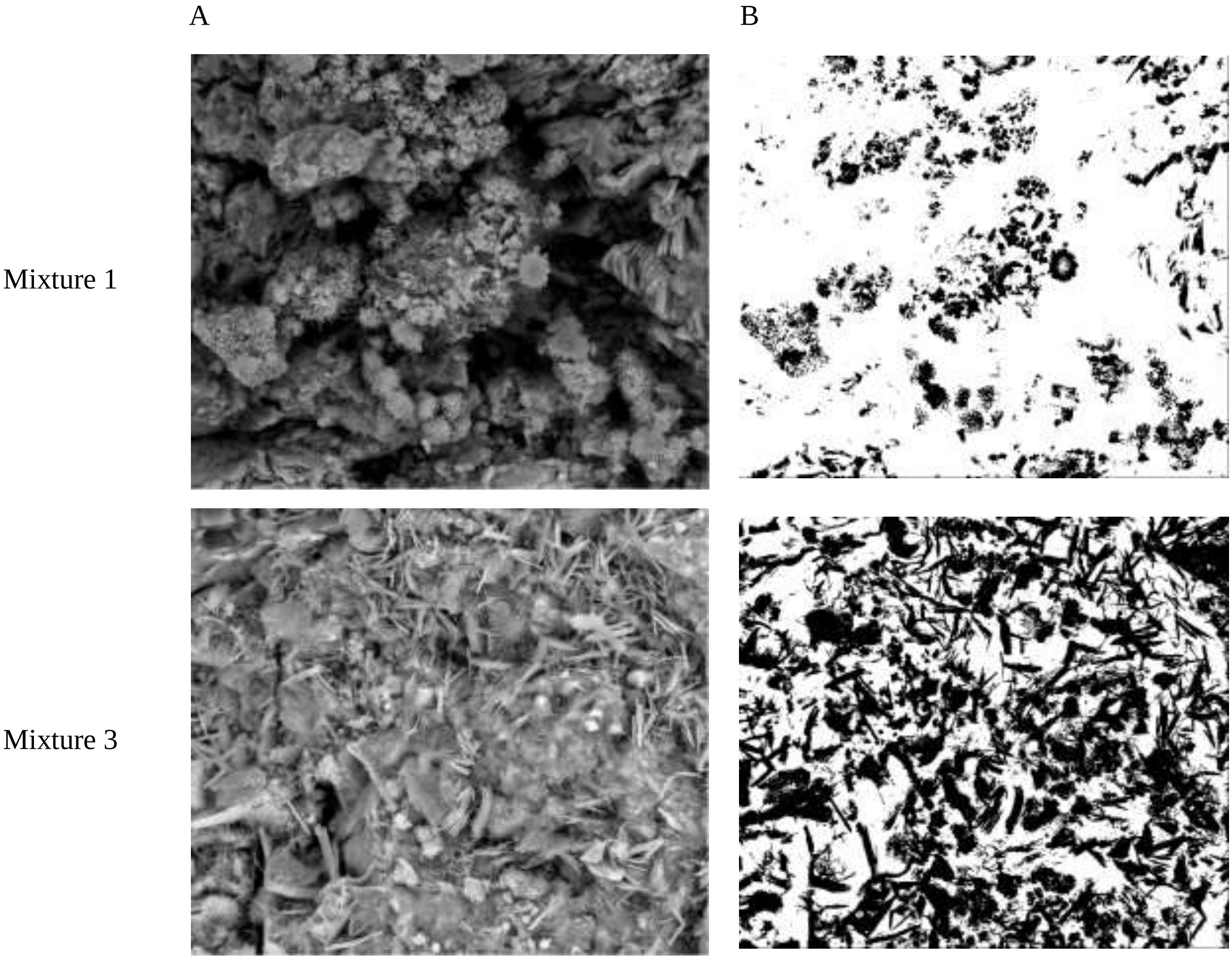


Figure 2-a. Image binarization for mixtures 1 and 3 at 7 days

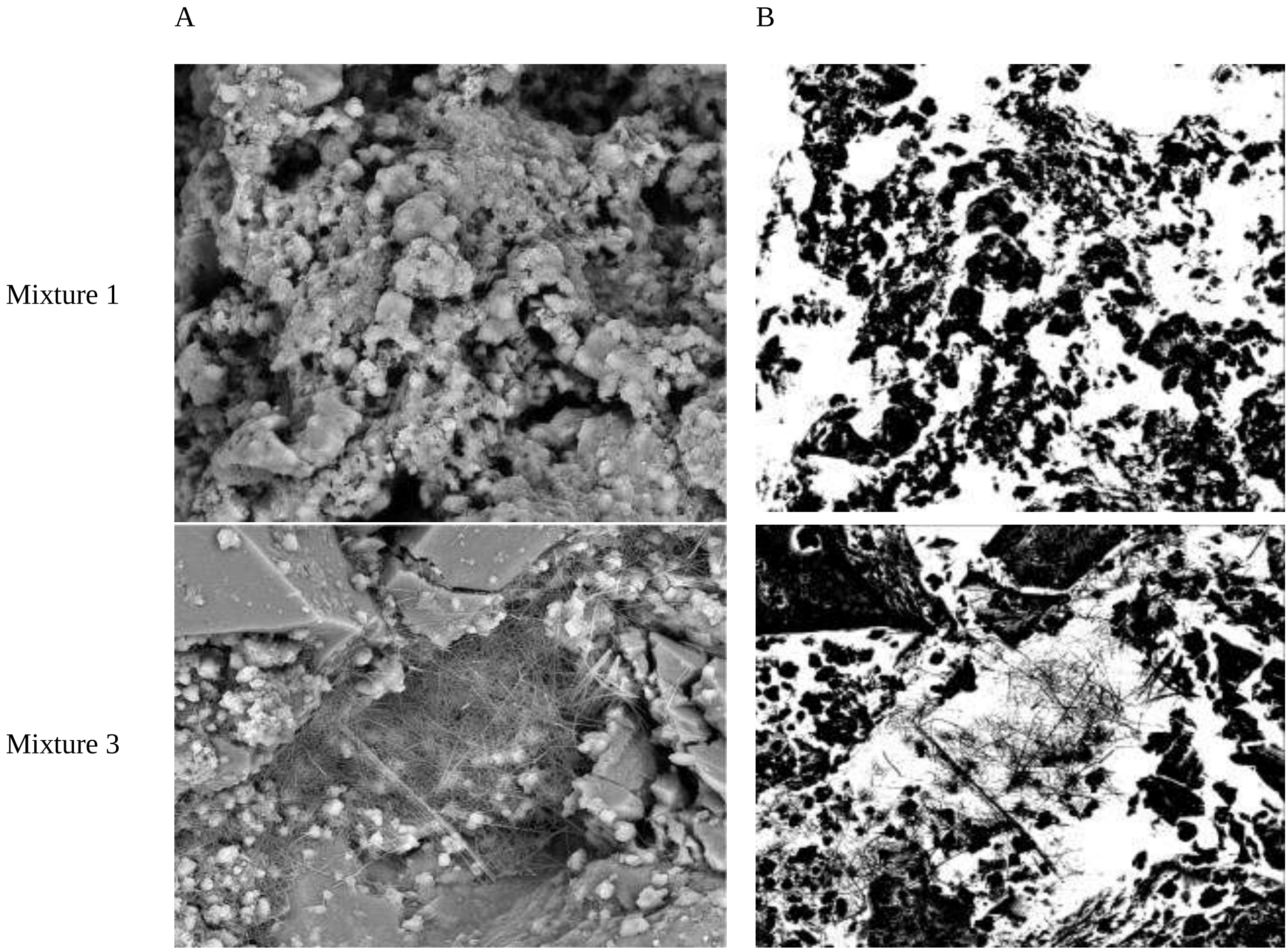


Figure 2-b. Image binarization for mixtures 1 and 3 at 28 days

3.3 Porosity analysis using 3D CT scan

In this experiment, a CT scan analysis was performed to show the internal pore structure of all the four mixtures under study in 3D. Figure 3 shows an example for a typical section in three perpendicular axes of the reference mixture (mixture1) in which disconnectivity of voids, number, distribution, total volume and total surface area of voids can be seen and determined. The blue colours refer to the pores inside the concrete.

Figure 4 (a) illustrates that the MK and hybrid polymers separately reduce the total volume of voids and number of voids in comparison with the control mixture at 56 days. However, the combined MK and hybrid polymers slightly reduces the volume of voids but not the number of voids when compared to the sample with MK alone. This might be attributed to a delay in cement hydration due to the polymers effect as observed in SEM micrograph study. Furthermore, the number of voids curve shows that the presence of micro cracks is significant as the polymers tends to fill the macro cracks. Also, the results show that the porosity values of the four mixtures are 2.89%, 2.72%, 2.43% and 2.50%, respectively, as shown in Figure 4-b. The results show that the porosity reduced by 20% for the modified concrete by adding MK (15%) and hybrid polymers (4% SBR+ 1% PVA) compared to the concrete of the reference mixture. In addition, the modified concrete (mixture 3) showed 18% lower surface area but not significant compared to concrete modified with MK alone. This leads to lower permeability results from reducing the pores and their size and hence the connectivity of the system.

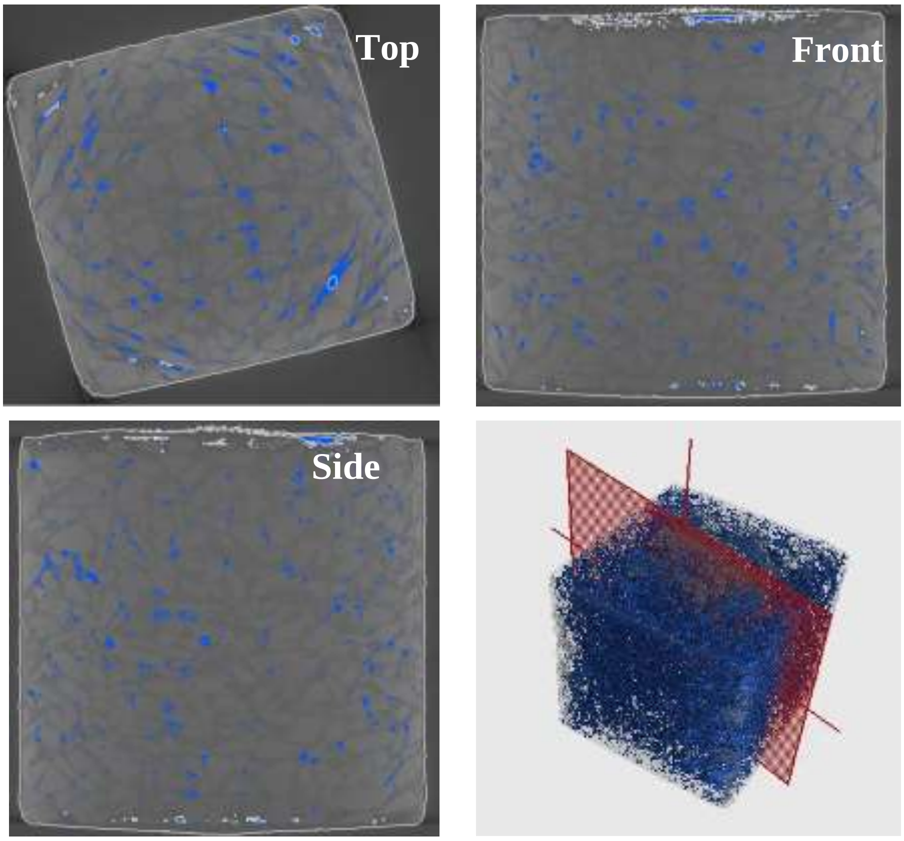
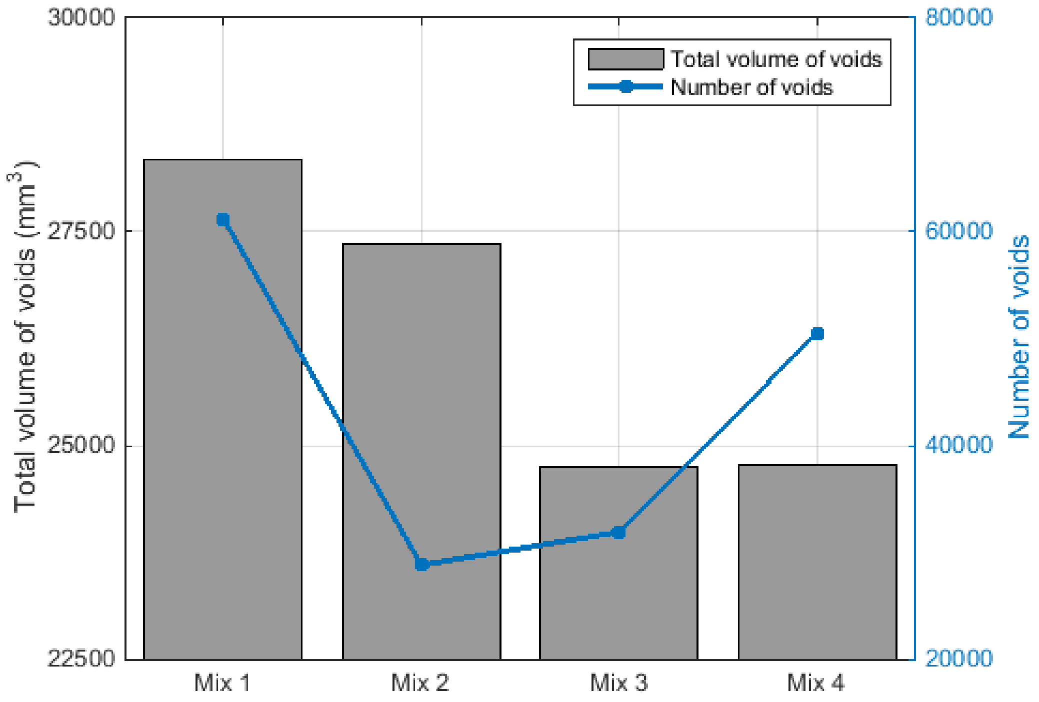


Figure 3. CT scan of mixture 1 concrete cube at age 56 days with 3D visualization of pores system in blue colour

Sphericity represents how closely the shape of the voids approaches that of a mathematically perfect sphere, where the value 1 represents a perfect sphere. Understanding the distribution of voids volume, surface area of voids and sphericity provides details about the internal structure of the voids. Figure 5 demonstrates the relationships between the volume of voids with the sphericity and the surface area of voids. The obtained findings indicated that the void volume is observed to be as spherical function. Also, small voids are closer to the sphere sphericity value of 1. It has been shown that the metakaolin and polymers reduces the larger voids by developing more solid phase in the cement. However, the combined metakaolin and polymers further reduces the larger volumes. Hence, more spherical voids were observed in the modified concrete with metakaolin and hybrid polymers (mixture 3), indicating the polymer effect and the pozzolanic activation of MK in reducing the amount and size of voids and hence increases the sphericity. Surface area and connectivity of the voids are the main factors governing concrete permeability. The surface area of voids within concrete must be reduced when concrete is exposed to extreme environments (e.g. concrete submerged into aggressive solution). There is clear evidence that the MK and hybrid polymers reduce the surface area of voids and complement to other.

Movement of water within concrete elements is governed by the pores, especially the size and interconnectivity of them. Figures 6 and 7 demonstrates the significance of the pore distribution for the concrete mixtures used in this study. Figure 6 presents the 3D voids size distribution for all the four mixtures at six groups of void volumes. On those six volume groups, the surface area of voids and corresponding porosity are shown in Figure 7. This study was conducted to investigate the distribution of voids in detail and to understand the changes in voids in the presence of MK and hybrid polymers. The results of visual inspection of all mixtures showed that the smaller void sizes appear more spherical than the larger sizes as summarised using Figure 5. It should be noted that the all the samples were cast using the same methods to minimise or eliminate the voids due to concrete compaction. In short, the compaction rate was controlled to keep this constant.

(a)



(b)

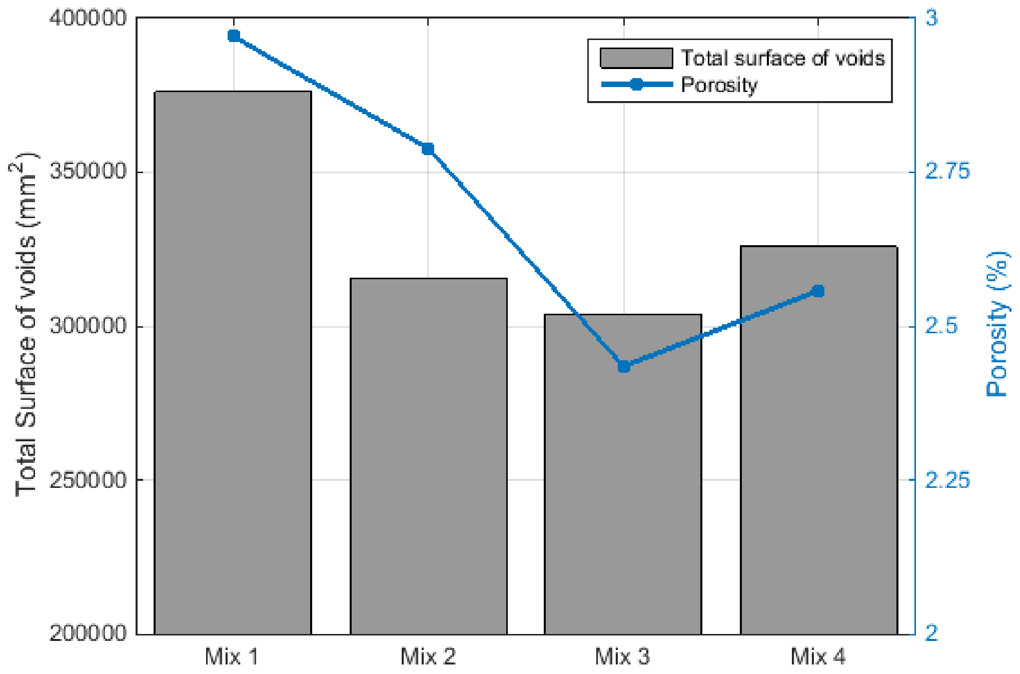


Figure 4. (a) Total volume of voids and total number of voids and (b) total surface area of voids and porosity of voids at age 56 days

The 3D images of mixture 2 have a low number of voids and the shape appear to be circular as the diameter and the surface area of the pores has decreased in comparison with the reference mixture (mixture 1), leading to gas and liquid porosity reduction. This is due to the contribution of the metakaolin reaction in producing more calcium silicate hydrate that fill the voids in the cement matrix and making them more spherical (see Figure 5).

It can be seen that the hybrid polymers (SBR and PVA) reduce the voids in the range between 25 mm3 and 125 mm3 in comparison to metakaolin (Figure 7). In addition, the capillary pore size was refined and the spaces between the voids were filled due to the polymer film formation, leading to a dense microstructure compared to the control concrete. In addition, the capillary pore size was refined and the spaces between the voids were filled due to the polymer film formation. However, the modified concrete with metakaolin and hybrid polymers (mixture 3) shows less and disconnected voids in comparison with the reference mixture (mixture 1) and modified mixes with metakaolin (mixture 2) and hybrid polymers (mixture 4). Also, the lower porosity results and surface area for voids of size larger than 25 mm3 were recorded for mixture 3 compared to the other mixtures.

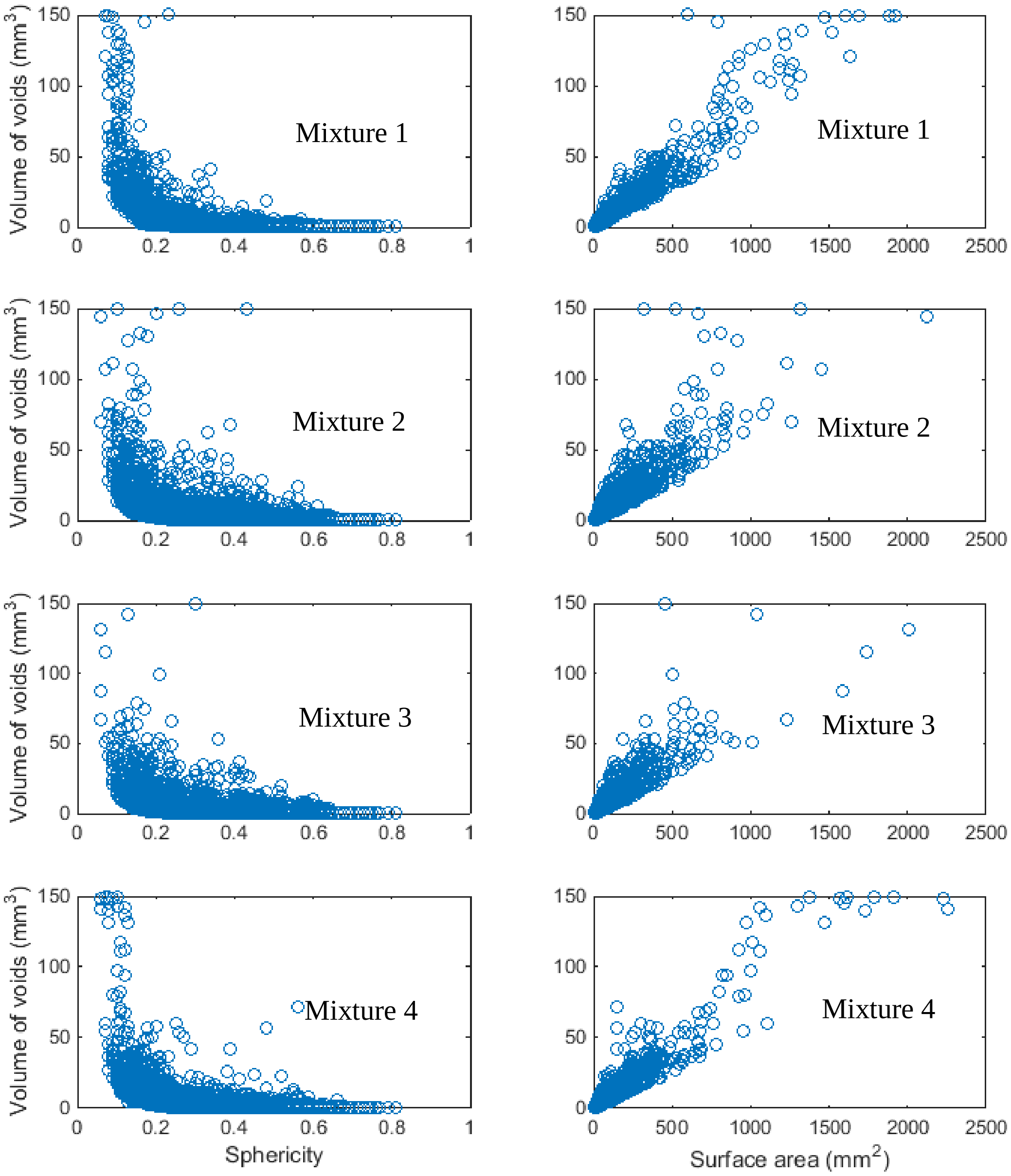


Figure 5. Correlation plots between volume of voids with the sphericity and surface area of voids of all four mixtures at the age of 56 days

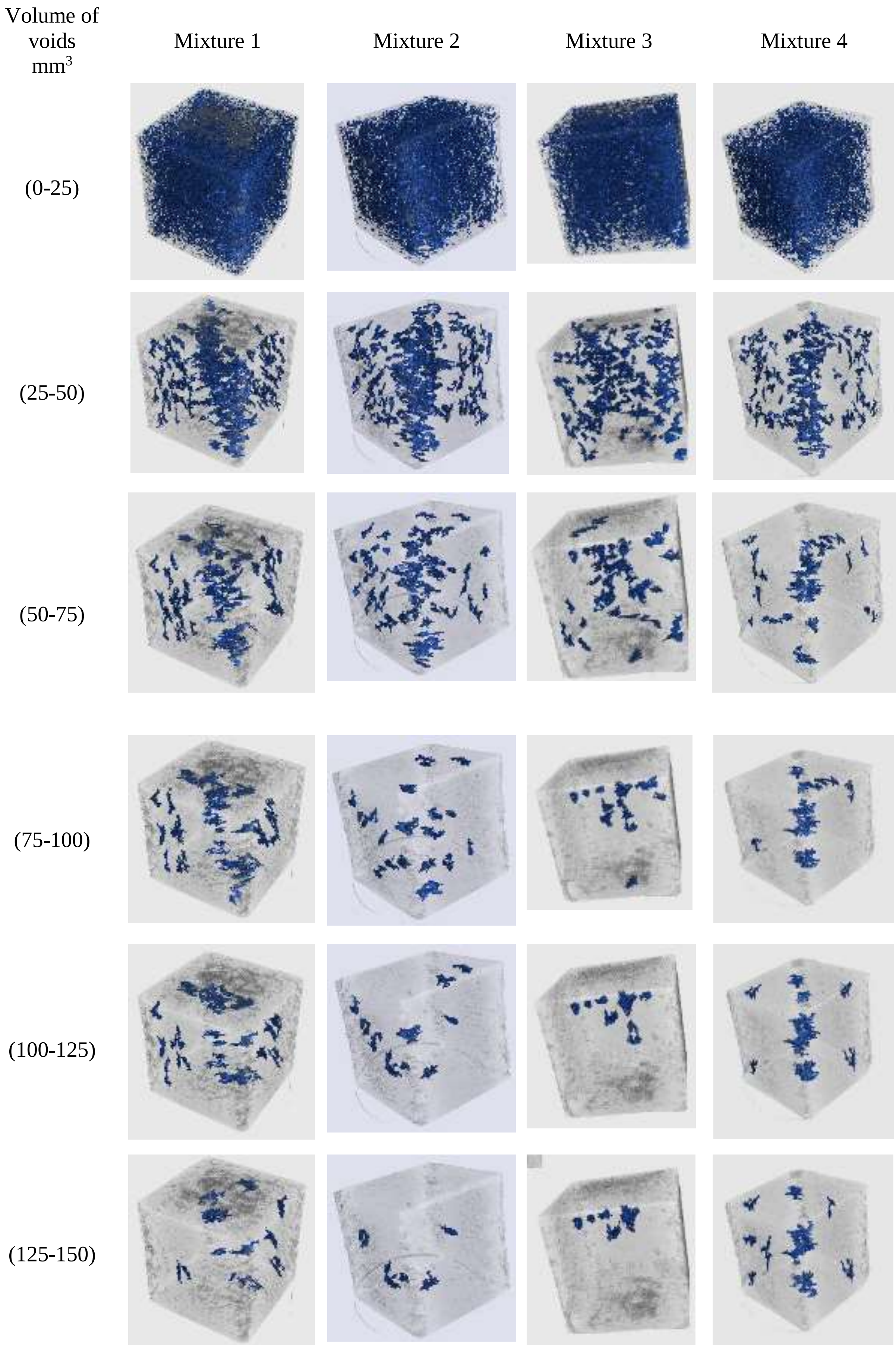


Figure 6. Voids size distribution

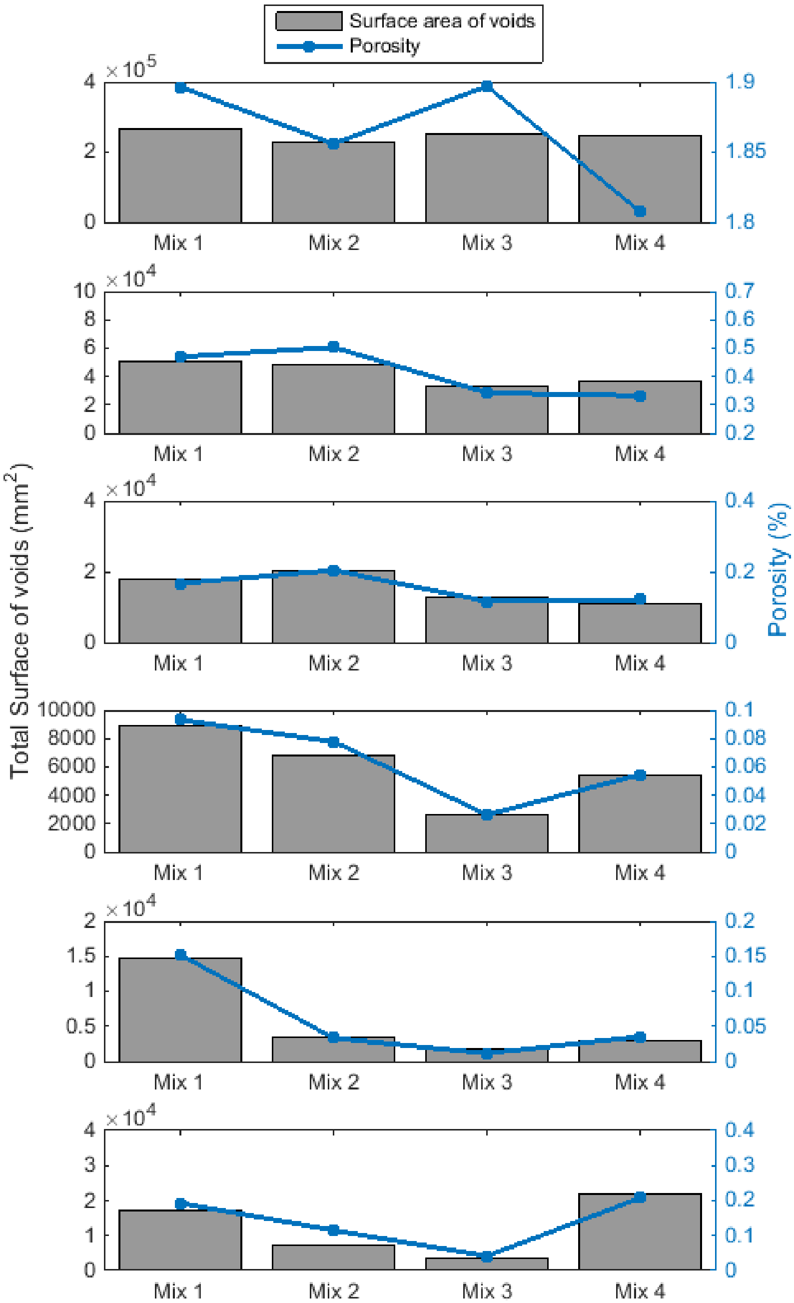


Figure 7: Surface area of voids and porosity

4. Conclusion

Changes in microstructure of concrete due to metakaolin and hybrid polymers were studied using SEM and CT-scan in this research. The visual observation of SEM image proves that the solid phases in the microstructure of the modified concrete has been increased. It can be also concluded that the polymer film formed around the solid phase, which delays the reaction of cement and metakaolin. However, the metakaolin continues to react with time and enhance the solid phase of the structure. In addition, CT scan results show that the metakaolin and the hybrid polymers contributed to refinement of the size, distribution and connectivity of voids. Especially in concrete mixture 3, voids with lower surface area were produced resulting in a decrease in the concrete porosity.

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