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Effect of (MgO/CaO) molar ratio on glassy phase viscosity and pyroplastic deformation in floor tiles

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In this study, effect of MgO/CaO molar ratio on the floor tiles properties was investigated. The viscosity of the bodies was successfully calculated by fleximeter analyses data. High MgO/CaO ratio causes enhancement of the densification temperatures and dissolution of the crystals in the floor tile body. The results showed a, during firing, high MgO/CaO ratio up to 6,505 value, formed, low viscosity liquid phase and allowed low sintering temperature approximately 20 °C when compared to the standard floor tile body. For YK_3 composition will be evaluated due to has allowable deformation amount for the production. This floor tile composition will be successfully produced in production line.

Keywords: Floor tile, Deformation, Viscosity, Sintering

Introduction

Ceramic floor tiles that are fired at high temperatures such as 1,150-1,180 °C for 30-45 min and have water absorption below 3%. Floor tiles can be produced either glazed or unglazed, or they can be produced as coloured body by adding color pigments to their initial compositions. Ceramic floor tiles are partially the vitrified product of mixtures of clay, quartz sand, and feldspar, after heat treatment at temperatures in range 1,150-1,180 °C. The primary purpose of these three components may be described as follows [1-3]: Clays provide plasticity to the body and provide dry strength. They gives the colour depends on their own color and impurities. After clays, feldspars have also critical role in the ceramic tile production sector. Feldspars are used as melting agents in the recipes. They are reduce the sintering temperature by forming liquid phase when the ceramic body is firing. In addition to the these raw materials which have plastic and melting properties in ceramic structures, there is a need for a non-plastic filler which will keep the body integrity in high temperature ranges. Quartz acts as a skeleton in the body. It is the main filler which is incorporated into the ceramic body as a real component or as a component from clay and feldspar. It constitutes the roughest particle size part of the structure. The large grain size interval provides resistance to cracks during drying and prevents deformation by forming a skeleton during firing [4, 5]. Maiti et al. [6], reported that during firing, tile body assists dissolution of quartz, recrystallization of secondary mullite and reduction of closed pores in the tile body. It has been also reported by Bull [7], alkaline earth materials in the tile composition resulted in the speedy glassy phase formation during fast firing cycle. During fast firing cycle, for some body compositions, glassy phase viscosity decreases suddenly and it could create some distortions and deformations on the sample during firing. Pyroplastic deformation is defined as deformation which occurs the effect of product weight during high temperatures [8]. By understanding the compositon effect on melting behaviour of the ceramic body, it can be understood that pyroplastic deformation, reactions and mechanical properties during fast firing [5]. Öztürk et al. [9] investigated the effect of alkaline oxides on porcelain tiles using factorial design method. MgO, CaO, Na2O and K2O were used in the new compositions. It was found that the strength increased, and water absorption decreased by means of alkaline oxide variation in the porcelain tile body. Rastelli et al. [10], studied effects of spodumene and zirconium based materials on the reology of the porcelain tile slurry. Nevertheless, in this study effect of these raw materials on the sintering behaviour body did not mentioned. n this study, the effect of these compositions on glassy phase viscosity on wall tile was not investigated and only wall tile was taken into consideration. Elmas et al. [11], studied about the effect of boric acid and lithium carbonate scombination on sintering and microstructure of single-fired wall tile bodies. They found that combination of the lithium-carbonate and boric acid provided low sintering temperature, and high strength values for single fired wall tiles. Sousa et. al. [12], investigated sintering behavior of porous wall tile bodies during fast single firing process. In this study, wall tile composition had red clay, limestone and

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quartz. Its technical properties and microstructure was evaluated considering the different sintering temperatures of the wall tile body.

Many studies about glassy phase viscosity of ceramic bodies have been reported. Porte et al. [13], studied about creep viscosity of vitreous china composition containing different mullite and quartz cystals. They used four point bend rig for creep measurement. However, they did not report any information about pyroplastic deformation relation with glassy phase viscosity. Tuna et al. [14], studied influence of porcelain tile starting composition containing spodumene on the pyroplastic deformation evolution during firing. They found that pyroplastic deformation was decreased with increasing Li_2O addition in porcelain stoneware tiles. Tuncel et al. [8], investigated effect of different Na_2O/K_2O and SiO_2/Al_2O_3 ratio affects the viscosity of the system as the amount of mullite increases. Other oxides that affect the vitreous phase viscosity in the ceramic bodies are magnesium oxide and calcium oxide. These oxides are generally used for allow the tiles firing at short firing cycle (24-30 min at 1,150-1,180 °C) and increasing sintering rate in the ceramic bodies. Dondi et al. [15], reported that magnesium accelerate the sintering and decrease the ripenning temperature of the body and with this way narrowed the firing interval of the body. On the other hand, magnesium containing porcelain stoneware tile compositions shows lower mechanical strength due to increasing porosity. Mukhopadhyay et al. [16], investigated the effect of talc component in illitic clay composition on thermal, mechanical properties and microstructure of the bodies. Talc is shown as $3MgO.4SiO_2.\ H_2O$ formula and it is magnesium silicate structure. It was observed that talc/feldspar composition reduced the vitrification temperature. MgO, which is incorporated by addition of talc provides more glassy phase formation with low glassy phase viscosity. Biasini et al. [17], designed porcelain tile composition containing different talc and chlorite components. The occurance of magnesium silicates does not affect the technological properties of semi-finished product, but it influences remarkably the firing behaviour. However, in these studies, the effect of glassy phase viscosity on pyroplastic deformation was not specified for floor tiles. Consequently, the research objectives of this study were the first to develop and understand about how viscosity of ceramic floor tile body changes as a function of alkaline earth oxides molar ratio, (MgO/CaO), the second objective was to investigate effect of viscosity on pyroplastic deformation of ceramic floor tiles an also understanding this compositional change on microstructure of the tile bodies.

Experimental Procedure

Starting from the standard ceramic floor tile body mix, different amounts of talc and calcite were added into the system. New compositions were denoted as YK_1, YK_2, YK_3 and YK_4. Chemical characterization was carried out by means of wavelength dispersive X-ray fluorescence spectrometry (XRF), using a Philips model PW 2400 XRF instrument fitted with an Rh white fluorescent tube. The samples were prepared as fused beads using a Philips PERL'X3 instrument. Chemical analyses of the compositions are shown in Table 1. Seger formulation was applied to prepare new compositions and MgO/CaO molar ratio was chosen as the main variable parameter to prepare the compositions and amount of total molar alkaline oxides (Na2O and K2O) was kept approximately constant in the compositions. Seger formulation details of the compositions are given Table 2. New compositions were wet milled by a laboratory ceramic jar mill containing 70 wt.% solid and 1.0 wt.% deflocculant, for 20 min. Slips were dried at 110 °C. Samples ($50 \times 50 \times 6$ mm^3) and ($60 \times 6 \times 6$ mm^3) were hydraulically compacted using uniaxial pressing at 300-350 kg/cm^2. The shaped samples were dried at 110-120 °C for 24 h till the moisture content less than 0.5%.

Sintering temperatures of the compositions were determined by flex point (i.e., temperature at which densification rate is maximum) using the optical

Table 1. Chemical composition (wt%) of ceramic floor tiles recipes.

Compositions	STD (Mean)(S.D)	YK_1 (Mean)(S.D)	YK_2 (Mean)(S.D)	YK_3 (Mean)(S.D)	YK_4 (Mean)(S.D)
SiO_2	70,39±2,0	62,2±2,0	62,1±2,0	62,27±2,0	61,40±2,0
Ti_2O	0,55±0,01	0,64±2,0	0,57±2,0	0,62±2,0	0,64±2,0
Al_2O_3	17,95±1,0	20,92±1,0	20,26±1,0	20,62±1,0	20,70±1,0
Fe_2O_3	0,75±0,01	1,22±0,01	1,11±0,01	1,22±0,01	1,20±0,01
MgO	0,93±0,2	2,19±0,2	2,54±2,0	3,18±2,0	2,55±2,0
CaO	0,74±0,2	1,12±1,0	1,16±1,0	0,14±1,0	1,12±1,0
Na_2O	2,67±0,2	5,27±0,2	5,31±0,2	5,05±0,2	5,18±0,2
K_2O	1,31±0,2	1,41±0,2	1,50±0,2	1,56±0,2	1,44±0,2
L.O.I	4,71±0,2	5,40±0,2	5,45±0,2	5,34±0,2	5,73±0,2

* L.O.I: Lost of ignition

Table 2. Seger formulations of the compositions.

Components	STD (Mean)(S.D)	YK_1 (Mean)(S.D)	YK_2 (Mean)(S.D)	YK_3 (Mean)(S.D)	YK_4 (Mean)(S.D)
MgO/CaO	4,990	5,41	4,450	6,505	5,103
Na_2O/K_2O	0,905	0,915	0,941	0,991	0,970

dilatometer (Misura 3.32, ODHT-HSM, Expert System Solutions, Italy). Samples were heated in an optical dilatometer at a rate of 50 °C/min up to 1,250 °C without soaking at peak temperature in air atmosphere condition to determine flex points as stated by Paganelli [18]. Total heat treatment was approximately 30 min and the peak temperature was 1,160 °C in roller kiln. The firing shrinkages were determined by measuring the diameter of the discs before and after sintering. The water absorption of the sintered disc was measured by a water displacement method according to ISO 10545-3.

The colour values of the new compositions and standard composition were measured by a spectrometer (Minolta CR, 300 Colormeter). The colorimeter operates on the CIELab method, which is utilized technique in the ceramic production to determine the whiteness and colour of the tiles by measuring three main parameters (Hunter parameters) L* (brightness) from absolute white L=100 to absolute black L=0, an (red–green), bn (yellow–blue) elaborated from the visible spectra. The bending strength of sintered samples was measured with an electronic universal tester (Model 5569, Instron Ltd.) by a three-point bending test with a lower span of 50 mm and crosshead speed of 1 mm/min, based on ASTM standard C1161-90. The crystalline phases in the fired samples were determined by XRD analyses. For XRD analyses, sintered samples were scanned from 2θ=5 to 70°, at a scanning speed of 2°/min, using a Rigaku Rint 2000 Series diffractometer with Cu Kα radiation at 40 kV and 30 mA. The crystalline phase composition was quantatively analysed with the software Material Analysis Using Diffraction (MAUD) based on the Rietveld method. Microstructural observations were performed on selected fired samples using a scanning electron microscope (EVO-50, Carl-Zeiss, Germany). Chemical etching was employed to reveal the presence of certain crystalline phases by immersing the relevant samples in 10% hydrofluoric acid (HF) solution at room temperature for 20 s. Qualitative EDX (Oxford Inst. 5108 Link) analyses were performed simultaneously with microstructural observations in order to distinguish the various phases. To determine the pyroplastic deformation behavior of the compositions, rod shapes samples having (80 mm × 7 mm × 7 mm) size were produced and fired using an optical fleximeter (Misura, ODLT Flex 1400-30) with a firing regime of 25 °C/min to 1,160 °C and waiting 5 min at the peak temperature. After fleximeter analysis, the pyroplastic index (PI) values of samples calculated according to Eq. (1) [8]. The viscosity of the ceramic floor tile bodies (η) was calculated using the results of fleximeter analysis according to Eq. (2) [8].

$$PI = (sb^2/l^4) \tag{1}$$

$$\eta = (5gl^4\rho b/32sb^2) \tag{2}$$

where s is the total deformation, b is the sample thickness, l is the distance between supports, ρb is the bulk density of the body, and g is the gravitational constant

Results and Discussion

The chemical and mineralogical compositions of the tiles affect the deformation behaviour of the tiles. For this reason, the crystalline phase compositions of samples fired at 1,160 °C were investigated based on XRD patterns. XRD pattern of standard composition is given in Fig. 1. Quartz, albite and anothite were present in standard floor tile. XRD analysis also was performed on the recipes with increasing MgO/CaO ratio. Comparison of the XRD patterns of the recipes was given in Fig. 2. According to the XRD patterns, the main crystalline phases were quartz, albite and anorthite. In order to determine the composition effect on the crystalline phases more clearly, amount of the crystalline phases and glassy phase were determined. The amounts of crystalline and glassy phases determined by the MAUD programme for all of the compositions are given in Table 3. Standard floor tile composition has 5 wt% albite, 10 wt% anorthite, 60 wt% glassy phase. Different MgO and CaO ratio affected the phase

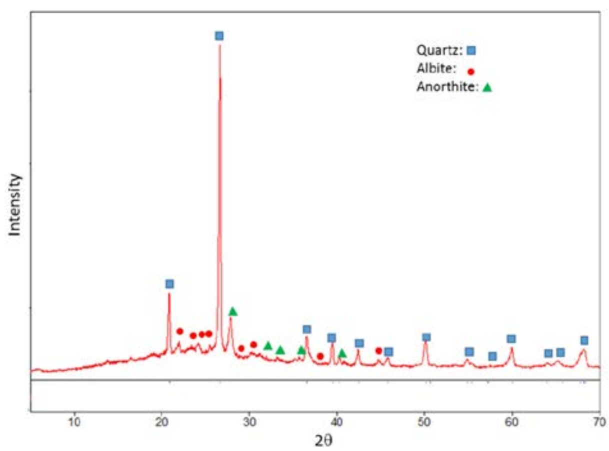

Fig. 1. XRD pattern of the standard (STD) composition.

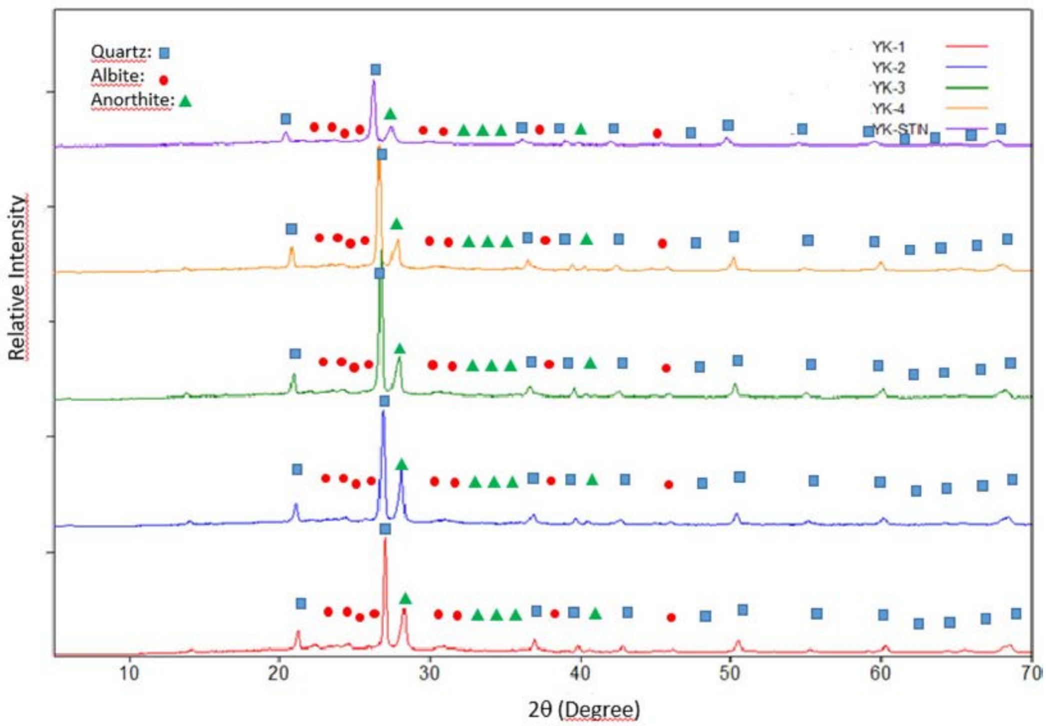

Fig. 2. Comparison of the XRD patterns of the floor tile compositions with standard floor tile body.

Table 3. Quantative mineralogical analyses of the floor tile bodies by MAUD method after firing at 1,160 °C (in wt %).

Compositions	STD	YK_1	YK_2	YK_3	YK_4
Quartz	25	19	27	15	18
Albite	5	8	6	5	9
Anorthite	10	8	9	5	8
Glassy Phase	60	65	58	75	65

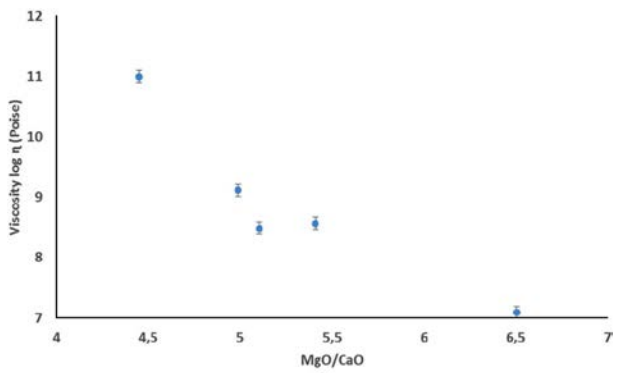

Fig. 3. Effect of MgO/CaO molar ratio on the viscosity of the floor tile bodies at 1,160 °C.

content of the floor tile bodies. When the MgO/CaO molar ratio reached 6,505 in YK-3, the amount of the quartz decreased compared to the STD, and the amount of albite remained constant and there was a decrease in anorthite crystals amount. The increase in the MgO/CaO ratio in YK-3 composition also affected the glassy phase viscosity. The amount of deformation during firing was determined and viscosity values were calculated according to Eq. (2) by using fleximeter. Fig. 3 shows the deformation behaviour of the floor tiles according to firing conditions and Table 4 shows the calculated viscosity values depend on the fleximeter analyses and technological properties of the compositions. The viscosity value of the YK_3 composition at 1,160 °C is 107,09 P, while the viscosity value of the YK_2 composition at 1,160 °C is 108,43 P, it can be showed that the crystalline phases are more effectively dissolved. With the increase in MgO/CaO ratio in the compositions, the increment of glassy phase fastened dissolution of the crystalline phases when compared the compositions have low amount of MgO/CaO ratio. When comparing deformation behaviours with fleximeter analysis (Fig. 4), especially for YK_3 composition, the sample started deformation movement after 36 min. During the sintering period, the deformation movement of the YK_3 composition completed movement after 51 min and total deformation amount is approximately 10,3%. For YK_2 composition with the lowest MgO/CaO ratio, deformation movement started after 45 min and this motion completed after 54 min. Total deformation is about 7.83%. YK_2 was then followed by YK_1, STD and YK_4 compositions. In addition to this, the effect of magnesium oxide and calcium oxide ratio on sintering was investigated by optical dilatometer analyses. In particular, the results of the analysis of the temperature at which the samples reach their maximum sintering point (Table 4). As MgO/CaO ratio increases,

Table 4. Calculated viscosity values & Technological properties of the floor tiles.

Properties	STD	YK_1	YK_2	YK_3	YK_4
Calculated Viscosity (1,160 °C) log η (Poise)	8,40	8,57	8,43	7,09	8,49
Water Absorption (wt.%)	1±0,01	2,5±0,01	3,08±0,01	0,97±0,01	3±0,01
Firing Shrinkage (%) (1,160 °C)	4,8±0,2	4,6±0,2	4,06±0,2	5,66±0,2	4,76±0,2
Flex Point (°C)	1160±2	1165±2	1170±2	1140±2	1165±2
L*	64,81±0,1	69,8±0,1	73,88±0,1	70,15±0,1	68,31±0,1
a*	3,76±0,1	2,8±0,1	4,14±0,1	4,81±0,1	4,92±0,1
b*	14,21±0,1	13,55±0,1	15,33±0,1	16,03±0,1	16,51±0,1
Bending Strength (N/mm^2)	40,20±2,0	41,41±2,0	37,22±2,0	35,67±2,0	39,97±2,0

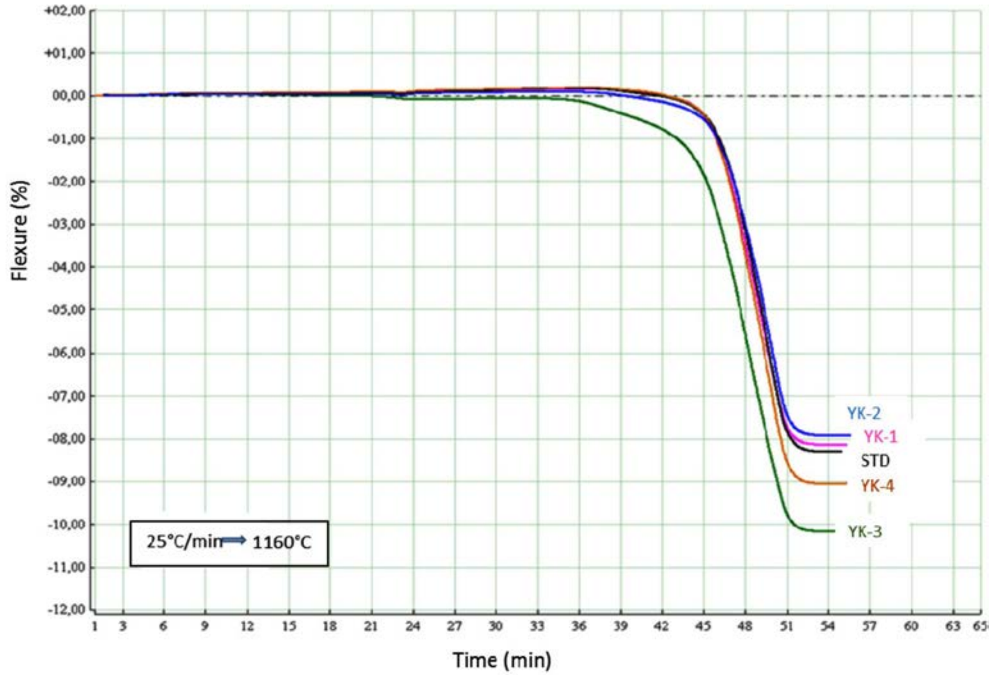

Fig. 4. Deformation behaviour of STD and new compositions.

the flex point of the bodies decreases. YK_2 composition has 4,450 MgO/CaO ratio and its flex point is approximately 1,170 ± 2 °C, while YK_3 composition has 6,550 MgO/CaO ratio and its flex point is approximately 1,140 ± 2 °C. This decrease in flex point is quite remarkable in the compositions. It is evident that by increasing the MgO/CaO ratio in the composition has a sintering accelerating effect. When investigated the literature, an a study performed Dondi et al., about porcelain tiles, the effect of magnesium silicates was emphasized [15]. They stated that magnesium accelerates the sintering of porcelain tile bodies and narrows the firing range of the body. In a study performed by Mukhopadhyay et al., the role of talc on porcelain sintering was investigated. They observed that the talc/feldspar composition reduces the vitrification temperature [16]. It has been determined that magnesium oxide which is incorporated by the addition of talc, provides more liquid formation with lower viscosity, decreases the maturation temperature but narrows the firing range of the body. Therefore, the results of this study are consistent with in the literature.

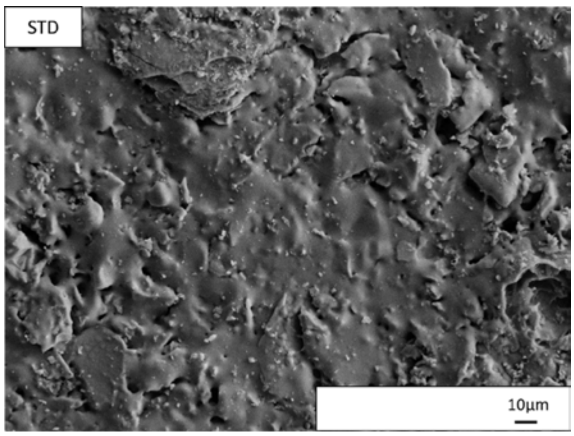

Fig. 5. SEM micrograph of the standard floor tile (STD).

SEM images taken from the polished surfaces of the industrially fired standard and new floor tile bodies are represented Fig. 5 and Fig. 6. When the surface microstructures were investigated, generally similar structures could be seen Fig. 6. Therefore, EDX analyses of the samples were carried out in order to see types and distributions of the crystalline phases, pores, etc. depend on the compositions. In addition, a typical SE (secondary electrons) image taken on the fractured surface etched with 10%HF solution for 20 s to selectively remove the glassy matrix shows some of the constituent crystalline phases. For standard floor tile body composition (Fig. 7), irregular shaped particles contain mainly silicon and oxygen so being quartz crystals (Fig. 7 (a)), presence of small spheroidal crystals forming clusters that contain

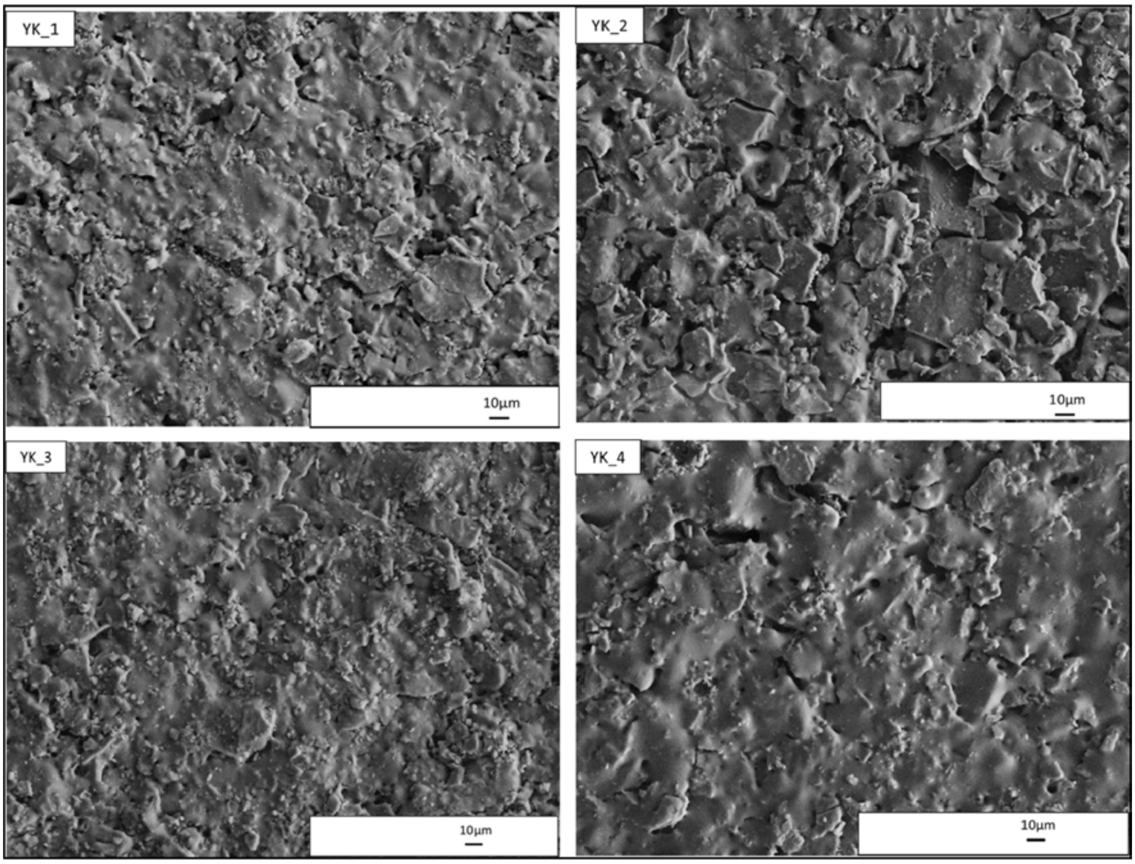

Fig. 6. SEM micrographs of the floor tile compositions.

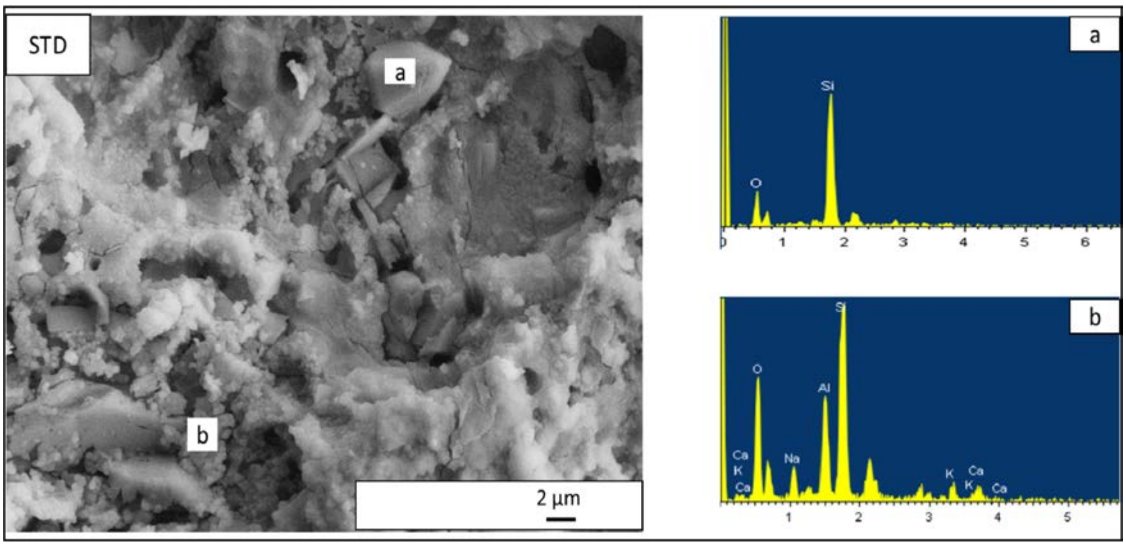

Fig. 7. EDX patterns taken from the standard floor tile (STD) compositon. (a) EDX analyses of irregular shaped crystal in STD composition, (b) EDX analyses of a cluster of spheroidal crystals in STD composition.

mainly calcium, sodium, aluminium, silicon and oxygen so being attributable to anorthite and albite crystals (Fig. 7(b)). Selected microstructures of the YK_2 and YK_3 compositions are shown in Fig. 8 and Fig. 9. The microstructure of the YK_2 composition is shown in Fig. 8. In this composition, according to the results of (a) EDX analysis of round crystalline clusters, it is seen that there is a region of albite and anorthite crystals and the grain sizes are around 1-2 microns. Irregular and large grains are also present (b), according to the EDX analysis taken from these regions, it is seen that these grains are quartz crystals. Microstructure of YK_3 composition is given in Fig. 9. This composition also contains quartz crystals (Fig. 9(a)), albite, anorthite (Fig. 9(b)) and but the crystalline dimensions are quite small (400-500 nm). Less viscous liquid phase and its able to eliminate larger pores and increase crystals dissolutions.

Conclusions

In this study, floor tile compositions which contain

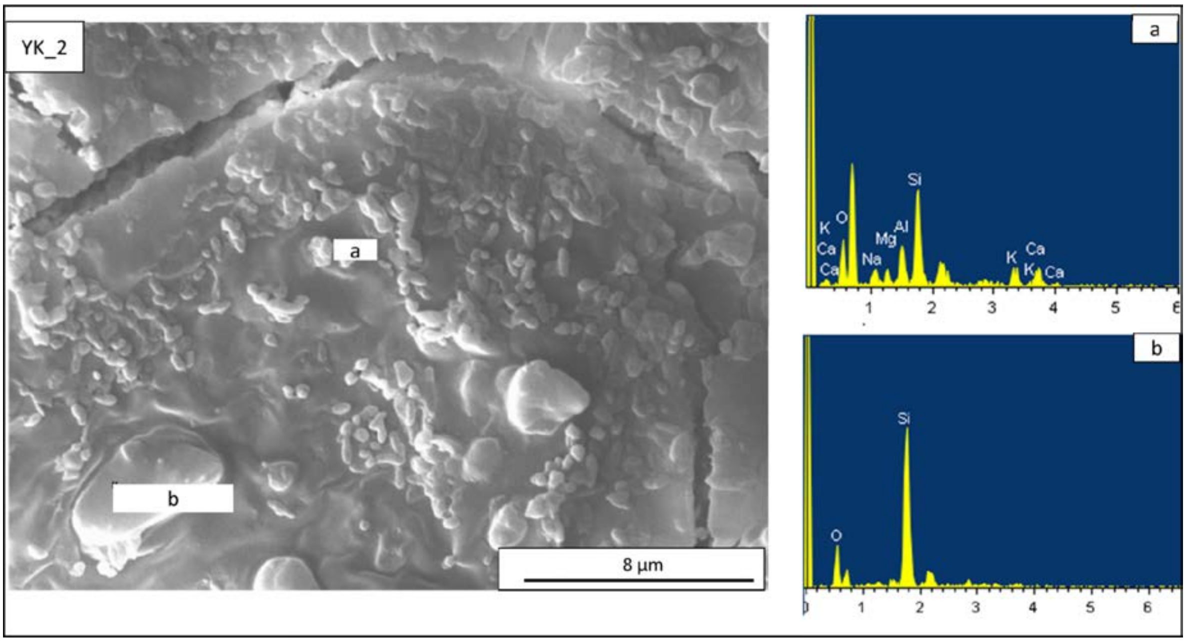

Fig. 8. EDX patterns taken from the newly developed porcelain stoneware tile (YK_2) composition. (a) EDX analyses of rounded shaped crystal in (YK_2) composition, (b) EDX analyses of a irregular shaped crystals in (YK_2) composition.

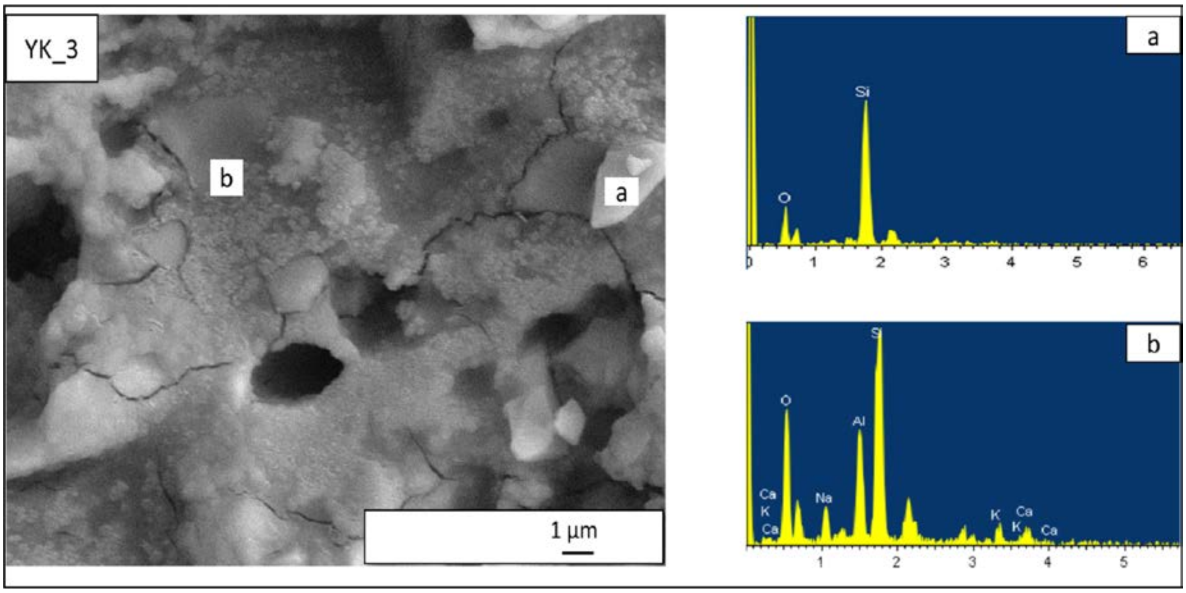

Fig. 9. EDX patterns taken from the newly developed porcelain stoneware tile (YK_3) composition. (a) EDX analyses of rounded shaped crystal in (YK_3) composition, (b) EDX analyses of a irregular shaped crystals in (YK_3) composition.

different MgO/CaO ratio, has been studied. It has been founded that MgO/CaO ratio affects the viscosity of the floor tiles and as the ratio increases the viscosity decreases. This viscosity decrease plays an important role for pyroplastic behaviour of the tiles. This means that when effect of compositional changes (in particular if there is any change in amount of liquid phase formers) on sintering of the tiles are investigated, the viscosity should be monitored and used as a key parameter during sintering of the tiles. For YK_3 composition will be evaluated due to has allowable deformation amount for the production. This floor tile composition will be successfully produce in production line.

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