Journal of Ceramic Processing Research. Vol. 17, No. 6, pp. 555~559 (2016)

J O U R N A L O F
Ceramic Processing Research

Microstructural characterization of mullite and anorthite-based Porcelain tile using regional clay

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The study focused on using of regional clay (Nevsehir/Turkey) instead of different clay and kaolin to prepare porcelain tiles along with dolomite and albite. Considering the variation of regional clay with other clay and kaolin the physical properties, phase-microstructure analysis and the determination of sintering temperatures by means of optical dilatometer of samples were studied. Uni-axially pressed samples were exposed to firing regime at 1205 °C for 42 min and tested to comply with ISO 10545 tile standards. The crystal phases were detected as quartz, anorthite and mullite. The mechanical strength was found to increase as the mullite content. When the Nevsehir's clay content in the starting composition added, glassy matrix became richer in kaolinite glass and earth-alkaline oxide favorably affected the sintering temperatures. Almost all technological properties and sintering behavior of new compositions demonstrated the suitability of Nevsehir clay as a potential raw material for ceramic tile industry. This regional clay is affect to microstructure and crystalline phases of tile bodies.

Key words: Porcelain tile, Kaolinite, Mullite, Anorthite, Processing.

Introduction

Porcelain tile is characterized by its high technological properties and improved aesthetic appearance, such as low water absorption (< 0.5%) and high strength (> 35 MPa), wear, frost and chemical resistance. These properties enlarged their usage area and increased its sales significantly compared to all other ceramic building materials [1-2]. These products are manufactured using the natural raw materials of clay, quartz and feldspar [3]. However, the high price of these raw materials and gradual exhaustion has a remarkable impact on the manufacturing of the end-product. The development of alternative materials would be a crucial task in the present and future [4]. Therefore, many of the recent studies related to ceramic tile compositions has focused on the substitution of the raw materials with other low cost minerals and wastes. The recent reports have shown the evidences that different industrial wastes [5-6], zeolite rich rocks [7-8], illite [9] quartzite clay [10], nepheline syenite [11] decreases the sintering temperature while improving properties of ceramics.

Porcelain tiles are sintered by fast single firing (< 60 minutes cold-to-cold, 1200 °C of maximum temperature and 5-10 minutes soaking time) whereby the resulting phases are new formed mullite and residual ones (quartz and feldspars) embedded in an abundant glassy matrix [2]. Hence, the microstructure evolution on firing could be explained dependent on the heating rate both crystallized fraction and the shape of mullite crystals [1] previous studies reported that microstructural approach is restricted to for porcelain tiles to describe mainly porosity evolution [12-13] or phases assemblages [14-15].

The aim of study was to investigate and re-demonstrate the possibility of regional clay (Nevsehir/Turkey) for fabrication of porcelain tile product as the clay fraction for replacing clay and kaolin. In this research the physical characteristics of porcelain tiles were investigated and also, phase- microstructural characterization, sintering behavior of the porcelain tiles presented. Porcelain tile bodies were characterized by X-ray diffraction (XRD) and secondary electron microscopy (SEM-EDS) for the evolution of new phases and structural changes. This study is important work both alternative clay material for ceramic tile industry in terms of feature of usage of this clay and taken into consideration changes of microstructure and sintering behavior of new tiles on after firing.

Experimental Procedure

The clay was obtained from about 4 km north east of the town of Avanos, Nevsehir of Turkey and the other raw materials used in porcelain stoneware tile body formulation provided by Yurtbay Ceramic Company (Eskisehir/Turkey). The chemical compositions of the initial materials used in this study are listed in Table 1. The chemical analysis of regional clay revealed the

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Table 1. The chemical analysis of raw materials (wt.%).

Raw materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	TiO_2	SO_3	BaO	L.O.I*
Regional clay	62.37	31.82	1.88	0.69	0.62	0.50	0.65	0.05	0.39	0.75	0.23	0.05
Kaolin1	66.84	23.47	0.19	0.45	0.18	0.09	0.29	–	0.45	0.07	–	7.97
Clay	57.87	25.28	0.83	0.37	0.47	2.24	2.20	–	1.40	2.29	–	7.05
Dolomite	10.32	1.97	0.70	3.32	39.80	0.75	0.17	–	0.09	0.80	–	42.08
Albite	68.66	18.91	–	0.61	0.54	10.02	0.29	–	0.24	-	–	0.73
Kaolin 2	73.29	18.00	0.34	0.09	–	0.38	0.22	–	0.19	0.42	–	7.07

*L.O.I: loss of ignition.

Table 2. Fractional (by unit weight) constituents of the compositions.

Compositions	Clay	Kaolin 1/2	Regional clay
A.0	26	12/15	–
A.1	13	12/15	13
A.2	26	0/15	12
A.3	26	12/0	15

presence of high quantities of SiO_2, Al_2O_3 and minor fractions of alkaline oxides compared with clay. On the other hand, regional clay contained smaller fractions of SiO_2 and higher quantity of Al_2O_3 than kaolins. Four porcelain tile compositions were formulated by using a mix of kaolin, clay, albite and dolomite. A.0 was the reference batch and the regional clay was replaced with clay and kaolins in the other batches. The changed raw materials were given in Table 2. All of the compositions were wet milled by a laboratory ceramic jar mill containing 70 wt.% solid and 1 wt.% deflocculant for 20 min. The slurries obtained were screened (residue < 2.5-3%, at 63 μm). The slip taken from mill were dried at 110 °C, crushed, ground, and then humidified with 6.5 wt. % of water. The granules were uni-axially pressed by a standard laboratory hydraulic press (Gabbrielli) at 130 bar in the form of rectangles (110x50x5 mm size). The pressed green bodies were dried at 110 °C and fired in industrial roller kiln at 1205 °C for approximately 42 min.

Linear shrinkage (LS%) and water absorption (WA%) determined by Archimedes' principle was performed on the industrial fired tiles. Strength values were measured by following ISO 10545-3 breaking strength standard. X-ray diffraction measurements were carried out of tiles by using Rigaku Rint 2200 diffractometer at 40 kV and 30 mA. Samples were scanned from 5 to 70 ° (2-theta), at a scanning speed of 2 °/min. The microstructure of the fired tiles was examined by scanning electron microscopy (Zeiss Supra 50 VP equipped with EDS).

Sintering temperatures of the compositions were determined by flex point using the optical dilatometer (Misura 3.32, ODHT-HSM Expert System Solutions). Paganelli stated that in order to determine flex point, samples were heated in an optical dilatometer at a rate of 50 °C/min up to 1250 °C without soaking at peak temperature in air atmosphere condition [16].

Table 3. The physical and mechanical properties of fired tiles.

Samples	Strength kg/cm^2	Water absorption wt. %	Linear shrinkage %
A.0	700.73	0.08	8.76
A.1	621.81	0.04	5.58
A.2	620.55	0.06	5.48
A.3	707.68	0.04	4.60

Results and Discussion

Physical characteristics

The firing behavior has been evaluated by the determination of shrinkage and water absorption. The physical characteristics of the fired samples were reported in Table 3. The linear shrinkage of modified samples was lower and more stable at 1205 °C compared to the reference. WA has to be relatively low, < 0.5% according to ISO 10545-3. In the present study WA values of the modified mixes were lower than the reference and reached 0.04 wt.% of WA at 1205 °C. The presence of new clay allowed increasing the sintering rate, thereby obtaining lower water absorption. The replacement of 13% and 12% of clay and kaolin 1 with regional clay allowed obtaining similar flexural strength values however these values were lower than reference (A.0) whereas only A.3 was showed an enhanced strength than the reference. Previous studies claimed that the high strength of anorthite based ceramic might also be due to the formation of high crystalline content in the matrix of the ceramic body [17-18]. On the other hand, mullite formation with different morphologies has been significantly favored to a diffusion mechanism [19]. Since the differences found in the mechanical characteristics cannot be explained only on the basis of the phase composition, a careful microstructural analysis was carried out [15].

Phase composition

The XRD analysis of regional clay and sintered tiles was conducted in Figs. (1-2). The main crystalline phases of regional clay were quartz, kaolinite, while sintered tiles were observed as quartz, mullite and anorthite. In comparison, the intensities of mullite peaks decreased whereas anorthite peaks increased in A.1 and A.2. Moreover, the mullite and anorthite peaks

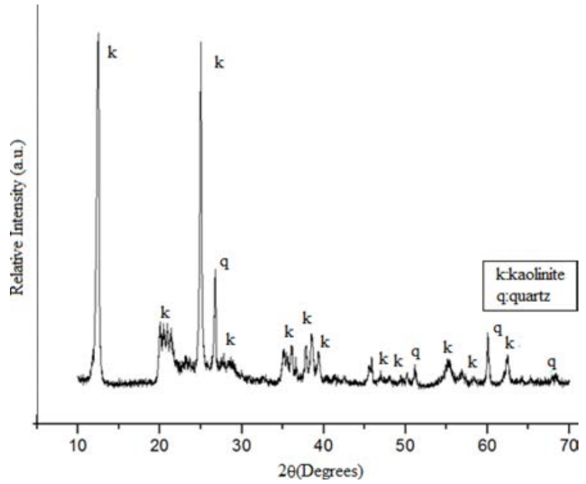

Fig. 1. XRD pattern of Regional clay.

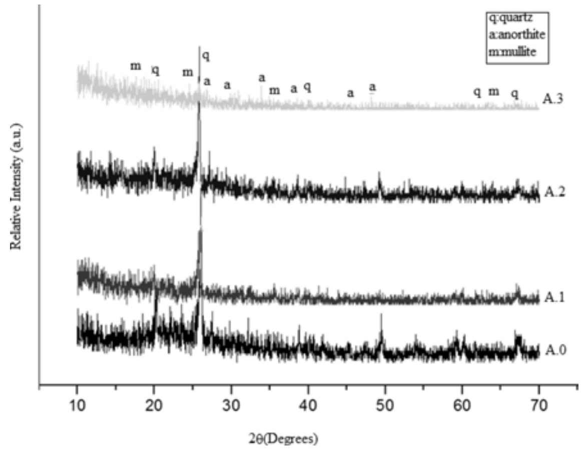

Fig. 2. XRD patterns of fired samples.

of reference and A.3 were slightly higher than the others, which means increasing mullite and anorthite amounts were crystallized and these crystals were proved to improve the mechanical strength of final products [20]. When the regional clay was added in the A.3, mullite crystal elevated with the increasing amount of Al_2O_3 in regional clay.

Microstructure analysis

Microstructures of fired tiles having quartz, anorthite and mullite composition were investigated with SEM. Diluted HF (5% wt.) etching was performed to analyze polished cross-section of tiles. Secondary electron (SE) mode was used to observe changes in the microstructure of samples. The images in Figs. 3 and 4 indicate the amount and size of anorthite and mullite crystals. Mullite crystals, approximately 0.5-1 μm in size, were present in their characteristic needle-like morphology and anorthite crystals found in the glassy matrix in Fig. 3(a-d). This distribution clearly indicates that the feltlike interlocking of fine mullite needles is responsible for the porcelain strength according to mullite hypothesis [21]. The images of A.1 were similar with A.2 composition's microstructure

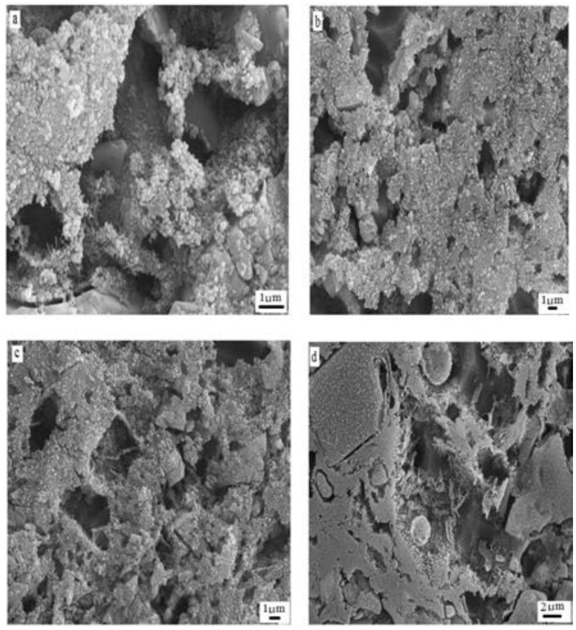

Fig. 3. SEM images of the porcelain tiles taken from surface of (a) A.0, (b) A.1, (c) A.2, (d) A.3.

in Fig. 4(b,c) and could not grow needle like mullite crystals while primary and needle mullite crystals can effectively grew in the glassy phase in Fig. 4(a,d). Therefore the strength values of A.0 (reference) and A.3 were increased.

According to SEM-EDS results of the standard porcelain tile anorthite regions contained 52.93 wt% SiO_2, 35.42 wt% Al_2O_3 5.12 wt.% MgO, 3.20 wt.%Na_2O and 3.22 wt% CaO in Fig. 3(a). Microstructure of A.1 was similar with A.2 tile composition's microstructure in Fig. 3(b,c). Anorthite regions contained 75.18 wt% SiO_2, 20.99 wt% Al_2O_3, 3.84 wt% CaO in A1 (Fig. 4(b)). On the other hand, these regions were detected as 67.95 wt% SiO_2, 28.98 wt% Al_2O_3 and 1.00 wt% CaO in A.2. For A.3, anorthite regions contained 54.27 wt% SiO_2, 34.05 wt% Al_2O_3 and 11.68 wt% CaO and mullite regions contained 63.17 wt% SiO_2, 36.83 wt% Al_2O_3 (Fig. 4(d)). A.3 has both clay and the regional clay thereby the highest amount of Al-containing mullite phase presented into A.3 composition. Therefore the microstructure of A.3 is considerably different from other compositions which containing high amount of SiO_2, Al_2O_3.

Sintering behavior

The sintering behavior of the reference bodies obtained by using of optical dilatometer, equipment particularly designed to reach a high heating rate to reproduce industrial firing cycles, was presented in Fig. 5. In the figure, graph was plotted with time on the x-axis versus the temperature and sintering percentage on the y-axis. Furthermore, the derivative of sintering curve (dy/dT) called as "flex point" temperature, corresponding to the

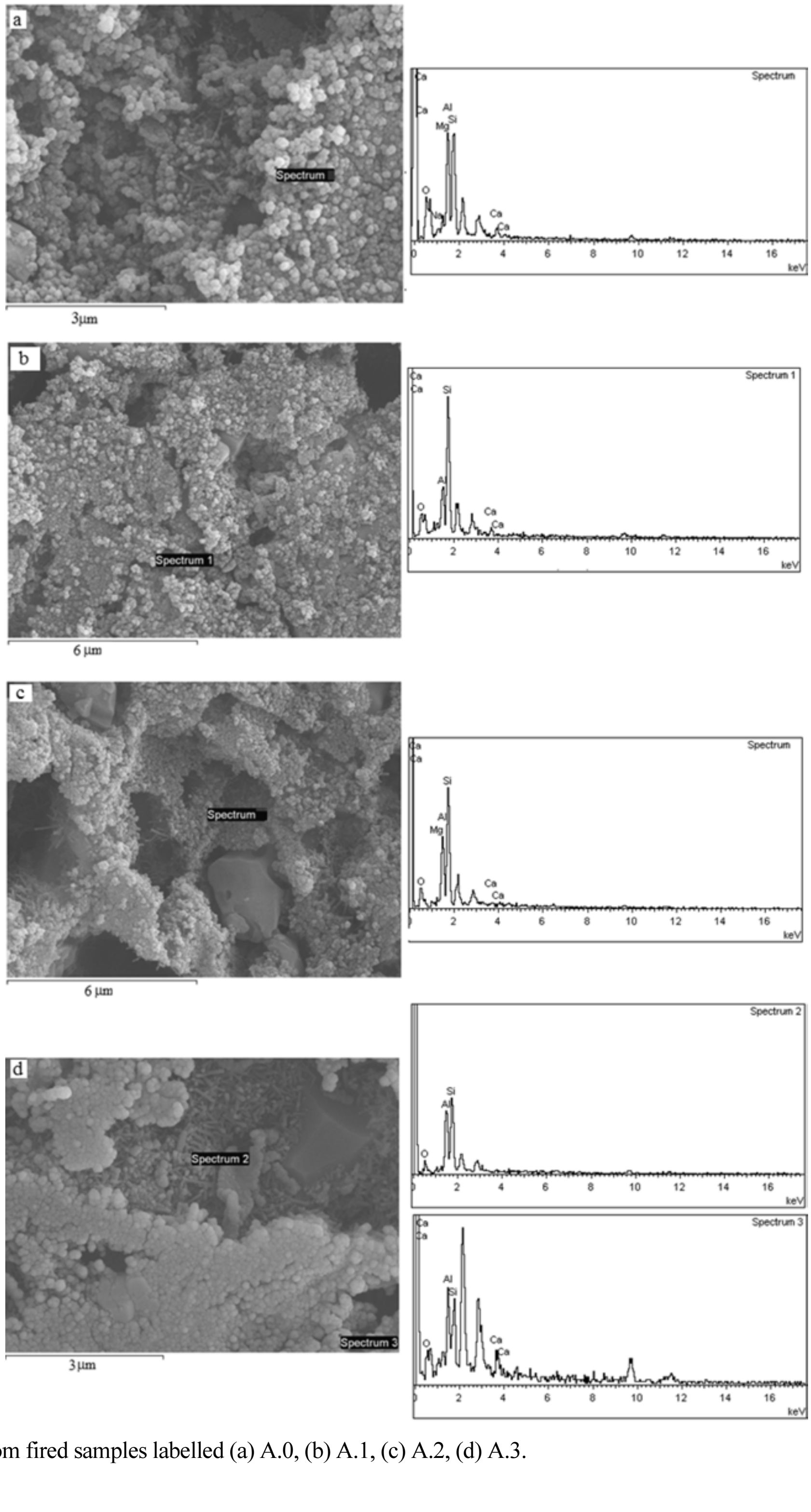

Fig. 4. EDX analyses from fired samples labelled (a) A.0, (b) A.1, (c) A.2, (d) A.3.

maximum amount of expansion, fastest sintering [14]. Flex point was 1216 °C for A.0.

The detailed optical dilatometer results (flex point and expansion value) of the reference and Regional clay added compositions are given in Table 4. When this table is examined, it is observed that the flex point temperatures were lower in regional clay added compositions than the reference (A.0). This phenomenon can be explained by an increase in fluxing of earth alkali oxides such as CaO, MgO with an increase of the Regional clay addition. The influence of earth alkaline- containing raw materials as sintering promoters on the vitrification of various

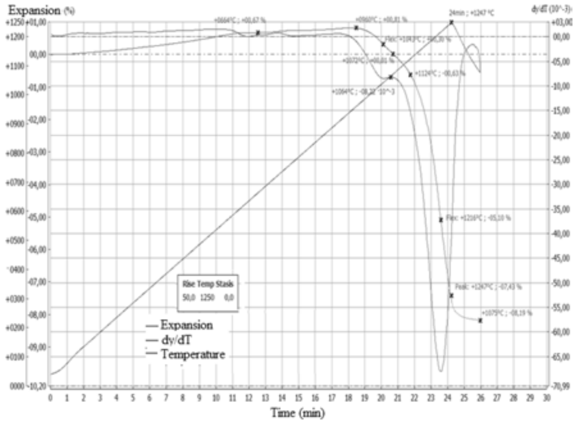

Fig. 5. The optical dilatometer result of reference sample.

Table 4. The results of optical dilatometer analysis.

Samples	Flex point (°C)	Expansion value (%)
A.0	1216	5.10
A.1	1204	4.47
A.2	1191	4.50
A.3	1191	4.29

compositions has already been shown in previous studies [22-25].

Conclusions

In the present study porcelain stoneware tiles containing regional clay were prepared and characterized. The predominant oxides in the Regional clay were SiO_2 and Al_2O_3, on the other hand the crystalline phases were quartz and kaolinite. The firing behaviors of porcelain tile composition containing Regional clay were evaluated by linear shrinkage, water absorption, strength, X-ray diffraction scanning electron microscopy and optical dilatometer. The results demonstrate that the usage of regional clay in compositions has lower water absorption and similar shrinkage and interestingly, only A.3 showed higher strength results than standard. The strength of A.1 and A.2 can be suitable for an industrial production of commercial tiles. On the other hand, the observed phases were quartz, anorthite and mullite post- firing of tiles. SEM micrographs showed the formation of enhanced anorthite in A.1 and A.2. Mullite crystals, approximately 0.5-1 µm in size, were present in their characteristic needle-like morphology and anorthite crystals found in the glassy matrix in A.0 and A.3. The presence of regional clay due to its earth alkaline oxides content was developed a low viscosity liquid phase, improved the sintering performance of samples. Hence flex temperature was reduced and favored the crystallization of anorthite and needle like mullite. In the scope of these evaluations regional clay can be used to produce anorthite and mullite based quality type porcelain tile body and this research was broaden usage areas and exhibition of Nevsehir's clays for ceramic tile industry.

Acknowledgments

This work was supported by the Scientific and Research Projects of Nevsehir Hacý Bektas Veli University Province (No: NEÜBAP14F14). Raw materials and analysis were supported by Yurtbay Ceramic Company and Anadolu University-Ceramic Research Center (Eskisehir).

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