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UTILISATION OF A LOCAL PEGMATITE IN MATT FLOOR TILE GLAZES

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Abstract

In this study, sodium feldspar, kaolin, quartz and zircon were replaced by a local pegmatite (Bilecik, Turkey) in an attempt to develop matt floor tile glaze formulations. Thermal behaviour of the formulated glazes prepared with and without pegmatite addition was investigated using hot stage microscopy. When the pegmatite ratio was in the range of 5 to 20 wt. %, no significant change in colour and brightness values was observed. In addition, there was no negative effect observed with the pegmatite incorporation on the technological properties such as thermal shock resistance, vapour pressure resistance, resistance to chemicals, abrasion resistance and stain resistance. X-ray diffraction (XRD) was used to analyse the phases formed after firing. Scanning electron microscopy (SEM) in combination with energy dispersive X-ray spectroscopy (EDS) was further employed in order to observe the microstructural characteristics of the selected fired samples. It was concluded that a feldspar type pegmatite raw material of local origin could be used in matt floor tile glazes in as a substitution of currently used expensive raw materials.

Key Words: Pegmatite, floor tile glaze, hot stage microscope

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1. Introduction

Ceramic tiles usually consist of two layers. Interior layer has a porous structure composed of sintered mixture of clay, feldspar and silicate particles. On the other hand exterior layer, called as glaze, contains various inorganic materials and covers the ceramic body [1, 2]. In recent years, the production of ceramic tiles with a matt finish has considerably increased. A review of the relevant literature shows that some studies have addressed the causes that produce such finishes and the variables on which these causes depend on [3−6].

Matt glazes present a higher surface roughness than that found in glossy glazes. This surface roughness causes multiple reflections of incident light, reducing the amount of light reflected in the specular direction and therefore producing a loss of gloss. Normally, surface roughness of the matt glazes is produced by the presence of crystals near or on the surface of the glaze. The crystals found in a matt glaze may come from; undissolved raw materials which remain in the glassy phase and crystallization of crystalline phases from the glassy matrix that forms during firing [7]. Tile glazes are prepared based on Li_2O-Al_2O_3-SiO_2, MgO-Al_2O_3-SiO_2 and MgO-CaO-SiO_2 terniary equilibrium diagrams [8−11]. Since the surface properties of glazed ceramic tiles are practically identical with glaze properties, it is desirable that properties of body covering glaze such as thermal shock resistance, autoclave and stain resistance be higher than its minimum standard limits. The resistance of the tile surface to the environment can be modified with the proper selection of the recipe provided that clean, homogeneous, fine grained and thermally treated special raw materials are used.

The aim of this study was to investigate the possible use of a local pegmatite in place of sodium feldspar, kaolin, quartz and zircon in a commercial matt floor tile glaze.

2-Experimental Studies

In order to investigate the effect of pegmatite incorporation on the properties of the commercial matt floor tile glaze (designated as M) used in the company, glaze recipes were calculated based on raw material chemical compositions. Pegmatite ratios of 5, 10, 15 and 20 wt % were used in the recipes (designated as M-5, M-10, M-15 and M-20) to meet the SiO_2 and Al_2O_3 ratio in the standard glaze. As the amount of pegmatite was increased in the recipes, the amounts of Na-Feldspar, Al_2O_3, quartz, kaolin and zircon were reduced accordingly. The as-received local pegmatite was ball-milled (60 wt % of solid loading) with sodium tripolyphosphate (STPP) as dispersant. The purpose of milling was to decrease the particle size of pegmatite to the level of all the other glaze raw materials. The milling time was set to 30 minutes. The glaze raw materials were weighted according to the glaze recipes, followed by a jet milling process, which involved the milling of the prepared mixtures with aluminum balls in a porcelain jet mill for 15 minutes. In the milled glaze slurries, solid loading was 50 wt. %. Sodium carboxymethyl cellulose (Na-CMC) and sodium tripolyphosphate (STPP) were used as binder and dispersant, respectively. The milled slurries were sieved down to 150 μm, and then their weight volume and the sieve residue values were measured. For the thermal behaviour of the investigated formulations, a hot stage microscope (Mısura 3.0 by Expert System) was employed with a heating rate of 50ºC/min. up to 800ºC and 10ºC/min. up to 1300ºC. The glazes were applied onto a commercial floor tile body with the commercial engobe of the same tile company by spraying. The dried tiles were fired in an industrial roller kiln under single firing condition of 1208^{o}C for 31min.from cold-to-cold. The brightness values of the fired samples were measured using Erichsen Pico Gloss 560. Furthermore, the chromatic coordinates of the fired samples was measured using a UV-Vis spectrophotometer (Minolta CR-300). The thermal shock resistance (Harkort test), vapour pressure resistance (Autoclave test), resistance to chemicals, abrasion resistance and stain resistance tests were applied on the samples according to following standards of TS EN ISO 10545-9, TS EN ISO 10545-11, TS EN ISO 10545-14, TS EN ISO 10545-13 and TS EN ISO 10545-7. Qualitative determination of the major crystalline phases present in the fired samples was achieved by X-ray diffraction (Rigaku,Rint 2000, Japan). Microstructural observations of the selected samples were performed on polished using a scanning electron microscope (Zeiss Supratam 50 VP) after sputtering with a thin layer gold-palladium alloy in order to prevent charging. Polishing was carried out in accordance with the standard procedures.

The chemical analyses of the raw materials used for the preparation of the glaze formulations are given in Table.1.

Table 1. Chemical analyses of the raw materials in wt. %

Oxide	Na-Feldspar	Al_2O_3	Marble	Magnesite	Quartz	Kaolin	Zircon	Pegmatite
SiO_2	69.95	5.55	-	-	99.10	51.30	32.80	73.45
Al_2O_3	18.60	92.65	-	-	0.15	34.20	-	15.60
TiO_2	0.20	0.03	-	-	0.05	0.20	-	0.30
Fe_2O_3	0.07	-	-	-	0.05	0.70	-	0.80
CaO	0.85	0.02	55.85	2.60	0.06	0.40	-	0.70
MgO	0.10	-	-	47.00	0.03	0.10	-	0.30
Na_2O	9.50	0.10	-	-	0.06	0.02	-	1.80
K_2O	0.35	0.02	-	-	0.10	0.85	-	2.55
ZrO_2	-	-	-	-	-	-	67.20	-
* LOI	0.40	1.65	44.15	50.80	0.40	12.25	-	4.50

* LOI : Loss on ignition

3. Results and Discussion

The sieve residue (%) and weight volume (g/l) values of the milled glaze slurries are summarized in Table 2. As can be seen, with increasing amount of pegmatite from 5 to 20 wt % in the standard glaze formulation, there was not any significant change in the mentioned properties.

Table 2. The sieve residue on 45 μm (%) and weight volume (g/l) values of the investigated formulations

Designation	Property	
	Sieve Residue (%)	Density (g/l)
M	1.20	1685
M-5	1.25	1680
M-10	1.28	1678
M-15	1.30	1673
M-20	1.45	1690

Based on the chemical composition of the standard glaze (M), four different glaze samples (M-5, M-10, M-15, and M-20) were prepared and their oxide composition is given in Table.3.

Table 3. Chemical composition of the investigated glazes (wt. %)

Designation		**M**	**M-5**	**M-10**	**M-15**	**M-20**
SiO_2		47.15	48.25	48.20	49.30	49.50
Al_2O_3		18.45	18.00	18.45	18.75	18.80
Fe_2O_3		0.10	0.10	0.20	0.30	0.30
TiO_2		0.10	0.10	0.10	0.10	0.10
CaO		13.30	13.30	13.30	13.40	13.40
MgO		4.40	4.40	4.45	4.45	4.50
Na_2O		2.20	2.35	2.40	2.40	2.70
K_2O		1.15	1.15	1.25	1.25	1.35
ZrO_2		9.40	8.60	7.80	6.30	5.55
B_2O_3		1.00	1.00	1.00	1.00	1.00
ZnO		2.75	2.75	2.75	2.75	2.75
Chromatic coordinates	*L**	85.52	84.25	84.19	83.09	83.78
	*a**	-0.04	0.09	-0.03	-0.02	0.01
	*b**	0.19	0.18	0.43	0.48	0.53
Gloss		14	17	16	17	20

(L*=0 black , L*=100 white, a*<0 green, a*>0 red, b*<0 blue, b*>0 yellow)

Fig. 1 shows the melting behaviour of all the investigated glazes. It is clear that the melting behavior of the pegmatite incorporated glazes is similar to that of the standard glaze. It was measured that the glazes started sintering at around 1130°C and showed a softening behaviour at 1180°C. Moreover, thermal shock resistance, vapor pressure resistance and stain resistance test results of the investigated glazes were determined to be good enough according to the relevant standards. The resistance to chemicals (i.e. resistance to HCl) was proved to be

A class, leading to the fact that the addition of the pegmatite into the composition had no negative effect on this particular property. Furthermore, abrasion resistance was found to be class IV (PEI method).

The crystalline phases present in the glazes were detected using XRD (Fig. 2). According to the results, all the glazes showed the presence of the same phases; namely, zircon ($ZrSiO_4$), residual quartz (SiO_2) and anorthite ($CaO.Al_2O_3.2SiO_2$) in similar amounts. The presence of these phases was also detected using SEM (Figs. 3 and 4).

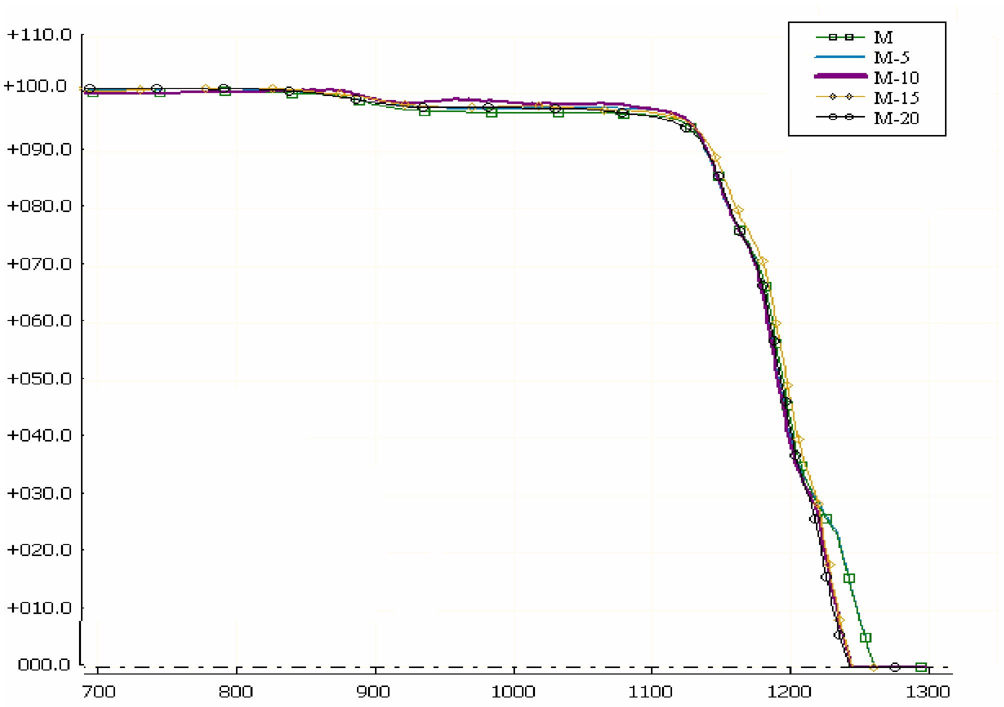


Fig. 1. The relation between temperature and area change (%) in the investigated glazes.

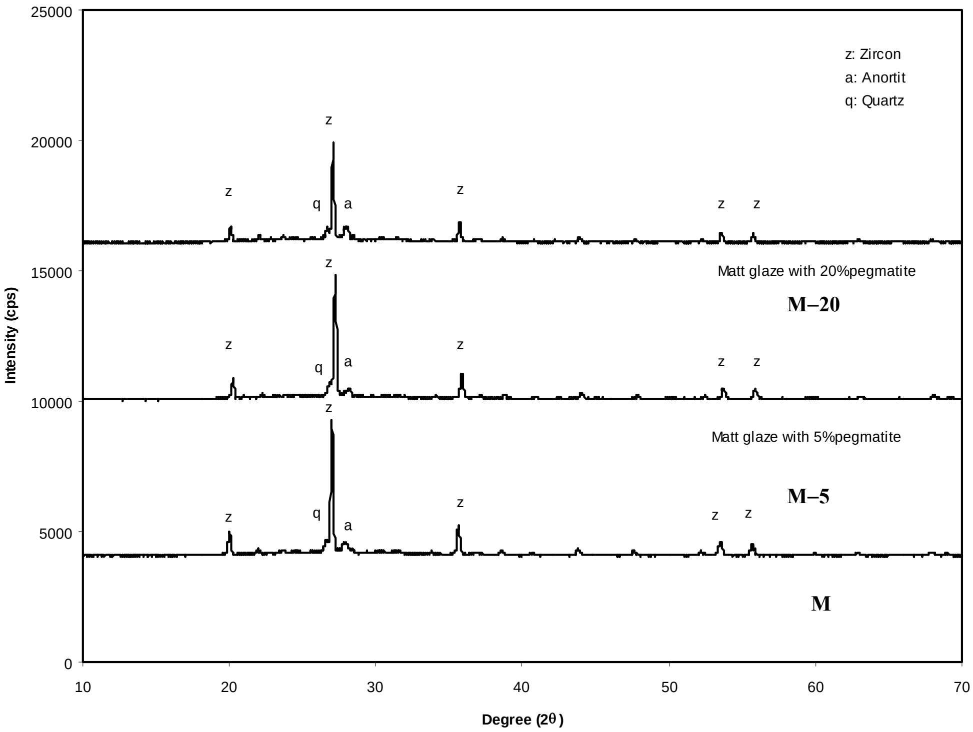
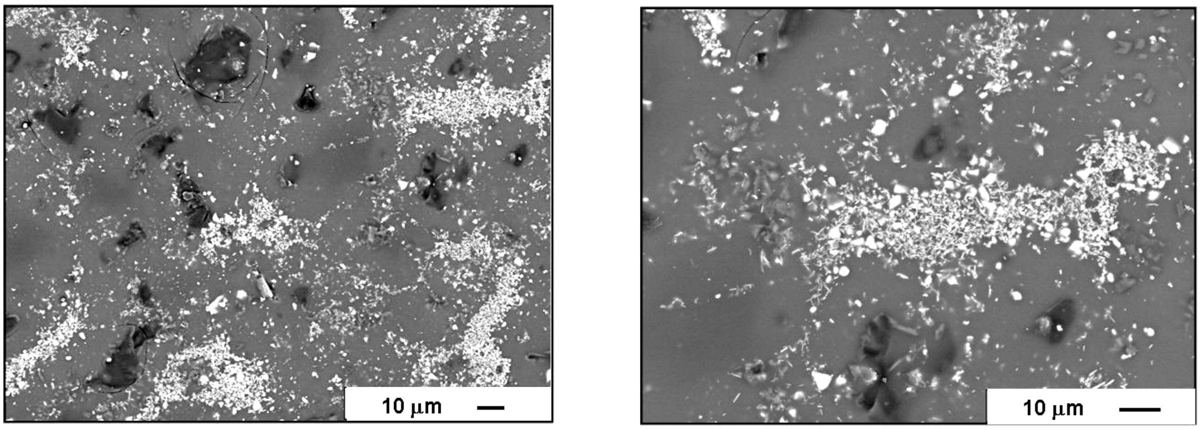
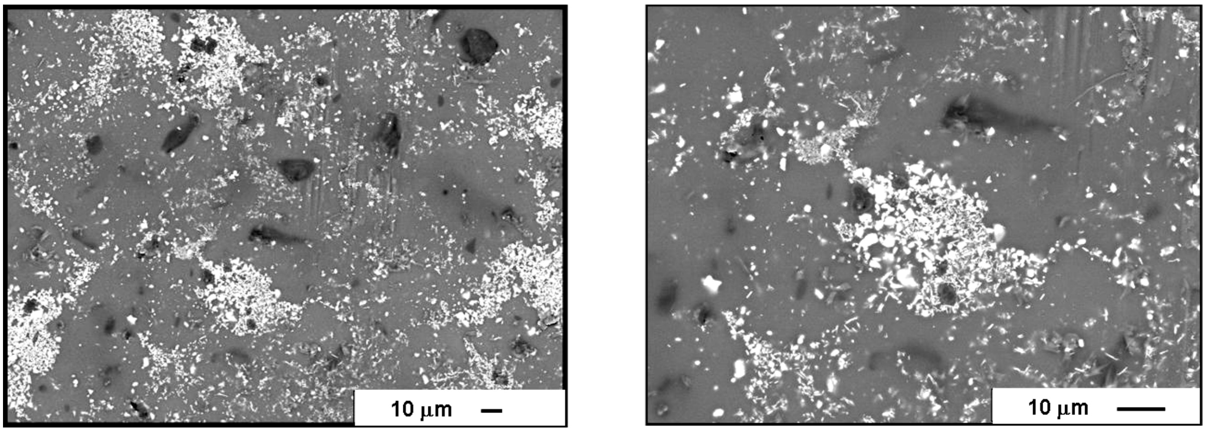


Fig. 2. Representative XRD spectra of M, M-5 and M-20 formulations



(a) (b)

Figure 3. Representative BE images of the standard formulation (M), (a) low, and (b) high magnification



(a) (b)

Figure 4. Representative BE images of the 20 wt. % pegmatite containing formulation (M-20), (a) low, and (b) high magnification

SEM investigation on selected formulations revealed that there was no considerable modification of the glaze microstructure with the incorporation of the pegmatite. In the particular BE images presented above, the areas with high contrast distributed randomly in the gray glaze matrix indicates the presence of zircon crystals. The dark areas are believed to be the unmelted quartz grains. Finally, the light gray phases are assumed to be the anorthite grains. The EDX was also employed to confirm the presence of relevant elements.

Conclusions

The results of the present study showed the possible use of a feldspar type local pegmatite in a commercial matt tile glaze in a controlled manner in order to induce similar degree of crystallization. It is expected that such use will bring cost savings to the company. However, before proceeding any further with industrial trials, the mechanisms of crystallization need to be further investigated and compared in detail in both the commercial and the pegmatite containing formulations.

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