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The role of viscosity on microstructure development and stain resistance in porcelain stoneware tiles

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Abstract

Effect of composition on viscosity of porcelain stoneware tiles and role of the viscosity on microstructure development and stain resistance in porcelain stoneware tiles were investigated. The viscosity of the tiles was successfully measured by a thermomechanical analyzer. Na_2O/K_2O ratio was used as a parameter to change the viscosity. As the Na_2O/K_2O ratio increases, the viscosity decreases. This reduction in the viscosity results in improvement of microstructure (i.e., spherical pore morphology and reduced closed porosity) and usually increases the stain resistance significantly. However, too low viscosity may also cause deformation of the tile during production. Therefore, the viscosity of the tiles should be carefully controlled and it should lie between a lower limit (in this study this value is between $10^{7.93}$ and $\sim 10^{8.35}$ P) and an upper limit (in this study this value is $10^{8.67}$ P) to achieve high stain resistant porcelain tiles with no deformation.

Keywords: Sintering; Microstructure; Stain resistance; Porcelain stoneware tile; Viscosity

1. Introduction

Recently, porcelain stoneware tiles have become very popular due to their outstanding technical and functional properties such as low porosity and low water absorption[1–4] (<0.5%). Porcelain stoneware tiles are glass-bonded materials and they can be classified as glazed and unglazed porcelain tiles in general. The unglazed porcelain tiles are usually utilized after a polishing procedure and hence they are also called as polished porcelain tiles. Utilization of glazed porcelain tile especially for outdoor applications is limited due to presence of double layer (i.e., glaze and body layers) nature of the product. As a result, polished porcelain tiles are much more advantageous than glazed porcelain tiles. Unfortunately, although the polishing process improves the aesthetical appearance, it often decreases stain resistance of the tiles. Stain resistance is one of the most important properties which determines applications of the polished porcelain tiles for both indoor and outdoor applications. Development of polished porcelain tiles with high stain resistance is critical to expand application areas of such materials. In polished porcelain tiles, stain resistance is controlled by surface characteristics such as surface roughness, open pore size, shape and aspect ratio.[1–3] Porcelain tiles generally exhibit almost 0% open porosity. On the other hand, they have 2–10% closed porosity in general.[1–3] Since the polishing process opens up some of the closed pores and they reduce the stain resistance, microstructure characteristics, in particular closed pore content, pore size, shape and aspect ratio should be controlled carefully to achieve high stain resistance in polished porcelain tiles. In the literature, there are several studies which focus on improvement of microstructure and hence properties via modifications in porcelain tile compositions. Junior et al.[5] studied influence of porcelain tile starting composition on the tile microstructure and mechanical properties. The compositions were prepared by using quartz, kaolinite and sodium feldspar. The researchers analyzed toughness and mechanical strength of the porcelain tiles as a function of the compositional design. The higher amount of quartz content resulted in greater difference between surface and total porosity. The detachment of the quartz particles during polishing was pointed out as main factor, increasing surface porosity. However, they did not report any information about stain resistance of the tile. Esposito et al.[6], investigated utilization of nepheline

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syenite as fluxing agent in porcelain tile composition. Starting from the reference mix compositions, 5.0, 10.0 and 15.6 wt% of sodium feldspar were replaced by the same amount of nepheline syenite. In addition, effects of milling time and soaking time at peak temperature during firing on microstructure development and mechanical properties of the tiles were studied. The presence of nepheline syenite improved densification kinetics. The modified compositions exhibited homogeneous microstructures which were characterised by smaller pores. However, the stain resistance characteristics of the tile were not investigated in that study. In another study, Tucci et al.[7], started from an industrial body mix of porcelain stoneware tiles, part of its fluxing agent, a sodium feldspar, was replaced by spodumene and they also used highly pure alumina powders in their initial composition. They claimed that the presence of spodumene, due to its capability to develop a low viscosity liquid phase, improves the sintering performances of the products, reduces porosity and favours the crystallization of elongated mullite which increase hardness and fracture toughness. However, no viscosity values were reported in that paper. Although there are several studies about effect of composition on microstructure development in porcelain stoneware tiles, there is very limited number of publications which discusses how viscosity changes quantitatively with compositional changes. Since porcelain stoneware tiles densify via viscous phase sintering mechanism, viscosity of the liquid phase plays a critical role on microstructure development and hence stain resistance characteristics. While too high viscosity is not desired due to very slow densification kinetics, too low viscosity may also bring some additional problems such as increasing closed porosity and/or pyroplastic deformation. Therefore, viscosity should be monitored as a function of compositional modifications to interpret effect of composition design on microstructure and properties of porcelain stoneware tiles, correctly.

There are many different techniques to measure viscosity of the glassy phase of the porcelain tiles. These techniques are generally using a hot stage microscope and a fleximeter. In literature, Dondi et al.[8], measured viscosity of glass phase by preparing glass phase compositions by using related phase diagrams. However, these results reflected only behaviour of the glass phase as a function of the temperature and composition. Raimondo et al.[9] also measured viscosity of porcelain stoneware tiles considering the pyroplastic deformation, they calculated uniaxial viscosity according to a mathematical equation, as previously reported by Lee et al.[10] Although this technique is useful to determine viscosity of the materials, viscosity could only be measured when the sample undergoes a pyroplastic deformation as a function of temperature. Another technique to measure viscosity is TMA (Thermomechanical Analyzer) analysis. TMA is a sort of thermal dilatometer which can be used to apply load on the sample during sintering.[11] This equipment has an important role to determine sintering pressure, elastic modulus and viscosity of the sintered samples. It can apply cyclic load with temperature on the sample. Cai et al.[12], calculated densification stresses in alumina and zirconia laminates by cyclic loading dilatometer and they also calculated uniaxial viscosity of alumina as a function of temperature. Green et al.[13], investigated densification and sintering viscosity of LTCC ceramics by using thermomechanical analyzer under different compression stresses. Xie et al.[14], reported experimental determination of the uniaxial viscosity of two commercially available low temperature co-fired ceramic (LTCC) powder compact by loading dilatometer. When TMA is applied to porcelain stoneware tiles, TMA analysis enables one to measure viscosity of the whole system (i.e., glass phase and crystalline solid phase) so that real impact of compositional design on the body viscosity and hence on densification kinetics can be evaluated clearly. According to the authors' knowledge, to date, TMA has not been used to determine viscosity of porcelain stoneware tile systems. Consequently, the research objectives of this study were first to develop an understanding about how viscosity of porcelain stoneware tile changes as a function of alkali ratio (Na_2O/K_2O) in a standard porcelain stoneware tile composition; the second objective was to evaluate effect of the viscosity on densification, microstructure development and hence stain resistance of porcelain stoneware tiles. The ultimate goal of this study was to determine an optimum viscosity range to achieve polished porcelain stoneware tiles with high stain resistance and no deformation for the studied standard porcelain stoneware tile composition.

2. Experimental procedure

In this study, porcelain stoneware body composition was prepared by using industrial raw materials. A formulation, used for the industrial production of porcelain stoneware tiles, was chosen as a standard body mix. Starting from the standard body composition, different amounts of sodium and potassium feldispathic sands were added into the system. The new compositions were denoted as N1, N2, N3, N4 and N5. Seger formulation was applied to prepare new compositions and Na_2O/K_2O molar ratio was chosen as the main variable parameter to prepare the compositions and amount of total molar alkali oxides (Na_2O and K_2O) was kept constant in the compositions. Chemical analyses of the compositions are shown in Table 1. New compositions were prepared by wet grinding. Slips were dried at 110 °C. The powders obtained were moisturised with 5 wt% water. The pellets with 50 mm diameter and 6 mm thickness were prepared by uniaxial pressing at a forming pressure of 44 bar (Nannetti Press, Hydraulic Laboratory Press Mignon S, Italy).

Sintering temperatures of the compositions were determined by flex point (i.e., temperature at which densification rate is maximum) analyses as stated by Paganelli[15] using the optical dilatometer (Misura 3.32, ODHT-HSM, Expert System Solutions, Italy). Total heat treatment was approximately 37 min and the peak temperature was 1220 °C. The viscosity of the porcelain stoneware tiles were measured by TMA (Thermomechanical Analyser-TMA-60H, Shimadzu, Analytical Measuring Instruments Division, Japan) equipment at 900, 1100 and 1200 °C. The compacts were tested in TMA with a vertical 3 mm diameter loading road. In this study, uniaxial compressive loads of 1 N, 2 N and 3 N were applied to sample surfaces at a constant loading rate. Axial strain rates of the samples under different uniaxial stresses were measured. A plot for axial strain rates vs. uniaxial compressive stresses was obtained and the reciprocal

Table 1
Chemical compositions (wt%) and Na_2O/K_2O ratio (molar%) of the recipes.

Compositions	STD (Mean) (S.D.)	N1 (Mean) (S.D.)	N2 (Mean) (S.D)	N3 (Mean) (S.D.)	N4 (Mean) (S.D.)	N5 (Mean) (S.D.)
SiO_2	67.0 ± 2.0	66.0 ± 2.0	67.0 ± 2.0	67.0 ± 2.0	68.0 ± 2.0	68.0 ± 2.0
Ti_2O	0.53 ± 0.01	0.56 ± 0.01	0.50 ± 0.01	0.59 ± 0.01	0.52 ± 0.01	0.56 ± 0.01
Al_2O_3	17.0 ± 1.0	20.2 ± 1.5	19.5 ± 1.0	21.2 ± 1.2	18.2 ± 1.0	21.8 ± 1.0
Fe_2O_3	0.58 ± 0.01	0.52 ± 0.02	0.47 ± 0.01	0.51 ± 0.01	0.38 ± 0.01	0.530 ± 0.01
MgO	0.69 ± 2	0.23 ± 2	0.20 ± 2	0.22 ± 2	0.4 ± 2	0.23 ± 2
CaO	2 ± 1.0	1.2 ± 1.0	1.8 ± 1.0	0.7 ± 1.0	0.70 ± 1.5	1.58 ± 1.2
Na_2O	3.2 ± 0.2	4.6 ± 0.8	5.5 ± 0.5	4.1 ± 0.5	6.6 ± 0.7	3.5 ± 0.9
K_2O	0.80 ± 0.2	1.0 ± 1.0	2.2 ± 0.9	3.2 ± 0.4	1.9 ± 1.6	1.1 ± 1.0
P_2O_5	0.1 ± 0.01	0.08 ± 0.01	0.09 ± 0.01	0.08 ± 0.01	0.1 ± 0.01	0.08 ± 0.01
Na_2O/K_2O	5.82	8.77	5.55	9.13	10.6	9.06

of the slope of the straight line yielded the uniaxial viscosity of the samples.[16]

Staining was created by marking on the sample surface with permanent marker. After cleaning the surface with water, the colour variation value (ΔE) was measured by a spectrometer (Minolta CR, 300 Colormeter). Staining agent was applied on the samples surfaces after polishing. Samples were polished by using polishing machine (Metkon-Forcipol-300-1N). Bulk density and open porosity were determined by water saturation under vacuum and Archimedes' principle (ISO 10545-3) by using related equations (Eqs. (1) and (2)). Total porosity of the samples was measured by using the relationship between bulk density and specific density of the material (Eq. (3)). Closed porosity was determined by using Eq. (4) and specific density of the samples was measured by a Helium pycnometer.

$$\text{Bulk density}\,(\rho_b) = \frac{w_d}{w_w - w_s} \times \rho_w \tag{1}$$

$$\%\text{Water absorption}\,(w_a) = \frac{w_w - w_d}{w_d} \times 100 \tag{2}$$

$$\%\text{Total porosity} = \varepsilon_T = \left(1 - \frac{\rho_b}{\rho_t}\right) \times 100 \tag{3}$$

$$\%\text{Closed porosity} = \varepsilon_c = \varepsilon_T - \varepsilon_o \tag{4}$$

where ρ_b, bulk density, w_d, dry weight of the sample, w_w, wet weight of the sample, w_s, weight of solid suspended in water, ε_c, closed porosity, ε_T; total porosity, ε_o; open porosity.

The sample microstructures were examined by scanning electron microscopy (EVO-50, Carl-Zeiss, Germany). In addition, as a function of the compositional changes, viscosity, microstructure and stain resistance variations of porcelain stoneware tile were compared and discussed.

3. Results and discussion

3.1. Role of Na_2O/K_2O ratio on viscosity of porcelain stoneware tiles

Fig. 1 shows the effect of Na_2O/K_2O ratio on viscosity of porcelain stoneware tiles. As the ratio increases, the viscosity decreases. While the viscosity of the composition with 5.55 Na_2O/K_2O ratio is $10^{10.35}$ P, the viscosity of the composition with 8.77 Na_2O/K_2O ratio is $10^{8.67}$ P. The change in viscosity decreases as a function of the ratio at above 8.77 Na_2O/K_2O ratio. Accordingly, the viscosity difference between the compositions with 8.77 and 10.60 Na_2O/K_2O ratios is only $10^{0.74}$ P. The reduction in the viscosity as a function of increase in the alkali ratio can be attributed to the network modifying characteristics of Na_2O and K_2O. Network modifiers provide extra oxygen ions but do not participate in the network. This extra oxygen allows the bridging oxygen between two tetrahedra to be disrupted and two nonbridging oxygen to terminate each tetrahedron. The effects of modifiers are directly analogous to the decreasing SiO_4 interconnectivity.[17] The loss of this connectivity results in decreased viscosity in the modified compositions. The liquid phase developed in presence of sodium and potassium feldspar, results in a lower viscosity in comparison with Standard and N2 compositions, this effect is probably due to smaller dimensions of the sodium with respect to potassium ions. These results show that changing compositions of the porcelain stoneware tiles results in viscosity change of the system which is expected to influence the sintering and microstructure development.

3.2. Role of viscosity on microstructure development and stain resistance

Table 2 shows sintering shrinkages as a function of the viscosity of porcelain stoneware tiles. The viscosity of the tile decreases with the increases of Na_2O/K_2O ratio, favours the

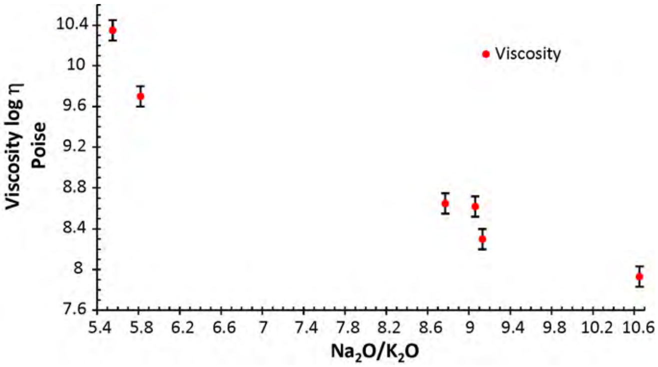

Fig. 1. Effect of the Na_2O/K_2O ratio on the viscosity of the porcelain stoneware tile at 1220 °C.

Table 2
Technical characteristics of the porcelain stoneware tiles.

Properties	STD	N1	N2	N3	N4	N5
Na_2O/K_2O	5.82	8.77	5.55	9.1	10.6	9.06
Water absorption (wt%)	0.03	∼0	∼0.03	∼0.005	∼0	∼0
Closed porosity (vol.%)	10.3	4.5	10.5	4.6	4.3	4.6
Firing shrinkage (%) (1220 °C)	7.6	8.3	7.2	9.1	10.0	10.2
Flex points (°C)	1220	1220	1222	1223	1223	1221
Viscosity (1220 °C) log η (Poise)	9.7	8.67	10.35	8.35	7.93	8.62

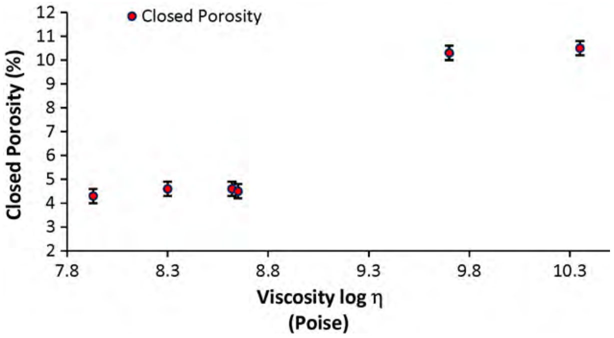

Fig. 2. Effect of the viscosity of the porcelain tile on closed porosity amount after sintering at 1220 °C.

sintering shrinkage. For example, the system with $10^{9.7}$ P viscosity exhibits 7.6% linear shrinkage; however, the system with $10^{8.67}$ P viscosity exhibits 8.3% linear shrinkage at 1220 °C. The shrinkage values are not changing significantly for the compositions with $<10^{8.67}$ P. The viscosity effect on shrinkage values also reflects on microstructure characteristics. Fig. 2 shows the effect of viscosity on closed porosity. For the systems which exhibit low viscosity (i.e., $\leq 10^{8.67}$ P), closed porosity is ∼4.5%. On the other hand, closed porosity values for the systems with $10^{9.7}$ and $10^{10.35}$ P viscosity values are 10.3 and 10.5%, respectively. Similarly, while 0.03% water absorption is observed for these systems, it is about 0% for the other systems with $\leq 10^{8.67}$ P viscosity (Table 2). This enhancement of densification rate ($d\rho/dt$) can be related to reduction in viscosity according to the

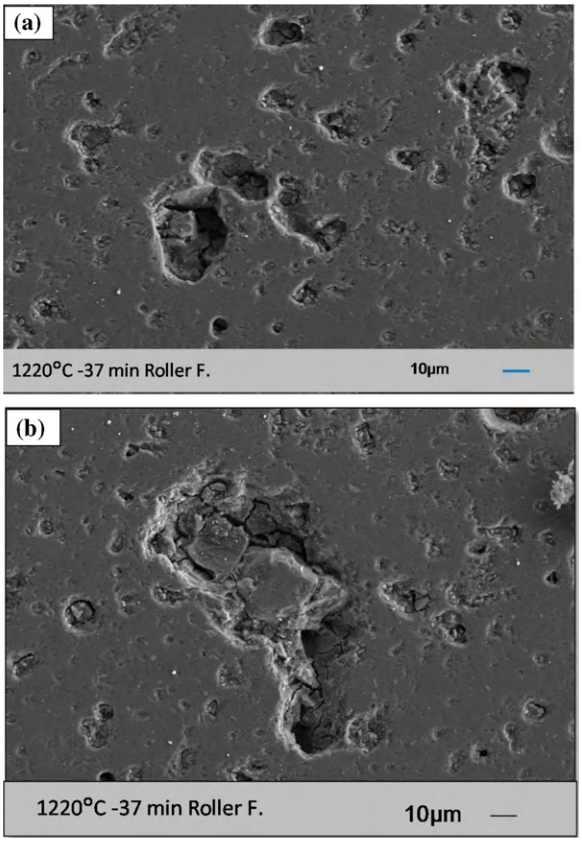

Fig. 3. SEM micrographs of the standard porcelain stoneware tile after sintering at 1220 °C (log η = 9.7 Poise at 1220 °C).

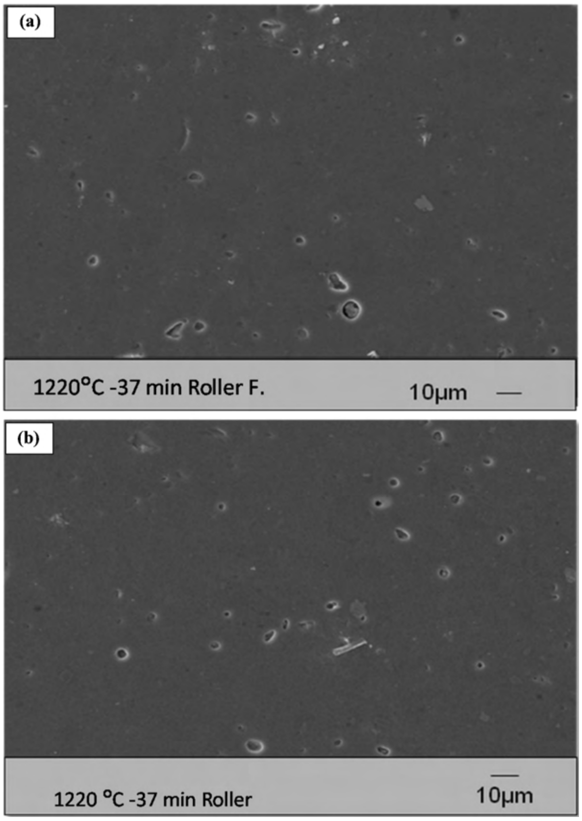

Fig. 4. SEM micrographs of (a) the N1 (log η = 8.67 Poise) and (b) the N5 (log η = 8.62 Poise) porcelain stoneware tile compositions after sintering at 1220 °C.

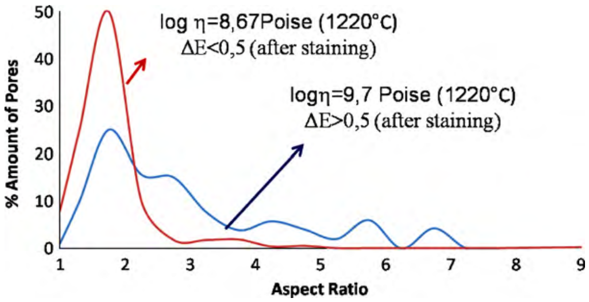

Fig. 5. Pore aspect ratio distribution for the standard (log $\eta = 9.7$ Poise) and the N1 (log $\eta = 8.67$ Poise) porcelain tile compositions after sintering at 1220 °C.

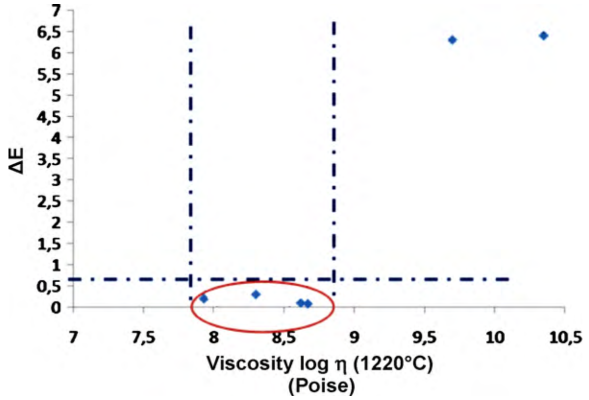

Fig. 6. Influence of the viscosity on the colour variation value (ΔE) for the porcelain stoneware tiles.

following equation[18]:

$$\frac{d\rho}{dt} = \frac{kn^{1/3}\gamma^{1/3}}{\eta}$$

where k and n are constants, γ is surface energy and η is viscosity. Surface energy does not change significantly with the compositional changes in the present study. As a result, viscosity remains as a key parameter to affect densification.

On the other hand, variation of the viscosity affected the microstructural properties of the porcelain tiles. Fig. 3(a) and (b) shows the microstructures of the system with $10^{9.7}$ P viscosity after sintering at 1220 °C. There are large and irregular pores in the microstructure which can reduce mechanical strength and stain resistance of the porcelain stoneware tiles. Fig. 4(a) and (b) exhibits microstructures of the systems with $10^{8.67}$ and $10^{8.62}$ P viscosity values after sintering at 1220 °C, respectively. In both cases, pore concentration is much lower than the system with $10^{9.7}$ P viscosity (Fig. 3). For the systems with $\leq 10^{8.67}$ P viscosity, pore morphology is more spherical. Fig. 5 shows the pore distributions in the systems with $10^{8.67}$ and $10^{9.7}$ P viscosity values as a function of aspect ratio. In accordance to the SEM images presented in Figs. 3 and 4, the latter system exhibits pores with large aspect ratio distribution while the former system exhibits narrower distribution. Although the system with $10^{9.7}$ P viscosity has pores with as high as 7.5 aspect ratio values, there is almost no pore with ≥ 4 aspect ratio in the system with $10^{8.67}$ P viscosity (Fig. 3). These results suggest that decreasing viscosity does not only result in less closed porosity but also favours spherical pore morphology which is critical for achieving porcelain stoneware tiles with high stain resistance.[3,19]

Fig. 6 shows the colour variation value (ΔE) as a function of the viscosity. For the systems with $10^{9.7}$ and $10^{10.35}$ P viscosity, the ΔE values are 6.2 and 6.4, respectively. This means that the marker stain cannot be removed by simple water cleaning from surfaces of these samples. Fig. 7(a) and (b) shows the pictures of the remaining stains (after water washing) over sample surfaces with $10^{9.7}$ and $10^{10.35}$ P viscosity. On the other hand, the samples with $\leq 10^{8.67}$ P viscosity, the ΔE value is below 0.5 which means that the marker stain can be removed from the surface after cleaning with water (Fig. 7c). These results show that to achieve high stain resistant porcelain stoneware tiles in the studied system, the composition should be tailored in such a way that the viscosity of the tile should be $\leq 10^{8.67}$ P at sintering temperature. This critical viscosity level forms the upper limit of viscosity to fill the pores effectively and densify the compact while modifying the pore morphology.

Although lower the viscosity results in less and spherical closed porosity with improved stain resistance, excess viscosity decrease (i.e., too low viscosity) can bring additional problems such as pyroplastic deformation of the tiles. Therefore, there should be also a lower limit for the viscosity below which the tile exhibits pyroplastic deformation. To determine the lower viscosity limit for the studied system, the samples' shape was

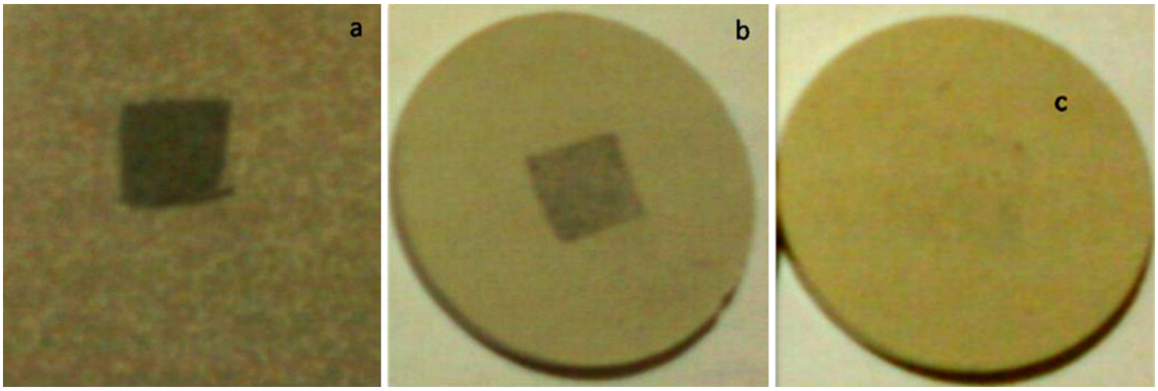

Fig. 7. Comparison of the stain resistance behaviours of (a) the Standard porcelain stoneware tile composition (log $\eta = 9.7$ Poise) (b) the N2 composition (log $\eta = 10.35$ Poise) and (c) the N1 composition (log $\eta = 8.67$ Poise).

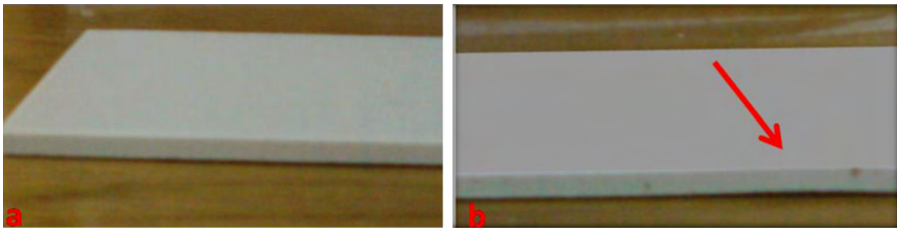

Fig. 8. Pictures of (a) the N1 and (b) the N4 porcelain stoneware tile samples after sintering at 1220 °C.

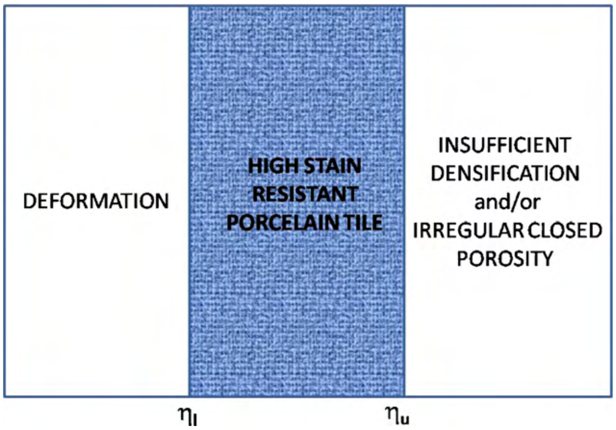

Fig. 9. Hypothetical map which shows the relationship between the viscosity of the tiles and microstructure development and subsequently stain resistance, and deformation.

analyzed whether there is any distortion or not after sintering. It has been observed that although the samples with $10^{8.67}$ and $10^{8.35}$ P viscosity do not demonstrate any deformation, the samples with $10^{7.93}$ P viscosity shows deformation (Fig. 8). These results suggest that the lower limit for the viscosity is somewhere between $10^{7.93}$ and $10^{8.35}$ P. That means the system with a viscosity below this limit exhibits deformation in the studied porcelain stoneware tile system.

4. Conclusions

In this study, it has been shown that thermomechanical analyses (i.e., sintering experiments under loading) can be successfully utilized to measure viscosity of the whole tile body. In addition, it has been found that the Na_2O/K_2O ratio affects the viscosity of the porcelain stoneware tiles and as the ratio increases the viscosity decreases. This viscosity decrease plays a significant role in microstructure development and subsequently it can be used to improve the stain resistance of the tiles remarkably. 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 to achieve high stain resistant porcelain stoneware tiles with no deformation. For the studied system and the viscosity range, two critical viscosity values have been noticed; (i) the upper viscosity limit above which insufficient densification occurs and/or irregular pore structure is observed and (ii) the lower viscosity limit below which the tiles exhibit pyroplastic deformation. If the stain resistance (as ΔE value), microstructure characteristics and deformation are drawn as a function of the viscosity on the same graph, the upper limit and the lower limit of viscosity can be drawn on this graph. Such a graph can be used as a map to achieve high stain resistant porcelain stoneware tiles with no deformation via tailoring viscosity of the tile composition as shown in Fig. 9. Such kind of maps should be developed for the tile systems to be studied so that they can be utilized as a guide to predict the densification characteristics and stain resistance properties of the tiles as a function of their viscosity. In the present study, the upper and lower viscosity limits were $10^{8.67}$ and a value between $10^{7.93}$ and $10^{8.35}$ P, respectively. Accordingly, for the studied system if the viscosity of the tile is in between these limits, then high stain resistant polished porcelain stoneware tiles can be produced readily without any deformation.

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