DEVELOPMENT OF PORCELAIN TILE COMPOSITION WITH HIGH IMPACT RESISTANCE

N. T. Selli, A. Tunali, T. Yagyemez, F. Duman, E. Talsik

Eczacıbasi Building Products Co. Innovation Center Bozuyuk/Bilecik, Turkey

1. ABSTRACT

Recently, porcelain stoneware tiles have become very popular due to their outstanding technical and functional properties, such as low porosity and low water absorption. However, besides these superior features, they also have some disadvantages, such as low impact strength. Especially in areas where human traffic is high, such as airports, supermarkets, etc., high-impact resistant tiles are preferred. The aim of this study is to design porcelain tile compositions with high impact strength. Newly developed compositions were obtained by changing SiO_2/Al_2O_3 ratio via standard porcelain body. Technical properties of the newly developed compositions were compared with the standard composition. SEM and XRD analyses were conducted. Impact resistance of the compositions was tested with the method stated in -CSTB - NF UPEC (French Quality Certificate) - Specification No: 2898 (Resistance of the tiles against the impact strength and 510 g mass) and the results were compared.

2. INTRODUCTION

The porcelain tiles that emerged at the end of the 1980s are becoming increasingly important, with the day-by-day development of their superior mechanical properties and standing in the ceramic tile market. Thanks to the technical properties (low water absorption value, high abrasion and scratch strength and high hardness value), porcelain tiles have been substantially developed. In addition to these properties, it is expected that porcelain tiles also have high resistance against instantaneous loads such as impact strength. Specific studies for the increasing impact strength of ceramic structures were especially discussed for ballistic applications. As also seen in literature and patent search, crystalline and vitreous phase amount, type, amount and size of crystalline phases are critical for the mechanical resistance of porcelain structures. However, in these publications, the effect of the type and amount of crystal phases on the impact strength of porcelain tiles was not discussed. Thus, there is a gap regarding studies for increasing the impact strength of porcelain tiles, both in literature and in application stage. In this study, the aim was to examine the effect of the control of crystalline phase (quartz, mullite, etc.) and vitreous phase amount occurring in the structure composition on the impact strength of porcelain tile.

3. METHODS AND PROCEDURES

Starting from the standard body mix, different amounts of sodium and potassium feldisphathic sands were added into the system and Al_2O_3 amounts were increased, while quartz amounts were decreased in the formulation. The new composition was denoted as D1. Chemical characterisation 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. New compositions were wet milled for 20 minutes by a laboratory ceramic jar mill containing 70 wt% solid and 1.0 wt% deflocculant. Slips were dried at 110°C. The discs 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) using the optical 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 1250°C, without soaking at peak temperature in air atmosphere condition to determine flex points as stated by Paganelli [20]. Total heat treatment was approximately 40 minutes and the peak temperature was 1220°C in roller kiln. Firing shrinkages were determined by measuring the diameter of the discs before and after sintering. Water absorption of the sintered disc was measured by a water displacement method according to ISO 10545-3. Crystalline phases in the fired samples were determined by XRD analyses. For XRD analyses, sintered samples were scanned from 2Φ= 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. Crystalline phase composition was quantitatively 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). EHT voltage was set to 20 kV. 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.

Porcelain tiles prepared with the developed composition (D1) and standard porcelain tiles were tested with the method stated in -CSTB - NF UPEC (French Quality Certificate) - Specification No: 2898 (Resistance of the tiles against the impact strength and 510 g mass) standard and the results were compared. The tile composition with no crack formation on the surface is classified as having high impact strength.

Compositions	STD (Mean)(S.D)	N1 (Mean)(S.D)
SiO_2	70.39 ± 2	62.2± 2
TiO_2	0.55±0.01	0.67± 2.0
Al_2O_3	17.95±1.0	25.92±1.0
Fe_2O_3	0.75±0.01	0.52±0.01
MgO	0.93±0.2	0.67±0.2
CaO	0.74±0.2	0.54±1.0
Na_2O	2.67±0.2	4.94±0.2
K_2O	1.31±0.2	1.31±0.2
L.O.I	4.71±0.2	3.20±0.2
SiO_2/Al_2O_3	5.797	4.730

Table 1. *Chemical composition (wt%) of standard porcelain tile (STD) and chemical composition (wt%) of newly developed porcelain tile (N1).*

Properties	STD	N1
Flex Points (°C)	1220	1220
Water Absorption (wt%)	%0.06±0.01	~0.01±0.01
Firing Shrinkage (%) (1220°C)	7.5±0.1	7.6±0.1

***Table 2**. Comparison of the technical properties of porcelain stoneware tiles.*

4. RESULTS AND DISCUSSION

In this study, newly developed N1 porcelain stoneware tile composition and standard porcelain stoneware tile compositions were characterised. The results were compared with standard porcelain stoneware tile in order to investigate applicability of N1 porcelain stoneware tile composition in the production line. To understand the densification behaviour, new compositions' and standard white porcelain stoneware composition's flex points were determined (Table 2). Fired samples' water absorption values are represented in Table 2. The water absorption values of sintered samples were almost zero, indicating that the fired body achieves the standard requirement. As a result of the quantitative analysis from XRD, amounts of crystal phases and vitreous phase occurring in standard composition and N1 composition were determined. Results are given in Table 3. It was found that standard white porcelain tile composition (STD) contained ~13.65 wt% quartz, ~13.31 wt% anorthite, ~0.41 wt% mullite with the remainder glassy phase (~72.63 wt%); N1 composition contained ~10.54 wt% quartz, ~14.10 wt% anorthite, ~7.16 wt% mullite with the remainder glassy phase (~68.2 wt%). According to these results, quartz amount and vitreous phase amount decreased in N1 composition compared to STD porcelain tile composition.

Phases and their content (wt%)	**STD**	**N1**
Quartz	13.65±0.3	10.54±0.3
Anorthite	13.31±0.2	14.10±0.2
Mullite	0.41±0.2	7.16±0.1
Glassy phase	72.63±0.5	68.2±0.5

***Table 3**. Phase composition of standard porcelain stoneware tile (STD) and N1 composition.*

Finally, at the comparison of these results, it can be said that the basic difference between N1 composition microstructure and standard porcelain tile microstructure is that there is quite a few mullite crystals, even in clustered form, in the N1 composition microstructure. In the new composition (N1), an impact strength test was performed to see the effect of the increased mullite crystals and decreased quartz crystals and vitreous phase on the impact strength.

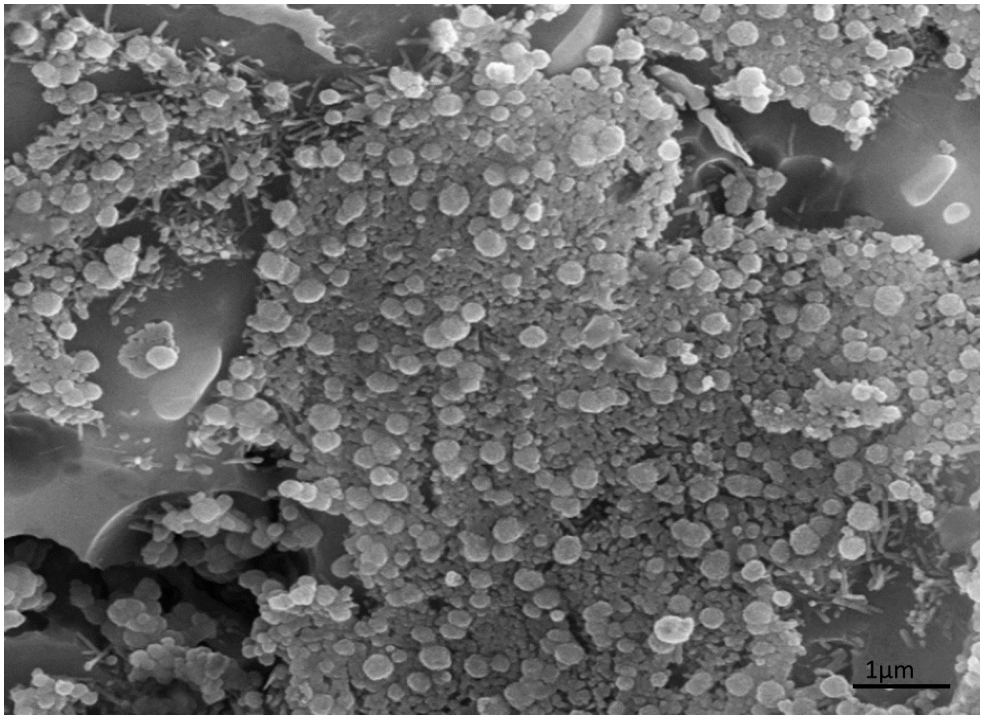

***Fig.1**. SEM micrograph of the standard porcelain stoneware tile (STD) composition.*

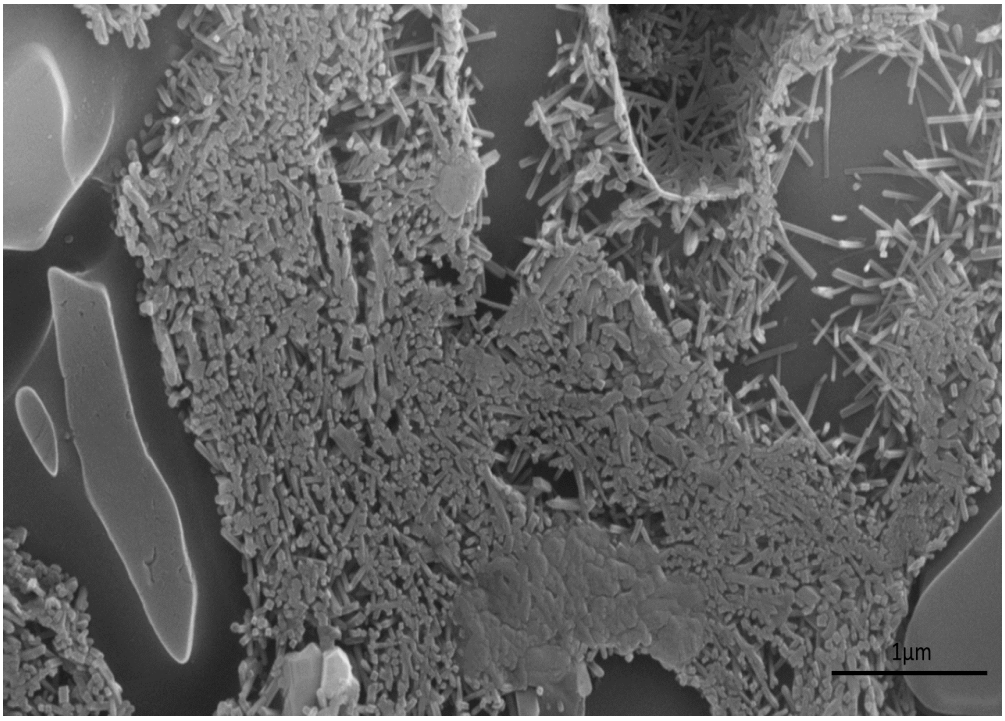

***Fig.2**. SEM micrograph of the newly developed porcelain stoneware tile (N1) composition.*

N1 composition compensated the porcelain tile standards with its technical properties, and standard porcelain tile compositions currently provided in the production were produced in pilot scale and pressed in a manner to have a 20 x 20 cm size and thickness of 14 mm, and fired in the operating oven at 1220^{0}C for 50 minutes. Then, the samples were subjected to impact strength test. Results obtained from the impact strength test are shown in Fig. 3. In the tiles produced with standard porcelain tile composition, crack was formed in the tiles in each of the experiments made 3 times. In the tiles produced with N1 composition, however, crack formation is not encountered in the 3 experiments as a result of the impact strength test. Thus, porcelain tiles produced with N1 composition passed the impact strength test.

5. CONCLUSIONS

Porcelain tiles prepared with the developed composition (N1) and standard porcelain tiles were tested with the method stated in -CSTB - NF UPEC (French Quality Certificate) - Specification No: 2898 (Resistance of the tiles against the impact strength and 510 g mass) standard and the results were compared. With the composition design made in the new composition, mullite amount was increased (~7.16 wt% mullite) compared to the standard porcelain tile structure; quartz amount (~10.54 wt% quartz) and vitreous phase amount (~68.2 wt%) were decreased. It can be interpreted that, along with the increase in mullite crystals and also the decrease in the amount of vitreous phase, the impact absorption effect was strengthened and thereby, the impact strength test was passed.

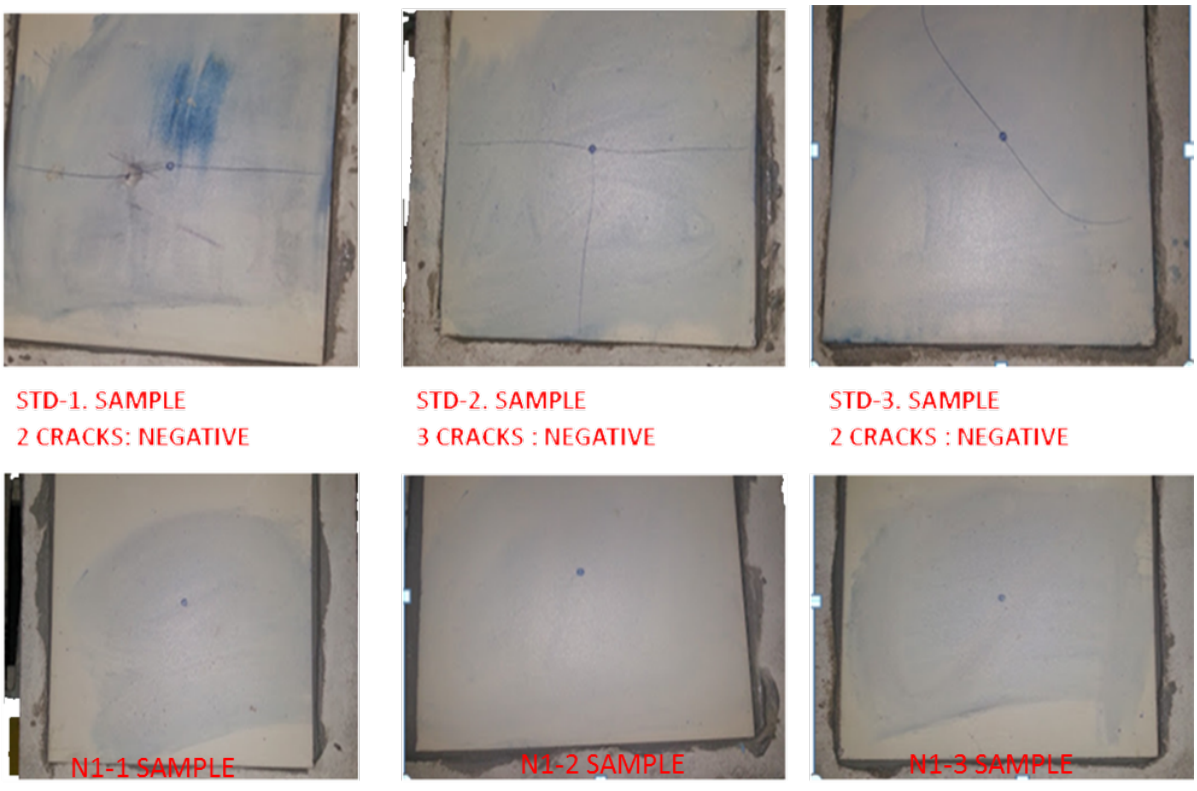

***Fig.3**. Pictures of (20 cm x 20 cm) standard (STD) and D1 porcelain stoneware tiles after impact test.*

6. ACKNOWLEDGEMENTS

I would like to thank Mr. Vedat Bayrak for his help and fruitful discussions throughout this study.

7. REFERENCES

[1] **Suvaci E., Tamsu N.,** The role of viscosity on microstructure development and stain resistance in porcelain stoneware tile, J. Eur. Ceram. Soc. **[30],** (2010), 3071-3077

[2] **Tunali A., Özel E., Turan S.,** Production and characterization of granulated frit to achieve anorthite based glass-ceramic glaze, J. Eur. Ceram. Soc. **[35]**, (2015), 1089–1095

[3] **Tamsu N.,** Enhancing the Stain Resistance of The Polished Porcelain Tile, Ph.D. Thesis, Anadolu University, Turkey (2010).

[4] **Kirchner H. P.,** Method of Improving Impact Resistance of Ceramic Bodies and Improved Bodies, USA Patent-3.953.636, (1976)

[5] **Cunha T.B., Wu J., Peitl O., Fokin V. M., Edgar D. Zanotto L., Iannucci A. R.,** Mechanical Properties and Impact Resistance of a New Transparent Glass Ceramic, Advanced Engineering Materials, 9, **[3],** (2007), 191-196

[6] **Li H. T., Fei W. D., Yang D. Z.,** Damage of aluminum borate whisker reinforced 6061 aluminum composite under impact of hypervelocity projectiles, Mater. Sci. Eng., 333 **[2],** (2002), 333-377

[7] **Nordberg M. E., Mochel E. L., Garfinkel H. M., Olcott J. S.,** Strengthening by Ion Exchange, J. Am. Ceram. Soc., 47 **[6],** (1964) 215-219

[8] **Junior A. N., Hotza D., Soler V. C., Vilches E. S.,** Influence of Porcelain Tile Starting Composition on Tile Microstructure and Mechanical Properties, Qualicer 2008, (2008), P. BC. 61-73

[9] **Amigó J.M., Clausell JV., Esteve V., Delgado J. M., Reventós M. M., Ochando L. E., Debaerdemaeker T., Martí F.,** X-ray powder diffraction phase analysis and thermomechanical properties of silica and alumina porcelains, J. Eur. Ceram. Soc. **[24],** (2004), 75-81

[10] **Mattyasovszky-Zsolnay L.,** Mechanical strength of porcelain, J. Am. Ceram. Soc. **[40],** (1957), 299-306

[11] **Hamano K., Wu Y.H., Nakawaga Z., Hasegawa M.,** Effect of grain size of quartz on mechanical strength of porcelain bodies, J. Ceram. Soc. Jpn. **[99]**, (1991), 149-53

[12] **Stathis G., Ekonomakou A., Stournaras C. J., Ftikos C.,** Effect of firing conditions, filler grain size and quartz content on bending strength and physical properties of sanitaryware porcelain, J.Eur. Ceram. Soc. **[24],** (2004), 2357-66

[13] **Zoellner A.,** Some chemical and physical properties of porcelain, Sprechsall **[41],** (1908), 471–473

[14] **Carbajal L., Rubio-Marcos F., Bengochea M. A., Fernández J. F.,** Properties related phase evolution in porcelain ceramics, J. Eur. Ceram. Soc., **[27],** (2007), 4065-9

[15] **De Noni Jr. A., Hotza D., Cantavella V. S., Sánchez E., Vilches E.,** Effect of quartz particle size on the mechanical behaviour of porcelain tile subjected to different cooling rates, J. Eur. Ceram. Soc., **[29],** (2009), 1039-46

[16] **Dondi M., Guarini G., Melandri C., Raimondo M., Cavalante P. M. T., Zanelli C.,** Resistance to deep abrasion of porcelain stoneware tiles: Key factors, Ind. Ceram. **[25],** (2005), 71-8

[17] **Leonelli C., Bondioli F., Veronesi P., Romagnoli M., Manfredini T., Pellacani G.C., Cannillo V.,** Enhancing the mechanical properties of porcelain stoneware tiles: a microstructural approach, J. Eur. Ceram. Soc., **[21],** (2001), 785-93

[18] **Sánchez E., Orts M.J., García-Ten J., Cantavella V.,** Porcelain tile composition effect on phase formation and end products. Am. Ceram. Soc. Bull., **[80],** (2001), 43-9

[19] **Esposito L., Salem A., Tucci A., Gualtieri A., Jazayeri S.H.,** The use of nepheline-syenite in a body mix for porcelain stoneware tiles, Ceram. Int.,**[31],** (2005), 233-240

[20] **Paganelli M.,** Using the optical dilatometer. Am. Cer. Soc. Bull., **[81],** (2002), 25-30