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Applied Clay Science 29 (2005) 137–143

www.elsevier.com/locate/clay

Technical Note

Shrinkage and strength behaviour of quartzitic and kaolinitic clays in wall tile compositions

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Received 19 August 2003; received in revised form 23 March 2004; accepted 14 October 2004

Abstract

Five different clays of Indian sources were characterized and its influence in wall tile compositions was evaluated. The results show that the compositions containing a higher amount of quartzitic clays possess lower shrinkage (<1.0%) in the temperature range of 1050–1150 °C. Body compositions containing higher amount of kaolinitic clays showed lowest water absorption and highest strength due to better densification. XRD studies conducted on fired tile specimens (1150 °C) show the formation of anorthite and quartz as major crystalline phases and monticellite and mullite as minor phases. SEM picture of a selected sample show the presence of uniformly distributed pores in the matrix. No cracks were seen around the quartz grain.

Keywords: Kaolinitic clay; Ceramic wall tile; Porcelain; Low shrinkage; Fly ash

1. Introduction

An optimum combination of various clays is the essential ingredient in ceramic wall tile compositions, which provides plasticity and green strength during forming stages and contribute substantially to the colour of the fired products depending upon the impurity oxides present. Two types of clays are generally used which are often termed as china clay and ball clay. Both are kaolinitic in nature; contain quartz as major impurity mineral along with iron oxide and titania as minor impurities. Ball clays are finer than china clay and often referred to as plastic clay as they provide greater plasticity in a ceramic body.

The formation, structure, mineralogical and other physico-chemical properties of various types of clay minerals are widely studied subject discussed in the literatures (Hinkley, 1962; Kingery, 1976; Murray and Keller, 1993; Moore and Reynold, 1997; Carty and Senapati, 1998). Other important materials that are traditionally used in making ceramic wall tiles are carbonates, which are commonly selected from chalk, limestone, marble and dolomite. These carbonate materials form a fusible eutectic with alumina and

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0169-1317/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.clay.2004.10.002

silica (Yatsenko et al., 1998) and also act as fluxing minerals. Controlling shrinkage on firing is one of the important criteria in wall tile manufacture because excessive shrinkage causes deforming of articles during firing. One of the methods for controlling firing shrinkage is the use of various calcium containing materials such as wollastonite, blast furnace slag and precalcined materials such as fly ash, a by-product of thermal power plants. Many authors (Marghussion and Yekta, 1994) reported the production of wall tiles containing iron slags with firing shrinkage less than one per cent and good mechanical properties. They produced single fired low shrinkage wall tiles possessing all requisite properties from blast furnace slag, different types of clays and sand filler. Other authors (Brusa and Bresciani, 1995; Dana and Das, 2002) reported new multi purpose bodies containing various clays, wollastonite and calcium carbonate, with or without pyrophyllite, feldspar and sand for both wall and floor tiles. Effects of partial substitution of clay by fly ash in porcelain compositions has been studied (Das et al., 1996; Kumar et al., 2001; Shah and Maity, 2001). The authors reported an increase in strength up to 25–30% fly ash addition, beyond which the strength decreased. Because fly ash is a calcined material, it has very low shrinkage which is beneficial in wall tile compositions.

In the present investigation, five different clay samples were characterised with respect to their chemical, mineralogical, thermal and fired properties. These clays were incorporated in different proportions in the wall tile compositions keeping other raw materials the same. The effect of these clays on the properties of the wall tile body was studied by measuring their linear shrinkage, bulk density, water absorption and flexural strength. A few selected samples were studied by XRD to identify the various phases developed on firing and SEM for micro-structural evaluation.

2. Materials and methods

Five clays collected from rural areas of West Bengal (Birbhum, South 24 Parganas and Bankura districts), India were characterized with respect to their chemical, mineralogical and thermal analysis. Fired characteristics of all the clays were studied separately by preparing rectangular bars (100×15×6 mm) from the respective clay powder followed by oven drying at 110 °C and firing at 1000 °C with 1 h soaking in an electric furnace. The fired clay bars were tested for linear shrinkage, bulk density, water absorption and colour. Non clay materials viz. fly ash, wollastonite and dolomite were also chemically analysed. Because fly ash is a precalcined material, it was subjected to XRD studies to identify the phases present.

One kilogram batch of each composition (Table 1) was prepared by wet milling. The slurries were dried and disintegrated. The dry powders were thoroughly mixed with 5–6 wt.% water and rectangular bars (100×15×6 mm) were prepared using uniaxial compaction at a pressure of 200–250 kg/cm^2. The compacted bars dried at 110 °C till the moisture content was reduced to less than 0.5 wt.% were fired in the temperature range of 1050–1150 °C for a soaking period of 1 h in an electric furnace. The fired samples were then subjected to various tests including linear shrinkage, bulk density, water absorption and flexural strength.

A gravimetric method was utilized to determine $SiO_2$and Al_2O_3, whereas Fe_2O_3, CaO and MgO were determined volumetrically (Hillebrand and Lundell, 1953). The crystalline phases present in the raw materials and fired samples were identified by XRD (Philips "X-Pert Pro" diffraction unit attached with secondary monochromator, automatic divergence slit and nickel filter to get monochromatic Cu-Kα). Differential thermal analysis (DTA) technique was used to study the thermal behaviour of all the clays (Netzsch STA 409C) at a heating rate of 10 °C/min. Bulk density and water absorption were determined by a boiling water method. An Instron 5500 R machine was utilized to determine flexural strength. Microstructural features of the fractured specimens were examined by SEM (LEO 430i). The color measurements were done by the method (Hill and Lehman, 2000) where a scanner (HP 2300c, Hewlett-Packard) attached to a computer was used. The scanner illumination source was maintained constant throughout the study. The values are expressed as "L" (lightness factor) and chromaticity

Table 1
Batch compositions (wt.%)

Raw materials	WT-1	WT-2	WT-3
Clay A	20	20	20
Clay B	10	20	NIL
Clay C	10	NIL	20
Clay D	10	20	NIL
Clay E	10	NIL	20
Fly ash	20	20	20
Wollastonite	10	10	10
Dolomite	10	10	10

Table 2
Chemical analysis of the clays (wt.%)

Oxide content (wt.%)	Clays				
	A	B	C	D	E
SiO_2	68.70	49.64	62.94	47.80	45.36
Al_2O_3	16.43	32.90	23.83	33.33	35.71
Fe_2O_3	3.41	1.27	0.62	1.21	2.46
TiO_2	0.38	0.65	0.93	0.81	1.35
CaO	1.64	Tr.	0.88	0.79	0.41
MgO	2.18	1.19	0.19	0.19	0.10
K_2O	0.13	1.43	0.52	0.90	0.19
Na_2O	1.70	0.29	0.45	0.63	0.31
LOI	5.00	12.44	9.25	13.97	13.80

Table 4
Chemical analyses of non-clay materials (wt.%)

Chemical constituents	Fly ash	Wollastonite	Dolomite
SiO_2	59.02	45.80	Tr.
Al_2O_3	27.59	1.27	0.80
Fe_2O_3	4.18	1.47	0.47
TiO_2	1.55	0.28	0.01
CaO	1.39	42.46	30.39
MgO	Tr.	0.58	21.62
K_2O	1.35	0.52	0.25
Na_2O	0.17	1.42	0.63
LOI	4.59	5.86	45.47

coordinates “a” (red) and “b” (yellow). Reproducibility in measurements was observed.

3. Results and discussion

3.1. Characteristics of raw materials

The chemical analyses of all the clays are provided in Table 2. It is observed from Table 2 that clays A and C contain SiO_2—62–68 wt.% and Al_2O_3—16–24 wt.%, while B, D and E contain SiO_2—45–50 wt.% and Al_2O_3—32–36 wt.%. The Fe_2O_3 content of clays A and E is on the higher side. XRD studies and chemical analysis show that clays A and C are quartzitic and clays B, D and E are kaolinitic. Also, DTA study revealed an endothermic peak in the temperature range of 509–570 °C due to removal of chemically combined water and an exothermic peak in the temperature range of 936–984 °C. The appearance of this exothermic peak is due to the formation of γ-Al_2O_3 spinel phase which was also predicted by other authors (Brindley and Nakahira, 1959; Grimshaw, 1971; Chen and Tuan, 2002).

The characteristics of the clay samples after firing at 1000 °C are given in Table 3. From Table 3, it is observed that percent linear shrinkage (%LS) of clays A and C at 1000 °C is significantly lower (0.3%) compared to other clays (>2%) and this is very advantageous for wall tile compositions. This may be due to the presence of more quartz in clays A and C. Lower ranges of percent water absorption (%WA 13–16) in clays A and C indicate better vitrification at 1000 °C compared to others. The fired colour of all the clays is expressed in terms of L, ‘a’ and ‘b’ values. The lightness in color (L value) of the clays used in the present study follow the sequence clay E>clay D>clay B>clay C>clay A. The wide variation in L, a and b values between the

Table 3
Characteristics of fired clay samples (1000 °C, 1 h soaking)

Clays	%LS	BD (g/cc)	%WA	Colour		
				L	a	b
A	0.30	1.81	13.0	53	25	30
B	2.11	1.62	22.7	80	9	12
C	0.30	1.81	16.4	75	4	19
D	2.89	1.58	25.3	84	6	14
E	2.74	1.51	29.05	85	7	12

Table 5
Oxide composition of experimental bodies (wt.%)

Constituent oxides	WT-1	WT-2	WT-3
SiO_2	50.70	49.61	51.78
Al_2O_3	21.59	22.26	20.92
Fe_2O_3	2.27	2.21	2.33
TiO_2	0.79	0.71	0.87
CaO	8.09	8.05	8.15
MgO	2.82	2.93	2.71
K_2O	0.67	0.84	0.52
Na_2O	0.75	0.76	0.73
LOI	12.30	12.61	11.89

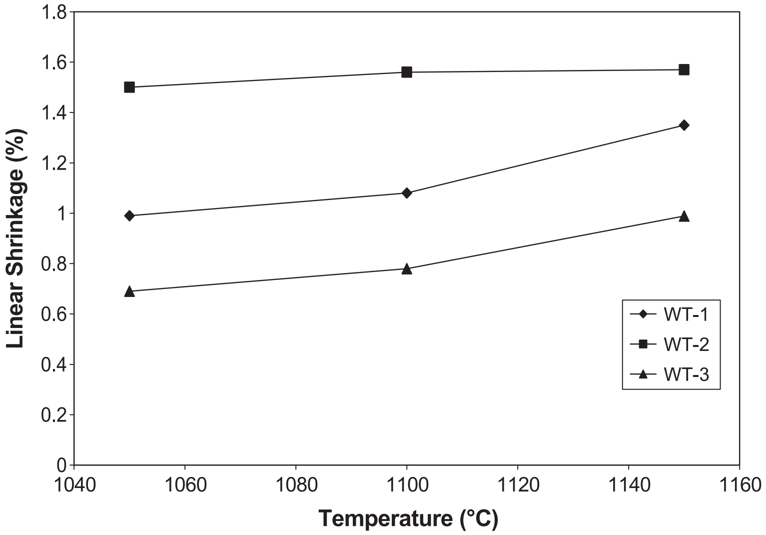

Fig. 1. Variation in linear shrinkage with temperature.

clays is due to the presence of colouring impurities (mainly Fe_2O_3 and TiO_2). The red color of clay gets stronger as the amount of Fe_2O_3 increases (Lee et al., 2002; Das, 2003). Clay A is reddish (lower L value and higher a, b values), while other clays are whitish (higher L value and lower a, b values).

Chemical analysis of non clay materials are shown in Table 4. It is noted that fly ash contains around 4% Fe_2O_3 and 4.6% wt. loss on ignition (due to unburnt carbon). Due to the presence of such high amounts of iron oxide and unburnt carbon, it is not advisable to use more than 30 wt.% fly ash in tile compositions as observed by many authors (Das et al., 1996; Kumar et al., 2001; Shah and Maity, 2001). An earlier study of the present authors (Das et al., 1996; Dana et al., 2004) confirms the presence of quartz and mullite in fly ash. The presence of such pre-synthesized mullite in

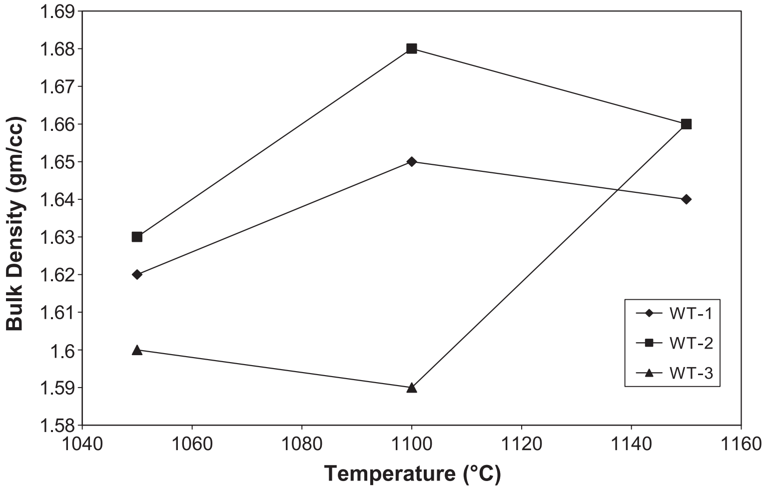

Fig. 2. Variation in bulk density with temperature.

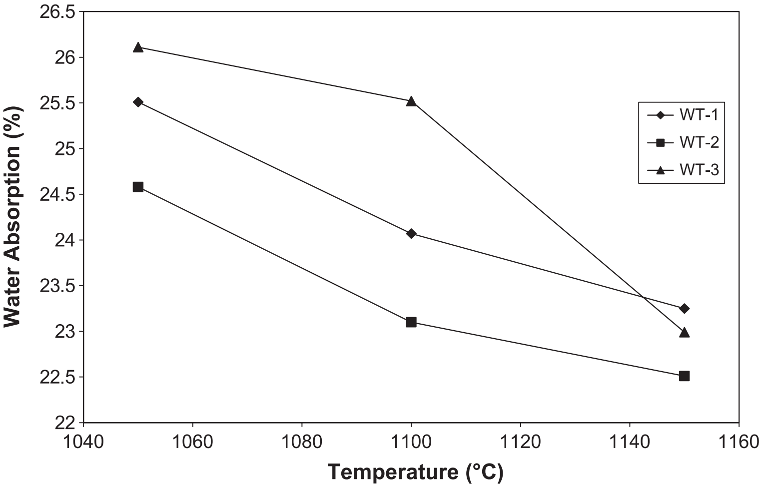

Fig. 3. Variation in water absorption with temperature.

tile compositions contributes towards strength improvement. The chemical analysis of wollastonite and dolomite show that they are more or less pure.

3.2. Characteristics of wall tile bodies

The oxide composition of the experimental wall tile bodies are given in Table 5. It is observed that there is no significant variation in the oxide constituents between the bodies due to the optimal combination of different clays used in the present study keeping other raw materials the same. However, due to differences in chemical and mineralogical behaviour among the clays, a significant variation in tile properties is expected on firing and this will be discussed in the later section.

Fig. 1 shows the results of linear shrinkage of the experimental bodies in relation to heating temperature. No significant increase in shrinkage is observed with the increase in firing temperature. WT-3 shows significantly less shrinkage (0.8%) in the temperature range of 1050–1100 °C (usual firing

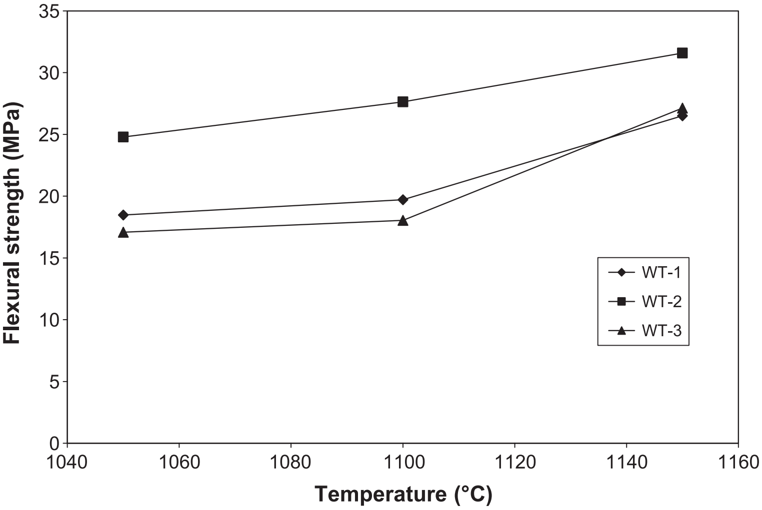

Fig. 4. Variation in flexural strength with temperature.

temperature of commercial wall tile bodies) due to the presence of a higher amount of siliceous clays A and C. Fig. 2 shows the variation in bulk density in relation to heating temperature. No significant variation is observed in bulk density values with heating temperatures. Similarly, the percent water absorption results (Fig. 3) also show no significant variation with heating temperature. WT-2 body containing a higher amount of kaolintic clay achieved the highest density and lowest water absorption compared to others. The results of flexural strength (Fig. 4) show an increase in strength with increase in temperature in all the specimens. Strength of WT-2 body was found to be significantly higher compared to WT-1 and WT-3 bodies at all the temperatures due to better densification. There is no major difference in strength values between the WT-1 and WT-3 bodies with temperature.

The XRD pattern (Fig. 5) of all the 1150 °C heated tile samples confirm the presence of anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$) and quartz ($SiO_2$) as major crystalline phases and monticellite ($CaO \cdot MgO \cdot SiO_2$) and mullite($3Al_2O_3 \cdot 2SiO_2$) as the minor phases. The microstructure of a selected specimen taken on the fractured surface is shown in Fig. 6. Pores are seen to be uniformly distributed in the matrix. No cracks are observed around the quartz grain.

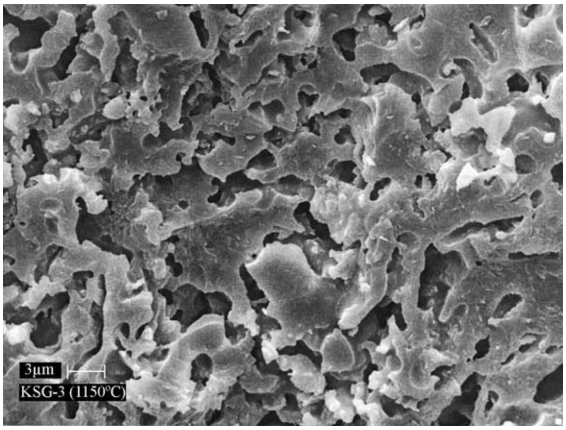

Fig. 6. SEM photomicrograph of a tile specimen heated at 1150 °C (fracture surface).

4. Conclusions

Five clays of West Bengal, India were used in formulating wall tile compositions along with other raw materials including fly ash, wollastonite and dolomite. The tile compositions with a combination

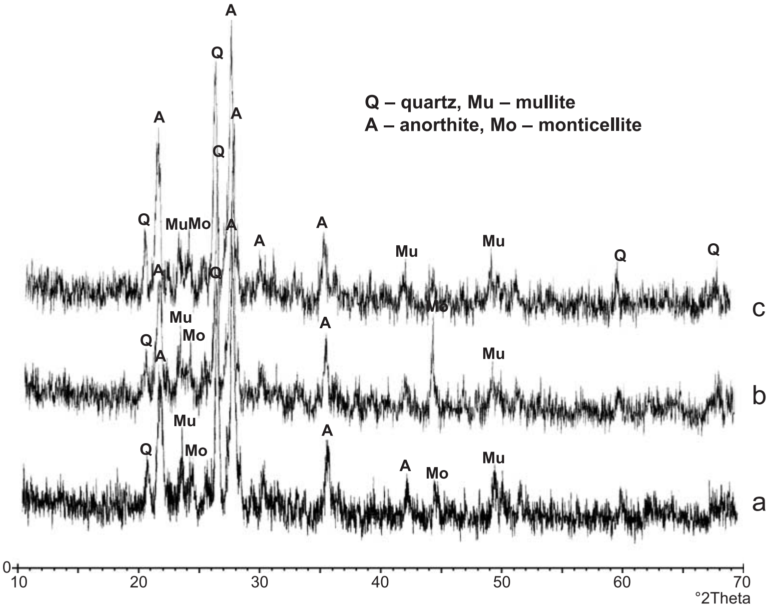

Fig. 5. X-ray diffraction pattern of tile specimens heated at 1150 °C (a: WT-1, b: WT-2, c: WT-3).

of more quartzitic clays show less shrinkage with adequate densification and strength values, whereas the compositions with more of kaolinitic clays show higher shrinkage, higher densification and strength values. Anorthite and quartz are the major phases formed while monticellite and mullite are the minor ones observed in the fired (1150 °C) samples of all the experimental bodies. Microstructure of a selected specimen show absence of cracks around the quartz grains and uniformly distributed pores in the matrix.

Acknowledgements

The authors wish to thank Dr. H.S. Maiti, Director, CGCRI, Kolkata, India for kind permission to publish this paper.

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