THERMAL COMPATIBILITY STUDIES OF VARIABLE BODY AND GLAZE COMPOSITIONS FOR GLAZED CLAY BASED COOKWARE APPLICATIONS

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Abstract

This study was focused on the development of a glazed red clay cookware with adequate thermal shock resistance for open flame cooking applications. Thermal compatibility of different red clay and fritted glaze compositions were investigated using thermal expansion and thermal shock resistance. Coefficients of thermal expansion and thermal shock resistance values of red clay bodies with different proportions of quartz were investigated. Commercially available lead free glazes were selected to satisfy the coefficient of thermal expansion and thermal shock resistance requirements. Thermal conductivity, modulus of rupture, and modulus of elasticity of each body and glaze were measured.Based on the test results, suitable red clay body and glaze compositions were selected and actual size cookware samples were fabricated.The red clay body with 25% quartz having a coefficient of thermal expansion of 60.31×10^{-7} K^{-1} and a thermal shock resistance of 0.97 kJm^{-1}s^{-1}, and the glazes having a coefficient of thermal expansion in the range of (49-51)×10^{-7} K^{-1} and thermal shock resistance in the range of (1.10-1.20) kJm^{-1}s^{-1} could be effectively used to manufacture a glazed red clay cookware product. Hence it could be concluded that a suitable body composition for glazed cookware could be formulated by incorporating quartz in a certain proportion to kaolinitic type red clay.

Keywords: Ceramic cookware, glaze, red clay, coefficient of thermal expansion

Introduction

Thermal compatibility of a ceramic body and glaze in a glazed ceramic product is of great importance in ceramic engineering to fabricate defect free glazed ceramic products. Body and glaze possess their independent expansion characteristics; the lack of compatibility between them is one of the major causes of defects in ceramic fabrication.As the glaze is fixed to the underlying body, expansion of the body and glaze should be compatible with each other to have a defect free object. However practically it is not possible to exactly match the expansion of the body and glaze. Glaze is a glassy material and can bear compressive stresses much better than the tensile stresses. Hence when matching, the glaze is kept in a

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state of slight compression.

Thermal shock resistance is another important property that should be considered during the fabricating of glazed ceramic cookware. The ability of a material to resist sudden temperature changes is known as its thermal shock resistance. Thermal shock occurs when a substrate is exposed to temperature extremes in a short period of time. Under these conditions, the substrate is not in thermal equilibrium, and internal stresses may be sufficient to cause fracture. The thermal stresses depend on the different factors including geometrical thermal boundary conditions and physical parameters, such as coefficient of thermal expansion, modulus of elasticity, thermal conductivity, and mechanical strength.

The term cookware refers to the commonly found utensils used in the kitchen for the purpose of cooking. Ceramic materials are most suitable for cookware applications because they do not contain materials harmful to the human body. Thermal shock resistance is an important factor for cookware as they are directly in contact with an open flame.Red clay, which is the major raw material of the traditional pottery industry in Sri Lanka is available in many parts of the country. Hence a glazed red clay product with enhanced thermal conductivity will be better for cookware. The main drawback of red clay is its low thermal expansion, thus making it difficult to match a glaze. It was found in the literature that the free quartz content in the ceramic body increases the coefficient of thermal expansion (Morgan, 1934). Hence, using quartz for this purpose, the research was carried out to develop a thermally compatible red clay body with leadless fritted glaze having adequate thermal shock resistance for cookware applications.

Materials and Methods

Materials

Sedimentary red clay from the Kelaniya region located in the western province of Sri Lanka was used for the research work since unglazed pottery industries exist in that area. Commercially available quartz powder of 200 mesh size was used. Lead free glaze frits (Johnson Matthey Plc, UK) were used for glaze preparation and sodium silicate was used as a deflocculant in slip preparation.

Experimental Method

The clay samples were dried and sieved through 53 μm test sieves made to British Standard specification BS 410/1986 (British Standards Institution, 1986). X-ray diffraction analysis Rigaku D Max (Rigaku Americas Corp., USA) and chemical analysis were done to analyze the clay samples.

Five clay bodies were formulated by incorporating different percentages of quartz in the red clay body which were 10%, 20%, 30%, 35%, and 40% by dry weight. Bodies were prepared by wet mixing using pot mill and a mechanical stirrer. The test samples were fabricated by slip casting using plaster moulds and fired at 1050^{o}C. The thermal conductivity of each body was measured using the Lee's Disk method (Van Vlack, 1964). Test samples were in the form of a disc with a thickness of 0.6 cmand diameter of 6 cm. Modulus of elasticity was determined using rectangular samples of 10×15×80 mm, both in bending and in compression by measuring the gradient of the linear part of the load-deflection curve just before fracture initiation. The coefficient of thermal expansion at 500^{o}C of each fired body sample was measured by thermo mechanical analyzer (Rigaku Thermoflex TMA). A square bar shape test sample was prepared with dimensions 20×3×4 mm. To calculate the thermal shock resistance (*R*) of a ceramic body, the formula derived by K.D. Kingery was used (Grimshaw, 1971):

$$R = \frac{K\sigma(1-\upsilon)}{E\alpha}$$

where

σ = Tensile strength of the material
K = Thermal conductivity
υ = Poisson's ratio

α = Coefficient of thermal expansion
E = Modulus of elasticity

The slip casting method was used to fabricate the actual size of cookware samples for selected body compositions. Models of actual size cookware utensils were designed using finite element analysis to minimize the thermal shock failure during direct heating. The thermal shock resistance test, as per ASTM C 554-77 method, (ASTM International, 2012) of the product and direct heating of the product on a gas cooker were performed to check the suitability.

Results and Discussion

The X-ray diffraction pattern and the chemical analysis data of the red clay samples given in Figure 1 and Table 1, respectively, confirm that red clay is of the kaolinite group with gibbsite, goethite, and quartz as accessory minerals (Velde, 1992; Van Olphen and Fripiat, 1979; Worrall, 1968).

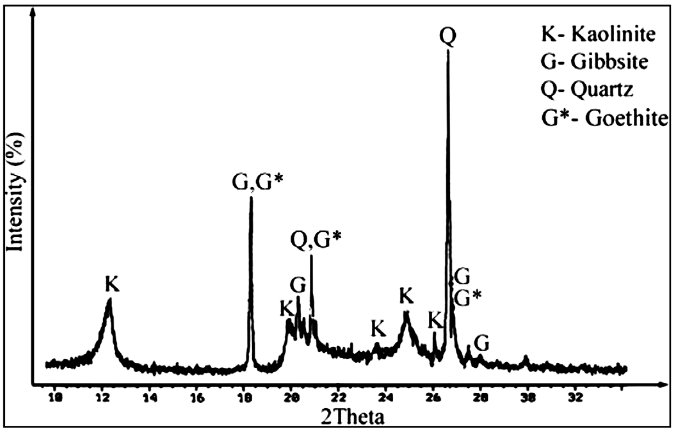


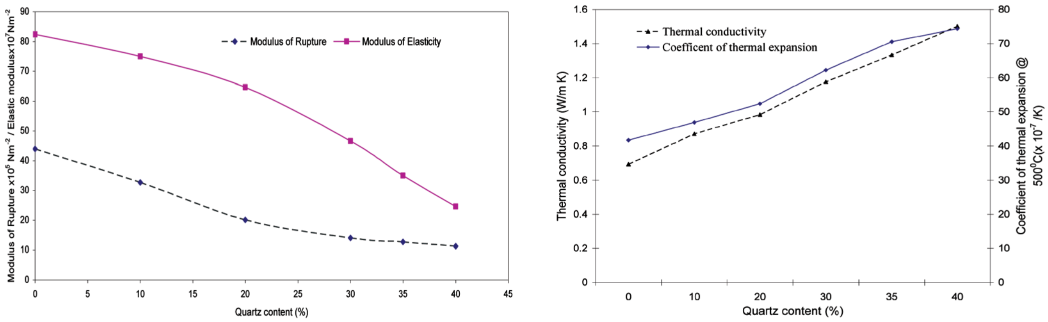
Figure 1. X -ray diffraction pattern of red clay sample

Table 1. Chemical analysis of red clay samples

Constituent	Weight %
SiO_2	41.10
Al_2O_3	31.48
Fe_2O_3	6.05
Na_2O	0.62
K_2O	1.77
CaO	0.28
MgO	0.35
P_2O5	0.21
MnO	0.02
TiO_2	1.49
LOI	16.58
Total	99.95

As shown in Figure 2(a), the modulus of rupture and modulus of elasticity of the red clay body decreased with an increasing quartz content. According to Figure 2(b), the coefficient of thermal expansion at 500°C and thermal conductivity increased with an increasing quartz content of the body (Jayawardene *et al.*, 2008). The thermal shock resistance of the body samples with different quartz contents and fired to a temperature of 1050°C is given in Figure 3. These results indicated that the thermal shock resistance decreased with increasing of the quartz content of the red clay body, but the variation is not uniform (Jayawardene *et al.*, 2009).

Since a body with less quartz content has high thermal shock resistance, it was decided to select a body with the least possible amount of quartz to match the thermal expansion of the glaze. It was necessary to use a glaze which has a lower coefficient of thermal expansion in order to avoid crazing and delayed crazing. However the tested transparent glazes no.1 and no.2 showed high coefficients of thermal expansion and they are not compatible with a body composition having the lowest quartz contents and lowest coefficient of thermal expansion which were found in the matt glazes as shown in Table 2. When using a matt glaze, the true color of the red clay will change to a dull color. However, it was decided to use a matt glaze



(a) (b)

Figure 2. (a) Modulus of rupture and modulus of elasticity vs. quartz content of red clay body (b) Coefficient of thermal expansion at 500^{O}C and thermal conductivity vs. quartz content of red clay body

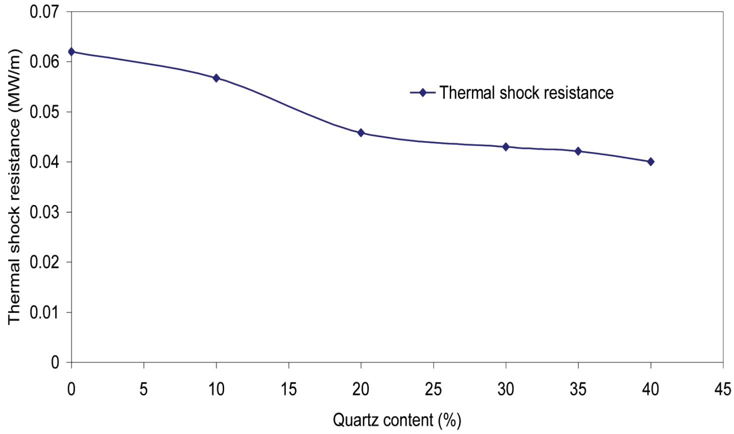


Figure 3. Thermal shock resistance vs. quartz content of red clay body

with a little amount of transparent glaze to make it translucent. Test glazes were prepared by mixing different proportions of matt glaze and transparent glaze. The optimum compositions of a clay body and glazes no. 4 and no. 5 given in Table 3 were selected observing the fired properties and coefficient of thermal expansion results of the tested body and glaze compositions.

The whole cookware item was glazed by the dipping technique and a patch of glaze was removed from the outer bottom surface over an area of 6 cm diameter where the flame directly hits the cookware. This is because if there is any moisture absorbed to the body previously through unglazed areas from the atmosphere, it can vaporize on subsequent heating and exert a pressure on the glaze surface. Therefore this pressure can be released through the unglazed area. Further, when heating on a gas cooker, the bottom glaze surface gets heated much faster than the body. Even though the expansion of the body causes cracking and the glazes are compatible, due to the temperature differences of the glaze and the body, stresses will form on the glaze which can initiate cracking.

According to the results of direct heating and thermal shock resistance tests as per ASTM C 554-77 method, actual size products with unglazed outer bottom surface were found to be the most successful for glazes no. 4 and no. 5. However as glaze no. 5 contains more of the transparent glaze, it gives a better red color appearance than glaze no. 4.

Therefore products of 25% quartz content body with glaze no. 5 were the most compatible products for cookware application. Chemical compositions of frits used to formulate transparent glazes no.1, 2, 3, and the matt glaze are given in the Table 4. This

Table 2. Details of glaze compositions

Name of the glaze	Compositions	(%wt)	Coefficient of thermal expansion @ 500°C
Transparent glaze no: 1	Fritt no1	93%	59.06×10^{-7} K^{-1}
	China clay	7%	
Transparent glaze no: 2	Fritt no 2	93%	59.75×10^{-7} K^{-1}
	China clay	7%	
Transparent glaze no: 3	Fritt no 3	93%	58.32×10^{-7} K^{-1}
	China clay	7%	
Matt glaze	Fritt no 4	93%	41.05×10^{-7} K^{-1}
	China clay	7%	

Table 3. Details of selected body and glaze compositions

Name	Compositions	Coefficient of thermal expansion @ 5000C
Body	Red clay -75% Quartz– 25%	60.31×10^{-7} /K
Glaze no: 4	Matt glaze – 55% Transparent glaze no:3- 45%	49.45×10^{-7} /K
Glaze no: 5	Matt glaze – 50% Transparent glaze no:3 -50%	50.31×10^{-7} /K

gives a better insight into the chemical nature of glazes no.4 and no.5. An optimized cookware design for better thermal shock resistance is given in Figure 4.

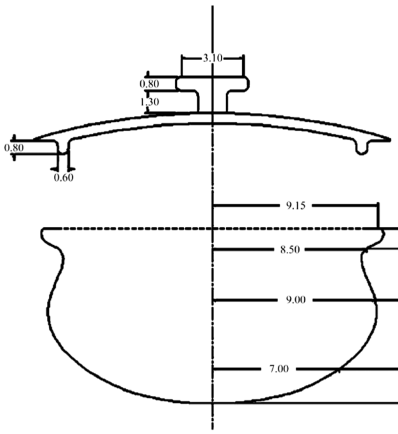


Figure 4. Schematic diagram of the cookware design

Conclusions

A suitable body composition for glazed cookware could be formulated by incorporating quartz in the correct proportion to kaolinitic type red clay. It can be concluded that the kaolinite type red clay body with 25% quartz and having a coefficient of thermal expansion 60.31×10^{-7} K^{-1} and thermal shock resistance 0.97 $kJm^{-1}s^{-1}$, and a glaze (consisting of 50% transparent glaze and 50% matt glaze) having a coefficient of thermal expansion in the range of $(49\text{-}51)\times10^{-7}$ K^{-1} and thermal shock resistance in the range of (1.10-1.20) $kJm^{-1}s^{-1}$ could be effectively used to manufacture a glazed red clay cookware product.

Acknowledgement

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Table 4. Chemical compositions of selected fritts

Name of the glaze	Compositions (%wt)		Chemical analysis of fritt	
Transparent glaze no. 1	Fritt no. 1	93%	Al_2O_3 – 10.0 %	CaO/MgO – 4.0%
	China clay	7%	B_2O_3 – 12.0 %	KNaO /Li_2O – 8.0 %
			SiO_2 – 65.0%	BaO – 1.0 %
Transparent glaze no. 2	Fritt no. 2	93%	Al_2O_3 – 11.0%	CaO/MgO– 5.5%
	China clay	7%	B_2O_3 – 11.1%	KNaO /Li_2O– 8.6%
			SiO_2 – 62.3%	
Transparent glaze no. 3	Fritt no. 3	93%	SiO_2 – 63.70%	Al_2O_3 – 5.10%
	China clay	7%	CaO- 10.64%	MgO– 1.74%
			Fe_2O_3 – 0.04%	P_2O_5 – 0.02%
			Na_2O-0.57%	K_2O – 2.66%
			ZnO -11.12%	TiO_2 – 0.08%
Matt glaze	Fritt no. 4	93%	SiO_2 – 54.54%	P_2O_5 – 0.02%
	China clay	7%	Na_2O-1.26%	TiO_2 – 0.09%
			K_2O – 2.72%	ZnO -14.56%
			Al_2O_3 – 10.04%	CaO- 7.61%
			MgO– 0.11%	Fe_2O_3 – 0.09%

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