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Investigation on Physico-Chemical Properties of Vitreous China Sanitary Ware from Local Clays

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Abstract

The cost of producing sanitary ware in Bangladesh is substantially low as compared to the advanced countries, because of low labour cost and abundance of basic raw materials. Ten sanitary ware compositions were prepared using Bijoypur clay, black clay, red clay, ball clay and china clay with fluxes and filler materials. Chemical compositions of the raw materials and the formulated batch compositions were determined. Physical properties (linear shrinkage, bulk density, apparent porosity, water absorption etc) and the modulus of rupture (MOR) of the prepared body compositions were also determined. The sample specimens were fired at 1150^{o}C and 1200^{o}C. Compositions S-3, S-4, S-5, S-7, S-8 and S-10 at 1150^{o}C were found to be of good quality.

Key words: Linear shrinkage, Bulk density, Water absorption, MOR, Red clay, Black clay.

Introduction

Sanitation remains one of the biggest development challenges in Bangladesh. Now a day, increasing concern for protection of health and environment has caused increased use of ceramic component all over the country. For manufacturing sanitary ware, the crucial state in this process is preparing the casting slip, which determines the moulding time and the quality of the finished products. Clays and kaolin are the principal raw materials which have a large effect on their technological properties for manufacturing sanitary ware (Khalev and Vlasov, 2007). Therefore the content of water and the dispersion of the solid phase should be optimized taking into account subsequent drying and sintering to ensure the maximally high parameters of the product. The main technological operations are as follows: pretreatment of raw materials, preparation of casting and glaze slips, casting a product, its setting, drying, glazing and firing. The chemical composition of the clay raw materials is one of the main indicators for selection of a component for the final mixture. Al_2O_3 has the largest effect on the properties of ceramic articles. As the Al_2O_3 content increases the refractoriness and mechanical strength of the material increases.

SiO_2 decreases the shrinkage and it also decreases refractoriness of the product. Colouring oxides iron and titanium oxides are strong fluxes, which decrease the viscosity of the liquid phase as well as the mechanical strength of the article (Khalev and Vlasov, 2007). The most effective method for decreasing the viscosity of a ceramic slip with a constant content of the dispersion phase (water) is the use of liquefying additives (electrolytes), which usually are salts of monovalent metals (Pishch *et. al.*, 2006). In this work, sodium silicate was used as electrolyte. Bijoypur clay, red clay, black clay, china clay and ball clay were used to prepare sanitary ware compositions. Sanitary ware used in domestic purpose can be classified as sanitary earthenware and vitreous china ware. It is found that, the range of firing temperature is from 1180^{o}C to 1200^{o}C and water absorption value 5-10% for earthenware and below 1% for vitreous china sanitary ware (Singer and Singer, 1963). There are some other basic physical properties such as linear shrinkage, bulk density, chemical compositions of the sanitary ware bodies play the main role in quality control parameters. Modulus of Rupture (MOR) is another important property for sanitary ware body. Investigations revealed the effect of qartzitic clay and kaolinitic clay on the properties of the products.

Thus the aim of this work is to develop cost effective and quality vitreous china sanitary ware for domestic use in rural area. Ten different batch compositions were prepared using different ratios of the raw materials. Chemical properties,

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physical properties (e.g. linear shrinkage, water absorption, bulk density etc) and Modulus of Rupture (MOR) of the finished products were evaluated.

Materials and Methods

Raw materials

Preparation of sanitary ware composition were done by using Bijoypur clay, ball clay, china clay, red clay, black clay, quartz and feldspar. Priority was given in the use of Bijoypur clay, red clay and black clay as these were available in huge amount in Bangladesh. Other ingredients namely ball clay, china clay, quartz and feldspar were purchased from local markets, but these are imported from abroad usually from India. The chemical composition of the clays was determined by X-ray fluorescence (XRF, PANalytical XRF, Model no. PW 2404), and the result is given in Table I. Sodium silicate was added to the mixture as dispersing agent.

Table I: Composition of different clays used in the sanitary ware body

Parameter measured (%)	BJC	RC	BLC	BC	CC
SiO_2	45.89	62.80	53.13	44.63	50.18
Al_2O_3	35.80	20.43	23.41	36.93	33.34
Fe_2O_3	1.89	6.07	4.97	0.96	1.88
TiO_2	2.51	0.99	0.98	3.57	0.01
MgO	0.15	0.95	1.20	0.44	1.05
CaO	0.09	0.15	0.79	0.17	0.94
Na_2O	0.36	0.09	0.23	0.11	0.81
K_2O	0.15	2.43	2.17	0.741	2.58
LOI	13.39	5.62	12.65	1.97	

Clays: BJC=Bijoypur clay, RC= Red clay, BLC= Black clay, BC= Ball clay, CC= China clay, LOI= Loss on ignition.

Preparation of compositions

Experiments were performed with ten compositions of the slurry with different ratio of raw materials. Formulated compositions are given in Table II. For the preparation of slurry the raw materials and distilled water were mixed. The mixture was then milled for 48 hours at 120 rpm. To obtain better dispersion (0.5%) sodium silicate was added to the slurry prior to mixing. The prepared slip was casted into plaster of Paris moulds at room temperature. To determine the linear firing shrinkage and other physical properties, 10 test pieces (50mm×50mm×10mm) were prepared from each mixture, rectangular bars (100mm×50mm×10mm) were prepared to measure the modulus of rupture (MOR). Test specimens of the sanitary ware S-1 to S-10 were prepared by slip casting method into plaster of Paris mould. After casting for a predetermined time the excess slip was poured away from the mould. After sometime the test specimens were removed from the mould and allowed to dry at 40^{o}C for 24 hours. The green bodies were sintered at 1150^{o}C and 1200^{o}C in a furnace, the temperature increasing rate was 3^{o}C/min and the soaking time was 15 minutes. The furnace was left free to cool to room temperature. A flow diagram of the processing steps is shown in Fig.1.

Sample characterization

Physical properties of the test specimens such as linear firing shrinkage, water absorption, bulk density were investigated after sintering of the specimens. Linear shrinkage was calculated by measuring the dimension of the bars before and after sintering following ASTM (designation: C326-82). Water

Table II: Ten compositions of sanitary ware body

Samples	BJC (wt%)	RC(wt%)	BLC(wt%)	BC (wt%)	CC(wt%)	Quartz (wt%)	Feldspar(wt%)
S-1	45	_	_	25	_	10	20
S-2	40	_	_	10	_	20	30
S-3	10	_	45	_	_	20	25
S-4	_	20	40	_	_	15	25
S-5	_	45	10	_	_	20	25
S-6	_	35	35	_	_	10	20
S-7	_	40	40	_	_	10	10
S-8	_	10	60	_	_	10	20
S-9	20	_	30	_	20	15	25
S-10	10	10	30	5	10	10	30

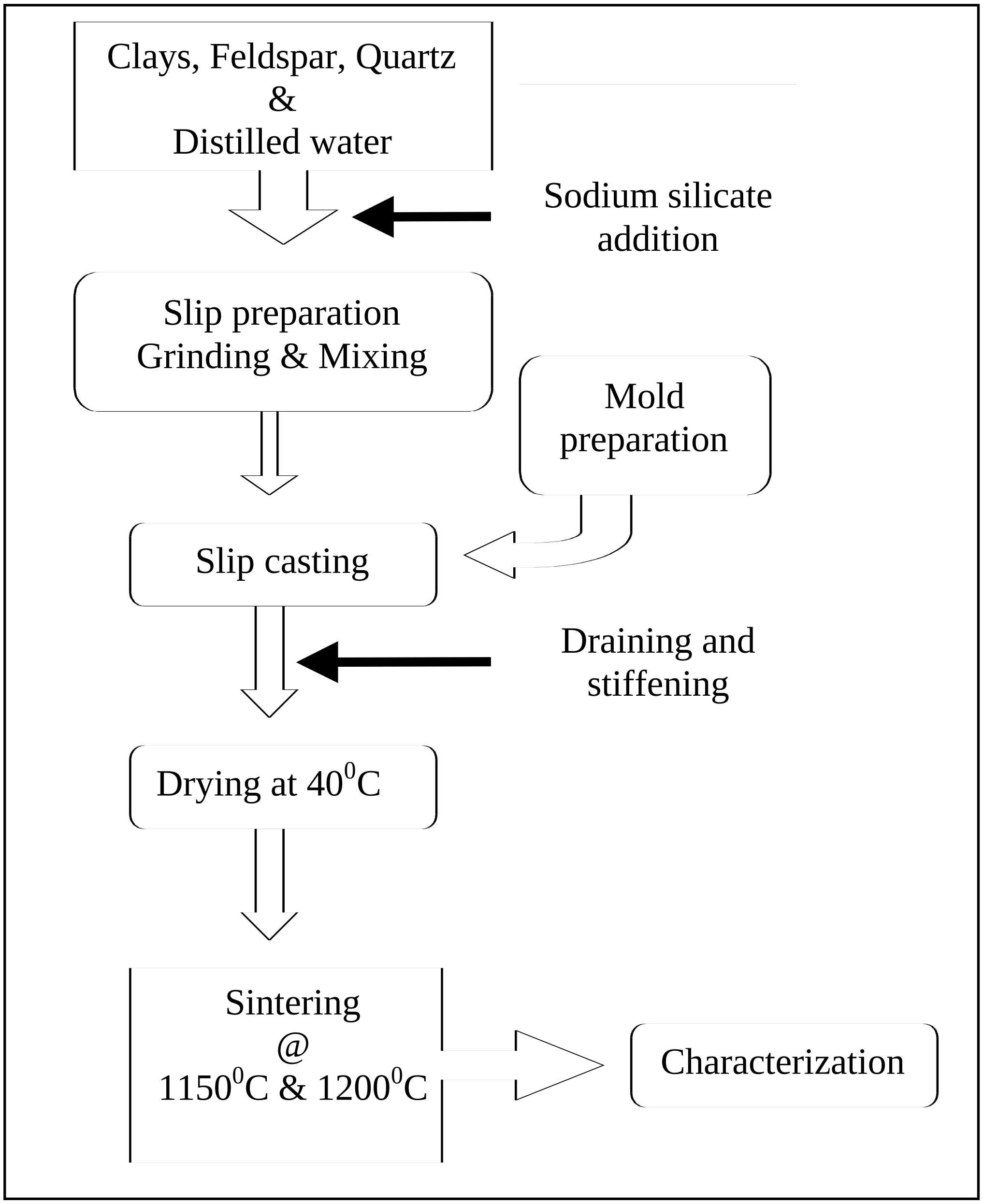

Fig.1: Flow diagram of the processing steps of sanitary ware

absorption was determined via boiling in water for 2 hours and by submerging in water for 24 hours. Then they were removed from water and weighed. The important physical properties (water absorption, bulk density) were determined by following ASTM (designation: C373-88). The modulus of rupture was measured using a 3-point loading method by Universal Testing Machine (Shimadzu UTM, model AUTOGRAPH AGS-10KNG). Chemical analysis of each composition was done by using both XRF and conventional gravimetric method. The chemicals used for this study were analar grade and Na_2CO_3, NH_4Cl, NH_4OH, HCl, $NH_4)_2HPO_4$ and ammonium oxalate were purchased from market either E. Merk or BDH.

Results and Discussion

Evaluation of raw materials

The chemical analysis shows that clays, quartz and feldspar used in the present study were of the common type. SiO_2 and

Table IIIa: Physical properties of sanitary ware compositions at 1150°C

Parameter	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	S-10
Linear shrinkage (%)	14.18	11.12	10.74	10.63	11.69	8.65	9.3	8.68	9.97	10.44
Water absorption (%)	2.78	4.63	0.02	0.02	0.07	1.97	0.01	0.33	0.45	0.28
Bulk density (gm/cc)	2.35	2.31	2.38	2.38	2.35	2.28	2.44	2.08	2.39	2.37
Apparent porosity (%)	6.53	10.64	0.04	0.04	0.06	4.46	0.02	0.72	1.06	0.68
Apparent sp. gravity	2.52	2.59	2.35	2.35	2.38	2.38	2.37	2.4	2.52	2.41

Table IIIb: Physical properties of sanitary ware compositions at 1200°C

Parameter	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	S-10
Linear shrinkage (%)	11.23	10.02	7.39	6.67	10.33	8.6	8.9	7.25	9.69	8.58
Water absorption (%)	0.02	0.04	0.03	6.32	0.75	0.76	0.43	0.50	0.27	3.01
Bulk density (gm/cc)	2.48	2.38	1.90	1.83	2.07	2.12	2.05	1.94	2.40	1.92
Apparent porosity (%)	0.06	0.04	0.08	11.52	1.53	1.6	2.94	0.96	0.71	7.11
Apparent sp. gravity	2.48	2.38	1.93	2.07	2.1	2.15	2.11	1.96	2.42	2.09

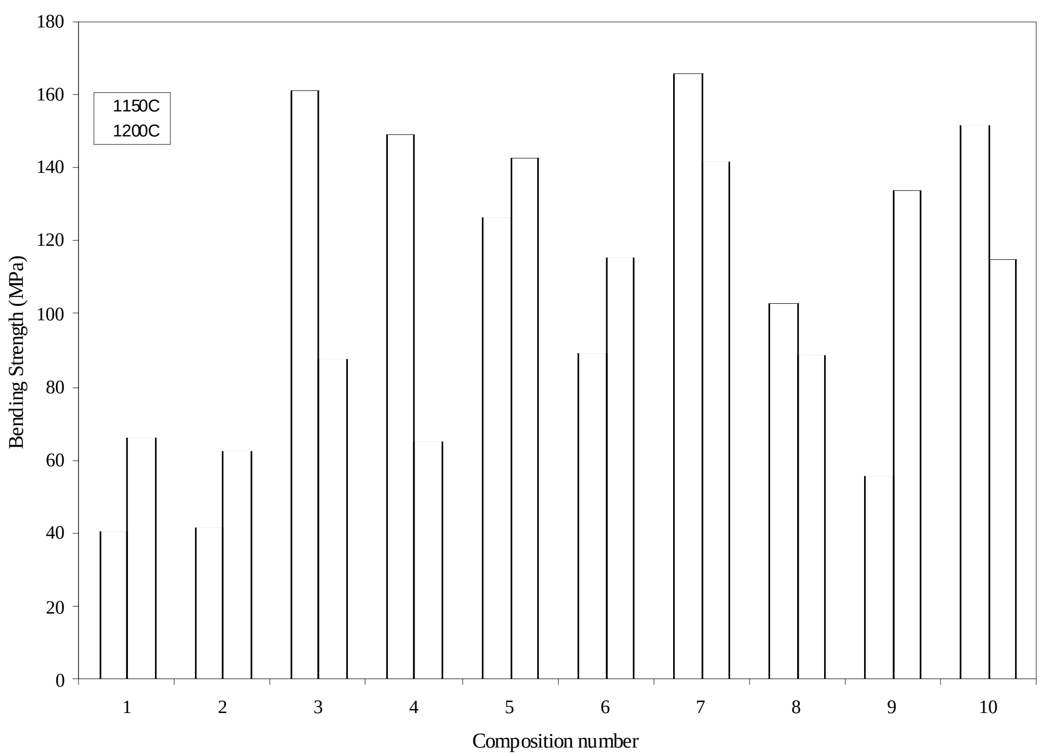

Figure 2: Modulus of Rupture (MOR) at 1150°C and 1200°C

Table IV: XRF result of sanitary ware compositions

Parameter measured (%)	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	S-10
SiO_2	70.35	61.83	62.20	68.54	72.50	67.24	67.96	67.76	65.07	63.54
Al_2O_3	21.44	25.43	25.43	13.99	11.78	17.89	15.18	16.85	19.37	17.68
Fe_2O_3	1.51	1.78	1.79	4.57	4.70	5.16	6.50	5.57	3.40	3.66
TiO_2	0.45	2.86	2.90	0.79	0.77	0.96	1.11	1.05	1.32	1.22
MgO	0.82	0.53	0.54	0.81	0.68	1.06	1.03	1.07	0.54	0.78
CaO	0.49	1.69	1.58	2.28	2.07	0.74	2.11	1.99	2.58	3.94
Na_2O	0.82	0.41	0.40	0.68	0.55	0.38	0.48	0.71	0.59	0.81
K_2O	2.81	3.92	3.94	6.82	6.19	5.48	4.47	6.25	5.99	7.08
Others	0.52	0.53	0.39	0.45	0.46	0.55	0.65	0.30	0.50	0.50
LOI	0.79	1.02	0.83	1.07	0.30	0.54	0.51	0.45	0.64	0.79

Al_2O_3 are the major constituents with Fe_2O_3 and alkali (K_2O+Na_2O) content. High Fe_2O_3 and TiO_2 content of clay reduce the quality of the product but offer higher plasticity and mechanical strength (Eygi and Atesok, 2008)). It is observed from Table I that RC and BLC contain 53-63 wt% of SiO_2 and 20-24 wt% of Al_2O_3. Again BC, BJC and CC contain 44-50 wt% of SiO_2 and 33-37 wt% of Al_2O_3. Chemical analysis and the Al_2O_3/SiO_2 ratio of BC and BJC show that these clays are kaolinitic as the Al_2O_3/SiO_2 ratio is around 0.8 which is very close to the theoretical ratio of pure kaolinite (0.85) (Halm, 1952)). From the chemical analysis, it is also observed that RC and BLC are quartzitic and they also contain higher amount of Fe_2O_3 and TiO_2.

Evaluation of the formulated bodies

The physical properties of fired specimens are summarized in Table IIIa and IIIb. The results of linear shrinkage of the experimental bodies at 1150^{o}C and 1200^o C show no significant change with firing temperature. S-6, S-7, S-8 and S-9 show low linear shrinkage value (below 10%) at both the temperature. But S-3, S-4 and S-10 show lower value of that only at higher temperature (at 1200^{o}C). Low linear shrinkage of the specimens is due to the presence of higher amount of quartzitic clays RC and BLC in the corresponding compositions. The most important parameter of sanitary ware body is water absorption. It is mostly controlled by the feldspar/quartz ratio and the water absorption value less than 1% for vitreous china sanitary ware is acceptable, as reported in the literature (Singer and Singer, 1963). At 1150^{o}C temperature S-3, S-4, S-5, S-7, S-8, S-9 and S-10 and at 1200^{o}C temperature S-1, S-2, S-3, S-7, S-8 and S-9 show the lower value of water absorption. Almost all the formulated compositions were found to be of good quality according to the water absorption values. Then other properties will help to select the better compositions among the ten. The results of modulus of rupture (MOR) (Fig. 2) depict the higher bending strength of S-5, S-7 and S-10 at both the temperatures. Again S-3, S-4, S-5, S-7 and S-10 show higher MOR values only at 1150^{o}C. A higher bending strength indicates a lower water absorption capacity. The fired body compositions show 61-73 wt% silica and 12-25 wt% alumina according to the XRF result (Table IV). The amount of fluxing oxide (i.e. Fe_2O_3+MgO+CaO+Na_2O+K_2O) shows a direct correlation with bulk density and an inverse relation with water absorption of the fired body. Presence of high concentration of fluxing components in the body permits a lowering of firing temperature. Thus S-3, S-4, S-5, S-7, S-8, S-9 and S-10 show a lower water absorption value at 1150^{o}C rather than at 1200^{o}C.

Conclusion

Five clays were used in the formulation of the vitreous china sanitary ware, of which three of them are local clays. Results of this study indicated that more quartzitic clays show less shrinkage with higher MOR values. Lowering of firing temperature due to the presence of higher concentration of fluxing components revealed the possibility of reducing the energy consumption during firing. As discussed in the previous section the water absorption values are within the range found in the literature and also mentioned in the technical specification sanitary ware products of various companies.Considering the firing temperatures with water absorption and MOR values S-3, S-4, S-5, S-7, S-8 and S-10 are of good quality. These six combinations out of 10 can be selected for further research on microstructure of the body compositions followed by preparing sanitary ware products on pilot plant scale.

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