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ScienceDirect

Ceramics International 41 (2015) 7097–7102

CERAMICS INTERNATIONAL

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LCD waste glass as a substitute for feldspar in the porcelain sanitary ware production

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Received 23 January 2015; accepted 4 February 2015
Available online 9 February 2015

Abstract

LCD glasses belong to the alkali-free alumino-borosilicate system and thus exhibit different properties from the traditional soda lime silicate glasses. In the present work, the replacement of feldspar by the waste glasses produced from LCD manufacturers was performed for porcelain sanitary ware. As the amount of LCD waste glasses increases, the sintered body showed a dense microstructure due to the rich liquid phase. Even under full replacement of feldspar, there was no pyroplastic deformation, except the exudation of liquid to the surface. The microstructure and mullite content were discussed in terms of the apparent viscosity and LCD glass composition, respectively. It is expected that LCD waste glasses enable the sanitary ware industry to save both raw material and energy simultaneously.

Keywords: Porcelain sanitary ware; LCD waste glasses; Feldspar; Glass viscosity; Glass composition

1. Introduction

The manufacturing of LCD panels applied to information display devices, such as televisions, monitors, and mobile phones, only occurs in four Asian countries, that is, China, Japan, Korea and Taiwan. In Korea, two LCD manufacturers are working and have a global share of approximately 50% [1]. A large amount of waste glasses (hereafter designated as LPWG: LCD Process Waste Glasses), approximately 40 kt/y, is being produced by LCD manufacturers. However, the reuse of LPWG as a raw material of the LCD glass itself is impossible because LPWG is contaminated by thin films such as a transistor, indium tin oxide and color filter. Furthermore, the composition of LPWG occasionally shows considerable fluctuation because it consists of glass products of five different manufacturers. Therefore, the recycling of LPWG is difficult in a field that is sensitive to composition change. In Korea, LPWG is now being recycled for use as a raw material in cement. Considering the composition and components of LPWG, however, it is not a valuable form of recycling.

LCD glass is alkali-free and composed of SiO_2, Al_2O_3, B_2O_3, and alkaline earth oxides. Therefore, its physicochemical properties are very different from those of the traditional soda lime silicate glass. Moreover, unlike the old LCD glasses produced before 2010, the current LCD glasses contain no toxic components such as arsenic- and antimony oxide [2,3]. Therefore, the resulting cullet and waste glass, such as LPWG, is environment friendly.

In fact, the waste glasses generated from the LCD industry can be divided into three categories: (1) LCD cullets from LCD glass manufacturers, (2) Foregoing LPWG from LCD panel manufacturers, and (3) End LCD waste glasses from end-of-life LCD devices. Among them, LCD cullet is being recycled as a raw material for commercial glasses, such as alkali-free alumino-borosilicate E glass and soda lime silicate white bottle glass in Korea [4,5]. The main raw material of B_2O_3 for E glass is LCD cullet, and two-thirds of white bottle glasses used in Korea contain B_2O_3. In the case of the end LCD waste glasses, however, the aforementioned toxic components contained in the old LCD glasses preclude their recycling [6], and thus they are

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http://dx.doi.org/10.1016/j.ceramint.2015.02.018

disposed as waste material. In relation to LPWG, there have been several studies on their recycling in the field of ceramic tile [7,8], glass–ceramics [9–11], foamed glass [12] and cement [13–15]. However, there have been no reports in which LPWG is applied to traditional porcelain such as sanitary ware.

Raw materials for traditional porcelain consist of clay, feldspar and quartz called tri-axial white ware [16]. It is well-known that hydrous aluminosilicate minerals such as clay and kaolinite contribute to the plasticity during formation and subsequent mechanical strength of the final porcelain body through the formation of the mullite during sintering. Quartz plays a role of the filler, which maintains the skeleton of the porcelain body during sintering. On the other hand, the alkali aluminosilicate feldspar called the fluxing agent plays a different role than the other raw materials. In general, the melting of the feldspar to the liquid occurs during sintering of the green body, and the amount of liquid phase depends on the type of feldspar [17–19] as well as clay. Here, the liquid phase during sintering moves into the alumina silicate ceramic powders by viscous flow, resulting in the bonding of powders and formation of a dense mass due to the deep inter-diffusion of phases [16]. The rest of the liquid phase is solidified without active crystallization during cooling, and thus the resulting porcelain is sometimes called a vitreous white ware. In relation to the foregoing role of the feldspar in the porcelain body, LPWG as an alternative raw material can be suggested. Although LPWG is contaminated with the aforementioned materials, its basic characteristics such as thermal properties are preserved; thus, it is a potential substitute for the feldspar used in the production of sanitary ware. In the present work, the influence of LPWG on some properties was examined in the porcelain body of sanitary ware, and the resulting data, including economic effects, were discussed.

2. Materials and methods

In Table 1 there are batch compositions of the raw materials used for commercial sanitary ware. The original batch consists of 75 wt% ready mixed powder of clay + quartz and 25 wt% feldspar supplied from the industry. The number at the end of LPWG means wt% of LPWG in total batch. The particle size of all the powder was in the range of 5–50 μm.

The viscosity (η) of 10^4 dPa s of LPWG was measured by using a rotating viscometer (VT-550 Haake Viscotester, Thermo Scientific, Germany) based on DIN 52312. The softening and transition temperatures corresponding to $10^{7.6}$ and $10^{14.5}$ dPa s were also determined by the methods described in ASTM C338 and E1545, respectively. The viscosity curve of LPWG and its corresponding sintering temperature were calculated by the Vogel–Fulcher–Tamann (VFT) equation based on the above three viscosity points [20].

The body mix was prepared by milling the ready mixed powder with feldspar and LPWG in the zirconia ball mill according to the batch compositions shown in Table 1. The green compacts were prepared in a disk form by uniaxial pressing at a forming pressure of 500 kg/cm^2. They were heated at a rate of 5 °C/min in an electric box furnace and sintered for 1 h at 1100 or 1200 °C. The volume shrinkage, density, water absorption and thermal expansion coefficient of the sintered body were measured to estimate the performance of the resulting ceramic product. Some detailed measuring procedures are described in the literature [18,19]. The crystalline phases in the raw materials and sintered body were analyzed by XRD. A quantitative analysis of the phases such as glass phase, mullite and quartz of the sintered body was performed using the Rietvelt-RIR method with aids of PANalytical Highscoplus (EMPYREAN, PANALYT, Netherlands) in which Si crystal was used as a standard phase.

Table 1
Experimental batches of sanitary ware (wt%).

Specimen code	Clay + quartz	Feldspar	LPWG	Total
LPWG0	75	25	0	100
LPWG5		20	5	
LPWG10		15	10	
LPWG15		10	15	
LPWG20		5	20	
LPWG25		0	25	

3. Results

3.1. Characterization of raw materials

The compositions of the ready mixed powder of clay + quartz, feldspar and LPWG are shown in Table 2. The crystalline phases for both natural raw materials identified by XRD are also described in the last column of Table 2. For the ready mixed powder of clay + quartz, there exists kaolinite, muscovite and quartz. The feldspar consists of albite and quartz. The composition of LPWG indicates some fluctuation in the respective component due to the existence of several different glass manufacturers. Table 3 and Fig. 1 show the temperatures corresponding to three viscosity fixed points and a rough viscosity curve of LPGW, respectively. To obtain a dense microstructure by sintering the glass powder, approximately 10^6 dPa s is normally required, as

Table 2
Compositions (wt%) and identified crystalline phases of raw materials.

Component	Clay + quartz	Feldspar	LPWG
SiO_2	61.0	75.0	58–64 (60.1)
Al_2O_3	26.1	14.0	15–20 (16.8)
TiO_2	0.34	0.12	–
B_2O_3	–	–	7–11 (10.3)
Na_2O	0.40	3.10	–
K_2O	2.40	4.50	–
MgO	0.33	1.20	0–4 (0.44)
CaO	0.20	0.80	3–8 (7.6)
SrO	–	–	0–8 (4.2)
BaO	–	–	0–5 (0.48)
Fe_2O_3	1.56	0.26	~0.025
L.O.I	7.61	~1.02	–
Crystalline phase	K, M, Q	A, Q	

K: kaolinite, M: muscovite, Q: quartz, A: albite.
(): The composition of LPWG used in the present work.