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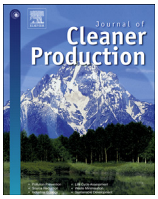

TFT-LCD cullet: a raw material for production of commercial soda lime silicate glasses

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ABSTRACT

Alkali free alumino-borosilicate display glasses that serve as the window in a TFT-LCD (hereafter LCD) device not only have few impurities but also high homogeneity to guarantee the quality of the display. These characteristics of LCD glasses enable the possibility of recycling LCD glass cullet as a raw material for commercial soda lime silicate glasses from the perspectives of the raw material costs and the energy saving. In the present work, several batches containing LCD cullet for two commercial model glasses were prepared and melted in the laboratory. According to several properties of the melts and the glasses, there was no serious change in the properties with up to 9 wt% replacement of the flint glass and 11 wt% replacement of the low iron flat glass by the LCD cullet. Currently, LCD cullet is being used successfully in a number of industrial plants for the production of flint glass in Korea. Two-thirds of flint bottle glasses contain B_2O_3 component derived from LCD cullet.

1. Introduction

In the glass industry, the cullet is generated during glass manufacturing and it is generally used as a strategic recycled material to save both raw materials and energy. In relation to LCD glass used in such products as televisions, mobile phones, and monitors, its manufacturing only occurs in four Asian countries: China, Japan, Korea and Taiwan. In Korea, five LCD glass manufacturers are operating, and they have a global share of approximately 50% of the glass production (Global Industry Analysts, Inc., 2011). The amount of LCD glass produced in Korea was estimated to be at 180 kt in 2010. Therefore, a large amount of cullet has been produced. However, the reuse of cullet as a raw material of the LCD glass itself is limited because of the strict quality control of the LCD glass. To guarantee the glass quality as a component of LCDs, a portion of cullet contaminated by melting defects is not usually reused and had been disposed as waste material. Such landfill disposal amounted to approximately 30 kt/y. This landfill disposal is still the primary waste management method. However, such disposal is undesirable from the viewpoint of environmental preservation. Recycling is the best solution.

LCD glass is alkali free and composed of SiO_2, Al_2O_3, B_2O_3 and alkaline earth oxides. The production technology and composition of LCD glass are described in detail in a review literature (Ellison and Cornejo, 2010). LCD glass not only has few impurities but also high homogeneity because the display quality must be guaranteed. In particular, unlike the old LCD glasses produced before 2010, the current LCD glasses contain no toxic components, such as arsenic and antimony oxide (Kim, 2013). Although the foregoing disposed LCD cullet exhibits certain melting defects, the two characteristics of high homogeneity and high purity can offer a possibility of recycling their cullet as a raw material for some commercial glasses that do not require strict display quality.

There have been several studies investigating the recycling of glass related to LCDs under consideration of WEEE directive (WEEE, 2012). However, these works were related to the waste glasses released from the LCD manufacturer (Lin et al., 2009, 2012; Fan et al., 2013; Lee, 2013) or the End-of-Life LCD device (Bihlmaier and Volker, 2013). Those waste glasses are contaminated by, for instance, thin-film transistors, indium tin oxide and color filters. Furthermore, their compositions can exhibit considerable fluctuations because they consist of glass products of different manufacturers. Therefore, the recycling of these glasses is difficult in a field that is sensitive to composition change. A recent paper (Kim and Hwang, 2011) by the present authors has reported the recycling

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of LCD cullet as a raw material for the alkali free alumino-borosilicate long fiber glass called E glass. This idea for E glass was realized and produced notably positive effects; for example, a reduction of the environmental burden of landfills and savings of both raw materials and energy with the accompanying reduction of CO_2 emissions. However, a serious obstacle to the use of LCD cullet for the production of E glass is that the compositions of LCD glass are different according to the different manufacturers. Under strict management of the LCD cullet source, the application of LCD cullet in an industrial glass plant was undertaken, and approximately two-thirds of the total amount of LCD cullet is being successfully recycled as a raw material for E glass in Korea.

Soda lime silicate glasses, such as bottle and flat glass, offer a significant possibility for the recycling of LCD cullet if their several components can be supplied from LCD cullet, and the resulting glass properties can be maintained or improved. In particular, unlike the case of E glass, it is not necessary for them to reduce the cullet to fine powder. It is sufficient for cullet to be in the form of fragments of several centimeters in size. In the present work, the influence of LCD cullet on certain properties of melt and glass was examined in two commercial soda lime silicate model glasses, and the resulting data, including the economic effect, are discussed.

2. Materials and methods

In the present work two types of LCD cullet, denoted by LF and LPV, were applied to flint glass and low iron flat glass. Flint glass is used as general beverage bottles and low iron flat glass is used as a cover or substrate in solar photovoltaic modules. Table 1 describes the compositions of LCD cullet (LF), flint model glass (LF0) and modified flint glasses with LF cullet (LF3~LF9). Flint glass batches consisting of various raw materials, including flint cullet and LF cullet, are shown in Table 2. Table 3 lists the compositions of LCD cullet (LPV), low iron flat model glass (LPV0) and modified low iron glasses with LPV cullet (LPV6, LPV11). Table 4 describes low iron glass batches consisting of various high-purity raw materials, such as sand, soda ash, calcite, dolomite, alumina, sodium sulfate and LPV cullet with only 175 ppm of Fe_2O_3. The number at the end of LF and LPV denotes wt% of LCD cullet in the total glass weight. The compositions of LF3~LF9 and LPV6, LPV11 in Tables 1 and 3 are theoretical values calculated from the experimental batches listed in Tables 2 and 4. The chemical analysis for the resulting glasses performed by XRF showed a negligible deviation from the target compositions.

Approximately 300 g of the glass batch was melted at 1550 °C in a Pt/20Rh crucible for 2 h, and the bubble-free melts were homogenized by a Pt/20Rh stirrer. The melt viscosity (η) was determined by using a rotating viscometer (VT-550 Haake Viscotester, Thermo Scientific, Germany) based on DIN 52312. The working temperature (T_W) corresponding to 10^4 dPa was calculated by the Vogel-Fulcher-Tamann (VFT) equation based on the viscosities measured at high temperatures as follows, $\log\eta = A+(B/T-T_0)$ where A, B and T_0 are constant and T is the temperature in ^{o}C (Scholze, 1988). The so-called devitrification or liquidus temperature (T_L) of glasses, which is related with the glass forming ability, was measured by using a gradient temperature furnace according to ASTM C 829-81. The glass powders placed into the platinum boat were soaked for 8 h. The primary crystalline phase was examined by a polarizing microscope, and the corresponding liquidus temperature was determined. The detailed descriptions for both the melt viscosity and the liquidus temperature are shown elsewhere (Hwang et al., 2000). The corrosion test for specific refractory products used in glass melting furnace was conducted in each melt of the LF series at a temperature corresponding to 10^2 dPa by the static finger method. The cross section of corroded refractory was observed by FE-SEM and EDX. The detailed experimental set up for refractory corrosion is described in literature (Kim et al., 2007). The so-called AZS refractory consisting of Al_2O_3, ZrO_2 and SiO_2, which are used frequently in the contact area with melts, were chosen for the corrosion test. The batch free temperature (T_{BF}), where all crystalline phases have disappeared in a glass batch, was determined by XRD analysis for four flint batches melted for 2 h at various temperatures. A number of low-temperature viscosities and thermal expansion coefficient of flint glasses were determined. Spectral transmission for low-iron glasses was determined in the UV–Vis–NIR range. The water resistance of low-iron glasses was estimated using the extracted Na_2O concentration in hot water based on ISO 719. The experimental procedure is presented schematically in Fig. 1.

Table 1
Compositions of LCD cullet (LF), flint model glass (LF0) and some modified flint glasses (wt%).

Glass code	SiO_2	Al_2O_3	B_2O_3	Na_2O	K_2O	MgO	CaO	SrO	SnO_2
LF	62.3	17.2	10.5	0	0	1.4	7.5	0.8	0.4
LF0	74.2	1.89	0	12.7	0.21	0.11	10.8	0	0
LF3	73.7	1.89	0.29	12.5	0.09	0.11	11.0	0.20	0.06
LF6	73.1	2.2	0.59	12.4	0.03	0.11	11.0	0.41	0.13
LF9	72.4	2.6	0.88	12.4	0.03	0.10	10.7	0.61	0.20

Table 2
Experimental batches of LF series for flint glass preparation (kg).

Raw material	LF0	LF3	LF6	LF9
Sand	222.5	224.29	211.95	186.48
Feldspar	48.95	15.92	0	0
Calcite	64.52	65.04	61.46	54.08
Soda ash	75.65	76.48	76.51	75.71
Sodium Sulfate	2.11	2.13	2.01	1.77
Flint cullet (65%)	646.1	646.1	646.1	646.1
LF cullet	0	30.05	60.19	90.44
Total batch	1059.83	1060.1	1058.22	1054.58
Total glass	1000	1000	1000	1000

Table 3
Compositions of LCD cullet (LPV), low iron flat model glass (LPV0) and some modified low iron glasses (wt%).

Glass code	SiO_2	Al_2O_3	B_2O_3	Na_2O	MgO	CaO	SrO	BaO	Fe_2O_3
LPV	60.1	16.9	9.9	0	0.35	7.8	4.7	0.54	0.0175
LPV0	72.5	0.39	0	13.9	3.9	8.7	0	0	0.02
LPV6	71.4	1.06	0.62	13.7	3.8	8.6	0.27	0.03	0.0194
LPV11	70.2	1.87	1.12	13.6	3.7	8.5	0.50	0.05	0.0190

Table 4
Experimental batches of LPV series for low iron flat glass preparation (kg).

Raw material	LPV0	LLPV6	LPV11
Sand	728.7	692.6	662.5
Soda ash	235.8	236.1	236.2
Calcite	64.1	55.5	48.4
Dolomite	175.5	174.9	174.4
Alumina	3.1	0	0
Sodium sulfate	7.2	6.9	6.7
LPV cullet	0	60.6	111.1
Total batch	1214.4	1226.6	1239.3
Total glass	1000	11,000	1000

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