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Improve melting glass efficiency by Batch-to melt conversion

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Abstract

Soda–lime silicate glasses are composition used recently in container, table ware, float glass, etc. Most of soda-lime silicate glasses are produced by major component sand (silica, SiO_2), soda ash (Na_2CO_3) and lime stone ($CaCO_3$) by adding effective minor additive such as dolomite ($CaMg(CO_3)_2$), sodium sulfate (Na_2SO_4), alumina (Al_2O_3), etc. During melting process, around 550 °C, soda ash is reacted with lime stone to produce sodium calcium carbonate, $Na_2CO_3(s) + CaCO_3(s) \Rightarrow Na_2Ca(CO_3)_2$, melting at 780 °C. Sodium calcium carbonate is reacted with sand generate formation of sodium silicate and wollastonite, $Na_2Ca(CO_3)_2 + 2SiO_2 \Rightarrow Na_2SiO_3 + CaSiO_3 + 2CO_2$, at 900 °C. The alternative way of Batch-to Melt conversion is to replace lime stone by natural wollastonite ($CaSiO_3$). This reaction has occurred by crossing over the step of the reaction $Na_2Ca(CO_3)_2$. This means that the melting process can be emerged easier than batch with lime stone; batch with wollastonite requires lower energy. From the calculated thermodynamic exploited heat of glass batch includes wollastonite which is required 10 % lower than using lime stone. When the lime stone is replaced by wollastonite, the kinetic is investigated by Thermal gravity and Differential Scanning Calorimeterv (TG/DSC). Then the next analysis is the melting process of both batches by using Batch-Free Time method with the same condition. The concern of wollastonite is minor impurity, especially iron oxide (Fe_2O_3), because iron can present in green color for clear glass production. From this experiment, wollastonite can be replaced lime stones and some parts of silica. Regarding to this experiment, batch containing wollastonite melts easier than lime stone batch. In conclusion, the results demonstrated that the two composite glasses were of the same properties.

Keyword: Melting glass; Soda-lime silicate glass; Glass batch; Wollastonite

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1. Introduction

Glass is a material to apply for any products because of outstanding properties. Glass products have more added value than other materials. Soda-lime silicate glass (main composition from Sand (SiO_2), Soda ash (Na_2CO_3) and lime stone ($CaCO_3$)) are common use in many products such as Table ware, container, sheet glass for construction, etc. The most problem in glass industry is energy cost because glass needs to be melted at high temperature (normally above 1450 °C) [1-2]. Currently, energy is the main cost effectiveness of glass industry. There are many solutions to reduce energy especially in the melting process such as increasing cullet in batch. The study of new technologies, for increasing the energy efficiency of glass furnace [3] was compared with different method found batch and /or cullet preheating by flue gases seem to be best solution and this technology are already commercial and new concepts are in development. The selective batching was proposed by Carty W. M. et al. [4] and controlled reaction paths, approach 1 batch component are prereacted to form an intermediate Na_2CO_3 + SiO_2 and $CaCO_3$ + SiO_2 ($CaSiO_3$, wollastonite). And approach 2 batch components are selectively agglomerated or pelletized to from small reaction volumes that promote specific reactions to generate silicate endpoints within the glass furnace. Montoya B. G. et al. [5] proposed new method of pre-reacted batches with out free silica Na_2CO_3 + $CaCO_3$ in temperature range 450-650 °C after investigated using X-ray diffraction been found formation of a double bicarbonate $Na_2Ca(CO_3)_2$. Compare with batch whereas CaO and SiO_2 are difficult to be reacted. A double bicarbonate increases the reactivity with silica and melting starts at lower temperature. According to Theodore D. T. et al. [6] was found the solid-state reaction of $Na_2Ca(CO_3)_2$ occurs very readily and it melt and reacts with the SiO_2 to form glassy melt, beginning at around 800 °C.

This study focuses on using natural wollastonite; mainly, it uses as ceramic raw material [7] such as ceramic tile body, glaze, combination with zircon to reduce sintering temperature, decreasing the firing shrinkage, increasing mechanical strength and thermal resistance. The problem is natural wollastonite occurs in small amounts and is highly contaminated by other minerals especially iron oxide (Fe_2O_3) and dolomite ($CaMg(CO_3)_2$). The study by Kotsis et al. [8] was synthesis of β-wollastonite by the chemical reaction $CaCO_3$ + SiO_2 (smoke produced at Zagyvarona Iron Alloys Factory) ⇒ $CaSiO_3$ + CO_2. Yet, the concern is the price is to high compare with natural wollastonite.

2. Theory

Standard of glass formula is soda-lime silicate glass, $74SiO_2$-$16Na_2O$-10CaO

The thermodynamic calculation uses to calculate the theoretical heat demand (exploited heat, H_{ex}) [9]. The exploited heat is composed of the so-called chemical heat demand ΔH^o_{chem} which is equivalent to standard heat of batch-to-melt conversion (at 25 °C, 1 bar)

$$\text{Batch (25 °C)} \Rightarrow \text{Glass + batch gases (25 °C)} \quad (1)$$

And the heat $\Delta H_{T(glass)}$ physically stroed in the glass melt (relative to 25 °C) at melting temperature

$$\Delta H^o_{chem} \Rightarrow H^o_{(glass)} + H^o_{(gas)} - H^o_{(batch)} \quad (2)$$

$$H_{ex} \Rightarrow \Delta H^o_{chem} + \Delta H_{T(glass)} \quad (3)$$

ΔH^o_{chem} is derived directly from the batch composition. The batch composition unambiguously determines the nominal oxide composition of the resulting glass, the gas species and the composition of the crystalline counterpart of the glass.

The reaction is occurred by difference raw material. First, glass composition (Glass A) is prepared by SiO_2, Na_2CO_3 and $CaCO_3$. The reaction is started by Na_2CO_3 and $CaCO_3$.

$$Na_2CO_3(s) + CaCO_3(s) \Rightarrow Na_2Ca(CO_3)_2 \text{ (occur between 450-650 °C) [5]} \quad (4)$$

And then double bicarbonate is react with silica.

$$Na_2Ca(CO_3)_2 + 2SiO_2 \Rightarrow Na_2SiO_3 + CaSiO_3 + 2CO_2, \text{ (react at 900 °C)} \quad (5)$$

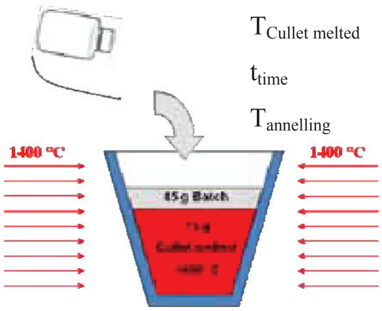
Second glass composition is prepared by SiO_2, Na_2CO_3 and $CaSiO_3$ (Glass B) the reaction can start easier than Glass A and produce lower CO_2 emission.

$$74SiO_2(s) + 16Na_2CO_3(s) + 10CaCO_3(s) \Rightarrow 74SiO_2\text{-}16Na_2O\text{-}10CaO_{(glass)} + \mathbf{26CO_2} \quad (6)$$

$$64SiO_2(s) + 16Na_2CO_3(s) + 10CaSiO_3(s) \Rightarrow 74SiO_2\text{-}16Na_2O\text{-}10CaO_{(glass)} + \mathbf{16CO_2} \quad (7)$$

3. Experimental

Raw materials used in batch to melt conversion are silicon dioxide (SiO_2, Riedel-de Haen), sodium carbonate (Na_2CO_3, Fisher scientific), calcium carbonate ($CaCO_3$, Carlo Erba) and natural wollastonite ($CaSiO_3$). Composition of two glasses was SiO_2-Na_2CO_3-$CaCO_3$ and SiO_2-Na_2CO_3-$CaSiO_3$ targeted as same composition $74SiO_2$-$16Na_2O$-$10CaO$. The experiment was separated into two parts: First, kinetic was studied by TG/DSC (Thermal gravity and Differential Scanning Calorimeter, Netzsch STA 449 F3 Jupiter). In experiment, Batch-Free Time method, feeded batch in melted cullet and kept in the crucible for different times, [10-11] was melted in electrical furnace (Carbolite BLF 17/3) and annealed at 570 °C in box furnace (Carbolite CWF 1100) (present in Fig. 1). Second, properties were investigated by comparing two batches by melting 150 g of glass at 1500 °C for 2 hours, and then samples were prepared after annealed. The experiment were performed the chemical composition by using Wavelength-dispersive XRF spectrometer, S8 Tiger, Bruker AXSX, thermal properties, dilatometeric method, NETZSCH DIL 402 PC and fiber elongation method, BÄHR 402 physical property, micro hardness testing, Shimadzu HMV 2000 and optical property, colors determination, UV/Vis spectrophotometer, Analytikjana Specord 250.



$T_{\text{Cullet melted}}$ = 1400 °C

t_{time} = 10, 30, 40, 50 and 60 minute

$T_{\text{annelling}}$ = 570 °C

Fig. 1. Batch-Free Time testing

4. Result and discussion

According to the thermodynamic calculation, and exploited heat (H_{ex}) were calculated by two glasses at melting temperature (T_{ex}, 1500 °C).

H_{ex} (Glass A) as 2.3 GJ/t_{glass} 10% higher than H_{ex} (Glass B) 2.1 GJ/t_{glass}.

From Fig. 2(a) TG and (b) DSC, the kinetic of the reaction in both glass batches demonstrated reaction of batch. The thermal gravity of Glass A (red line) showed characteristic during heating; according to equation 4, Na_2CO_3 reacted with $CaCO_3$. To compare with Glass B (green line), it didn't show any reaction from the temperature range. Next both batches, A and B, presented similar characteristic as equation 5. The difference between these batches was Glass A lighter than Glass B which was explained by using equation 6 and 7. As TG curve from Fig. 2(b) showed the difference of both batches, Glass A formation of $Na_2Ca(CO_3)_2$ around 750 °C reacted with SiO_2. In other hand, Glass B in the batch already had $CaSiO_3$; therefore, the reaction of melting occurred around 900 °C. During melting glass process (above 1000 °C), Glass B indicated lower energy to form glass structure than Glass A.

The kinetic of the reaction from the Batch-Free time experiment presented in Fig. 3 confirmed that Glass A held in the furnace for 30 and 40 minutes and it still remained batch on the surface. Therefore, this supported that it took longer time to melt the batch. The comparison Glass B held in the furnace as the same time and condition presented quite clear glass for 30 minutes and completely clear for 40 minutes. This means replaced lime stone by natural wollastonite melted easily and lower energy requirement.

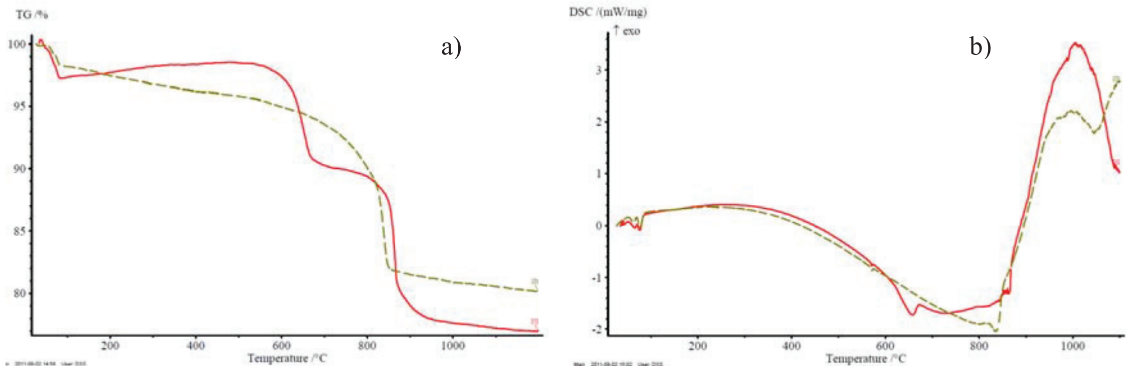


Fig. 2.a) Thermal gravity b) Differential Scanning Calorimetric curves (Glass A red line and Glass B green line)

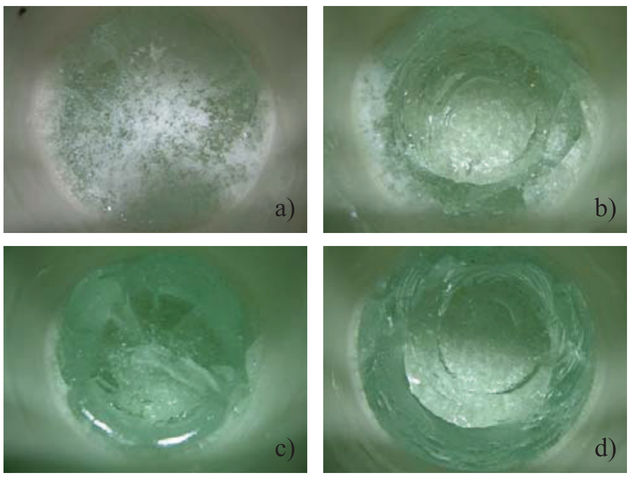


Fig. 3. Batch-Free Time testing a) Glass A 30 min b) Glass A 40 min c) Glass B 30 min d) Glass B 40 min

The chemical composition presented in Table 1, both batches showed slightly the same composition as wollastonite can replace completely calcium carbonate in batch. Only minor components are difference such as magnesium oxide (MgO) and iron oxide (Fe_2O_3) because there is normally impurity of natural wollastonite.

Table 1. Chemical composition of glasses

Composition (weight %)	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	ZrO_2
Glass A	15.63	0.09	0.27	74.67	0.05	9.16	0.07	0.04	0.01
Glass B	16.61	0.40	0.31	73.61	0.05	8.88	0.06	0.06	0.01

Figure 4 presented the thermal properties investigated by dilatometeric method. This showed thermal expansion, glass tranformation temperature and dilatometric softening point by dilatometeric method (Glass A, red line and Glass B, green line). Both of glasses presented quite similar behavior of thermal expansion data see in Table 2.

Table 2. Thermal properties by dilatometric method

Thermal properties by Dilatometric method	Glass A	Glass B
The coefficent of thermal expansion 50-300 °C (COE, $°C^{-1}$)	10.18×10^{-6}	9.95×10^{-6}
Glass tranformation temperature (°C)	543	540
Dilatometric softening point (°C)	619	619

Table 3. Vickers Micro hardness testing

Glass	Vickers Hardness (HV)
A	509 ± 16
B	516 ± 11

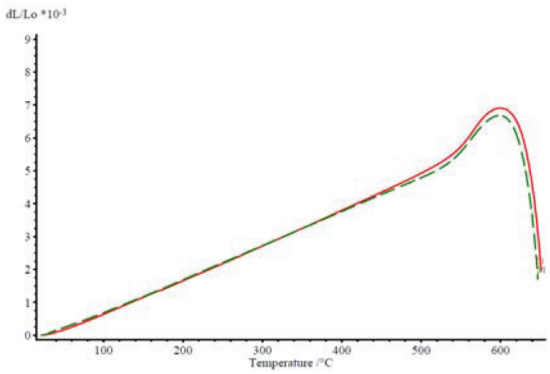


Fig. 4. The thermal properties by dilatometeric method. (Glass A, red line and Glass B green line)

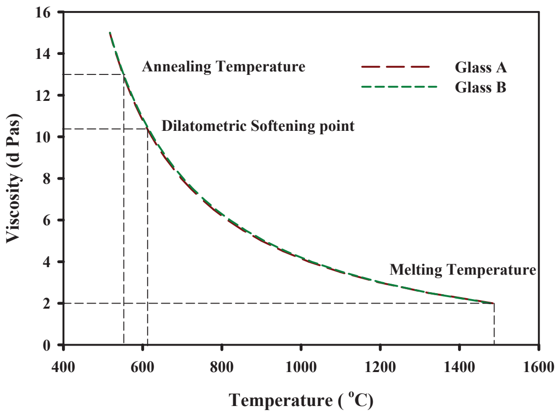


Fig. 5. Viscosity curve (Glass A, red line and Glass B, green line)

From this property, glasses were normally soda-lime silicate glass. The glass tranformation temperature and dilatometric softening point were very close to the same point. COE were not distinct; thus, this point was not significantly different. This result could be confirmed by fiber elongation method and calculated by Vogel-Fulcher-Tammann (VFT) equation [12], presented in Fig. 5. These curves presented exactly similar viscosity properties of both glasses.

The physical property was performed by Vickers micro indentation testing. This method showed mechanical property on glass surface, and soda-lime silica glass prefer hardness in range 450-550 HV [13] depended on glass composition. Table 3, the result of both glasses presented the values obtained quit nearby. Table 3, the result of hardness values obtained for both glasses are comparable.

The last experiment of both glasses was color determination by UV/Vis spectrophotometer. After calculated color from glass transition in CIE L* a* b* system were found Glass A L*(lightness) 86.24, a* -1.17 and b* 0.65 and Glass B L* 89.19, a* -1.28 and b* 0.85 respectively. The result of a* and b* was one of the most concern in glass industry because these values presented color of the glasses. From the color of Glass B, wollastonite was a little greenish but still in the range that it can be control using decolorizing or reducing agent.

5. Conclusion

This research results represented efficiency of the melting glass by Batch-to melt conversion. From thermodynamic calculation, wollastonite replaced lime stone can be reduced approximately 10% of energy requirement. The kinetic investigation was used to confirm this study. Moreover, the properties experiment of glasses from both batches showed composition and properties giving the same result. This meant that replacing wollastonite in soda-lime silicate glass batch can improve energy efficiency and also reduced CO_2 emission on glass melting process.

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