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Alternative Soda-lime Glass Batch to Reduce Energy Consumption

Ekarat Meechoowas [a], Kanit Tapasa [b] and Tepiwan Jitwatcharakomol [c]

Thailand Center of Excellence for Glass, Department of Science Service, Bangkok, 10400, Thailand

[a]ekarat@dss.go.th (corresponding author), [b]kanit@dss.go.thl, [c]tepiwan@dss.go.th

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Abstract. Soda-lime glass is produced by melting sand (SiO_2), soda ash (Na_2CO_3), lime stone ($CaCO_3$) together with effective additives such as dolomite ($CaMg(CO_3)_2$) and an important structural modification, alumina (Al_2O_3) in which the melting temperature is very high around 1500°C. With this reason, to dissolve alumina, high amount of energy is needed. Consequently, one of possibilities to reduce the melting energy is replacing alumina by the raw material with a lower enthalpy of melting. The heat required for melting the batch of raw materials from atmosphere temperature to melting temperature is called exploited heat (H_{ex}), which can be calculated from chemical enthalpy (H°_{chem}) and heat content (H_{melt}) at reference temperature (T_{ex}). From thermodynamic approach, chemical enthalpy of alumina is higher than feldspar ($KAlSiO_3$) or pyrophyllite ($Al_2Si_4O_{10}(OH)_2$). For the glass batch with alumina, the calculated exploited heat is 540 kWh/ton while the batch with feldspar or pyrophyllite is lower, namely 534 and 484 kWh/ton, respectively. This means that the melting process can be emerged easier than the batch with alumina because the melting point of feldspar is around 1200℃ and pyrophyllite dehydroxylates around 900℃. The kinetic properties of batch melting were investigated by Batch-Free Time method, which defines the melting ability of the modified batch. According to thermodynamic calculation, it was found that both alternative batches were melted easier. The study showed that feldspar or pyrophyllite could be used instead of alumina without significant changes in glass chemical composition and physical properties. The concern of using feldspar or pyrophyllite is the quantity of minor impurities which affect to the color appearance especially in clear glass products.

Introduction

Glass production is required massive energy especially in melting processes required 70 - 80 percent of energy [1]. In glass production, batch is absorbed about 75 to 90 percent of total amount of heat during the first hour [2], which means batch is strongly effect on energy required. Now a day energy cost is rising and this is a major problem effecting to glass industry. Almost glass productions in Thailand are using soda-lime silicate glass produced from sand (SiO_2), soda ash (Na_2CO_3), and dolomite ($CaMg(CO_3)_2$)) adding with alumina (Al_2O_3). They are usually used in many products such as tableware, sheet glass, container, etc. There are many solutions to reduce energy consumption. R. Beerkens et al [3] study shows that batch and/or cullet preheated by flue gases could be reduced up to 25 percent of the energy requirement. The highly energy-efficient melter was developed by applying modular glass melting concepts and by separating the three essential processes: components-melting, refractory grain dissolution, and bubble removal [4-5]. The advantage of modular glass melting concept is to reduce residence time for glass melting process by avoiding seed and bubble, but still on developing process to the large-scale production. The selective batching and pre-reacted batches were proposed by Carty W. M. et al. and Montoya B. G. et al [6-7]. The selective batching was controlled by the reaction paths. For the first batch component was pre-reacted by intermediate form and then selective agglomeration started reaction to generate silicate endpoint within the glass furnace. From pre-reacted batched, the reaction started without free silica $Na_2CO_3 + CaCO_3$ in temperature range 450 – 650 ℃ formation of double bicarbonate $Na_2Ca(CO_3)_2$ before this compound reacted with silica and other components. The double bicarbonate increased the reactivity with silica and melting started at lower temperature.

According to Theodore D. T. et al. [8], the study was found that the solid-state reaction of $Na_2Ca(CO_3)_2$ occurred readily and $Na_2Ca(CO_3)_2$ melted and reacted with SiO_2 to glassy form, beginning at around 800 °C. The alternative way is to replace raw materials such as lime stone [9] by using wollastonite instead. As the result, this can be reduced approximately 10 percent of energy requirement and increased batch melting ability approved by Batch-Free Time and Differential Scanning Calorimetric/ Thermogravimetry investigation.

According to thermodynamic approach, this study used either feldspar ($KAlSiO_3$) or pyrophyllite ($Al_2Si_4O_{10}(OH)_2$) to replace alumina which have higher chemical enthalpy [10]. The potential of reducing energy consumptions was indicated by thermodynamic calculation and kinetic investigation.

Theory

The Glass composition is soda-lime silicate glass, $71SiO_2$-.$14Na_2O$-$8CaO$-$6MgO$-$1Al_2O_3$ which used alumina source from alumina (Al_2O_3), feldspar ($KAlSiO_3$) and pyrophyllite ($Al_2Si_4O_{10}(OH)_2$) target slightly same glass composition.

$$71SiO_2 + 14Na_2CO_3 + 6CaMg(CO_3)_2 + 2CaCO_3 + Al_2O_3 \Rightarrow$$
$$71SiO_2\text{-}14Na_2O\text{-}8CaO\text{-}6MgO\text{-}Al_2O_3 + 22CO_2 \qquad (1)$$
$$69SiO2 + 13Na_2CO_3 + 6CaMg(CO_3)_2 + 2CaCO_3 + 2KAlSiO_3 + 2.5O_2 \Rightarrow$$
$$71SiO_2\text{-}13Na_2O\text{-}8CaO\text{-}6MgO\text{-}K_2O\text{-}Al_2O_3 + 21CO_2 \text{ (}K_2O\text{ replace }Na_2O\text{)} \qquad (2)$$
$$67SiO2 + 14Na_2CO_3 + 6CaMg(CO_3)_2 + 2CaCO_3 + Al_2Si_4O_{10}(OH)_2 \Rightarrow$$
$$71SiO_2\text{-}14Na_2O\text{-}8CaO\text{-}6MgO\text{-}Al_2O_3 + 22CO_3 + H_2O \qquad (3)$$

The chemical reaction can be changed by using different raw materials.

The thermodynamic calculation

The thermodynamic calculation is used to calculate the theoretical heat demand (exploited heat, H_{ex}) [11,12]. The exploited heat is composed of the chemical heat demand ΔH^o_{chem} which is equivalent to standard heat of batch-to-melt conversion (at 25 °C, 1 bar)

$$\text{Batch (25 °C)} \Rightarrow \text{Glass + batch gases (25 °C)} \qquad (4)$$
$$\Delta H°_{chem} \Rightarrow H°_{(glass)} + H°_{(gas)} - H°_{(batch)} \qquad (5)$$

And the heat content H_{melt} is the enthalpy different between the glass at 298 K and the glass melt at melting temperature T_{ex}.

$$H_{melt} \Rightarrow H_{Tex(glass)} - H°_{glass} \qquad (6)$$
$$H_{ex} \Rightarrow \Delta H°_{chem} + H_{melt} \qquad (7)$$

$\Delta H°_{chem}$ 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.

Experimental

Soda-lime silicate glass were produced by sand (SiO_2),sodium carbonate (Na_2CO_3), dolomite ($CaMg(CO_3)_2$, alumina (Al_2O_3), feldspar ($KAlSiO_3$), and pyrophyllite ($Al_2Si_4O_{10}(OH)_2$). The chemical composition of raw materials presents in Table 1 and glass batch formula presents in Table 2 targeted as comparatively same composition.

Table 1 Raw materials composition

Composition (%wt)	Sand	Sodium carbonate	Dolomite	Alumina	Feldspar	Pyrophyllite
SiO_2	99.44	-	0.09	0.06	65.32	72.34
Al_2O_3	0.26	0.08	-	99.59	17.92	20.43
Na_2O	-	61.24	-	0.02	3.06	-
K_2O	0.06	-	-		13.09	0.12
CaO	0.04	0.03	34.92	0.08	0.22	0.23
MgO	0.03	-	18.35	-	-	0.08
Fe_2O_3	0.04	-	0.01	0.05	0.05	0.37
L.O.I	0.08	38.65	46.55	-	0.2	6.13

Table 2. Glass batches formula

Formula	Composition (%wt)					
	Sand	Sodium carbonate	Dolomite	Alumina	Feldspar	Pyrophyllite
1	60.30	20.50	18.10	1.10	-	-
2	56.35	19.95	18.10	-	5.60	-
3	56.45	20.45	18.10	-	-	5.00

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). From experiment, Batch-Free Time method (comparing melting ability of different batch), which feeded batch in melted cullet in electrical furnace (Carbolite BLF 17/3) and kept it in the crucible for different times (present in Figure 1). [9] After annealed at 550 °C were investigated the appearance. Second, glass properties were investigated by melting 150 g of glass at 1500 °C for 2 hours, and the sample of the glasses prepared after annealed. The chemical composition of glasses were using Wavelength-dispersive X-ray fluorescence spectrometer, S8 Tiger, Bruker AXSX. The thermal properties were using fiber elongation method, BÄHR 402. And the optical property with colors determination investigated by UV/Vis spectroscopy, Analytikjana Specord 250.

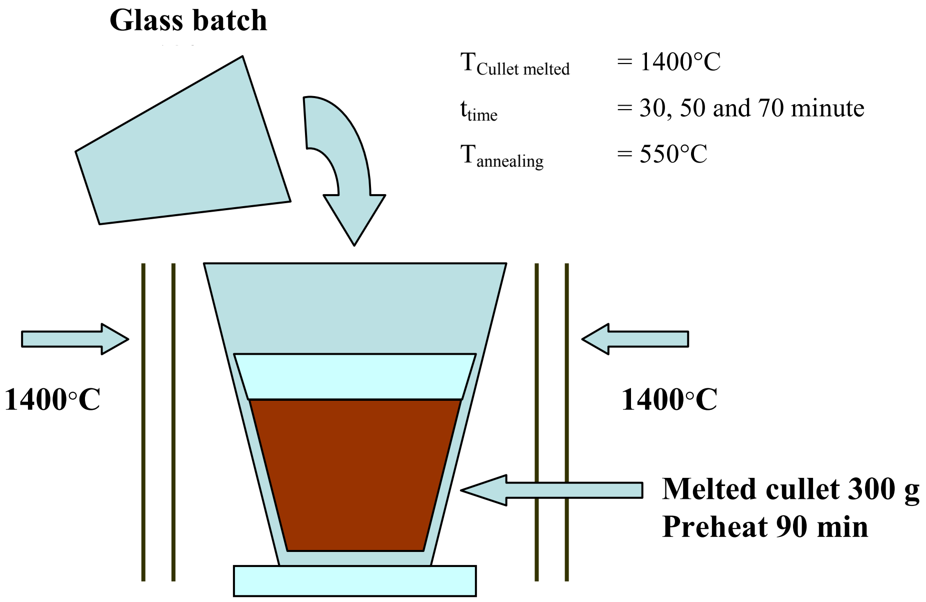

Figure 1 Batch-Free Time testing

Result and discussion

From the thermodynamic calculation, the exploited heat (H_{ex}) of difference glass formula showed the result of 540, 534 and 484 kWh/ton respectively. The original batch (Formula 1) had higher exploited heat (H_{ex}) than alternative batch (Formula 2 and 3). That has potential to reduce energy consumption.

The result of TG/DSC present in Figure 2 show that mass changed during heating and the reaction of formation occurred around 700°C. Then batches melted nearly 900°C, endothermic peak calculated as 276, 207 and 180.5 J/g for Formula 1, 2 and 3 respectively. According to the thermodynamic calculation, both alternative batches are required lower energy than original batch. They clearly showed that the Batch-Free Time testing in Figure 3 gave the result held in the furnace at the same time as formula 1, remained batch particle more than Formula 2 and 3. This means that replacing alumina by either feldspar or pyrophyllite melted easily and lower energy requirement.

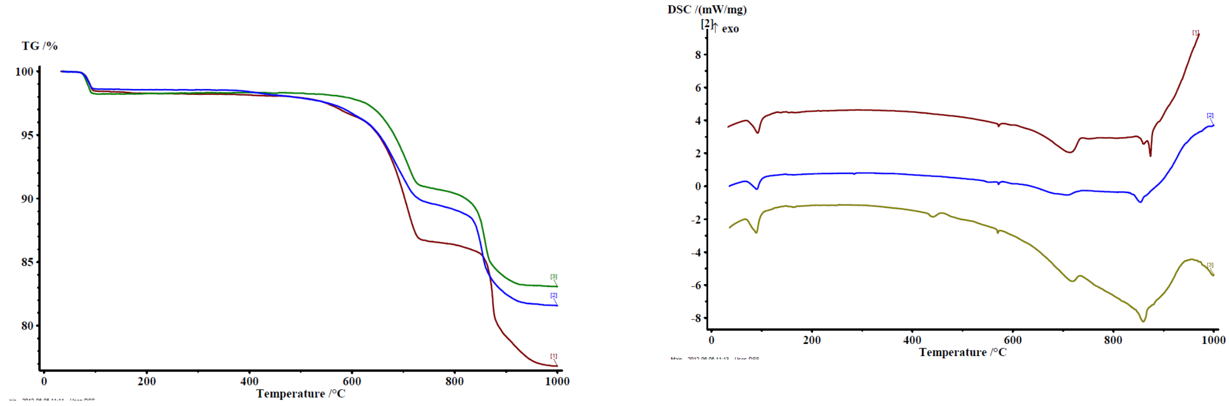

Fig.2 a) Thermal gravity and b) Differential Scanning Calorimetric curves (Formula 1 red line, formula 2 blue line and formula 3 green line)

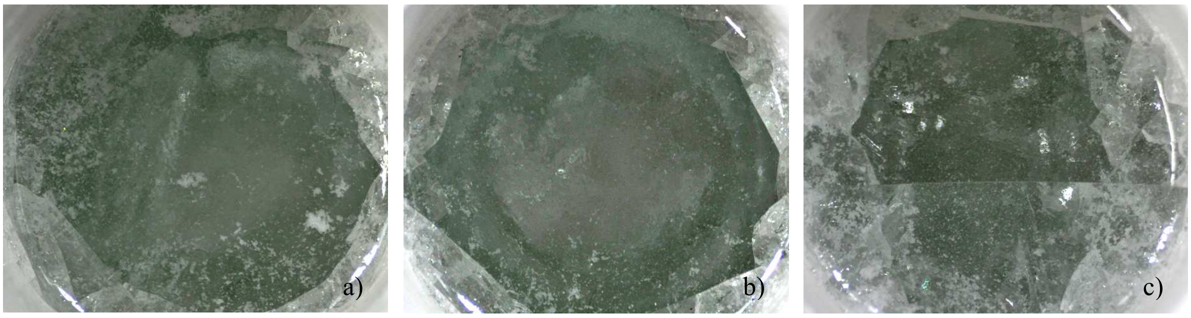

Fig. 3 Batch-Free Time testing 70 min a) Formula 1 b) Formula 2 c) Formula 3

From the Table 3, the glass composition of Formula 2 and 3 is slightly different from original composition because only Formula 2 was included feldspar (potassium feldspar) which presented K_2O in glass composition.

Table 3. Chemical composition of glasses

Composition (weight %)	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	SO_3
formula 1	13.72	4.81	1.82	73.01	0.02	7.02	0.01	0.02	0.15
formula 2	13.66	4.74	1.54	72.62	0.80	6.94	0.01	0.02	0.18
formula 3	13.86	4.81	1.49	73.22	0.03	6.98	0.02	0.03	0.16

Figure 4 and Table 4, the thermal property was investigated by fiber elongation method (weight the glass fiber in the furnace, fiber is elongated with increasing temperature) and the result were calculated by Vogel-Fulcher-Tammann (VFT) equation.

$$\log \eta = A + B/(T-T_0)$$

η is viscosity. Term of A, B and T_0 are constants, T_0 was introduced into the Boltzmann relation which represents a correlation of temperature T [13]. These viscosity curves presented exactly similar and viscosity temperatures slightly difference, both alternative batches given lower temperature than original batch.

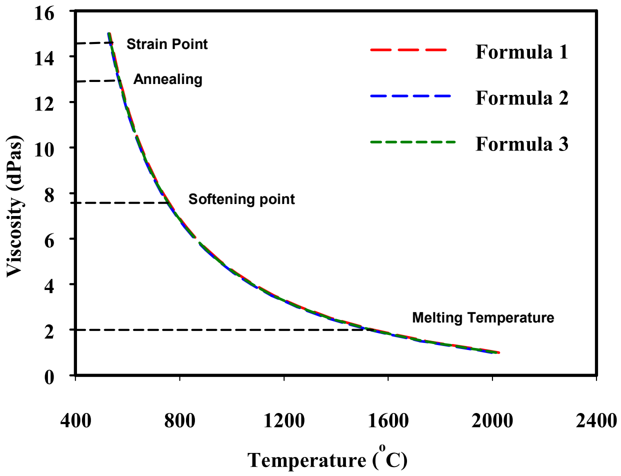

Figure 4 Viscosity curve (Formula 1, red line Formula 2, blue line and Formula 3, green line)

Table 4. Relative between viscosity and temperature of glasses

Viscosity of glass	Relative temperature (°C)		
	Formula 1	Formula 2	Formula 3
Strain point, 14.5 dPas	540.2	535.5	537.7
Annealing point, 13 dPas	570.0	565.2	567.4
Dilatometric softening point, 11.3 dPas	642.5	637.4	639.8
Working point, 4 dPas	1081.6	1072.6	1077.3
Gob temperature, 3 dPas	1260.8	1249.4	1255.6
Melting temperature, 2 dPas	1538.2	1522.2	1531.3

The last experiment of all glasses was color determination by UV/Vis spectrophotometer (Figure 5). After calculated color from glass transition in CIE L* a* b* system, the study was found in the Table 5 L* is lightness, a* present green-red and b* present blue-yellow color. 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 Formula 2, using feldspar glass was quite whiter than the Formula 1 but for the Formula 3, pyrophyllite was a little greenish due to high concentration of iron oxide. However, it is still in the range that can be controlled by using decolorizing or reducing agent.

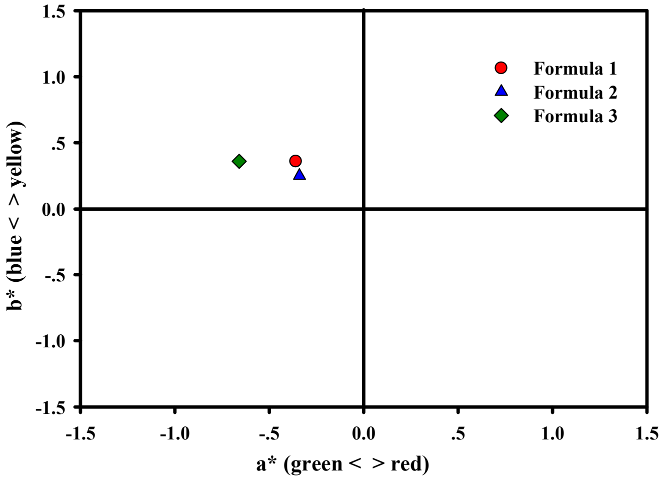

Figure 5 Color determination by UV/Vis spectrophotometer in CIE L* a* b* system

Table 5. Calculated glasses color in CIE L* a* b* system

Glass	Color		
	L*	a*	b*
Formula 1	96.41	-0.36	0.36
Formula 2	96.38	-0.34	0.25
Formula 3	96.17	-0.66	0.36

Conclusion

This experiment represented the alternative batches to reduce energy consumption. From thermodynamic calculation, either feldspar or pyrophyllite replaced alumina can be reduced approximately 2% and 10% of energy requirement respectively. In the mean time the kinetic investigation also was used to confirm this study. The properties experiment of glasses from both batches showed composition and properties giving the same result. This meant that replacing alumina in soda-lime silicate glass batch can reduce energy consumption and also improves melting ability on glass melting process.

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