



Recycling of exhausted dust from regenerator of glass furnace in glass batch melting

Jitlada KUMPA¹, Pitcharat INEURE², Parinya CHAKARTNARODOM³, Benya CHERDHIRUNKORN¹, Edward A LAITILA⁴, and Nuntaporn KONGKAJUN^{1,*}

¹ Department of Materials and Textile Technology, Faculty of Science and Technology, Thammasat University, Pathum Thani, 12120, Thailand

² Glass Bridge Company Limited, Bangkok, 10230, Thailand

³ Department of Materials Engineering, Faculty of Engineering, Kasetsart University, Bangkok, 10900, Thailand

⁴ Department of Materials Science and Engineering, Michigan Technological University, Houghton, MI, 49931, USA

*Corresponding author e-mail: n-kongkj@tu.ac.th

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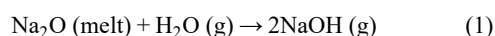
Thermal properties

Abstract

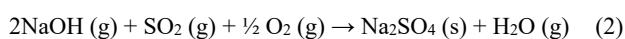
In soda-lime glass manufacturing, evaporation of volatile compounds from glass melt is the origin of the dust emission from glass tank furnace. The exhausted dust then is deposited on the regenerator and is needed to be removed. Thus, this study focuses on using the dust from melting glass in glass production. The glass batches were prepared from 0 wt% to 10 wt% of the exhausted dust from soda-lime glass production as a substitution of the total raw materials. The analysis of phase and chemical composition of the dust by x-ray powder diffraction (XRD) and x-ray fluorescence technique (XRF) indicated that it consisted mainly sodium sulphate. Thermal analysis (TG/DSC) revealed that the addition of exhausted dust reduced the temperature of the melting reaction of the glass batches. The optimum amount of the exhausted dust, which made it possible to obtain the glass with the lowest number of remaining bubbles, was 2 wt%. From CIE lab and dilatometry results revealed that up to 2 wt% replacement of total raw materials by the exhausted dust in the glass batch did not affect the glass color, thermal expansion coefficient, glass transition temperature and dilatometric softening point of glass samples.

1. Introduction

Soda-lime glass is one of the materials that is widely used such as the production of container glass, flat glass and utility glass [1]. In glass manufacturing, a tank furnace generally consumes about 70% to 80% of total energy. The fuel is spent to provide high temperature for glass melting. Heat recovery from flue gas is in the form of preheating air using a generator for the combustion of a fuel. However, evaporation of volatile compounds from glass melts is the origin of the dust emission from glass tank furnace. This is related to chemical reaction during melting of glass batch [2-3]. For glasses based on soda-lime-silica, alkali and alkaline oxide, such as sodium compounds, are easy to evaporate from the surface of the glass melt. Volatile sodium hydroxide is formed by reacting with water vapor at temperature around 900°C. These chemical reactions can be expressed as Equation (1).



Highly reactive sodium hydroxide gas tend to recombine when the flue gas such as SO₂ and O₂ cools down to form sodium sulphate particles [4-6] (Beerkeens 1995). The reaction is given by Equation (2).



The condensation of volatile compounds is in the form of exhausted dust emission. The dust from flue gas derived from the tank furnace then deposits in the regenerator. The regenerator recovers about 60% of total input heat by building up the waste heat of flue gas and then delivering it to preheat the combustion air. The deposition of exhausted dust can cause reduction in heat transfer area and deteriorate regenerator efficiency. The clog of dust deposits are found on both the doghouse side and non-doghouse side of the regenerator [7]. The dust is collected from the regenerator during glass melting.

Composition of the dust varies on its source. Besides Na₂SO₄, other components of exhausted dust emission may be in the form of chloride, fluoride, oxide and carbonate [8]. The previous works reported that the major chemical composition of the dust produced from containing glass composes of sodium sulphate and potassium sulphate which can be used in the glass fining agent [9-10]. The previous studies showed that the replacement of fining agent such as sodium sulphate in glass batch with the dust had no significantly affect the thermal properties of the glass batches [11-12].

In Thailand, the glass manufacturing company needs to remove about 6000 tons of dust from regenerator each year. Besides, the cost of dust removal is about 2,000 baht per ton. To date, there is no any study on the replacement of total glass batch with the exhausted dust. Thus, this research is focus on using the exhausted dust from melting glass to glass production to reduce production costs, reduce energy

for melting glass and recycle the waste for maximum benefit. The replacement of total glass batch with the exhausted dust is considered in this work. Subsequently, the focus will be on the influence of the exhausted dust content on the glass batch reaction, glass color, thermal expansion coefficient, glass transition temperature and dilatometric softening.

2. Experimental procedure

The glass batch of standard mixtures were prepared from the following raw materials; silica sand (SiO_2), dolomite ($\text{CaMg}(\text{CO}_3)_2$), soda ash (Na_2CO_3) and sodium sulphate (Na_2SO_4). Sodium sulphate was added to the batches as a fining agent. The exhausted dust samples were collected from the regenerator in glass tank furnace of a glass factory, Rayong province, Thailand. The batch mixtures with different content of exhausted dust were prepared comprising 0, 1, 2, 3, 4, 5 and 10% exhausted dust as a substitution of the standard mixture. Six mixtures were prepared; STD, D1, D2, D3, D4, D5 and D10. STD is standard glass from glass batch plant factory. The letter D is an abbreviation of the exhausted dust and each number show percentage of the exhausted dust used in the standard glass batch as seen in Table 1. Chemical composition and phase analysis of the exhausted dust were monitored by X-ray fluorescence spectroscopy (Phillips PW2404) and X-ray diffractometry (Phillips X'pert X-ray diffractometer). To obtain the batch melting reaction data, thermal analysis (TG/DSC) was conducted at heating rate at $10^\circ\text{C}\cdot\text{min}^{-1}$ in air by NETZSCH STA 449 F5 thermal analyzer. The density of glass was determined by Archimedes' method. The measurement of the refractive index of glass was conducted by Abbe refractometer (T1 Atago).

Each glass batch of glass was thoroughly mixed and preheated in Al_2O_3 crucible at 550°C for 15 min to reduce intense thermal shocks in crucible. Then, the melt was heated at 1450°C for 3 h. The glass samples were then annealed at 550°C for 15 min to remove internal stress. After the melting and annealing, the glass melts were ready for observation of the remaining bubbles. Observation of the bubbles was performed by optical microscope. The bubble counting determination was from the sample area of 1 cm^2 for 5 areas and taking an average.

To observe the color parameter performed by CIELab analysis (UV-VIS spectroscopy Shimadzu: UV-1700, the specimens were cut and fine polished. Optical transmission spectra were recorded between 300 nm and 1100 nm. The ferrous-feric redox ratio ($\text{Fe}^{2+}/\text{Fe}^{3+}$) can be

calculated using the Equation (3) where A1000 and A380 are the absorbance value at 1000 nm and 385 nm [13].

$$\frac{\text{Fe}^{2+}}{\text{Fe}^{3+}} = 0.133 \left(\frac{A_{1000}-0.036}{A_{385}-0.036} \right) \quad (3)$$

Dilatometric plot were obtained on glass samples with dimensions of $5\text{ mm}^3 \times 5\text{ mm}^3 \times 20\text{ mm}^3$ at a heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$ in the temperature range of room temperature to 1000°C . The coefficient of thermal expansion (COE) was determined in the temperature range of 100°C to 400°C . The glass transition temperature (T_g) was obtained from the change in the slope of the plot. The dilatometric softening point (T_d) was obtained from the maximum of the expansion of the plot.

3. Results and discussion

3.1 Phase and chemical composition of the exhausted dust

The results by X-ray fluorescence analysis showed that the exhausted dust mainly composed of SO_3 (37.6 wt%), Na_2O (32.7 wt%), CaO (8.8 wt%), Al_2O_3 (6wt%), MgO (4.9wt%) and SiO_2 (4.4%) as shown in Table 2. The main phase compositions of the dust were analyzed by XRD diffraction technique. The main phases of dust were sodium sulfate (Na_2SO_4) and the minor phases were calcium silicate (CaSiO_3), silica (SiO_2) and ZnS as presented in Figure 1. From the previous work, besides Na_2SO_4 , the dust may consist of low concentration of other components with high vapor pressure such as Zn, and Pb [8].

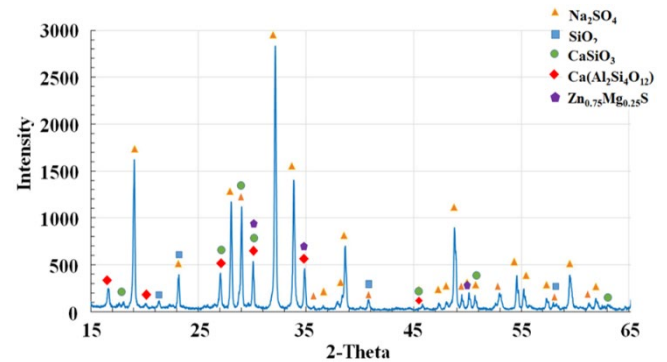


Figure 1. XRD pattern of the exhausted dust.

Table 1. Formulations for sample preparation.

Materials	Composition (wt%)						
	STD	D1	D2	D3	D4	D5	D10
silica sand	61.74	61.12	60.51	59.89	59.27	58.65	55.57
dolomite ($\text{CaMg}(\text{CO}_3)_2$)	19.07	18.88	18.69	18.50	18.31	18.12	17.16
soda ash (Na_2CO_3)	18.12	17.94	17.76	17.58	17.40	17.21	16.31
sodium sulphate (Na_2SO_4)	1.07	1.06	1.05	1.04	1.03	1.02	0.96
Exhausted dust	0	1	2	3	4	5	10

Table 2. Chemical composition of the exhausted dust as determined by XRF.

Oxide	SiO_2	Al_2O_3	ZrO_2	CaO	MgO	Na_2O	K_2O
wt%	4.43	6.02	0.21	8.77	4.94	32.72	1.37
Oxide	Fe_2O_3	SO_3	Cr_2O_3	P_2O_5	ZnO	Sb_2O_3	PbO
wt%	0.61	37.61	0.26	0.28	1.80	0.64	0.07

3.2 Reaction of the exhausted dust content in glass batch

Figure 2 shows number of bubbles versus the concentration of the exhausted dust. The bubbles remaining in the samples mainly came from the batch reaction such as carbonate decomposition of raw materials. By the addition of 2 wt% to 3 wt% exhausted dust in the standard batch, the number of bubbles remaining in the glass sample decreased. When the concentration of exhausted dust was greater than 3 wt%, the number of bubbles left in the glass sample significantly increased. This indicates that the addition small amount of exhausted dust can facilitate to homogenize the melt.

Figure 3 shows the optical images taken from the surface of the samples prepared from various dust contents. It shows the significant decrease of bubble number in glass surface as the dust level of 2% to 3% were introduced. The exhausted dust containing mainly sodium sulphate reacts as a fining agent to expand the small gas bubbles by releasing SO_2 and O_2 gases at elevated temperature. This also brings vigorously stir in melt resulting in mixing and homogenization. Then, the expanded bubbles are able to leave the melt surface by buoyancy. In addition, sulphate melt could form as a melt film on molten glass surface. This film may assist quartz grain dissolution and bubble release from melt surface. However, high amount of the dust addition containing sodium sulfate could pile up as thicker layer on molten glass surface that may suppress bubble release during fining process [14-15].

Figure 4(a) and 4(b) show the thermograms of glass batch with 0 wt% and 2 wt% of the dust added. The results were recorded in the form of DSC/TG curves in the function of temperature to study the behavior of the batch during heating. The first endothermic peak

at 90°C was resulted from evaporating moisture contained in raw material was found in both STD and D2 mixture. The amount of moisture was about 3 wt% of loss of mass. At temperature about 424°C, an endothermic reaction between sodium carbonate (soda ash) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) causing the formation of double carbonate $\text{CaNa}_2(\text{CO}_3)_2$ and $\text{MgNa}_2(\text{CO}_3)_2$ were observed in both STD and D2. A few loss of mass was resulted from the carbonate reaction with quartz and releasing of CO_2 . At temperature of 574°C for STD and D2 mixture, the β -quartz to α -quartz transition was observed. This can initiate endothermic reaction (650°C to 660°C) of sand (SiO_2) with sodium carbonate (Na_2CO_3) and then form Na_2SiO_3 and CO_2 . The results corresponded to the previous work by Kusnierz *et al* [16].

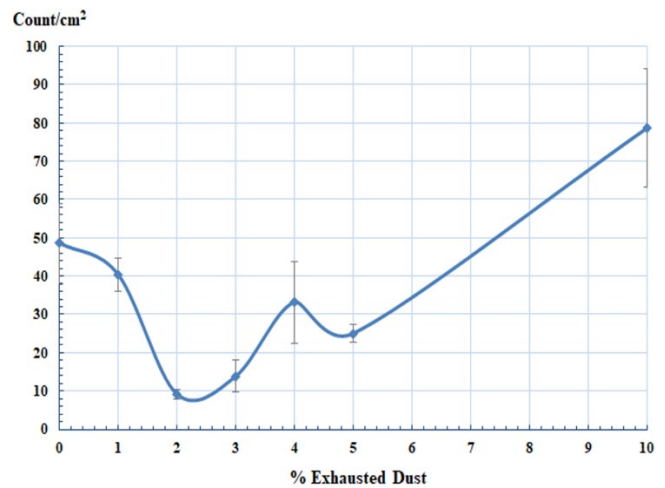


Figure 2. Chart of bubble counting against % exhausted dust.

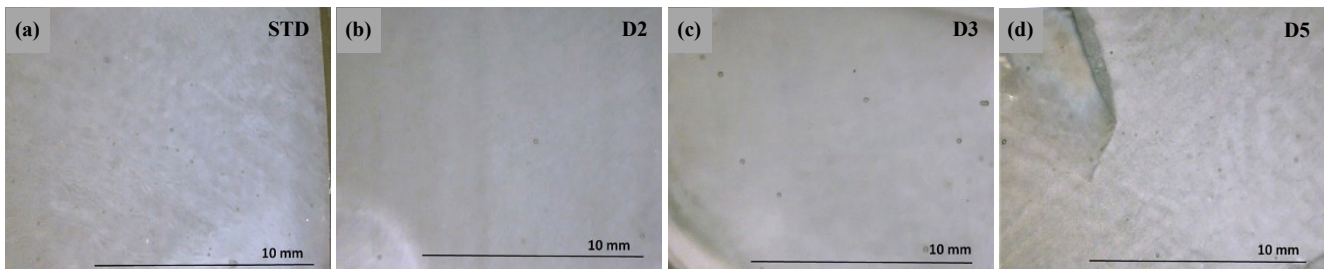


Figure 3. Image of bubbles on the surface of the samples which prepared from various dust contents (a) standard, (b) D2, (c) D3, and (d) D5.

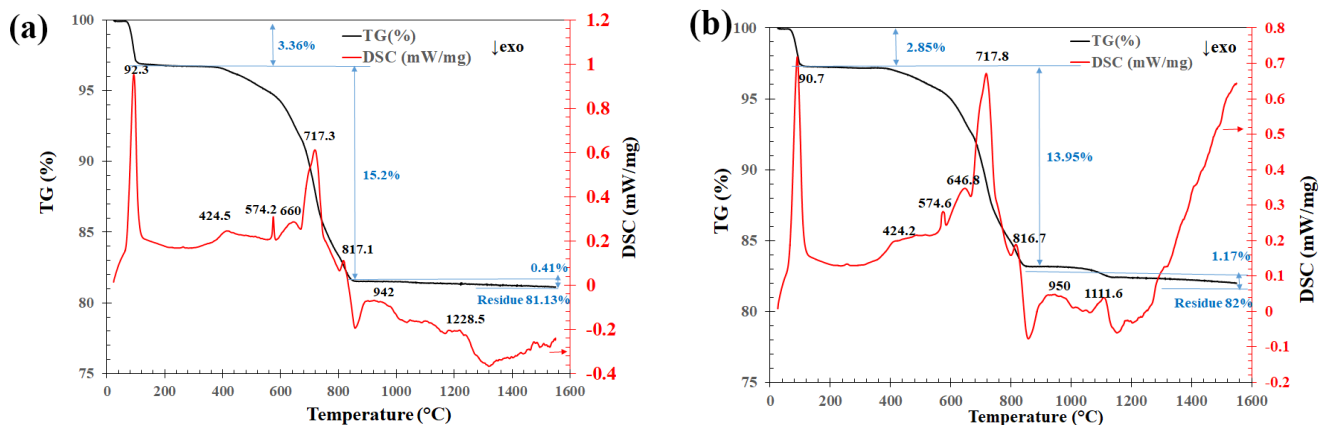
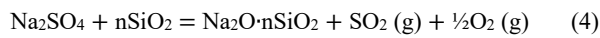


Figure 4. TG/DSC thermograph of the glass batch with the dust incorporated (a) 0% and (b) 2%.

By further increasing temperature, two-step decomposition of dolomite was found on endothermic peak for both STD and D2 mixture at 717°C and 817°C. The total amount of the released gaseous component from 100°C to 850°C was equal to 15.2 wt% in standard batch and 14 wt% in D2 formula. At temperature of about 950°C to 1250°C, the eutectic melt was formed along with Na, Ca and Mg silicate. The dissolution of SiO₂, CaO and MgO in eutectic melt was observed as the board endothermic reaction. By the addition of small amount of the exhausted dust to the batch (D2 mixture), the endothermic peak of DSC peak indicated that there was a shift of endothermic peak to the left. The change in kinetics of the process and the lower reaction temperature from 1228°C in STD batch to 1111°C in D2 batch were observed.

According to Merkerji [10], sodium sulphate reacts with coarse silica grains remaining by the following reaction at temperature above 1200°C.



In the stage of melting and formation of homogeneous melt (above 1000°C), the TG results revealed higher amount of gas evolution (1.17%) in the batch with exhausted dust (D2 batch) compared to the STD batch (0.41%). From Equation (4), the evolution of gases brings further melt stirring and facilitates in mixing, homogeneity and dissolution of sand particles [15]. Thus, it confirmed that the addition of small amount of exhausted dust reduced the temperature of the melting reaction of the glass batches. This corresponds to a decrease in bubble number found in the presence of small amount of the exhausted dust in glass batch due to a lower energy consumption during batch melting.

3.3 Physical properties of glass specimens

Figure 5 presents the optical spectra of the glass samples. The optical spectra of the glass samples containing the exhausted dust exhibited the absorption peak at 380 nm due to the Fe³⁺ ions, around 650 nm due to Cr³⁺ ions, and a very broad band around 1100 nm due to the Fe²⁺ ions. From XRF result, the exhausted dust contained 0.61% iron oxide and chromium oxide 0.26% as shown in Table 2. That means higher amount of the dust addition in the glass batch, the higher amount of iron oxide and chromium oxide content in the glass sample. Iron oxide and chromium oxide in glass batch affect the glass color according to the redox reaction [17].

Table 3 shows the values of CIE Lab, Fe²⁺/Fe total, and refractive index as the function of percentage of the exhausted dust. According to the CIE system, the +a* axis corresponds to the red color and -a*

corresponds to the green color. The +b* axis correlates with the yellow color and -b* correlates with the blue color. The lightness L* ranges from 0 (black color) to 100 (white color). The yellow component (+b*) and the green component (-a*) increased with increasing the amount of the exhausted dust in the standard batch. When the concentration of exhausted dust was greater than 2 wt%, the glass color changed from colorless to yellow green tone corresponded to CIE Lab values as seen in Figure 6.

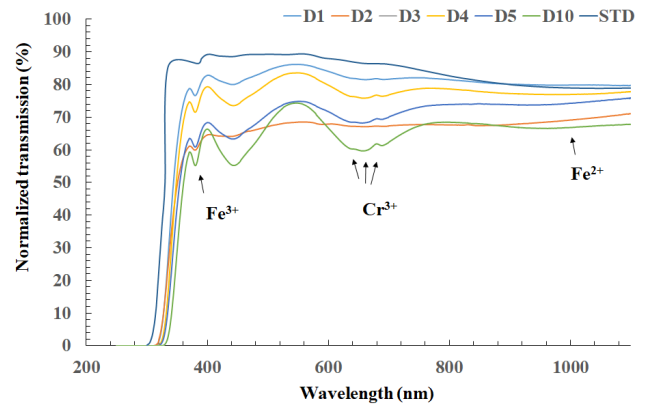


Figure 5. UV-VIS spectra of the glass samples.

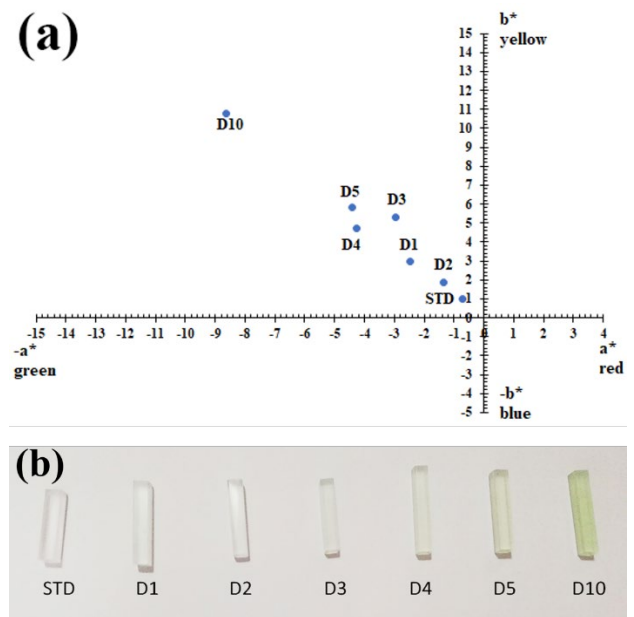


Figure 6. Color measurement by UV-VIS spectroscopy (a) CIE Lab analysis results of glass samples which prepared from various dust contents, and (b) the photo of glass samples.

Table 3. Results of colorimetric analysis of glass samples according to CIE system, Fe²⁺/Fe total ratio and refractive index of glass samples.

%DUST	L*	a*	b*	Fe ²⁺ /Fe Total	Refractive index
0	93.22	-0.71	0.99	0.2150	1.516
1	92.64	-2.48	2.99	0.0935	1.518
2	87.36	-1.35	1.89	0.0816	1.516
3	86.64	-2.95	5.33	0.0720	1.519
4	91.69	-4.25	4.75	0.0864	1.518
5	85.61	-4.40	5.85	0.0650	1.519
10	82.25	-8.63	10.80	0.0769	1.520

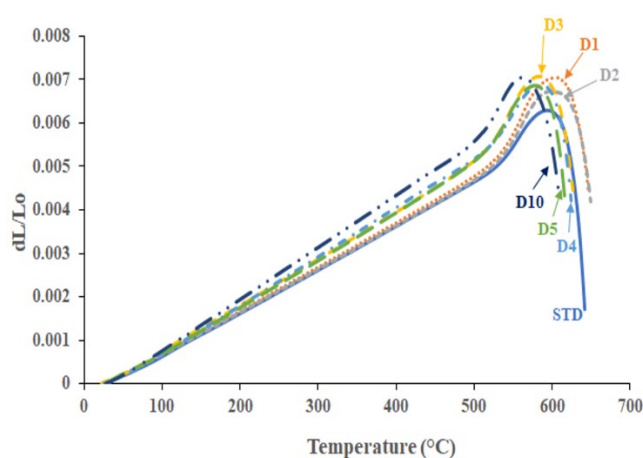
Table 4. The summary results from dilatometric plots and density of glass samples.

% DUST	COE ($10^{-6} \times 1/^\circ\text{C}$)	T _g ($^\circ\text{C}$)	T _d ($^\circ\text{C}$)	Density ($\text{g}\cdot\text{cm}^{-3}$)
0	9.97	530.96	598.09	2.4846
1	10.12	533.16	607.30	2.4959
2	9.95	529.8	601.90	2.4930
3	10.74	517.02	586.37	2.5043
4	11.19	515.4	590.78	2.4935
5	11.10	518.49	580.70	2.4855
10	12.04	505.96	564.24	2.5028

From Table 3, the value of Fe^{2+}/Fe total decreases with the increasing amount of exhausted dust. According to equation (4), more evolution of O_2 gases could be from the exhausted dust. Thus, ferric ions (Fe^{3+}) was more stable. The intense band due to ferric ions at about 385 nm resulted in a yellow-green color as shown by the samples in Figure 6. However, the amount of the exhausted dust did not affect the value of refractive index of the glass. The value of refractive index of the glass samples was in the range of 1.516 to 1.519.

Coefficient of thermal expansion (COE) in the temperature range of 100°C to 400°C , T_g and T_d were determined from the thermal expansion curves (Figure 7) and the results were summarized in Table 4. For Standard sample, COE, T_g and T_d are $9.97 \times 10^{-6}/^\circ\text{C}$, 531°C and 598°C respectively. Up to 2 wt% replacement of total raw materials by the exhausted dust in the glass batch did not affect the thermal properties of glass samples. When the dust were introduced more than 2% into the glasses, the COE of glasses (D3 to D10) were greater than that of STD glass. But, T_d and T_g of glasses (D3 to D10) were lower than that of STD glass. T_g and T_d of glass samples decrease with increase Na_2O content from the exhausted dust.

The observed decrease in T_g and T_d and increase in COE of the glass samples suggested that Na_2O led to the decrease in the cross linking of glass network. Na_2O content in the exhausted dust acted as network modifiers and increased the number of nonbridging oxygen (NBO), signifying weaker a glass network [1]. The amount of the exhausted dust did not affect the density of the glass samples. The value of density of the glass samples was in the range of $2.4846 \text{ g}\cdot\text{cm}^{-3}$ to $2.5028 \text{ g}\cdot\text{cm}^{-3}$ as shown in Table 4.

**Figure 7.** Thermal expansion curves from dilatometry technique.

4. Conclusions

Based on the results in this study, exhausted dust can be recycled in glass batch to reduce production costs and energy for melting glass. The following conclusion can be drawn.

The analysis of phase and chemical composition of the dust indicated that it consisted mainly sodium sulphate which can be used in the glass fining agent. The glass made with exhausted dust yielded a decrease in the remaining bubbles and the temperature of the melting reaction of the glass batches.

The optimum amount of the dust, which made it possible for glass batch melting was 2 wt%. From the results revealed that up to 2 wt% replacement of total raw materials by the exhausted dust in the glass batch did not affect the value of density, refractive index and thermal properties of glass samples. The CIE lab values of the sample containing 2 wt% the exhausted dust was close to the color of standard sample referred to glass batch plant factory.

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