Vitrification of fly ash from municipal solid waste incinerator

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Abstract

Fly ash from municipal solid wastes (MSW) incinerators in Korea contains a large amount of toxic materials and requires pertinent treatments. However, since fly ash in Korea has a high chlorine concentration, it is difficult to apply cementation and chemical treatment techniques. In this study, we report the vitrification of fly ash along with the properties of the glasses and leaching characteristics of heavy metal ions.

Fly ash can be vitrified by melting at 1500 °C for 30 min with the addition of >5 wt.% of SiO_2. Glasses showed Vickers hardness of 4000–5000 MPa, bending strength of 60–90 MPa and indentation fracture toughness of ~ 0.9 MPa m$^{1/2}$. Glasses also showed the excellent resistance against leaching of heavy metal ions with $Cd^{2+} < 0.04$ ppm, $Cr^{3+} < 0.02$ ppm, $Cu^{2+} < 0.04$ ppm and $Pb^{2+} < 0.2$ ppm. These results indicate that the vitrification technique is effective for the stabilization and recycling of toxic incinerator fly ash. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

One of the major problems in developed countries is treatment of a large amount of municipal solid wastes (MSW). Especially, in countries where the population density is high and space for landfilling is limited, MSW treatment poses a serious problem. The best method for waste treatment is recycling and reuse. But the amount of waste that can be recycled is limited to less than approximately 40% of the total volume [1]. Landfilling is known to be the most expedient, inexpensive method to dispose non-recyclable solid

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wastes. However, this simple method causes many problems, for example, groundwater pollution from landfill leachate, odor emission and soil contamination. Furthermore, any toxic materials present in the original waste will remain in an unknown, uncontrolled form inside the landfill. Thus, incineration of MSW has been considered as a new strategy in many countries, such as Japan and several European countries. Incineration reduces the volume of the waste as much as 90% and does not produce further problems from leachate and odor. Moreover, this is a sanitary method for treatment of MSW that does not cause biological problems.

On the other hand, incineration has some disadvantages compared with landfilling. Incineration requires high energy consumption and leaves a large amount of fly and bottom ash, which are produced in the proportion of 10–30 wt.% of the original amount of waste. Of these, high energy consumption is being compensated with the rising economic and environmental costs of landfilling. But ash treatment remains unsolved. Particularly, fly ash must be detoxified or decontaminated because it contains significant concentrations of heavy metals [2], such as lead, chromium, copper, zinc, as well as organic pollutants such as dioxins. Several techniques to treat these incinerator ashes have been proposed. These include cement-based techniques, wet chemical treatment and thermal treatment including vitrification. Except for vitrification, it is difficult to apply these techniques to fly ash from MSW incinerators because of the high concentrations of chlorine compounds existing in the forms of dioxins and alkali chlorides. Dioxins are difficult to destroy or stabilize by cementation or chemical treatment [3] since alkali chlorides hinder hydration of cement. The increasing tendency for MSW incineration makes it essential to search for new options for treatment of fly ash, and vitrification is the most promising solution of the various available technologies. If fly ash is melted at a temperature in excess of 1300 °C with the proper amount of glass-forming additives, relatively inert glasses are produced and dioxins are completely destroyed. Heavy metals can also be stabilized through incorporation into the glass matrix. Moreover, the inert vitreous products can be used for landscaping or building materials.

Recent papers from Germany [4] and Spain [5] demonstrated that it was possible to vitrify filter dust from incinerators with some additives. There was also a report [6] on the vitrification of ash from MSW incinerators without any additives. However, these works dealt with ashes which are relatively easy to vitrify because of high silica concentration of >35 wt.% with a low alkaline chloride content (5–15 wt.%). In addition, most of the previous works [4–8] did not consider the toxicity of ash and vitrified products. This paper reports the stability and the characteristics of vitreous products made of fly ashes from MSW incinerators. Thermal and mechanical properties of the glasses were evaluated and toxicity characteristic leaching procedure (TCLP) was used to evaluate the chemical stability.

2. Materials and methods

Fly ash used in the experiments was sampled from a stoker-type incinerator in Da-Dae MSW Disposal (Pusan, Korea). The fly ash collection system was an electrostatic precipitator (EP) with a capacity of 60,000 Nm³/h. Fly ash appeared as a fine powder, gray in color. The

chemical composition of fly ash was analyzed with a combination of inductively coupled plasma–atomic emission spectroscopy (ICP–AES) and X-ray fluorescence spectroscopy (XRF). Specimens for XRF analysis were prepared in the form of pellets to reduce loss of volatile materials. Phase constitution was examined with X-ray diffractometer (XRD) using Cu Kα radiation.

Glasses were prepared from MSW fly ash by melting in an alumina crucible at 1500 °C for 30 min in consideration of viscosity. Melts were poured onto a copper plate in air and the glasses were annealed at 700 °C for 1 h and slowly cooled to room temperature. Glasses could not be formed by melting of fly ash itself so that addition of SiO_2 as a glass former was required. Also, in consideration of recycling of inert vitreous products, conversion of glasses into glass-ceramics is necessary to improve the mechanical properties. Furthermore, addition of MgO can significantly increase the formation of diopside crystals upon re-heating, and improve the thermal and mechanical properties. The glass-forming region, with the addition of these two additives, was investigated. Detailed analysis on the formation of diopside upon re-heating is ongoing and will be reported elsewhere.

The mechanical and physical properties were assessed by several techniques. The density of glasses was measured by the Archimedes method. Hardness and fracture toughness were analyzed with specimens (10.0 mm × 5.0 mm × 5.0 mm) by the indentation method using the Vickers indenter [9]. Vickers hardness was measured with a load of 200 g and loading time of 10 s. In the case of fracture toughness, the values of fracture toughness, K_{IC}, were calculated by the equation suggested by Evans [10]. Loads of 1 kg were used with the loading time of 10 s. To determine modulus of rupture, four-point bending strength was measured from specimens (5.5 mm × 3.0 mm × 48.0 mm) with the spans of 20 and 40 mm at the cross-head speed of 100 μm/min, as designated by the American Society of Testing Materials (ASTM) [11]. For analysis of mechanical properties, the specimens were polished with No. 2000-sand paper and 1 μm-diamond polishing paste.

The thermal expansion coefficient (α) and dilatometric softening point were measured by a thermomechanical analyzer (TMA). Glass transition (T_g) and crystallization (T_x) temperatures were determined from the differential scanning calorimetry (DSC) thermograms. Thermal analysis was performed at a heating rate of 10 °C/min in an alumina cell in an air atmosphere using alumina powder (99.9999%) as a reference.

Chemical stability of fly ash and glasses was estimated by the TCLP method of the US Environmental Protection Agency (EPA). Glass samples for the leaching test were ground and sieved to a particle size <45 μm, similar to the size of fly ash, so that a direct comparison becomes possible. For the analysis of the heavy metal concentration in the leached solution, inductively coupled plasma–atomic emission spectroscopy (ICP–AES) was used.

3. Results and discussion

Table 1 shows the composition of fly ash from a MSW incinerator in Korea. Major components, as determined by XRF, were Na, Cl and K. It is unique that the chlorine portion is high compared with other compositions reported [12] due to the high concentration of salty food waste and plastic materials in MSW (Fig. 1). Also, there was a significant weight

Table 1
Composition of as-received fly ash

Component	Concentration[a]
Major compositions	
Na	23.1
Mg	2.0
Si	5.1
S	5.7
Al	2.6
K	13.6
Ca	9.8
Cl	29.0
P	1.7
Zn	3.0
Ti	0.8
Total	96.8
Heavy metals	
Cd	629
Cr	332
Cu	1653
Mn	680
Pb	758

[a] Concentrations for major compositions are in wt.% and for heavy metals in ppm.
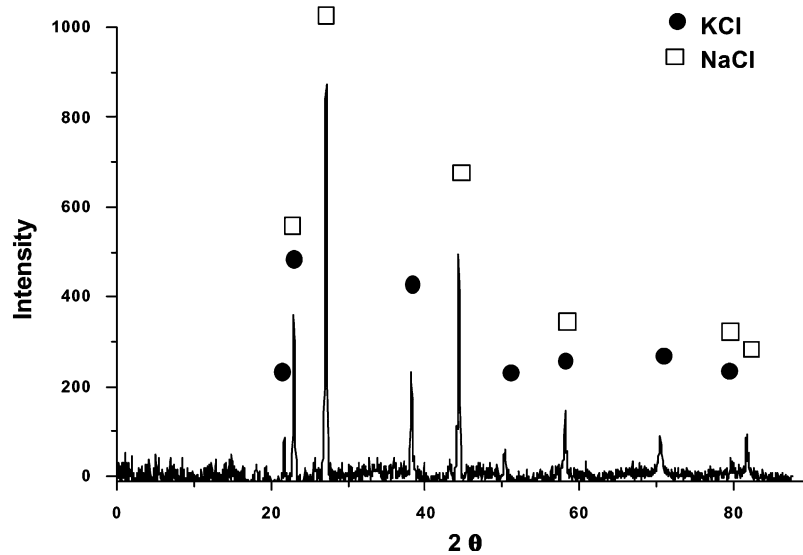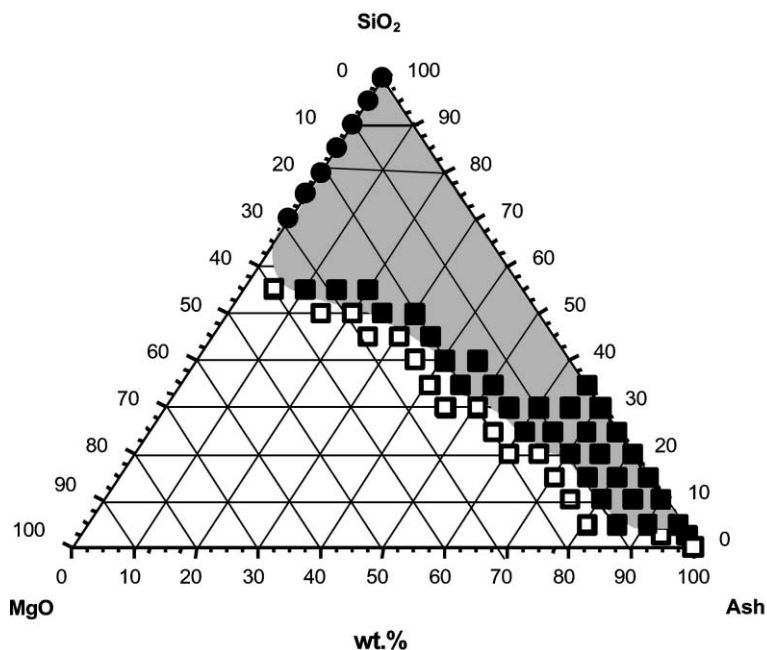

Fig. 1. X-ray diffractogram of fly ash.

Fig. 2. Fly ash–SiO$_2$–MgO ternary diagram of glass formation. (●) Glass (Mazurin et al. 1987) [13]; (■) Glass (experiment); (□) Crystallized glass (experiment).

loss (∼65% in weight) on heating to 1500 °C by TGA, which was probably due to loss of volatile materials associated with the decomposition of the chlorine compounds. The shape of the fly ash is round and is a few microns in diameter. An X-ray diffractogram of the fly ash is given in Fig. 1 and shows that KCl and NaCl are the major phases of the chlorine compounds.

Fig. 2 is the ternary diagram that shows the glass-forming region when SiO$_2$ and MgO were added. Melt containing fly ash only does not have enough glass formers, and therefore cannot achieve glass formation. With the addition of 5 wt.% SiO$_2$, however, the melt formed dark brown glasses upon cooling. As the portion of SiO$_2$ increased, the color of the glasses changed to light green.

Fly ash used in this study had a high concentration of heavy metals and chlorine compounds, as shown in Table 1. However, these chlorine compounds (KCl and NaCl) are relatively non-toxic in comparison with dioxins and are highly volatile at temperature of 1500 °C, where the experiments were carried out. Therefore, chlorine concentration in the glasses were considerably lower than that in the as-received fly ash. In Table 2, we can find that glasses do not contain chlorine compounds after melting. These volatile materials cause a significant weight loss, up to 65 wt.% of the fly ash, after melting. These volatilized chlorine compounds need to be treated using air pollution prevention facilities.

Table 2
Composition of glasses prepared from fly ash and additives

Nominal composition (wt.%)	SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	K_2O	Na_2O	P_2O_5	TiO_2
Ash + silica										
100 Ash–0 SiO_2	18.84	34.76	2.43	0.23	23.23	5.90	1.17	7.67	5.43	2.79
90 Ash–10 SiO_2	38.43	19.73	1.86	0.16	17.33	4.10	1.80	8.93	3.89	2.08
80 Ash–20 SiO_2	49.32	16.06	1.46	0.13	13.76	3.05	2.35	8.81	2.98	1.49
70 Ash–30 SiO_2	58.53	5.47	1.17	0.12	12.48	2.85	3.10	8.50	2.40	1.23
Ash + 10% MgO + silica										
80 Ash–10 SiO_2–10 MgO	37.44	7.90	1.66	0.16	16.89	22.59	0.75	5.51	3.89	1.93
70 Ash–20 SiO_2–10 MgO	44.01	5.29	1.20	0.12	12.36	17.82	1.37	5.64	2.64	1.29
60 Ash–30 SiO_2–10 MgO	49.70	3.87	1.03	0.09	10.02	15.57	2.08	5.97	1.92	0.95

Leaching of heavy metal ions decreased as the portion of SiO_2 increased. In general, chemical stability is consistent with the progressive formation of a more compact and interconnected glass network structure with the addition of the glass formers [14]. Therefore, addition of SiO_2 strengthens the chemical stability of the glasses. On the other hand, heavy metals leached more with MgO addition, which weakens the network structure. However, the results in Table 3 indicate that the vitrification method is effective in reducing the toxicity of fly ash. Particularly, we can find that vitrification is most effective for Cr, Cd and Pb which are highly toxic. The results of leaching tests satisfy European and American as well as Korean regulatory standards [15].

Although, the leaching of heavy metal ions was limited to well below the environmental regulation, several other properties of glasses with different concentrations of additives were evaluated to assess the potential applications of the vitrified products. Density decreased as the amount of SiO_2 addition increased (Fig. 3) because the density of silica glass (2.2 g/cm^3) is lower than that of the solid prepared by melting fly ash only (3.0 g/cm^3). Decrease in density also resulted in decrease of microhardness (Fig. 4). Vickers microhardness in glasses made from fly ash and SiO_2 decreased from 4730 to 3920 MPa as SiO_2 content increased.

Table 3
Results of leaching tests by TCLP (ppm)

Glasses (wt.%)	Cd	Cr	Cu	Mn	Pb	Zn
Korean regulatory standard (leachate)	0.1	2.0	3.0	10.0	1.0	5.0
90 Ash–10 SiO_2	0.004	0.015	0.026	0.161	0.16–8	3.548
80 Ash–20 SiO_2	0.004	0.008	0.025	0.116	0.076	2.528
70 Ash–30 SiO_2	ND[a]	0.004	0.025	0.089	0.059	1.594
80 Ash–10 SiO_2 –10 MgO	0.038	0.008	0.066	1.440	ND	18.100
70 Ash–20 SiO_2 –10 MgO	0.033	0.007	0.033	0.582	0.131	8.600
60 Ash–30 SiO_2 –10 MgO	0.027	0.007	0.032	0.115	0.104	1.940
60 Ash–30 SiO_2 –15 MgO	0.010	0.005	0.039	1.123	1.167	1.900
60 Ash–30 SiO_2–20 MgO	0.012	0.007	0.052	1.176	1.370	2.640
Fly ash (as-received)	25.490	0.030	24.020	1.630	9.740	362.100

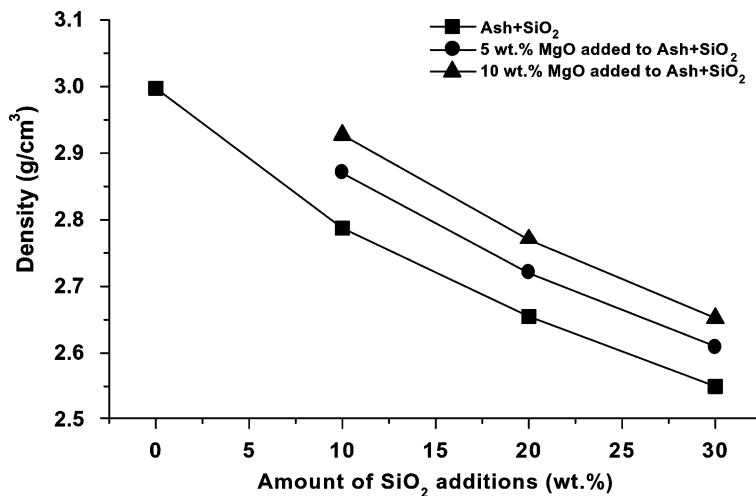[a] Not detected (detection limit: Cd, 0.003 ppm; Pb, 0.009 ppm).

Fig. 3. Changes in density with SiO_2 and MgO addition.

Upon the addition of MgO, density and microhardness increased since the density of MgO is $3.6\,g/cm^3$. Values of microhardness in these glasses are high in comparison with window glass (4100 MPa) and fused silica glass (4675 MPa) [16].

Bending strength was proportional to SiO_2 addition and shows a different pattern from the changes in Vickers microhardness (Fig. 5). This indicates that SiO_2 acts as a network former, which enhances the network connectivity of the glass matrix [17]. In addition, bond energy of a network former is much higher than that of a network modifier. When MgO was added, there was a small increment in bending strength. It is
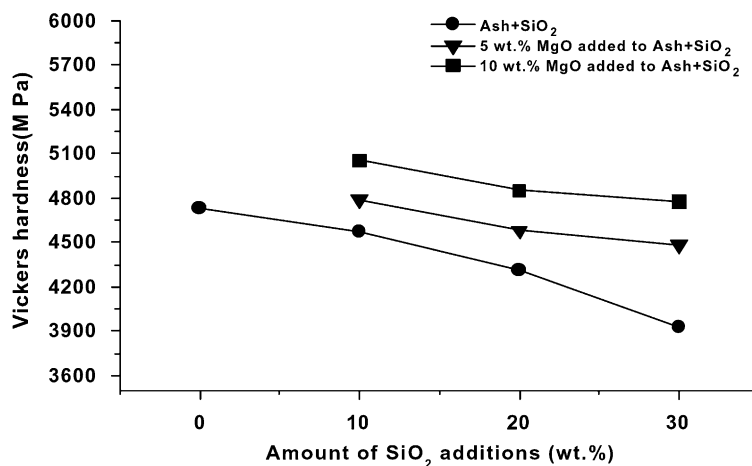

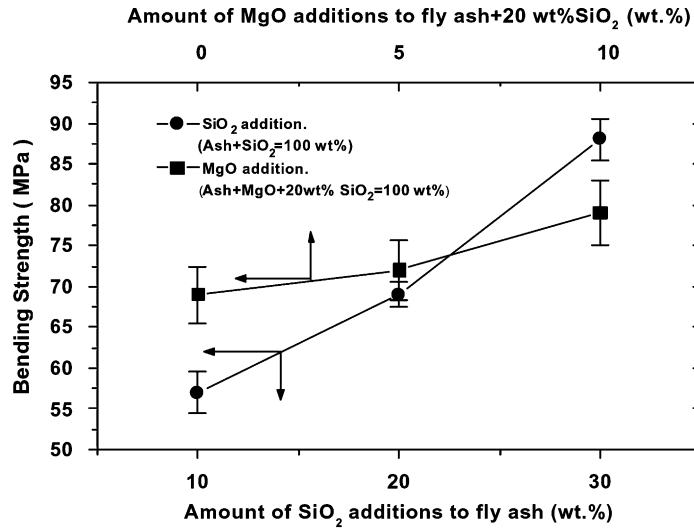Fig. 4. Changes in Vickers microhardness with SiO_2 and MgO addition.

Fig. 5. Changes in bending strength with SiO_2 and MgO addition.

reasonable to anticipate that a part of Na–O and K–O was substituted by Mg–O, and bond energy increased slightly due to the difference in bond energy. Bond energies of Na–O, K–O and Mg–O are 20, 13, and 37 kcal/mol, respectively [18]. Toughness was not largely affected by additions of SiO_2 and MgO, with values approximately 0.9 MPa m$^{1/2}$ (Fig. 6).
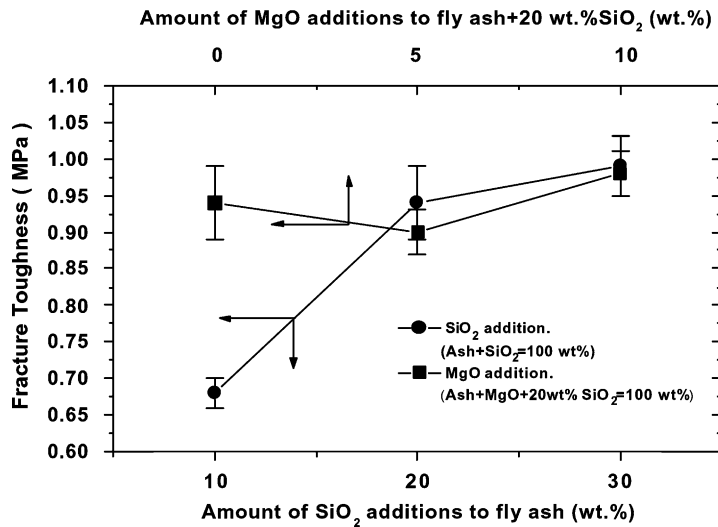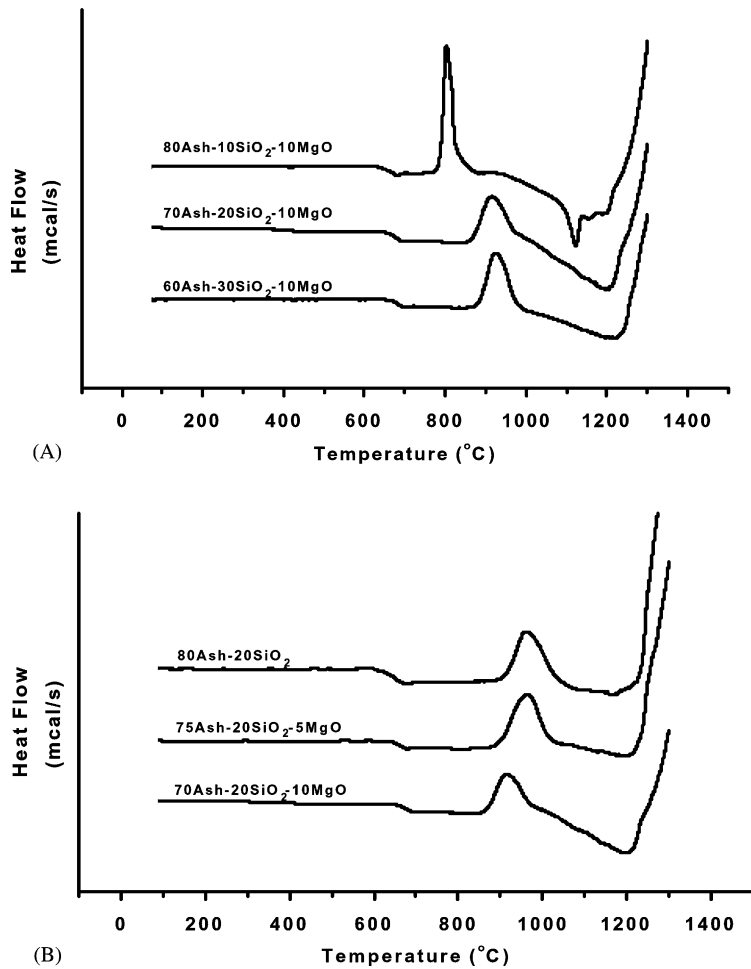

Fig. 6. Changes in fracture toughness with SiO_2 and MgO addition.

Fig. 7. DSC curves of glasses as the amount of (A) SiO$_2$ and (B) MgO changed.

Glass transition temperatures (T_g) of all glasses were similar within a range from 654 to 664 °C. On the other hand, crystallization temperatures (T_x) and temperatures of the maximum exothermic reaction (T_c) increased as the amount of SiO$_2$ increased. The reverse is true with MgO addition (Fig. 7). The glass-forming ability (S) can be evaluated [19] by the equation:

$$S = \frac{(T_c - T_x)(T_x - T_g)}{T_g} \tag{1}$$

In the glasses made from fly ash and additives, glass-forming ability tends to improve with increases in SiO$_2$ content and with decreases in MgO concentration. Thermal expansion also showed the same tendency. Thermal properties were summarized in Table 4.

Table 4
Summary of thermal properties of glasses

Glasses (wt.%)	T_g (°C)	T_x (°C)	T_c (°C)	α ($\times 10^{-6}$ °C^{-1})	S[a]
Ash + silica					
90 Ash–10 SiO$_2$	654	840	924	9.13	16.39
80 Ash–20 SiO$_2$	655	916	1011	8.77	25.86
70 Ash–30 SiO$_2$	658	932	1079	7.92	42.66
Ash + 10% MgO + silica					
80 Ash–10 SiO$_2$–10 MgO	653	788	805	9.98	2.48
70 Ash–20 SiO$_2$–10 MgO	659	868	915	9.33	10.54
60 Ash–30 SiO$_2$–10 MgO	664	885	932	8.72	11.08

[a] [19].

4. Conclusions

Fly ash containing a large amount of heavy metals can be vitrified with the addition of >5 wt.% SiO$_2$. Glasses made with fly ash and additives, SiO$_2$ and MgO, were effective in confining heavy metal ions from leaching. These glasses also showed high Vickers hardness, 3920–5100 MPa, and bending strengths of 57–88 MPa with a toughness of 0.9 MPa m$^{1/2}$. The coefficients of thermal expansion of the glasses were (7.92–9.98) $\times$ 10^{-6} °C^{-1} and were comparable to the normal window glasses.

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