

An alternative approach for reusing slags from a plasma vitrification process

Yi-Ming Kuo^{a,*}, Ho-Jung Tseng^b, Juu-En Chang^{c,d},
Jian-Wen Wang^a, Chih-Ta Wang^a, Hung-Ta Chen^d

^a Department of Safety Health and Environmental Engineering, Chung Hwa University of Medical Technology, 89, Wenhwa 1st St., Rende Shiang, Tainan County 71703, Taiwan, ROC

^b Department of Foundry Engineering, National Tainan Industrial Vocational High School, Tainan 71075, Taiwan, ROC

^c Department of Environmental Engineering, National Cheng Kung University, Tainan 70101, Taiwan, ROC

^d Sustainable Environment Research Center, National Cheng Kung University, Tainan 70101, Taiwan, ROC

Received 5 October 2007; received in revised form 13 December 2007; accepted 13 December 2007

Available online 23 December 2007

Abstract

Vitrification is widely applied to transform hazardous materials into inert slags. Raising the value of the recycled slag is an important issue from an economic point of view. In this study, an alternative approach for mixing a plasma slag with unsaturated polyester resin for making the dough-like molding composites is proposed. Physical properties, including ultimate tensile strength, Rockwell hardness, and the elongation at break, were measured to evaluate the characteristics of the composites. A scanning electron microscope and an X-ray diffractometer were used to examine the micro characteristics of the specimens. The chemical stability of the composites was estimated using the toxicity characteristic leaching procedure and a hot water bathing process. In an optimal slag loading (mass ratio of slag to unsaturated polyester resin) ranged from 0.1 to 0.2, the slag powder improved the physical properties of the composites. With an increased slag loading, excess slag powder weakened the structure of the resin, reducing the ultimate tensile strength and Rockwell hardness. The acid and water bathing tests indicated that the resin is decomposed in a hot environment. However, the slag was not destructed nor were the hazardous metals leached out. The results show that the molding method is an effective technology to recycle the slag.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Slag; Composite; Unsaturated polyester resin; Vitrification; Reuse

1. Introduction

Vitrification is widely applied to treat hazardous materials, such as fly ash and sludge [1,2]. The thermal melting process has several advantages: decomposition of organic toxic substances, volume reduction of waste, recovery of metals, and transformation of hazardous materials into inert slags [3–5]. A previous study showed that the mechanical strength of vitrified slag was improved after a crystallization step [6]. In such a process, the physical properties of the slags are more important than the chemical stability. These types of slags are most commonly used as construction or road-building materials or are converted

into glass ceramics [7,8]. A previous report stated that a water-quenched glassy slag offered better encapsulation of hazardous metals [9]. In the treatment of toxic substances, the immobilization of hazardous materials is the first concern prior to the reuse of slags. However, the physical strength of such an amorphous structure is often not strong enough to meet the requirements of building materials or other reuse purposes [10]. Hence, the applications for reuse of amorphous slags are usually limited in scope. It is very difficult to give equal consideration to both chemical stability and physical properties because the appearance of the amorphous phase weakens the structure of the slags [11]. Nevertheless, raising the value of the reused slags in a real scale plant is an important issue from an economic point of view [12].

This study proposes to find a new approach to directly reuse plasma slags. The effect of vitrification on laboratory waste was

* Corresponding author. Tel.: +886 6 2674567x854; fax: +886 6 2675049.
E-mail address: yiming@mail.hwai.edu.tw (Y.-M. Kuo).

not our focus; the slags were directly sampled without any effort to improve their physical properties during the vitrification process. Blends of slag powder and unsaturated polyester resin mixture were molded into the desired form. There are several potential applications for these composites. One can form statues or other decorative objects using this molding procedure, which is expected to greatly elevate the value of the composite. In addition, recycling the composite as a building material or apparatus components that have no strength requirements is another application to consider. The physical properties and chemical stability of the composites were estimated to show the safety and practicality of this approach.

2. Experimental section

2.1. Materials preparation and molding procedure

The slag used in this research was sampled from a batch-type plasma furnace in the Resource Recycling and Management Research Center, National Cheng Kung University. The flow chart of the vitrification system, including feeding, furnace, and air pollution control devices, is shown in Fig. 1. The feeding material of the plasma furnace was mainly laboratory waste from universities located in southern Taiwan. The raw materials had an extremely complicated composition which included liquids, solids, and organic and inorganic laboratory waste. After a sorting and separation process, the solid inorganic waste was fed into the furnace. The temperature of the plasma torch was $>1500\text{ }^{\circ}\text{C}$, with no excess air in the chamber during the operation. For a batch of the melting process (12 h), 1200 kg of waste and 480 kg of cullet were mixed and vitrified. The molten material was discharged from the bottom of the furnace, quenched by water, and collected as a slag. The plasma slag was dark green, sharp-edged, and porous.

The plasma slag was sampled and pulverized to a size that passed through a 100-mesh sieve ($149\text{ }\mu\text{m}$) for the subsequent molding and analysis process. The plasma slag powder was hermetically digested with an acid mixture ($3\text{ mL HNO}_3 + 5\text{ mL HClO}_4 + 1\text{ mL HBF}_4$) in a Teflon vessel at $210\text{ }^{\circ}\text{C}$ for 1 h. The digested mixture was added up to 25 mL with deionized water. The concentrations of the metals in the diluents were analyzed to determine the metal composition of the plasma slag.

An unsaturated polyester resin mixture containing 60–70% unsaturated polyester resin, 10–20% styrene, and 10–20%

organic solvent was mixed with the slag powder. The blend was mixed with a mechanical stirrer for 30 min to disperse the powder. The blend was then poured into a mold made of a rubber containing silicone ($\sim 4\text{ mm}$ thickness) and allowed to polymerize for 6 h. Specimens with various slag loadings (mass ratio of the slag powder to the unsaturated polyester resin) of 0, 0.1, 0.2, 0.3, 0.4, and 0.5 were labeled as S-0, S-1, S-2, S-3, S-4, and S-5, respectively for testing.

2.2. Estimation of physical and chemical properties

The ultimate tensile strength (UTS) of samples was obtained using a Computer Sever Tensile Testing Machine (Cometest Test Machines Co., Ltd., QC-505A1) following the procedure given in CNS 2112-G2014 at a crosshead speed of 0.1 mm/min [13]. After the sample was pulled into two pieces, the UTS of the specimen was calculated according to the ratio of applied force to cross section area. The elongation at break was estimated at the same time. The Rockwell hardness (HRB) was measured using a Rockwell indenter which indented the polished surfaces of the test material with a 1.59 mm hardened steel ball indenter with a load of 100 kg. To ensure the reliability of the heterogeneous nature of the samples, the UTS, the elongation at break, and the HRB of each specimen were all measured in triplicate to estimate their standard deviations, which are marked on the figures respectively.

One way to use recycled composites is to make outdoor decorations by mixing the resin and slags as a raw material. Therefore, it is important to ensure the stability of the composites in a thermal environment. To evaluate the thermal stability of the composites, the specimens were bathed in hot water from 50 to $90\text{ }^{\circ}\text{C}$ for 1 h. The COD in the solutions was determined using a standard procedure given in the Federal Register [14]. The surface characteristics of the water bathed specimens were also examined by a scanning electron microscope (SEM).

The toxicity characteristic leaching procedure (TCLP) was carried out to evaluate the mobility of hazardous metal species in the plasma slag. The extraction and digestion process of TCLP followed the detail procedure given in the SW846 Method 1311 [15]. The concentrations of metal species in the digests of the slag and the TCLP extracts were all determined using inductively coupled plasma-atomic emission spectrometry (JY-38 Plus ICP-AES).

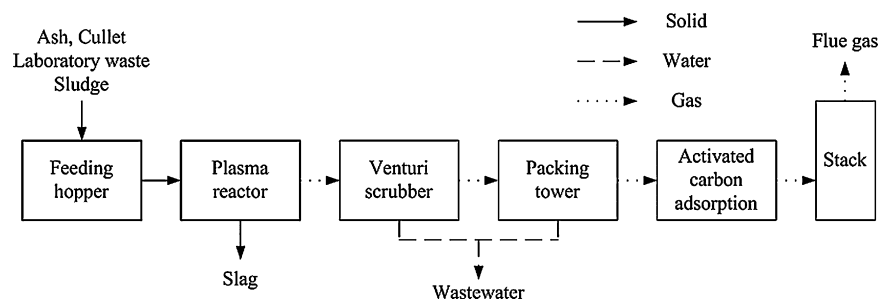


Fig. 1. Flow chart of the plasma vitrification system.

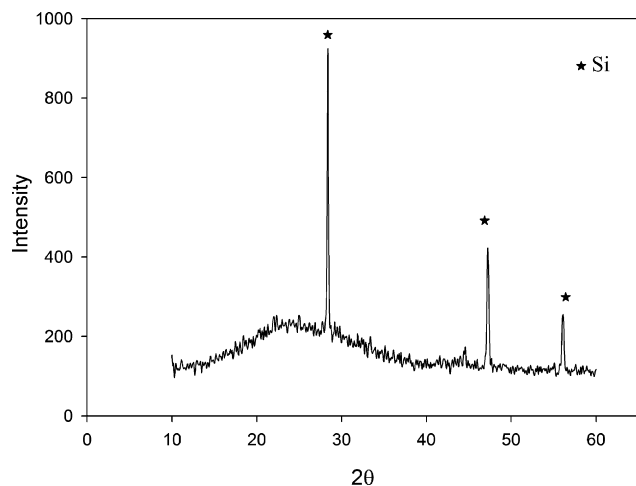


Fig. 2. XRD pattern of plasma slag.

2.3. Analysis of crystalline and microstructure characteristics

The crystalline phases in the slag were determined using X-ray diffraction (XRD) analysis, which was carried out by a powder diffractometer (Geigerflex 3063) with Ni-filtered Cu K α radiation at a particle size <20 μm , at 4° min⁻¹, in the 2 θ = 10–60° range. The volume fraction of the crystalline phase in the slag was determined using quantitative XRD analysis with an internal standard method [16]. High-purity silica powder was mixed with the specimen, with a Si/sample mass ratio of 0.1, to serve as an internal standard. The quantitative XRD analysis was performed to measure the approximate amount of the crystalline phase; a similar procedure was also applied in our previous report [17]. The amount of crystalline phase was determined according to the area of the specific peaks. The amorphous volume fraction (AVF) of the slag was then calculated using the following equation:

$$\text{AVF} = 1 - \sum_{i=1}^{i=n} \text{CP}_i \quad (1)$$

CP_{*i*} is the volume fraction of *i*th specific crystalline phase.

Scanning electron microscope–energy dispersive spectroscopy (Jeol JXA-840 SEM-EDS) was used to quantitatively examine the characteristics of the composites' surface with a working distance of 15 mm. Pulverized samples were adhered on a metallic plate, and then coated with Au using an ion sputter coater. The specimens were scanned by electron beams accelerated with a voltage of 25 kV to generate SEM images with a magnification factor of 10,000.

3. Results and discussion

3.1. Composition and crystalline characteristics of slag

The composition and crystalline characteristics of the plasma slag are shown in Table 1. The major components in the slag are Al (4.64%), Ca (21.0%), and Si (13.1%), which are also the com-

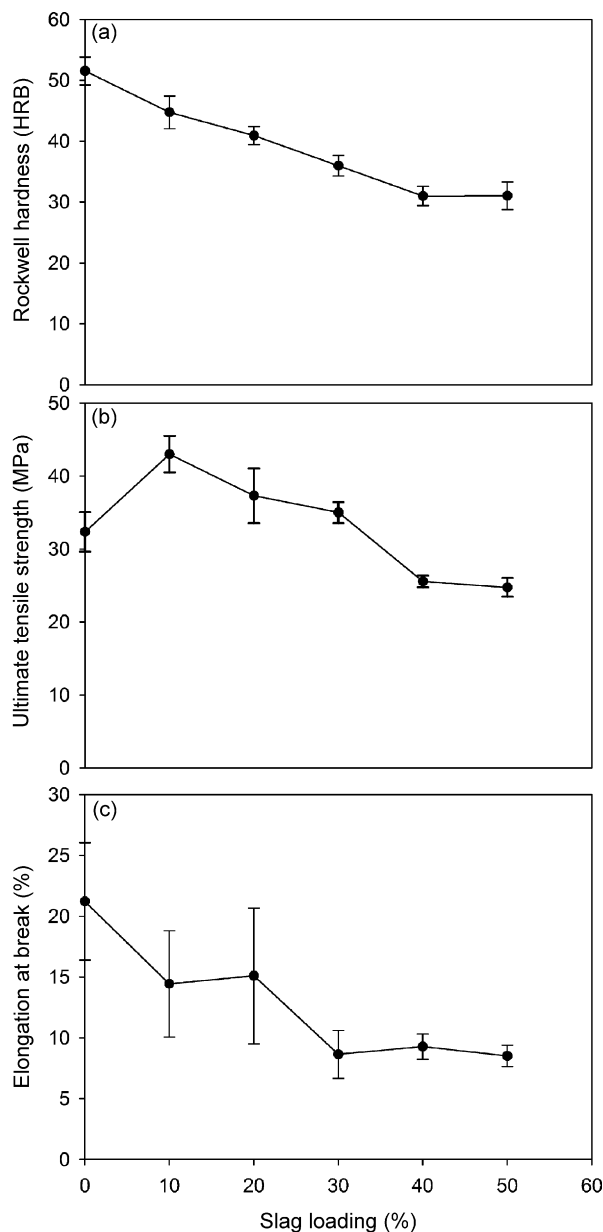


Fig. 3. Physical properties of the composites with various slag loadings (a) Rockwell hardness; (b) ultimate tensile strength; (c) elongation at break.

mon constituents of a slag matrix [18]. Anthropogenic metals, including Cd, Hg, and Pb, were present in trace amounts or below the detection limits, but Cu (69 mg/kg) and Zn (126 mg/kg) were found in relatively high amounts. Metals with a high boiling point (Al, Ca, Cr, Cu, Fe and Si) remained in the slag, whereas vaporization-oriented metals (Cd, Hg, Pb and Zn) vaporized into the flue gas. The profile of metal content in the plasma slag was similar to that from another vitrification process [19]. In addition, the leaching concentration of hazardous metal species of specimens was well below the regulated limits in Taiwan, making it safe to directly reuse the plasma slag. During thermal treatment, metal species with a lower boiling point, such as Cd, Hg, Pb and Zn, are vaporized. Therefore, these metals are present in the slag in trace amounts. The vaporized metal species are absorbed onto the fly ash, which is collected by the

Table 1
The metal content and TCLP results of the plasma slag

Category	Crust metal (wt%)					Anthropogenic metal (mg/kg)						Crystalline characteristics	
	Al	Ca	Fe	Mg	Si	Cd	Cr	Cu	Hg	Pb	Zn	Basicity	AVF (%)
Species													
Content	4.64	21.0	2.34	1.3	13.1	N.D.	38	69	N.D.	18.4	126	1.06	85.1
TCLP result (Standard*)	–	–	–	–	–	N.D. (1.0)	N.D. (5.0)	0.34 (–)	N.D. (0.2)	0.35 (5.0)	N.D. (–)	–	–

(N.D.) Non-detectable, (–) not available.

* Regulated standard in Taiwan.

air pollution control devices or emitted directly into the ambient air with flue gas [20].

The XRD pattern of the slag is shown in Fig. 2, on which the internal standard, Si, is marked. In the slag, the crystalline phases were all insignificant and the amorphous volume fraction was 85.1%, indicating that the structure was glassy amorphous. The basicity (CaO/SiO_2 mass ratio) of the slag was 1.06. The slag was cooled by water quenching. From our previous experience, it is reasonable to obtain a slag with such an amorphous structure which is suitable to encapsulate hazardous metals [21].

3.2. Physical properties of specimens

Fig. 3 illustrates the physical properties, including the HRB, the UTS, and the elongation at break, of the composites with various slag loadings. The error bars attached with these curves represent the standard deviation of these properties. Fig. 3(a) shows that the value of the HRB gradually decreased from 51.6 to 30.0 with an increase of slag loading. Fig. 3(b) shows that the UTS of pure unsaturated polyester resin is 32.3 MPa. The addition of 10% slag powder strengthened the specimen to a

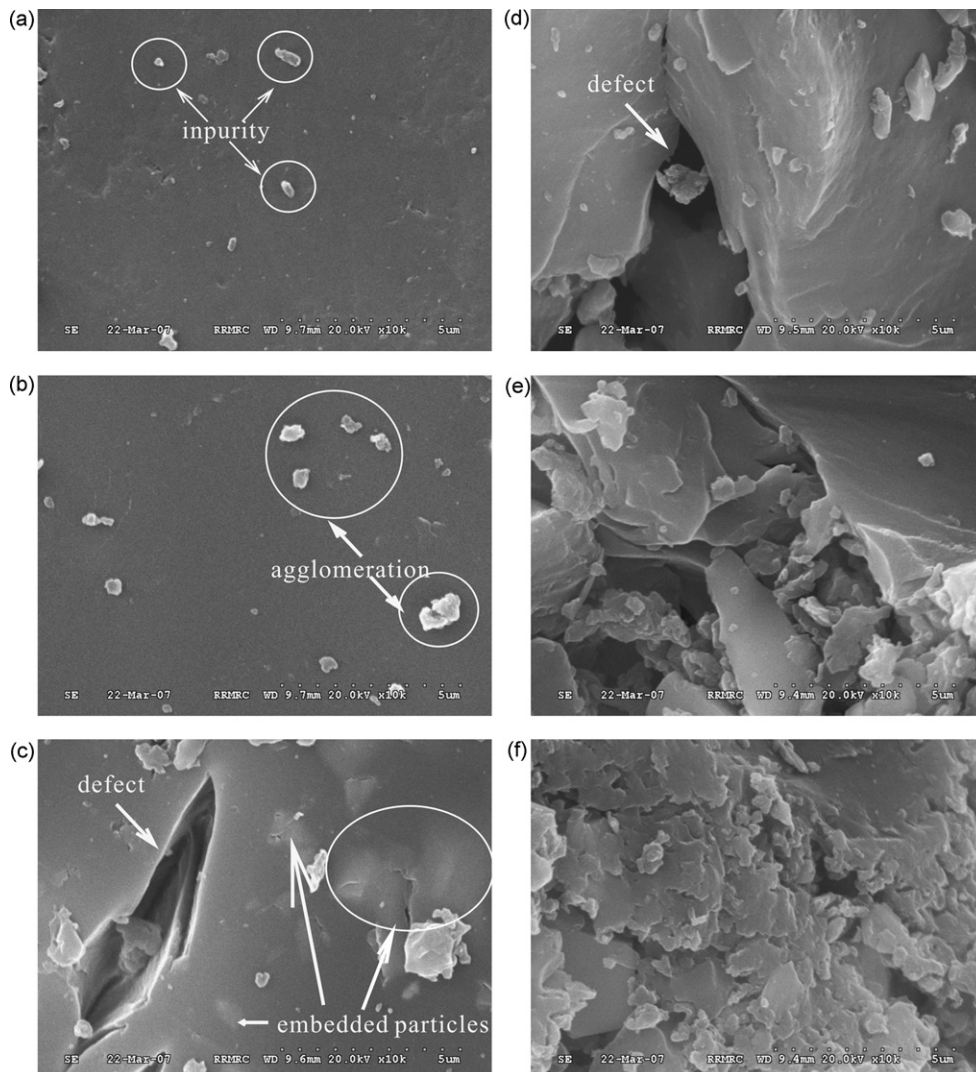


Fig. 4. SEM images of composites (a) S-0; (b) S-1; (c) S-2; (d) S-3; (e) S-4; (f) S-5.

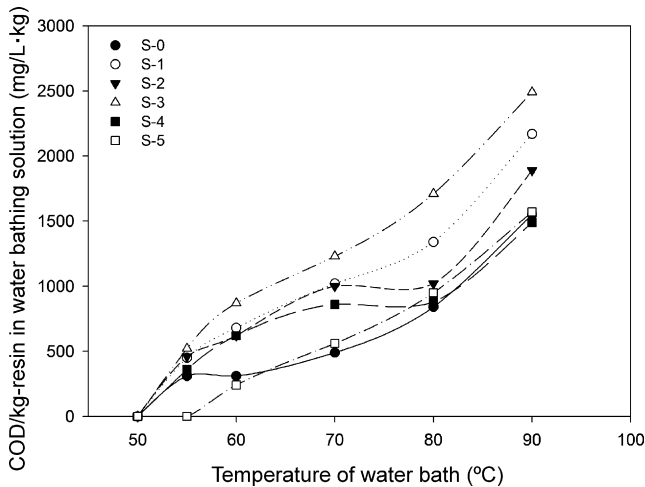


Fig. 5. Decomposition behavior of composites with various slag loadings.

UTS of 43.0 MPa. When the slag ratio increased to 20–30% and 40–50%, the UTS of the specimens decreased to ~ 35 and ~ 25 MPa, respectively. This shows that the slag powder first increased the strength, but then caused two declines with increasing slag loading. Fig. 3(c) shows that the elongation of pure unsaturated polyester resin is 21.2%, revealing that the material is very elastic. When more slag powder was added, the elongation of the composites gradually decreased to 15% and finally to $< 10\%$.

From the physical properties, it is obvious that the hardness and the elongation of the composites decreased due to the heterogeneous structure caused by the addition of the slag powder. It was also found that an appropriate slag loading (10–20%) increases the strength of the composites. However, an excess addition of slag powder weakens the composite's structure. A previous study supports these results; it reported that an adequate amount added minerals reinforced unsaturated polyester resin composites, but the structures were gradually weakened as more minerals were added [22].

Fig. 4 illustrates the SEM images of the composites. Fig. 4(a) shows that the structure was uniform and some particles deposited on the flat surface of S-0. These particles were probably impurities which were originally contained in the unsaturated polyester resin. For S-1, agglomeration due to the addition of the slag powder is visible. In Fig. 4(c) and (d), the agglomeration of particles and the defects are obvious (marked on the figure). In addition, it was found that some particles were embedded in the unsaturated polyester resin, indicating that the resin could serve as a material for macro-encapsulation to further immobilize hazardous metals in the slag.

In Fig. 4(e) and (f), single and pure agglomerations of the slag powder are not clearly visible and it is difficult to distinguish the slag powder from the unsaturated polyester resin. This shows that the excess slag powder drastically disturbed the polymerization of the resin, weakened the structure, and thus reduced the physical strength of the specimens. According to the microphotographs of the composites, the addition of the slag powder makes the resins heterogeneous and reduces the HRB of the composites. This was probably caused by the binding force

between the slag and the resin being smaller than the self-binding force of the resin.

The SEM images show that there is only a bit of powder on the surfaces of S-0 and S-1. For S-2 and S-3, the defects on the surface of the composites are clearly visible. With an increasing slag loading, the structure of the composites became more heterogeneous, making it difficult to distinguish the slag powder from the resin. Such a heterogeneous structure is expected to be weaker than a homogeneous structure. The SEM images look similar to each other between S-0 and S-1, S-2 and S-3, and S-4 and S-5. This finding coincides with the two stage declines in the UTS of the composites at the slag loading of 20–30% and 40–50%, respectively. This indicates that the slag loading governs the structure and the physical properties of the composites, which is supported by the transformation of the structure observed in the SEM images.

3.3. Thermal stability of composites

During the water bathing process, the mass losses of the composites were all under 0.1%, making it difficult to estimate the results. Therefore, the specific chemical oxygen demand (COD/kg-resin) in the water bathing solutions was taken as an index to represent the decomposition behavior of the composites. Fig. 5 illustrates the specific COD of the water bathing solution of the composites in the temperature range of 50–90 °C. It was observed that the composite began to be decomposed upon

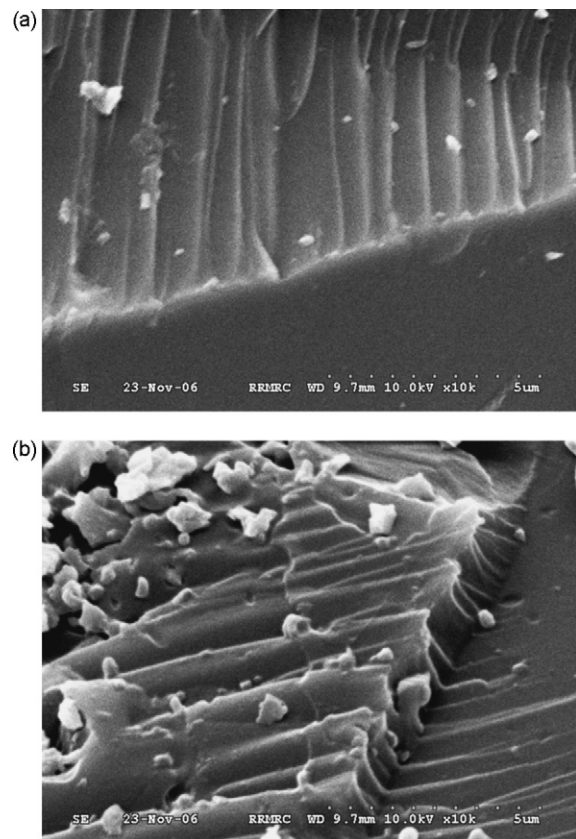


Fig. 6. SEM images of S-1 after 50 °C water bathing (a) pure water; (b) acid solution (pH 5).

reaching 55 °C and a further elevation of water bathing temperature enhanced the decomposition. Among the composites, S-0 and S-5 showed the best ability to resist heat decomposition, while the heat resistance of S-3 was relatively poor. The concentrations of metal species, including Cd, Cr, Cu, Hg, and Pb, in the water bathing solutions were analyzed. They were all below the detection limits, indicating that a water bathing process only decomposed the unsaturated polyester resin instead of the slag powder.

Fig. 6 shows the SEM images of S-1 after the bathing in water and in an acid solution (pH 5). For specimens bathed in water, signs of wear by hot water were almost invisible. The acid solution caused significant corrosion on the unsaturated polyester resin, but no signs of corrosion were observed on the slags. This indicates that the composites decompose upon reaching a water bathing temperature of >55 °C. The results of the metal concentrations (all were N.D.) in the water bathing solution reveal that heavy metals encapsulated in the resin were not leached out.

4. Conclusions

The results indicate that blending unsaturated polyester resin and plasma slag could be effectively used to make molding composites. In an optimal range (0.1–0.2) for the slag loading of the composites, the slag powder improved the physical properties. With an even higher slag loading, the excess slag powder made the structure of the resin heterogeneous, and thus decreased the physical strength. The SEM images of composites show that the slag powder were macro-encapsulated by the unsaturated polyester resin. In a hot environment (immersed in water hotter than 55 °C), the structure of the resin was initially damaged, with only the unsaturated polyester resin decomposed and dissolved in water. However, the resultant slag was not destroyed, and thus the encapsulated hazardous metals were not leached out. Therefore, the proposed approach is feasible for mixing slag powder and unsaturated polyester resin to a desired form. The value of the slags as a decoration or statue material is much higher than that as a building material. Thus, implication of the present technology is the next step. In addition, other materials, such as epoxy, could also be taken into consideration as an alternative material for the molding technology.

References

- [1] Y.M. Kuo, T.C. Lin, P.J. Tsai, W.J. Lee, H.Y. Lin, Fate of polycyclic aromatic hydrocarbons during vitrification of incinerator ash in a coke bed furnace, *Chemosphere* 51 (2003) 313–319.

- [2] P. Kanchanapiyaa, T. Sakanoa, C. Kanaokab, T. Mikunia, Y. Ninomiyac, L. Zhongc, M. Masuid, F. Masamia, Characteristics of slag, fly ash and deposited particles during melting of dewatered sewage sludge in a pilot plant, *J. Environ. Manage.* 79 (2006) 163–172.
- [3] H. Ecke, H. Sakanakura, T. Matsuto, N. Tanaka, A. Lagerkvist, Effect of electric arc vitrification of bottom ash on the mobility and fate on metals, *Environ. Sci. Technol.* 35 (2001) 1531–1536.
- [4] C.T. Li, Y.J. Huang, K.L. Huang, W.J. Lee, Characterization of slags and ingots from the vitrification of municipal solid waste incineration ashes, *Ind. Chem. Eng. Res.* 42 (2003) 2306–2313.
- [5] Y.M. Kuo, T.C. Lin, P.J. Tsai, Immobilization and encapsulation during vitrification of incineration ashes in a coke bed furnace, *J. Hazard. Mater.* B133 (2006) 75–78.
- [6] M. Erol, S. Kuüçükbayrak, A. Ersoy-Meriçboyu, Characterization of coal fly ash for possible utilization in glass production, *Fuel* 86 (2007) 706–714.
- [7] K. Koichiro, Ash melting system and reuse of produce by arc processing, *Waste Manage.* 16 (1996) 423–430.
- [8] J.M. Kim, H.S. Kim, Processing and properties of a glass-ceramic from coal fly ash from a thermal power plant through an economic process, *J. Eur. Ceram. Soc.* 24 (2004) 2825–2833.
- [9] K.E. Haugsten, B. Gustavson, Environmental properties of vitrified fly ash from hazardous and municipal waste incineration, *Waste Manage.* 20 (2000) 167–176.
- [10] M. Romero, J.M. Rincón, R.D. Rawling, A.R. Boccaccini, Use of vitrified urban incinerator waste as raw material for production of sintered glass-ceramics, *Mater. Res. Bull.* 36 (2001) 383–395.
- [11] F. Peng, K.M. Liang, A.M. Hu, Nano-crystal glass-ceramics obtained from high alumina coal fly ash, *Fuel* 84 (2005) 341–346.
- [12] E. Ecke, H. Sakanakura, T. Matsuto, N. Tanaka, A. Lagerkvist, State of the art treatment processes for municipal solid waste incineration residues in Japan, *Waste Manage. Res.* 18 (2000) 41–51.
- [13] Taiwan Bureau of Standards Metrology and Inspection, Test pieces for tensile test for metallic materials, CNS No. 2112-G2014, 2005.
- [14] Federal Register, Chemical Oxygen Demand, National Archives and Records Administration, April 21, 45 (1980) 26811–26812.
- [15] Environmental Protection Administration of United States, Toxicity Characteristic Leaching Procedure: SW846 Method 1311, 1992.
- [16] B.D. Cullity, S.R. Stock, *Elements of X-ray Diffraction*, third ed., Prentice Hall, Upper Saddle River, 2001.
- [17] Y.M. Kuo, J.W. Wang, C.H. Tsai, Encapsulation behaviors of metals in slags containing various amorphous volume fractions, *J. Air Waste Manage.* 57 (2007) 820–827.
- [18] Y.M. Kuo, J.W. Wang, C.T. Wang, C.H. Tsai, Effect of water quenching and SiO₂ addition during vitrification of fly ash. Part 1: on the crystalline characteristics of slags, *J. Hazard. Mater.* 152 (2008) 994–1001.
- [19] S.I. Sakai, M. Hiraoka, Municipal solid waste incinerator residue recycling by thermal processes, *Waste Manage.* 20 (2000) 249–258.
- [20] Y.M. Kuo, T.C. Lin, P.J. Tsai, Metal behavior during vitrification of incinerator ash in a coke bed furnace, *J. Hazard. Mater.* B109 (2004) 79–84.
- [21] Y.M. Kuo, J.W. Wang, H.R. Chao, C.T. Wang, G.P. Chang-Chien, Effect of cooling rate and basicity during vitrification of fly ash. Part 2: on the chemical stability and acid resistance of slags, *J. Hazard. Mater.* 152 (2008) 554–562.
- [22] B. Singh, M. Gupta, A. Verma, Polyester moulding compounds of natural fibres and wollastonite, *Compos. Part A* 34 (2003) 1035–1043.