Plasma vitrification and re-use of non-combustible fiber reinforced plastic, gill net and waste glass

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Abstract

Fiber reinforced plastic (FRP) composite material has widespread use in general tank, special chemical tank and body of yacht, etc. The purpose of this study is directed towards the volume reduction of non-combustible FRP by thermal plasma and recycling of vitrified slag with specific procedures. In this study, we have employed three main wastes such as, FRP, gill net and waste glass. The thermal molten process was applied to treat vitrified slag at high temperatures whereas in the post-heat treatment vitrified slags were mixed with specific additive and ground into powder form and then heat treated at high temperatures. With a two-stage heat treatment, the treated sample was generated into four crystalline phases, cristobalite, albite, anorthite and wollastonite. Fine and relatively high dense structures with desirable properties were obtained for samples treated by the two-stage heating treatment. Good physical and mechanical properties were achieved after heat treatment, and this study reveals that our results could be comparable with the commercial products.
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1. Introduction

Fiber reinforced plastics (FRP) was found to be the most common composite materials in yachts or fishing boats, etc. In recent years, good amount of fishery industrial activity is growing in the coastal areas of Taiwan. Most parts of the body of the fishing boats/yachts in Taiwan are made up of FRP. FRP is a kind of composite material with good strength and high fatigue stability. A large number of yachts are manufactured in Taiwan which in turn produces large quantities of FRP wastes. Since the melting point of FRP is greater than 1100 °C, it is considered as non-combustible waste and should be treated using certain procedures other than incineration.

Non-combustible gill net disposal has also become a challenging problem in Taiwan recently. Several studies have been published on the thermal treatments of various wastes [1–3]; but, to our knowledge, no information is available on the thermal plasma treatment and reuse of these wastes. In this study, FRP, gill nets and waste glass were mixed and treated by thermal plasma. According to literature survey [4,5], the thermal plasma system would generate lesser gas than conventional incinerator and the thermal plasma processing has very strong chemical reactivity that has been expected to reduce or decompose toxic gaseous contaminants in gas phases such as NOx, SOx. In addition, dioxins, furans, and other toxic species are shown to be destroyed at high temperatures generated by the thermal plasma, as reported by Cubas et al. [6].

The vitrification slag was further heat treated to form the glass ceramic sample with proper post-heat treatment and adding additives. The present study is directed towards the optimization of waste stream for plasma vitrification treatment and reuse of vitrification slag. The study is aimed to treat the non-combustible fishery wastes such as, FRP, gill net and waste glass. Thermal plasma was used as a heating source at 1250 °C. The plasma furnace (DC non-transfer type) built by the Institute of Nuclear Energy Research (INER, Taiwan) was used. Our prior studies [7]

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show that the vitrification process is a safe and efficient method for treating hazardous and radioactive wastes. The plasma vitrification has been proved to be a viable technology for combustible and non-combustible wastes in which the end products are in the form of inert and nonleachable slags with good volume reduction that could be safely disposed [7].

After the plasma vitrification, the slag was characterized by scanning electron microscopy (SEM) for microstructure/morphology observation, X-ray diffractometry (XRD) for crystal structure/chemistry determination, and inductively coupled plasma atomic emission spectrometry (ICP/AES) for chemical microanalysis. The treated products were subjected to toxicity characteristic leaching procedure (TCLP), followed by a leachability analysis for the selected elements using ICP/AES.

For the reuse process, vitrified slag was treated into glass ceramic materials with addition of nucleating agent and post-heat treated at high temperatures. Two-stage post-heat treatment was used in this study for nucleation and grain growth that resulted in an end product with a predominantly crystalline microstructure.

2. Experimental

The schematic description of DC thermal plasma system is shown in Fig. 1. Argon was used initially for generating plasma and air was then used as the main ambient gas during the vitrification process. The crucible was placed in the middle of the chamber to achieve uniform temperature distribution. The plasma vitrification process was carried out for 1-h duration at 1250 °C with heating and cooling rates of <7 °C/min. The furnace temperature was controlled by adjusting gas flow, plasma current and voltage.

Crystal structures of the vitrified slags and glass ceramic were determined using an X-ray diffractometer with Cu Kα radiation. Morphological features and compositions of the slag were analyzed with a scanning electron microscope (SEM) and inductively coupled plasma–atomic emission spectrometry (ICP/AES), respectively. Differential thermal analysis (DTA) for
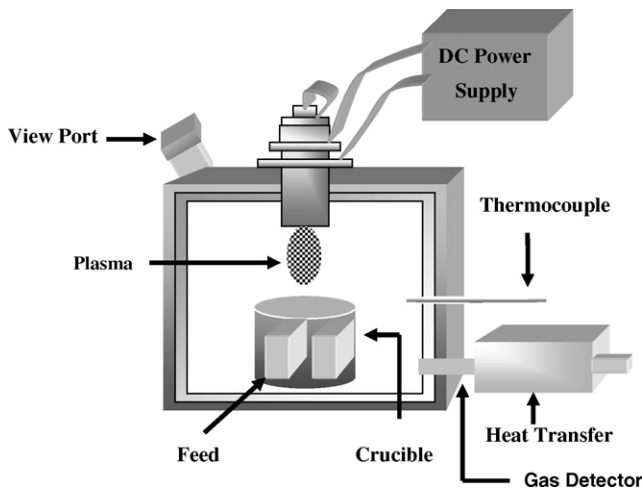

Fig. 1. A schematic description of INER plasma vitrification system used in this study.

Table 1
List of feed weights and slag properties

Samples	Weight of feed (g)			Slag chemical composition (wt.%)										Slag density (g/cm³)	Corrosion rate of SAE1022 (mm/year)[a]	Vitrified slag leachate (mg/l)	
	FRP	Gill net	Glass	SiO$_2$	Na$_2$O	K$_2$O	CaO	MgO	B$_2$O$_3$	Al$_2$O$_3$	TiO$_2$	CuO	Fe$_2$O$_3$			Fe	Al
FNG2/1/32[b]	20	10	320	–	–	–	–	–	–	–	–	–	–	2.49	–	–	–
FNG1/1/12	25	25	300	68.14	21.97	1.18	15.96	6.97	0.32	2.42	0.11	0.51	0.29	2.49	2.54	0.1	0.1
FNG1/0/0	200	0	0	49.29	–	0.05	10.07	–	6.51	3.65	2.27	0.15	0.11	2.57	2.48	0.5	0.9
FNG4/1/1	130	30	40	55.93	4.97	0.17	11.14	1.41	3.83	4.95	1.28	0.06	0.25	2.31	1.32	0.2	0.4
FNG7/1/1	200	30	30	55.07	3.13	0.18	11.51	0.60	4.48	5.38	2.10	0.61	0.16	2.48	1.66	0.1	0.4

F: FRP; N: gill net; G: glass.
[a] Corrosion rate of SAE1022 without slag (blank test) is 0.92 mm/year.
[b] Some analyses on this sample are not performed because it contains a higher glass content to be worthy for further study or reuse applications.
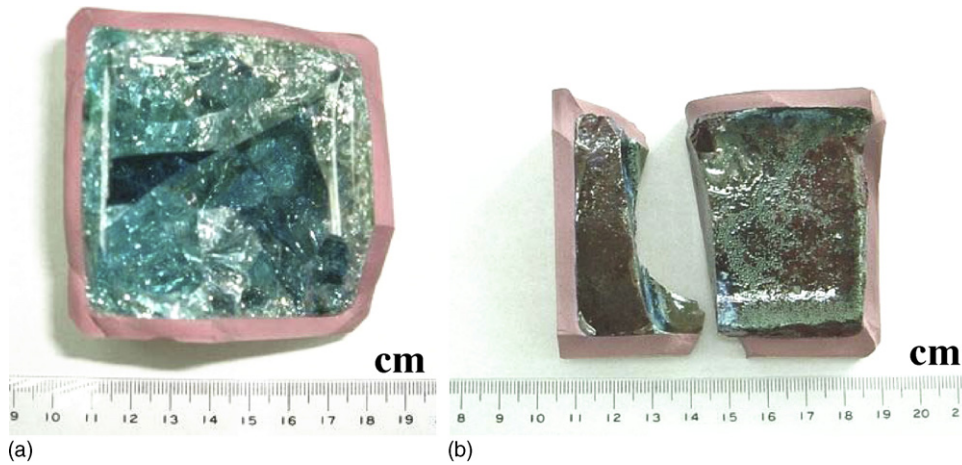
Fig. 2. Typical photographs of slags for FNG2/1/32 (a) and FNG7/1/1 (b) after plasma vitrification.

thermal analysis and Vicker hardness tester for surface hardness determination were employed. The leachability of the slag is evaluated by subjecting the slag for toxicity characteristic leaching procedure (TCLP). FRP, gill net and glass were used as feed materials in this study. The feeds listed in Table 1 are used in the present study because these feeds yield better results of volume and weight reductions, according to our previous study [8]. The chemical analysis results of these wastes indicate that the major components of glass are Si, Na, Ca and Mg in the form of oxides. FRP consists of Si, Al, B in the forms of oxides, while the gill net is made of polymers with major elements of C, O, Si, Fe, Al and Ca.

3. Results and discussion

3.1. Vitrified slags formed after thermal plasma treatment

The slags were formed after plasma vitrification treatment and two typical slag samples are shown in Fig. 2. FNG2/1/32 in Fig. 2(a) exhibits the transparent appearance because of more glass feed. FNG7/1/1 is the one with more FRP feeds and shows the opaque and deep dark appearance in Fig. 2(b).

Table 1 lists the leachability of Al and Fe elements of FNG1/1/12, FNG1/0/0, FNG7/1/1 and FNG4/1/1 are lower (<1 mg/l) and it interesting to note that the lower leachability leads to a better environment security. It reveals that these elements would be present either as network forming oxides or as network modifier oxides. The addition of glass not only supplies more Si element to bond metal element but also reduces the melting point of waste mixture. The densities of four slags of feeds were all around 2.46 g/cm^3, and corrosion test of TCLP leach solution to SAE1022 stainless steel is below regular value of 6.35 mm/year, as shown in Table 1.

Fig. 3 shows the structure of all of slags that are amorphous, and no major crystalline structures or phases are observed. FNG1/0/0 appears with an amorphous structure indicating that the pure FRP feed after process could result in a vitrified slag without adding any glass. ICP/AES results confirm the presence of SiO$_2$, Na$_2$O, Al$_2$O$_3$ and CaO in glassy slag, as shown in

Table 1. It is noticed that FNG1/1/12 contains more Na$_2$O due to the addition of more waste glass enriched with Na. FNG1/0/0, FNG4/1/1 and FNG7/1/1 showed less Na elements due to the presence of more FRP feed.

3.2. Glass ceramics formed by the post-heat treatment

Thermal studies (DTA) of slags were carried out to select the suitable temperature for post-vitrification heat treatments. FNG1/1/12, FNG1/0/0, FNG7/1/1 and FNG4/1/1 are observed to be not sufficient to form a complete crystalline structure without the additive. DTA curves shown in Fig. 4 indicate that with Ca(OH)$_2$ as the additive, the T_g glass transition onset temperature is well defined. In addition, the onset temperature of Ca(OH)$_2$-added sample is increased to 629 °C from 603 °C with-
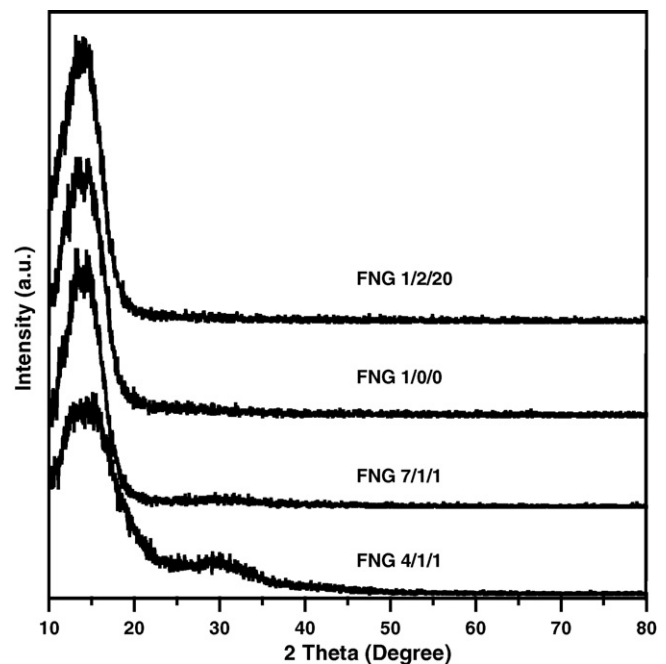

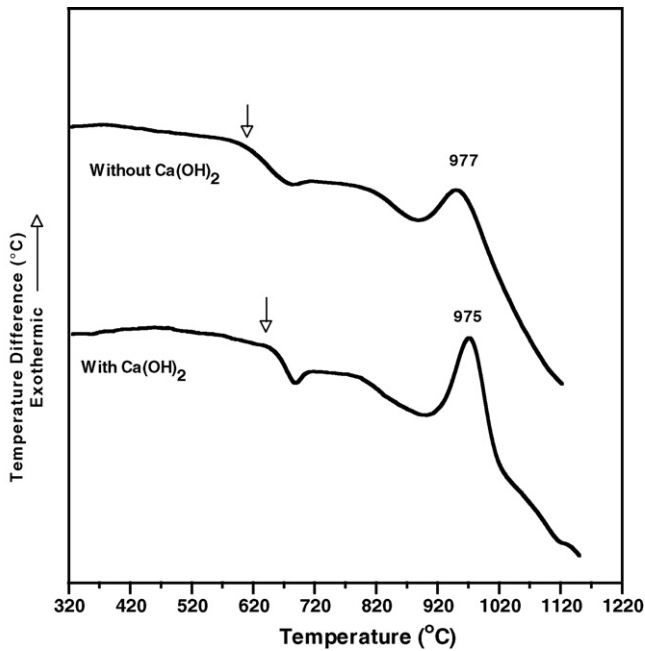Fig. 3. XRD patterns obtained from the slag samples for various feed ratios.

Fig. 4. DTA curves in the glass-based ceramic crystallized at a temperature rate of 40 °C/min. Arrows in the figure indicate the locations for T_g glass transition onset temperatures.
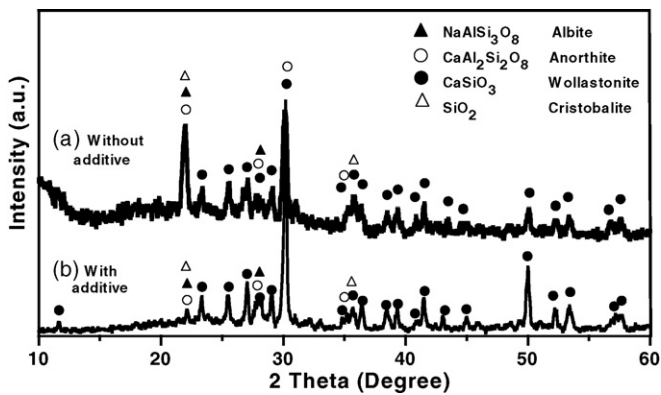

Fig. 5. XRD patterns of FNG4/1/1 with and without additive after post-heat treatment.

out additive. According to DTA results and our prior study [9], we selected 850 and 950 °C as post-heat treatment temperatures in the present study. The post-heat treatment duration is 1 h at each temperature.
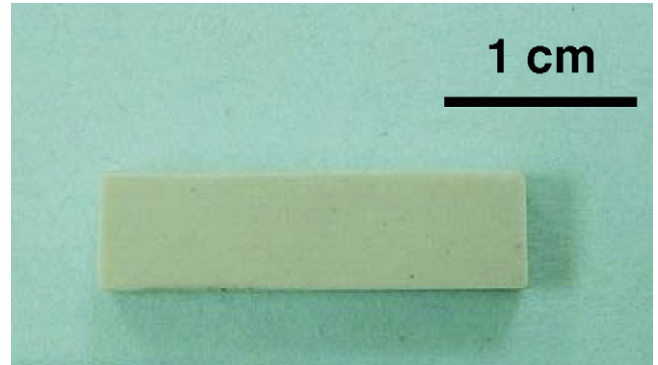

Fig. 7. Photograph of S1 sample after post-heat treatment.

After heat treatment, FNG4/1/1 powder without additives appeared in four crystalline phases and one amorphous phase are shown in the XRD pattern in Fig. 5. The four crystalline phases were cristobalite, albite, anorthite and wollastonite, respectively. A higher Si content is found to present in the FNG4/1/1 sample. Therefore, we can add 13.2 wt.% $Ca(OH)_2$ as the additive with FNG4/1/1 sample to adjust its composition. After adding the additive in FNG4/1/1 (sample name: S1), the XRD pattern of S1 revealed an amorphous phase with the decay of cristobalite phase and buildup of the peak of wollastonite phase. It is thus believed that the calcium hydroxide additive modifies the composition of the wastes leading to a system with the predominant presence of Ca-containing crystalline phases. SEM result of S1 shows more crystalline phases than those observed with FNG4/1/1 without additives, as shown in Fig. 6. XRD results indicate that the additives can decrease the amorphous and cristobalite phases in FNG4/1/1 sample after heat treatments. Fig. 6(b) shows the needle shaped natural wollastonite with a density corresponding to 2.8 g/cm^3 [10].

Fig. 7 shows the appearance of S1 glass ceramic sample, and majority of phase belong to wollastonite. Also, the wollastonite material available commercially is white as shown in Fig. 7. The properties of the product S1 and its commercial counterpart were listed in Table 2. A comparison of properties could be made between S1 and new cristone, natural marble and natural granite. The table shows that S1 is lighter than others, and however, it possesses larger bending strength than other commercial products. Although its compressive strength is weaker than new cristone, it shows better strength than other natural minerals.
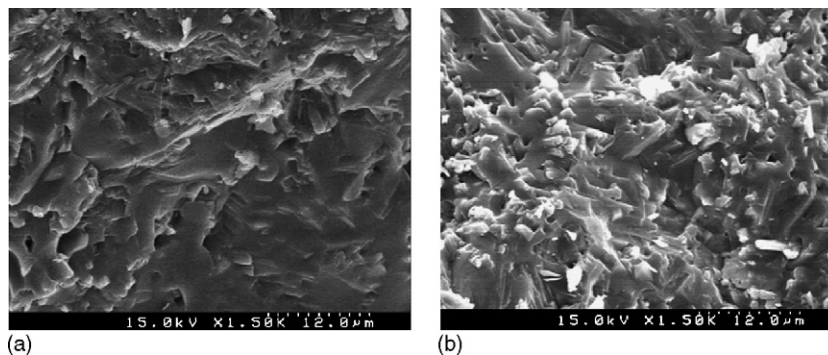

Fig. 6. SEM micrographs of FNG4/1/1 without (a) and with (b) additive after post-heat treatment.

Table 2
Properties of S1 glass ceramic and other commercial products

Properties	S1	New cristone[a]	Marble[a]	Granite[a]
Density (g/cm^3)	2.6	2.7	2.7	2.7
Four-point bending strength (MPa)	82	51	17	15
Compressive strength (MPa)	297	490	88–225	59–294
Water adsorption (%)	0	0.02	0.30	0.35
Resistance to chemical solutions				
1 wt.% H_2SO_4	1.79	0.08	10.3	1.0
1 wt.% NaOH	0.12	0.03	0.30	0.10

[a] Data taken from China Glaze Co. are included for comparison.

The property of resistance to acid solution is better than that in alkali solution since wollastonite is alkaline mineral in nature.

4. Summary and conclusions

All the slags in this study are fully vitrified. TCLP results indicate that the safety of the slag and hardness increases with FRP amount. The vitrification slag was further heat treated to form the glass ceramic with proper post-heat treatment and adding some certain additives. Therefore, fine and relatively dense structures with desirable compressive strength of ~297 MPa and bending strength of up to 82 MPa properties are obtained after the heating treatment, and have good resistant of chemical solutions. So a new and useful glass ceramic material was thus obtained with desirable properties. Hazardous waste treatment applications exploit the plasma's ability to rapidly initiate a variety of chemical reactions such as evaporation, decomposition, and oxidation. Inorganic materials can be heated to high temperatures where they melt and are transformed into molten slag and metal phases. Plasma vitrification using argon as well as ambient atmospheres is likely to be environmentally and economically feasible for large scale waste treatment applications and also comparatively advantageous than the other similar technologies.

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