Volatile Organic Compounds (VOCs) Distribution from PCB Waste and Vitrification by Reacting with Flux Agents

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ABSTRACT

Resin, the part of printed circuit board (PCB) waste, consists of harmful elements and volatile organic compounds (VOCs) and can cause pollution, but it can also be potentially treated through vitrification. Hence, the purpose of this study is to investigate the distribution of VOCs and analyze the effects of different flux agent types, pyrolysis duration, flux agent ratio, and effect of different carrier gases to vitrify resin waste in an atmospheric-pressure microwave plasma reactor. The resins to the flux agents - shell powder, limestone and quartz sand ratio of 50:50 and 25:75 gave the best results for the vitrification compared to the ratio of 75:25 and control (absence of flux agent). Furthermore, the crystalline structures of CaCO₃ and SiO₂ dominated the final residue, and this confirmed the vitrification of the resin. Flux agents also can reduce the distribution of propylene and benzene from the plasma pyrolysis. A longer duration of the pyrolysis, a higher flux agent ratio and flux agent types can be recommended for plasma pyrolysis applications even though they have no significant impact on the inertization of the elements statistically. Shell powder is thus suggested as a cost-less flux agent which can create vitrification and inertization of the contaminants from resin in plasma discharges.

Keywords: CaCO₃, Flux agents, Resin, SiO₂, Vitrification, VOCs

1 INTRODUCTION

The use of plasma technology, the fourth state of matter (Fridman, 2008), has become a promising method to tackle several issues of hazardous waste (Sanito et al., 2020b; Gomez et al., 2009; Cubas et al., 2015; Sanito et al., 2020a, c). It allows for the abatement of harmful compounds, such as organic, inorganic, and volatile organic compounds (VOCs) because of ionization from plasma discharge generates high energy atoms that collide to low energy atoms, thereby causing excitation, attachment, and molecular transfer. As a result, contaminants can be degraded entirely (Fridman, 2008; Mattox, 2010). The benefits of plasma technology are useful for the study installation of plants, reactor start-ups, stabilization of final products, energy saving, faster heat transfer compared to other jets, and a usable application in the industry (Heberlein and Murphy, 2008; Kuo et al., 2018). For this reason, plasma technology may be considered to deal with the management of hazardous waste.

Studies looking at plasma technology for degrading harmful compounds have been performed by some researchers (Cubas et al., 2014, 2015; Sanito et al., 2020b; Heberlein and Murphy, 2008; Sanito et al., 2020c, 2021). In their study, Heberlein and Murphy (2008), noted that plasma...
technology had been considered as a prominent technology for solving the waste disposal issues and recovering precious co-products. Cubas et al. (2015) confirmed that thermal plasma degraded Zn and Mn by more than 95% in the batteries waste. Likewise, Cubas et al. (2014) found that the inertization of elements from galvanic sludge, namely, Cr, Fe, and Zn ranging from 98%–100%, respectively, in thermal plasma. Sanito et al. (2020b) found that the elimination of metals and metalloids in the resin can be reduced by more than 96%. In this process, all the elements are perfectly degraded. Murphy (1999) also pointed out that degradation of ozone depleting substances that creates CF₄ and CF₂Cl exists during in plasma pyrolysis. In this regard, plasma technology should be applied as a suitable system for treating hazardous wastes and air pollutions.

The use of shells powder is a potential flux agent to deal in treatment of hazardous waste, especially, resin that contained metals and metalloids. Sanito et al. (2020b) showed that shell powder from the snails (Babylonia formosae; BF) is useful for treating metals, metalloids and volatile organic compounds (VOCs) from resin waste in an atmospheric-pressure microwave plasma reactor. Accordingly, inertization and vitrification of metals and metalloids happen. Some studies have shown that the addition of flux agents creates vitrification, and it is a safer procedure for managing hazardous wastes, such as electroplating sludge, medical waste, bottom ash, and fly ash. It is a safe process for transforming harmful compounds to less harmful ones, eliminate them, create amorphous structures, and more stable, for example; slag, from e-waste, radioactive waste, biologically hazardous waste, unused weapon, resin from PCB scrap waste, and chemical separation (Colombo et al., 2003; Bingham and Hand, 2005; Li et al., 2007; Karamanov et al., 2017; Lee and Lin, 2007; Celary et al., 2016; Park and Park, 2017; Tsakalou et al., 2018). Thereby, flux agents play an important part in vitrifying waste handling. However, there is still lack of information about the proper ratios of flux agent, different type of shell powder, and comparison study with commercial flux agent, that the insight has not been fully investigated properly, since some authors Wang et al. (2021a); Wang et al. (2012b) and Hu et al. (2013) have mentioned that optimal quantities of Ca play a crucial role to dealing with hazardous waste in thermal treatment. Also, there is no report of other flux agents from shell in reduction of VOCs. Hence, there is a need to conduct a further study so as to compare the use of shell powder in plasma pyrolysis to commercial flux agents for vitrification of elements.

In this study, natural shells, namely, Babylonia formosae (BF) and Haliotis diversicolor (HD) were prepared to powder form, and then used in the plasma pyrolysis. The flux agent of powder form was then applied as the flux agent for the plasma pyrolysis of resin drawn from the PCB scraps. The efficiency of the natural flux agent was then compared to that of the commercial flux agent. A microwave plasma reactor operating at atmospheric pressure was utilized for creating a plasma jet for the treatment of resin waste. Following this, the effect of shell types, the ratio of flux agents, and the duration of the plasma pyrolysis were examined so as to assess the inertization of the elements. This study also provided the information on degradation of volatile organic compounds (VOCs) of resin from the addition of different flux agents. Finally, the characterizations of the functional groups and crystalline phases derived from the resin, flux agents, and final residues were then presented for understanding the insight of mechanism of resin vitrification in plasma pyrolysis, potential reuse in the further environmental application and compared findings with previous studies.

2 MATERIALS AND METHODS

2.1 Collection and Preparation of the Samples

Resin from the PCB scraps was obtained from company in Taoyuan, Taiwan. The resin was sourced from a solvent distillation of the PCB scraps during the recycling process. Two types of snail powder were used as flux agents in the experiment namely, Babylonia formosae (BF) and Haliotis diversicolor (HD). The commercial flux agents, namely, quartz sand (Ferak) and limestone (MERCK) were obtained from the chemical company.

Before using the flux agent, the shells were washed with distilled water to clean the dirty particles on the shell surface. The shells were then dried in the oven for 24 hours at 100°C to evaporate the water. The shells were then crushed to small sizes (2 cm × 2 cm). A pulverizing machine was used for crushing the shell powder, quartz sand and resin at 30,000 rpm (Rong
Fig. 1. Schematic diagram of plasma experiments using different flux agents and atmospheric-pressure microwave plasma reactor system.

Tsong 0-2B, Taiwan) so as to obtain a smaller size particle of less than 0.100 mm (Cubas et al., 2015; Sanito et al., 2020b). The limestone was not crushed with the pulverizing machine because of its particle size. Following this, shell powder of 0.074 mm was obtained by using a 200 mesh sieve. Afterwards, all powder materials were stored in containers at room temperature (25°C). In order to prepare the samples for treatment in an atmospheric-pressure microwave plasma reactor, the resin and flux agents were weighed on a standard analytical scale (Shimadzu AUY-220, Japan) before being placed in the reactor. Fig. 1(a) displays the schematic diagram of plasma experiments using different flux agents.

2.2 Analysis of Initial Concentration and the Final Concentration

To analyze the concentration of the elements in the resin, the NIEA S321.63B method (TEPA, 2019) was used to extract the elements. Approximately 3 g of resin was placed in a 500 mL flask in a batch condition. The HCl 37% and HNO₃ 70% were added into the flask in the amount of 21 mL and 7 mL, respectively. The selection of the HCl and HNO₃ based on their good performance in dissolving elements as described in Sanito et al. (2020b).

To determine the concentration of the elements, an analysis was done using an inductively coupled plasma analysis (ICP-AES, Shimadzu ICPE 9820, Japan). The flow rate of argon gas was maintained at 10 L min⁻¹ while the auxiliary gas was carried out at 0.60 L min⁻¹, and carrier gas was set up at 0.31 L min⁻¹. The calibration curve of elements was measured in a calibration line using the standard solution (MERCK, Germany), with serially diluted of standard solution, and
with considering dilution factor with concentration of 5, 2.5, 1.25, 0.625, and 0.3125 mg L$^{-1}$. The $R^2$ of elements calibration curve shows 0.981–0.999. The power of the ICP-AES was maintained at 1.20 kW, and the exposure time was arranged at 30 seconds (Sanito et al., 2020b). The percentage rate was calculated under the initial and after the treatment value of ICP-AES analysis, as shown in the formula:

$$\text{% Removal} = \frac{\text{Initial Concentration} - \text{Final Concentration}}{\text{Initial Concentration}} \times 100\% \quad (1)$$

### 2.3 Analysis of Sample Characterization

In this study, the characterization technique, namely, SEM-EDX was performed only for the best vitrification results. The best vitrification result based on the crystalline structure from the peak analysis using the XRD. A scanning electron microscope energy dispersive X-ray (SEM-EDX: Hitachi S-4800, Japan) was used to analyze the morphology surface and the elemental composition of the final residue. The percentages of elemental composition from EDX analysis represent the final residue (Cubas et al., 2015; Sanito et al., 2020b).

The functional groups’ analyses of the resin, shell powder, limestone, and quartz sand were then performed with the Fourier transform infrared spectroscopy (FTIR-6600 JASCO, USA). The wavenumbers were used from 400–4000 cm$^{-1}$. Before analysis, the samples were mixed with KBr using the quick press KBr pellet kit until a 1 mm size of thickness (Sanito et al., 2020b).

The crystallinity of resin was determined before and after treatment using X-ray diffraction (XRD; Bruker D8 Advance Eco, Germany). The samples were scanned for 5 min within a range of 10$^\circ$–80$^\circ$. The X-rays originated from the modular components. The XRD’s voltage, power, and current were maintained at 40 kV, 1000 W, and 25 mA, respectively. The crystalline structures of the residues were shown at the 2$\theta$ peaks (Cheng et al., 2011; Sanito et al., 2020b).

### 2.4 Pyrolysis of Resin

An experiment was performed on the analysis of different flux agents for vitrification of resin (Fig. 1(b)). The resin’s pyrolysis was performed in a crucible of 20 cm$^3$ in volume, 4 cm in height, and 2.5 cm in diameter. The flux agents—the shell powder, quartz sand, and limestone, were mixed into the resin with various concentrations. They were then placed in the crucible for melting the material and it was operated in batch feeds. The selection of the quartz sand and limestone/shells represented SiO$_2$ and CaCO$_3$, which need to maintain lower melting points (U.S. EPA, 1992). The resin’s composition with the flux agents was as follows: 75:25, 50:50 and 25:75 (all ratio in %), with a total of 2 g in the crucible. The control was the treatment without the flux agents. In the experiment, nitrogen was selected as the carrier gas discharged from the magnetron propagate, which generate the plasma jet. The gas pressure, microwave power, and flow rate were controlled at 30 psi, 1000 W, 6 L min$^{-1}$, respectively. The pressure of carrier gas was set up at 30 psi from the 40 L of the gas tube. The duration of the pyrolysis was conducted at the 5 min and 7 min intervals. Pyrolysis duration less than 10 min considers energy consumption. The distance of the crucible from the copper wire where the plasma jet discharged was 5 cm. The plasma parameters used in the experiments are given in Table 1, and experimental design, replication and parameters of this study are shown in Table S1.

### Table 1. Summary of parameters in an atmospheric-pressure microwave plasma reactor.

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<td>Size of resin and flux agents</td>
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</table>
2.5 Analysis of Volatile Organic Compounds (VOCs)

A gas chromatography (GC; Agilent 6890 N-USA) was used for analyzing the VOCs composition in the treatment. 5 L gas bag (Tedlar, CKS) was used for capturing the gas from the plasma exhaust system. The temperature of GC oven was controlled at 32°C and increased to 200°C. The GC column size was 60 m × 0.25 mm × 1 µm. R² > 0.99 indicated a correct linear gas standard.

2.6 Statistical Analysis

The effects of shell types, flux agent ratios, and pyrolysis duration were statistically evaluated by the one-way ANOVA, with the IBM Minitab statistics, version 16, at the confidence level of 95%. The one-way analysis of variance (ANOVA) is usually used for determining the significant differences of the means of three or more independent (unrelated) groups. The number of p-values explains the effect of each parameter in the elimination of the elements. Tukey’s and Fisher’s method were used to analyze the pairwise comparisons from each parameter (Khan, 2013).

3 RESULTS AND DISCUSSION

3.1 Effect of Flux Agents for Degrading Volatile Organic Compounds (VOCs)

Fig. 2 gives the information of percentage distribution of VOCs. From the analysis, VOCs are generated from the treatment of resin as a result of plasma pyrolysis. The percentages of propylene, chloromethane, acetone, benzene, toluene and p-xylene were 7.78%, 1.69%, 5.23%, 72.52%, 12.16%, 0.62%, respectively, from the control (with an absence of flux agents). Benzene had the highest composition from the control with the value 72.52%, followed by toluene at the value 12.16% (Fig. 2(a)). Thereby, the reduction of benzene must be considered in this study.

The addition of shell powder derived from Babylonia formosae indicated a lower composition on the degradation of benzene at the value 68.23%, which was 4.29% higher than the control. This result is similar to Sanito et al. (2020b) which the concentration of benzene with the addition the powder of Babylonia formosae is lower compared to other flux agents. The removal rate of benzene was 7.30%, which was 0.48% higher than the control. The removal rates of benzene and propylene were obtained at 11.17% and 11.59%, respectively, from the control (with an absence of flux agents). Benzene had the highest composition from the control with the value 72.52%, followed by toluene at the value 12.16% (Fig. 2(a)). Thereby, the reduction of benzene must be considered in this study.

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Figs. 2(b–e) give the information of final percentage of VOCs composition with the mixing of different flux agents. Highest percentages of pollutant were propylene, with values at 41.11%, 49.56%, and 52.94%, respectively, which are quartz sand, Haliothis diversicolor, and limestone. The benzene was remained at value of 68.23% with the fuse of Babylonia formosae, higher compared to other flux agents because the lower percentage of other VOCs distribution, such as toluene (14.8%), propylene (7.3%), p-Xylene (0.8%) and chloromethane (1.7%). Besides, p-Xylene, with the addition of flux agents, had the lowest composition at 7.3%. The addition of Haliothis diversicolor, quartz sand and limestone show better results on degradation of chloromethane and acetone at 100% removal rate. Flux agents are therefore having different effects on the distribution of VOCs after plasma pyrolysis.

The study of Li et al. (2020) found that an eggshell CO₂/O₂/CaCO₃ catalyst showed a promising result on the conversion of benzene at value of approximately 100%. Adsorption of benzene occurs because of the presence of OH radicals in the shells as the catalyst for attacking pollutants (Harling et al., 2008; Wesenbeeck, 2016). Thus, the composition of VOCs will be changed.

3.2 Mechanism on the VOCs Degradation

The addition of the catalyst in the plasma system has an important role in degrading pollutants. Reactive species is generated from the plasma gas. Wesenbeeck (2016) stated that adsorption capacity of the catalyst depends on surface area, affecting the number of site. Exposure of plasma results in an increase or decrease of the surface area. Because of these results, it affects the
Fig. 2. Composition of VOCs in the material with addition of different flux agents in percentage (a) Control (resin only), (b) Resin: *Babylonia formosae*; (c) Resin: *Haliothis diversicolor*; (d) Resin: Quartz sand; (e) Resin: Limestone.

plasma catalytic background process. OH radicals oxidize VOCs pollutants, such as formaldehyde, acetone, peroxy radicals, hydroperoxyl and alcohol (Saunders *et al.*, 2003; Bloss *et al.*, 2005; Waring and Wells, 2015). In this study, there are reduction of benzene and propylene concentration with the addition of *Babylonia formosae* shell powder maybe due to the presence of OH hydroxyl in the material. The illustration of degradation is described in Fig. 3.

### 3.3 Effects of Pyrolysis Durations, Flux Agent Types and Flux Agent Ratios on Inertization of Elements

Fig. 4 and Table S2 show the initial concentration of resin derived from the ICP-AES analysis. Highest concentration of element in resin was Zn while the concentration of other toxic metals
such as As, Cd, Cr, Cu, and Pb, were less than 1.1 mg L\(^{-1}\). Although the concentration of toxic metals was lower, it should be managed seriously because of its harmful effect to the environment. The previous research of Sanito et al. (2020b) confirmed that concentration of Zn in resin was 77.65 ± 0.071 mg L\(^{-1}\). In this study, analysis of elements concentration by the ICP-AES confirmed that Zn had concentration with the value 75.3 mg L\(^{-1}\). The highest concentration of Zn in the residue could be attributed because of its function as a mechanical barrier, associated with the coating technology (Selvaraj et al., 2009). In this regard, resin requires a proper treatment to eliminate harmful elements.

The effects derived from the pyrolysis duration, flux agent types and flux agent ratios on the inertization of the elements were investigated. Fig. 6 illustrates the further outcome of the resin’s pyrolysis. Figs. 6(a–d) give information about the comparison of elements degradation in absence of flux agent and with the addition of flux agent, namely, control, 75:25, 50:50, and 25:75, respectively. In this study, the longer pyrolysis comprising 7 min showed a better result of the residue elements compared to the 5 min pyrolysis. Nonetheless, the duration had no significant effect on the inertization of the elements because it was fit the model of \(\alpha \) (F(1.49) = 0.223, \(p > 0.05\)) (concentration versus pyrolysis duration) with confidence level 95%. Moreover, statistical analysis showed that flux agent types and flux agent ratios had no significant impact on the inertization of the elements for values of \(\alpha \) because the duration fits the model (F(2.21) = 0.068, \(p > 0.05\)) (concentration versus flux agent ratio) and F(1.27) = 0.508, \(p > 0.05\)) (concentration versus flux agent type), respectively. The most influential parameter for the flux agent ratio was 25:75 (resin:flux agent) with a mean 0.884, and it was followed by 50:50 of ratio (mean 0.663). BF and limestone indicate a better type of flux agent for the inertization of elements because of a higher mean with value 0.992 and 0.924, respectively (Table S3). It is also supported with the better vitrification results from XRD analyses in Figs. 6(c) and 6(d) despite statistically have no significant impact on the elimination of elements. Flux agent types and flux agent ratios showed no difference in the vitrification and inertization of elements because the groups interval do not
Fig. 4. Concentration of resin after treatment with different ratio of flux agents. (a) Absence of flux agents; (b) Ratio of Resin:flux agents with composition 75%:25%; (c) Ratio of resin: flux agents with composition 50%:50%; (d) Ratio flux agents 25:75.

overlap in the Tukey’s and Fisher’s group comparison analysis. Moreover, the absence of flux agent (Control) and addition of *Babylonia formosae* maybe gave the different impact on inertization of elements, while the Fischer methods indicated that a quartz sand gave a different result on inertization of elements. However, the addition of flux agents has no significant impact on the inertization and vitrification ($0.508 > 0.05$). Thereby, the parameters are relatively at the same levels of this study. P-value indicators confirm that there are differences between the two groups (*Khan*, 2013). The statistical analysis is shown in Table S4, and the concentration of the final residue of the elements is presented in Table S5–Table S17.

Turning to the control, the removal efficiency of Zn at 5 min and at 7 min, was noted at 97.37% and 98.87%, with final concentration being $1.98 \pm 0.13$ mg L$^{-1}$ and $0.85 \pm 0.13$ mg L$^{-1}$, respectively. The removal efficiency of Zn with the fusing of flux agent in diverse ratios (HD, BF, limestone and quartz sand) for the pyrolysis duration of 7 min was obtained at 96.26%–99.38% whereas in the 5 min ratio (HD, BF, limestone and quartz sand), the removal efficiency was obtained at 94.58%–98.31%. In the removal efficiency of toxic elements, namely, As, Cd, Cr, Cu, Pb, and diverse results were exhibited. The removal efficiencies were obtained from 47.72%–100% in the pyrolysis
duration of 7 min. In contrast, removal efficiency was only achieved at 37.39%–99.77% in the pyrolysis duration of 5 min. The higher removal efficiencies of the elements were obtained due to the longer pyrolysis duration, which had generated a higher energy excitation. During this process, a collision of atoms from the plasma and the elements occurred; atoms from the elements are ionized by the high energy reaction (Sanito et al., 2020b). This is noted by Mattox (2010), who mentioned that collision of metastable atoms from carrier gas placed a significant impact on the ionization of atoms from the elements. The increase of temperature become the energetic (Fridman, 2008), and elements can be degraded perfectly (Mattox, 2010). The ionization reactions are explained as follows:

\[
\begin{align*}
N \text{ (Metastable)} + \text{As} & \rightarrow N + \text{As}^+ + e^- \\
N \text{ (Metastable)} + \text{Cd} & \rightarrow N + \text{Cd}^+ + e^- \\
N \text{ (Metastable)} + \text{Cr} & \rightarrow N + \text{Cr}^+ + e^- \\
N \text{ (Metastable)} + \text{Co} & \rightarrow N + \text{Pb}^+ + e^- \\
N \text{ (Metastable)} + \text{Pb} & \rightarrow N + \text{Pb}^+ + e^- \\
N \text{ (Metastable)} + \text{Zn} & \rightarrow N + \text{Zn}^+ + e^- 
\end{align*}
\]

In this research, the effect of flux agents in the different ratios (50:50 and 25:75) indicated better results when associated to the effect of flux agent ratio of 75:25. Fig. 6(d) highlights the inertization of the elements with a higher flux agent ratio (25:75), showing that higher ratio of flux agents always indicates better vitrification results (see ratio 75:25 in Fig. 6(b) and ratio 50:50 in Fig. 6(c)). The concentrations of elements were less than 4 mg L\(^{-1}\). However, the addition of quartz sand in the treatment also indicated better results. The different ratios of the flux agents, namely, HD, BF, and limestone in the treatment, can also achieve better results, except for the one with a ratio of 75:25. This outcome may be due to the high composition of quartz sand, which cannot be easily melted in the pyrolysis, affecting the metals’ final concentration. A study by Zhang et al. (2016) noted that the mixture ratio of fly ash to flux agents (red ceramic clay:field spar:gang sand) should be 20:60:10:10 as optimum composition. This was also confirmed by Cubas et al. (2015) who noted that the higher ratio of moist paste batteries with quartz sand (1:2) indicated a better inertization of Zn and Mn. In the current study, the same sample ratio compared to the resin (50:50) showed the important impact in the inertization of the metals and metalloids. Thus, a suitable composition of flux agents needs to be taken into account for plasma treatment. In this analysis, the elimination of Zn when fused with HD at the ratio of 50:50, can be obtained at the value of 0.48 mg L\(^{-1}\), when fused with BF, it can be received at 1.45 mg L\(^{-1}\), when fused with limestone, 1.87 mg L\(^{-1}\) was a total concentration, and when fused with quartz sand, it can be acquired at 1.52 mg L\(^{-1}\). Thereby, shells powder suggests a better outcome compared to limestone.

### 3.6 Characterization and Vitrification of Materials before and Resin after Treatment

Fig. 5 describes the surface of resin before and after treatment. Fig. 5(a) shows the surfaces areas of resin are spherical, irregular, and smooth. The elements composition in resin are explained in Table 2. In resin, the percentage of Ca, O, Si and Zn were 0.23%, 42.61%, 22.56% and 14.35%, respectively. For other elements were not detected because of their low concentration or below detection limit (0%). The detections of Si and Zn are related to the function of the thermosetting of resin and the primary composition of resin (Chrusciel and Lesniak, 2015). According to Li et al. (2019), polysiloxanes, silanes, silsesquioxanes, silica and silicate improves stability of PCB for the function as the flame retardant (Anjaneyulu et al., 2015). In resin, Zn has a function as the mechanical barrier related for coating technology, especially for better adhesion (Selvaraj et al., 2009). Thereby, the composition of C, Si and Zn are higher compared to other elements.
Fig. 5. Scanning electron microscope results. (a) Resin before treatment; (b) Control; (c) Resin the fuse of HD; (d) Resin with the fuse of BF; (e) Resin with the fuse of limestone; (f) Resin with the fuse of quartz sand.
The results of 0% are below the detection limit.

Table 2. Elemental composition resin before and after treatment.

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* the results of 0% are below the detection limit.

Figs. 6(a2–d4) explains the characterization of resin from the plasma post-treatment. The result showed a different pattern compared to the resin before treatment, with every ratio of flux agents (75:25, 50:50, 25:75) (Fig. 6(b1)–6(b4), Fig. 6(c1)–6(c4), Fig. 6(d1)–6(d4)) because of the absence of flux agents. The peaks were detected at 12.17°, 15.62°, and 22.98°, respectively, which explains the formation of the small crystalline structure. Figs. 6(c–f) indicate the surface of the resin after treatment in combination with the flux agents, except in Fig. 6(b). In Figs. 6(b–f) the surfaces were more compact because of the fusing of the flux agents in the materials, which transforms the chemical composition, and converting the form of surface, while the control indicated the larger shape and formation (Fig. 6(b)). This result is similar to previous study by Sanito et al. (2020b) which confirmed that there is no vitrification of materials with absence of flux agent. The information of flux agents surface material is shown in Fig. S1. Distribution of elements and percentages are shown in Fig. S2 and Table S18, respectively.

Figs. 6(b–d) explain the addition of shells powder, limestone and quartz sand in resin with a comparison of 75:25, 50:50, 25:75 (resin:flux agent). Fig. 6(b1–b4) displays the small peaks of the flux agents in the residue. The values were detected at 12.21°, 12.66°, 12.97°, and 13.07°, respectively. However, crystallization was not perfect, probably due to the small percentage of the resin’s flux agents. Interestingly, the patterns were different from the initial resin powder (Fig. 6(a1)). Du et al. (2018) stated that black extraction of samples is associated with the non-inerting characteristic. This states lower vitrification of the final residue because of the black color, thereby confirming the low inert product.

Figs. S3 and S4 display the different vitrification results of resin with the flux agents in different ratios. Fig. S3(a), Fig. S3(d), Fig. S4(a), and Fig. S4(d) indicate lower vitrification results of the resin when fused with the flux agents (black residue). Fig. S3(b), Fig. S3(e), Fig. S4(b), and Fig. S4(e) show better vitrification results of the resin when fused with the flux agents (greyer residue). From Fig. S3(c), Fig. S3(f), Fig. S4(c), and Fig. S4(f) display the best results of the vitrification when fused with the flux agents with grey powder. Sanito et al. (2020b) confirmed that when more flux agents were added, the vitrification effect is better - extractions are less black, thereby reflecting the characteristics of higher residues, which as reported by Du et al. (2018) and Kuo et al. (2009) that showed the similar information. In this study, higher ratios of the shells powder, limestone, and quartz sand in the resin play a key role in the vitrification of the materials. It also showed that the inert residues and the materials were greyer, where Du et al. (2018) had mentioned that the low quality of vitrification (non-inerting) can be recognized from the color of extractions of final residue, that usually is indicated with black color. Thus, good vitrification of resin can be obtained in plasma pyrolysis when mixing is done in the proper ratio of the waste and the flux.
agents. Furthermore, XRD analyses of final residue prove that the transformation of material occurs and change the peaks from the post-treatment. Thereby, the vitrification of resin can be obtained.

The ratio information of resin:flux agent (50:50) is outlined in Fig. 6(c). The final residues were dominated by CaCO$_3$ (Figs. 6(c1, c2, and c4)) and SiO$_2$ (Fig. 6(c3)). This crystalline structure confirmed...
the residues’ vitrification because of the findings of CaCO$_3$ (PDF No. 1-873) and SiO$_2$ (PDF No. 14260). The higher composition of the flux agents to resin, in the ratio of 25:75 (resin:shells) indicated a similar pattern of crystalline structure in the residue. Fig. 6(d) displays the XRD results of the higher ratio of the flux agents (25:75). Figs. 6(d1, d2, and d4) shows the spectra’s pattern that were associated with the findings of the CaCO$_3$ crystalline structure. Fig. 6(d3) shows the SiO$_2$ domination of the crystalline structure in the final residue. Interestingly, the formation of the SiO$_2$ showed a different residue. It is caused by the higher composition of quartz sand in the treatment of the resin. Other elements were not detected in the crystalline structure because of their amorphous structure. The fusing of resin and flux agents with the ratio of 50:50 exhibited the highest crystalline structure, which peaked at 29.62° (BF and HD), 31.13° (limestone), and 21.80° (quartz sand), respectively, represents the CaCO$_3$ crystalline structures. When in the ratio of 25:75, the highest peak of CaCO$_3$ from BF, HD and limestone can be detected at 29.62°. For quartz sand, the highest peak can be obtained at 26.74°. Thus, the fuse of different composition of flux agents provides a different crystalline structure. Fig. S5 indicates the different structures of flux agents that affects the results of vitrification.

Fig. 7(a) shows the mechanism of elements degradation and vitrification and Fig. 7(b) displays the vitrification of the final residue. The mechanism of vitrification is associated with the ionization (Fig. S12), which creates the collision from carrier gas with atoms from all the elements (metals and metalloids). It creates encapsulation of elements, and trap it in the layer, creates bonds with

Fig. 7. Mechanism of metals degradation and vitrification of resin in an atmospheric-pressure microwave plasma reactor. (a) Degradation of elements in resin and (b) Vitrification of resin in flux agent.
Ca, and Si from flux agents. Elements, for example, Zn, other metals and metalloids, are not detected in the surface of final reside due to its amorphous structure and volatile characteristics. In this research, final residue in XRD analysis mostly consist of Ca crystalline structure (BF, HD and limestone as flux agents) and Si crystalline structure (quartz sand as flux agent). Cubas et al. (2016) confirmed that the concentration weight of Si was obtained at 34.4% with the fuse of quartz sand, higher 33.79% after treatment of moist paste batteries. In this study, the weight of Ca and Si can be obtained at 30.2% (fused of quartz sand), and 33.47%, 33.32%, and 32.61% (fuse of shells powder and limestone). Thereby, vitrification of resin can be acquired.

### 3.7 Comparison of Functional Groups in Resin and Final Residue

Fig. 8 illustrates the comparison of the chemical structure of untreated resin, control (no flux agent) and the mixture of the shell flux agent ratio with the range of wavenumbers, from 400 cm⁻¹—4000 cm⁻¹. Fig. 8(a) presents the functional groups of the resin. From the analysis, halogen groups (C-Br) can be detected at the wavenumber, ranging from 500 cm⁻¹—600 cm⁻¹ and 900–1300 cm⁻¹ as the similar study from Guan et al. (2008) who have stated that stretching vibration of C–Br from resin is assigned at 579 cm⁻¹–688 cm⁻¹. Further, the wavenumber band between 1000 cm⁻¹—1100 cm⁻¹ also highlighted the phosphorous groups’ presence. Peak was detected at 788.51 cm⁻¹.

**Fig. 8.** Comparison results of FTIR analysis after treatment with the ratio composition of resin: flux agents. (a) Resin; (b) Control; (c) 75% of limestone; (d) 50% of limestone; (e) 25% of limestone; (f) 75% of quartz sand; (g) 50% quartz sand; (h) 25% of quartz sand; (i) 75% of HD; (j) 50% of HD; (k) 25% of HD; (l) 75% of BF; (m) 50% of BF; (n) 25% of BF (25:75).
which presented the phosphorus groups (P=S). The function of phosphorous-containing epoxy resin creates flame-retardant epoxy resin (Ratna, 2009). Thereby, phosphorus groups (P=S) can be found in the analysis. At the same time, Imine groups (C=N) can be detected in the final residue based on the control and the addition of flux agents. Some peaks may also be detected from the range of 1332 cm⁻¹–1481 cm⁻¹. The detections of peak number are shown at 1354 cm⁻¹ (Fig. 8(b)), 1356.67 cm⁻¹ (Fig. 8(c)) and 1384.39 cm⁻¹ (Fig. 8(d)). The main composition of epoxy resin contains of nitrogen (Ellis, 1993; Ratna, 2009). Liu et al. (2017) noted that the structure of N atom has high degree conversion and may reacted with –OH groups at high temperatures. In this study, the finding of the C=N bond may be due to the collision of the nitrogen atom with the carbon atom during plasma treatment and formed the C=N covalently. In the final residue, the C-Br functional group (halogen groups) and the P=S functional group (phosphorous groups) were not detected. This is due to the breakage of the organic compounds, which collided with the atoms because of high ionization energy. Guan et al. (2008) confirmed that cleavage of C-Br occurs to simpler compounds. Nonetheless, the atoms of the organic compounds were perfectly ionized to less harmful compounds (Mattox, 2010). Thereby, C-Br functional groups and P=S functional groups were not detected.

The strong bands were identified at the wavenumbers ranging from 400–580 cm⁻¹ with the stretching vibration types. The 460 cm⁻¹ refers to the silica glass structure (Si-O) bonding (Silva and Mello-Castanho, 2007). This stretching appears because the fuse of quartz sand in the materials. Thus, the wavenumbers in this analysis represent Si structures in the final residue. These results also indicate that the different functional groups or different patterns from Fig. 7(a) because of vitrification. This study’s striking finding is associated with the –OH groups, which can be found at approximately 3400 cm⁻¹ in the resin, in the control samples, and the fusing of all flux agent ratios, except at the 25% (75:25) ratio of HD. In the final residue, the band corresponding of –OH groups can be detected at 3619.73 cm⁻¹ (Fig. 8(a)), 3419 cm⁻¹ (Fig. 8(b)), 3412 cm⁻¹ (Fig. 8(c)), 3416.27 cm⁻¹ (Fig. 8(d)), 3430.74 cm⁻¹ (Fig. 8(e)), 3427.81 cm⁻¹ (Fig. 8(f)), 3404.70 cm⁻¹ (Fig. 8(g)), 3444.24 cm⁻¹ (Fig. 8(i)), 3443.27 cm⁻¹ (Fig. 8(j)), 3477.28 cm⁻¹ (Fig. 8(m)), and 3470.22 cm⁻¹ (Fig. 8(n)), except in Fig. 8(k), where the –OH groups were not detected. The advantage of shell powder and limestone addition is creating the high composition of the –OH groups. It was also noted by Ratna et al. (2009), Sanito et al. (2020b), and Tran et al. (2019), Tran et al. (2020), who reported that the –OH groups can be widely found at approximately 3400 cm⁻¹–3500 cm⁻¹ of the wavenumbers (Fig. S6). The –OH groups play a major role in adsorption of organic pollutants, acting as a catalyst for the reduction of volatile organic compound concentration (VOCs) (Huang et al., 2011). In this regard, residues can potentially be used to absorb or adsorb organic pollutants, both as a recycling material and a cost-less absorbent or adsorbent. Nonetheless, the releasing of harmful metals to the environment needs to be taken into the account.

Figs. 8(f–h) depict the functional groups of the final residues after the fusing of quartz sand with different ratios. A detection of the peak can be obtained at 404.10 cm⁻¹ from the analysis, thereby confirming the presence of Si, with Si-O-Si bonds in the residue. The detection of Si can be obtained at the range of 400 cm⁻¹–580 cm⁻¹ of the wavenumbers. This is similar to the study of Silva and Mello-Castanho (2007), who noted that 460 cm⁻¹ wavenumber represents the Si-O, in similar range for the detection of Si. Thus, it can be associated with the Si bonds and other elements that elements have been transformed to oxide formation when the atoms of Si bound with oxygen, thereby generating oxide formation. The finding of oxygen in the silica bond resulted in a durable product. This process was associated with the composition of oxygen with silicon in the resin material (U.S. EPA, 1992; Sanito et al., 2020b). The percentages of oxygen and silicon in the residue were 43.50% and 22.60%, respectively (Table 2). Cubas et al. (2015) observed that the presence of oxide formation in the elements was linked with oxide formation in the moist paste battery’s vitrification with quartz sand. In this context, Si plays a crucial role in the vitrification of the residue.

The discovery of Ca and Si referred to their vitrification function, where chemical bonding and encapsulation occurs. Their presence inhibited the ability of harmful elements from being released from the vitrified product to the environment. Higher ratios of the flux agents show an inert residue because of the high composition of Si and Ca (U.S. EPA, 1992). In this regard, a good vitrification of the residues can be achieved during the plasma treatment.
4 CONCLUSION

In this research, shell powder, limestone, and quartz sand were applied in the resin treatment as flux agents. They showed a significant impact on vitrifying the resin, and for eliminating elements in the residue when processed in an atmospheric-pressure microwave plasma reactor. They can thus be considered as the alternative flux agents. The high flux agent ratio improved resin vitrification when compared to the lower ratio. The addition of shell powder and quartz sand generated calcite formation (CaCO₃), and silicon formation (SiO₂) because of the amorphous structures of other elements from plasma post-treatment. This study also confirmed that the duration of the pyrolysis, the flux agent ratios, and the flux agent types had no significant effect on the inertization of the elements in the final residue. However, a longer pyrolysis duration, a higher ratio of flux agents, and the addition of different flux agents may be considered as important parameters during the treatment of resin in the atmospheric-pressure plasma reactor. Flux agents can be used to vitrify the resin through the ionization, creates collision with atoms of elements and bonds with Ca and Si. This process resulted in encapsulation and transformation of elements, which supported as the key in a vitrification. Shell powder can be suggested as low cost flux agents for the VOCs reduction from resin compared to other flux agents, especially in the abatement of benzene, propylene and toluene emission from plasma pyrolysis. Also, this is based on the concept of circular economy by transforming food waste into cost-less flux agents compared to the commercial ones. Future research should be focused on combining different flux agent ratios, microwave power modification, the flow rate of gases and samples composition.

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SUPPLEMENTARY MATERIAL

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REFERENCES


