Recycling of waste glass fiber-reinforced plastics using pyrolysis with KOH

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Abstract. Glass fiber-reinforced plastics (GFRPs) are composite materials with high strength and flame retardancy; however, their disposal process is expensive, causing illegal dumping. Herein, recycling of waste GFRPs using pyrolysis with KOH under an inert atmosphere was attempted by the gasification of resin and conversion of glass fibers into soluble silicate. The pyrolysis behavior of the GFRP, characteristics of the obtained residue, composition and yield of the generated gas, and extracted amount of silica in the solution obtained using KOH were investigated. The results indicated that the gasification of the resin and conversion of the glass fiber into soluble silicate were promoted by pyrolysis with KOH. With an increase in the heating temperature, KOH addition amount, and heating time, the yield of gases, especially flammable gases (H2 and CH4), and the extracted amount of silica increased, whereas the residual rate decreased. The amount of silica extracted using 1 M HCl is higher than that extracted using distilled water. Compared with those obtained using NaOH, the yield of gases and specific surface area of the residue achieved using KOH are superior, while the extracted amount of silica obtained using NaOH is higher than that acquired using KOH.

1. Introduction

Glass fiber-reinforced plastic (GFRP) is a composite material consisting of a resin (mainly a thermosetting resin such as epoxy resin and phenol resin) and glass fiber, and CaCO3 is generally used as a filler for resins to improve their reinforcement, heat resistance, and economic efficiency [1]. GFRPs have been widely used for boats, bicycles, helmets, and bathtubs because of their high strength, lightweight, and excellent corrosion resistance. Currently, in Japan, 300,000–400,000 tons of GFRPs are treated as wastes annually; however, the crushing and burning of waste GFRPs are difficult because of their high strength and the high content of glass fibers, respectively. Therefore, more than 90% of GFRPs are landfilled [2]; nevertheless, the landfill cost increases annually due to the shortage of land in Japan. Consequently, illegal dumping of GFRPs has increased, causing social problems. Therefore, the development of an effective treatment method for waste GFRPs is required. The pyrolysis or melting of the resin portion using a high temperature (800 °C) and high pressure (20 MPa) has been studied as a treatment method for GFRPs. However, the long processing time, high cost, and complex handling of the remaining glass residue have limited the practical applications of this method [3, 4].

The authors have tried to recycle various wastes using NaOH. For example, the recovery of tantalum from tantalum capacitors by the pyrolysis of the covered resin in the presence of NaOH [5] and the pyrolysis/gasification of the resin and solubilization of the glass fiber a waste glass wool insulator to reduce the volume of the residue [6] have been studied. Moreover, the gasification of the resin portion...
of waste GFRPs by pyrolysis with NaOH and solubilization of the glass fiber by alkali fusion were simultaneously performed; additionally, the reduction of the waste GFRP by the carbonization of the resin component and extraction of the glass component in distilled water were successfully conducted [7].

In the alkali-activation method, the reactivity of KOH is higher than that of NaOH, and the specific surface area of the residue acquired using KOH is higher than that achieved using NaOH. Therefore, the development of a high-performance process using KOH rather than NaOH can be anticipated [8, 9, 10]. Herein, to develop a new recycling technology for waste GFRPs, pyrolysis with KOH was performed, and the results were compared with those obtained using NaOH. The waste GFRP was heated under an inert atmosphere together with KOH, and pyrolysis and alkali fusion were simultaneously carried out to recover the combustible gas, residue, and silica component. The pyrolysis behavior of the waste GFRP, properties of the residue, and extraction of silica using HCl and distilled water were investigated.

2. Experimental

2.1. GFRP sample
The waste GFRP generated in Japan was used for the experiment, which is a typical waste GFRP containing epoxy resin. The composition calculated via thermogravimetric/differential thermogravimetric analysis (TG/DTA) is provided in Table 1. The resin component calculated from the weight loss at around 400 °C, which is caused by the burning of resin, is approximately 36 wt.% of the total weight. The weight loss and heat flow observed around 700 – 800°C were due to the decarbonization of CaCO₃. Using this weight loss, the amount of CaCO₃ was calculated to be approximately 36 wt.% of the total weight, and other components, including the glass fibers, accounted for approximately 28 wt.% of the total weight.

| Table 1. The composition calculated via TG/DTA. |
|-----------------------------------------------|
| Content (wt.%)                                |
| Resin                                        |
| 36                                           |
| CaCO₃                                        |
| 36                                           |
| Others                                       |
| 28                                           |

2.2. Pyrolysis with hydroxide
The experimental procedure is as follows (Figure 1): Waste GFRP was cut into 1 × 1 × 0.2 cm³ specimens. The experimental conditions were determined based on the previous studies conducted in the same laboratory. Waste GFRP (4 g) and KOH powder (0 – 8 g) were placed in a stainless reactor and subjected to nitrogen replacement (100 mL/min for 45 min). Then, the resulting mixture was heated at 400 – 600 °C for 0 – 120 min at a nitrogen flow rate of 20 mL/min followed by natural cooling for 40 min. The gas generated during the experiment was collected using a gas pack. The yield of the gas recovered by pyrolysis was measured, and the components of the recovered gas were analyzed using a gas chromatograph (GC-8A, SHIMADZU). After recovering the gas, the solution (distilled water or 1 M HCl) was added to the reactor for washing, and then filtered. The filtrate from which the silica component was extracted was recovered. The silica concentration in the filtrate was evaluated using an atomic absorption spectrometer (AAS, AAAnalyst 200, Perkin Elmer) to calculate the extracted amount of the silica component. The solid was dried in an oven to obtain the residue. The weight, specific surface area, surface morphologies, and crystal phases of the residue were examined using an electronic balance, a specific surface area measuring device (Macsorb Model-12, Mountech), a scanning electron microscope (SEM) (JSM-6510A, JEOL), and an X-ray diffraction device (XRD) (MiniFlex 600, Rigaku), respectively.
3. Results and discussion

The effects of temperature and KOH addition amount on gas generation, residue weight, and extraction of silica in distilled water were examined at the heating time of 60 min. The gas yields obtained under each condition are shown in Figure 2. With an increase in temperature, the gas yield increased, indicating that the gasification of resin is more effective at higher temperatures. When the KOH addition amount was increased, the yield of the fuel gases (CH$_4$ and H$_2$) increased, implying that the addition of KOH promotes the generation of these gases.

![Figure 2. Yields of the gases generated during pyrolysis.](image)

![Figure 3. Extracted amounts of silica under each condition.](image)

![Figure 4. Residual rates obtained after pyrolysis under each condition.](image)
The extracted amount of silica in distilled water under each condition is shown in Figure 3. When the KOH addition amount was increased, the extracted amount of silica increased possibly due to alkali fusion between KOH and glass fiber.

The residual rates acquired under each condition are shown in Figure 4. The residual rate decreased with the increasing heating temperature regardless of the KOH addition amount.

Effects of the heating time on gas generation, residual rate, and extraction of silica using KOH were examined and compared with those observed using NaOH. Note that the hydroxide addition ratio was 1:2. The gas yields acquired under each condition are shown in Figure 5. The gas yield increased with the increasing heating time. When KOH was used, the gas yield became almost constant when the heating time was more than 30 min. When NaOH was used, the gas yield became almost constant when the heating time was more than 15 min. After 30 min, the gas yield obtained using KOH was approximately twice of that achieved using NaOH. These results indicate that KOH is more effective than NaOH for the gasification of the resin.

The extracted amounts of silica in 1 M HCl and distilled water under each condition are shown in Figure 6. When NaOH was used, the extracted amount of silica increased with the increasing heating time and became constant after 15 min, regardless of the solvent used for extraction. The extracted amount of silica obtained using HCl is higher than that achieved using distilled water. When silica extraction was performed with distilled water and KOH, the extracted amount became constant regardless of the heating time. When 1 M HCl was used, the extracted amount of silica gradually increased with the heating time and became equal to the extracted amount acquired using NaOH in 120 min. Based on these results, it can be concluded that the alkali fusion of glass fiber with NaOH is more favorable than that with KOH.

The residual rates achieved under each condition are shown in Figure 7. When NaOH was used, the residual rate obtained using HCl and distilled water were almost constant (0.1 and 0.7 g/g, respectively), regardless of the heating time. When KOH was used, the residual rates in both the cases gradually
decreased and became constant at approximately 0.1 and 0.7 g/g for 1 M HCl and for distilled water, respectively, after heating for 30–60 min.

Figure 7. Residual rates after pyrolysis under each condition using (a) 1 M HCl and (b) distilled water.

The images of the residues acquired using KOH and NaOH followed by washing with distilled water and drying are shown in Figure 8. The treatment conditions are as follows: hydroxide addition ratio: 1:2; heating temperature: 600 °C; and heating time: 60 min. Both residues after heating and cooling were fixed at the bottom of the reactor as solid phases and could be recovered as powdery residues by adding distilled water to the reactor to dissolve the samples after heating and cooling.

Figure 8. Images of the residues obtained using (a) KOH and (b) NaOH followed by washing with distilled water and drying.

Figure 9 shows the XRD patterns of the residues achieved using KOH and NaOH followed by washing with distilled water and drying. The presence of calcite was confirmed in both the residues.

Figure 9. XRD patterns of the residues obtained using KOH and NaOH followed by washing with distilled water and drying.
The images of the residues acquired using KOH and NaOH followed by washing with 1 M HCl and drying are shown in Figure 10. The colors of both the residues were closer to black than that of the residue obtained using distilled water, and the residue acquired using KOH was more black than that achieved using NaOH.

![Image of residues acquired using KOH and NaOH](a) (b)

**Figure 10.** Images of the residues achieved using (a) KOH and (b) NaOH followed by washing with 1 M HCl and drying.

Figure 11 shows the XRD patterns of the residues acquired using KOH and NaOH followed by washing with 1 M HCl and drying. The presence of calcite was not confirmed in both residues probably because the CaCO$_3$ derived from the GFRP dissolved in HCl. The presence of quartz was confirmed in the residue achieved using KOH, while no peaks of quartz were obtained for the residue acquired using NaOH possibly due to insufficient alkali fusion of glass fiber with KOH than that with NaOH.

![XRD patterns of residues acquired using KOH and NaOH](a) (b)

**Figure 11.** XRD patterns of the residue acquired using KOH and NaOH followed by washing with 1 M HCl and drying.

SEM images of the residues obtained using HCl are shown in Figure 12. Multiple holes were confirmed in the residue acquired using KOH (Figure 12(a)), while aggregation of particles was noticed in the residue achieved using NaOH (Figure 12(b)). The specific surface areas of the residues achieved using KOH and NaOH were 666 and 316 m$^2$/g, respectively.

Chemical activation is promoted by intercalating an alkali metal into a graphite layer. Potassium intercalates the entire portion including graphite with high crystallinity, whereas sodium can intercalate the portion with low crystallinity, excluding graphite. Therefore, KOH promoted gasification, and the obtained residue had a higher specific surface area than that in the case of NaOH [10]. Alkali hydroxides react with glass fiber due to the hydroxide ion. As the proportion of the hydroxide ion in NaOH is larger than that in KOH, the alkali fusion of glass fiber with NaOH is more effective than that with KOH, promoting the extraction of SiO$_2$ [11].

![SEM images of residues acquired using KOH and NaOH](a) (b)
Figure 12. SEM images of the residues obtained using (a) KOH and (b) NaOH followed by washing with HCl and drying.

The extracted amounts of Ca in 1 M HCl and distilled water analyzed using an AAS are shown in Figure 13. Ca did not dissolve in distilled water and remained in the residue obtained using distilled water, whereas it dissolved in 1 M HCl.

Figure 13. The extracted amount of calcium.

4. Conclusion
Herein, a new technology for recycling waste GFRP using KOH is proposed. By pyrolyzing the waste GFRP using KOH under an inert atmosphere, the thermal decomposition of the resin and alkali fusion of the silica components inside the waste GFRP were simultaneously conducted to recover the combustible gas, residue, and silica component. The gasification of the resin and conversion of the glass fiber into soluble silicate were promoted by pyrolysis with KOH. With an increase in the heating temperature, hydroxide addition amount, and heating time, the yield of the gases, especially flammable gases (H₂ and CH₄) and the extracted amount of silica increased, whereas the residual rate decreased regardless of the type of hydroxide. The amount of silica extracted using a 1 M HCl solution was higher than that extracted using distilled water. Furthermore, the sample obtained after pyrolysis could be pulverized into a powdery residue mainly comprising CaCO₃ by adding distilled water. When 1 M HCl was used, the CaCO₃ derived from the GFRP reacted with HCl, and the weight of the residue reduced to approximately 10 wt.% of the original weight of the waste GFRP. The gas yield and specific surface area of the residue achieved using KOH were higher than those acquired using NaOH; however, the extracted amount of silica obtained using NaOH was superior to that achieved using KOH.

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