Korean J. Chem. Eng., **28**(1), 449-454 (2011)
DOI: 10.1007/s11814-010-0394-1

Circulating flow reactor for recycling of carbon fiber from carbon fiber reinforced epoxy composite

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(*Received 2 July 2010 • accepted 30 July 2010*)

Abstract−For the purpose of development of a chemical recycling process for carbon fiber from carbon fiber reinforced epoxy composite, a new chemical recycling system using nitric acid aqueous solution has been proposed. The recycling system is composed of hexahedral circulating flow reactor made of quartz, Teflon supporter, acid resistance pump and auxiliaries. Epoxy matrix in the composite was effectively decomposed by nitric acid aqueous solution in the circulating flow reactor and carbon fiber could be recycled without any tangle or disturbance. Optimum conditions for the recycling process have been experimentally established. Tensile strength loss of recycled carbon fiber and composition of liquid phase decomposition products were analyzed.

Key words: Recycling, Carbon Fiber, Epoxy Composite, Circulating Flow Reactor, Nitric Acid, Decomposition

INTRODUCTION

Recently, thermosetting composite materials have been diversely developed and used in a various industrial applications. At the cheaper end, polyester resins are combined with short glass fibers and low cost fillers to produce molding compounds for applications where high mechanical properties are not required. For more demanding uses, carbon fiber reinforced epoxy composites are used for critical applications, such as aerospace and vehicle industries. Although there are many successful uses for the thermosetting composite materials, recycling at the end of the life cycle is a more difficult issue because thermosetting polymers are cross linked, and cannot be melted down and remolded as what is done in the thermoplastics industry.

A number of recycling technologies, including liquid phase cracking [1-3] and pyrolysis [4-6], have been proposed and developed for thermosetting composite materials. Chemical recycling process [7-9], which decomposes thermosetting resin to their original constituents, is one of the potential options.

Among the fiber reinforced plastics (FRP), carbon fiber reinforced epoxy composite has excellent mechanical and chemical properties but causes industrial concerns. Epoxy resins, one of the versatile thermosetting plastics, are characterized by the presence of a three-membered cyclic ether group commonly referred to as an epoxy group, 1,2-epoxide, or oxirane. The most widely used epoxy resins are diglycidyl ethers of bisphenol A derived from bisphenol A and epichlorohydrine [10].

Fortunately, it is known that epoxy resin can be decomposed by hot nitric acid aqueous solution and some research has been reported. Bisphenol F type epoxy resin [11] and glass fiber reinforced epoxy resin [12] cured with amine could be effectively decomposed by nitric acid aqueous solution, and the liquid decomposition products undergo neutralization with sodiumcarbonate, extraction, refinement and dryness for preparation of recycled resin. Bisphenol A type epoxy resin [13] and carbon/epoxy composites [14] also could be decomposed by hot nitric acid aqueous solution.

However, for the recycling and reuse of carbon fiber from carbon fiber reinforced epoxy composite waste, no mechanical agitation should be applied during the decomposition of epoxy matrix in the composite in order to prevent tangle of recycled carbon fiber.

In this research, a new chemical recycling system for the carbon fiber from carbon fiber reinforced epocxy composite using nitric acid aqueous solution has been proposed. The recycling system is composed of hexahedral circulating flow reactor made of quartz, Teflon supporter for the composite, acid resistance pump and auxiliaries. Proposed circulating flow reactor effectively decomposed the epoxy matrix and recycled carbon fiber without any tangle or disturbance. Optimum conditions for the recycling process have been experimentally established and tensile strength loss of recycled carbon fiber and composition of liquid phase decomposition product were also analyzed.

EXPERIMENTAL

1. Materials

Carbon fiber reinforced epoxy composite was kindly supplied by Hankuk Fiber Co. Ltd in Korea. The composite was initially prepared for the application to new railway vehicles. Epoxy resin, whose average molecular weight is 430, was cured with an amine compound. The epoxy composite was reinforced with 52 wt% carbon fibers and 8 wt% glass fibers. Glass fibers were applied to outer layers of the carbon fibers to enhance adhesion ability with epoxy resin.

Extra pure grade nitric acid purchased from Junsei (Japan) was chosen as a decomposition solvent. Hexahedral circulating flow reactor and supporter for the composite specimen were made of

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quartz and Teflon, respectively.

2. Configuration of Circulating Flow Reactor System

For the purpose of recycling undisturbed carbon fibers from carbon fiber reinforced epoxy composite, circulating flow reactor and Teflon supporter for the composite specimen were designed and used for decomposition of epoxy matrix in the composite and recycling of carbon fiber.

The circulating flow reactor was composed of hexahedral decomposition chamber (5.8 cm×15.8 cm×18.6 cm) and its cover, and these are made of quartz. The decomposition chamber has an inlet for circulating nitric acid aqueous solution at bottom and an outlet at top. The cover has three taps for thermometer, condenser and nitrogen gas inlet. Band heater and PID temperature controller were installed for heating the reactor. Acid resistance pump and reservoir were also installed for proper circulating nitric acid aqueous solution. A schematic diagram of circulating flow reactor system is shown in Fig. 1.

Hexahedron Teflon supporter for composite specimen was prepared. The supporter could hold four composite specimens (10 cm×8 cm×0.4 cm) between separating baffles at a time. Circulating flow reactor with Teflon supporter is shown in Fig. 2.

3. Experimental Procedures

Carbon fiber reinforced epoxy composite was cut into suitable size and mounted in a Teflon support, and the support was placed in a circulating flow reactor. After complete purging oxygen with nitrogen gas for preventing oxidation of decomposition products, nitric acid aqueous solution flew into the circulating flow reactor at bottom and out at top by acid resistance pump. The nitric acid aqueous solution was stored in the reservoir and re-circulated through the reactor.

The reactor was heated to decomposition temperature by band heater. Vapor phase materials generated from hot nitric acid aqueous solution was trapped back by condenser. As the decomposition of epoxy matrix in the composite proceeded, the color of circulating nitric acid aqueous solution turned to dark brown, and the extent of the decomposition was continually monitored by measuring the absorbance of the circulating solution by spectrophotometer. The absorbance was increased with decomposition time and finally reached equilibrium value when decomposition was completed.

After complete decomposition of epoxy matrix, solid phase materials containing carbon fiber and glass fiber could be obtained via washing and drying. Weight loss of the composite specimen was measured by precision balance. The components of liquid phase decomposition product were analyzed by GC/MS. Recycled carbon fibers were examined by SEM, and the tensile strength of the carbon fiber was analyzed by universal test machine.

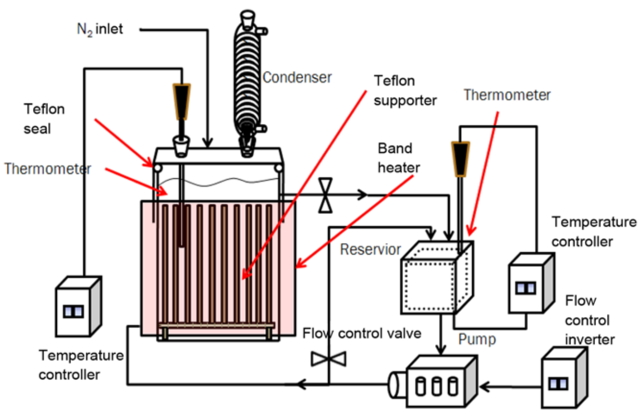


Fig. 1. Schematic diagram of the circulating flow reactor system.

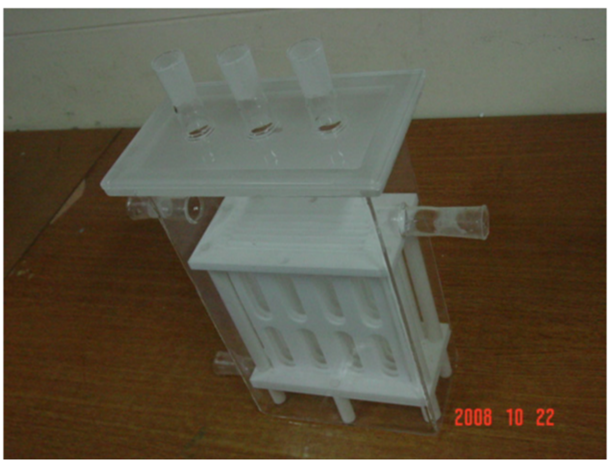


Fig. 2. Circulating flow reactor with Teflon supporter.

RESULTS AND DISCUSSION

Experimental researches on the decomposition of epoxy matrix and recycling of carbon fiber from carbon fiber reinforced epoxy composite in circulating flow reactor were performed. Operating parameters examined were decomposition temperature, concentration of nitric acid aqueous solution, linear flow rate of circulating nitric acid aqueous solution and the amount of nitric acid aqueous solution per 100 g of the epoxy composite.

The progress of decomposition of epoxy matrix was continually monitored by measuring absorbance of the circulating nitric acid aqueous solutions. The absorbance was steadily increased with decomposition time and finally reached equilibrium value when the decomposition is completed.

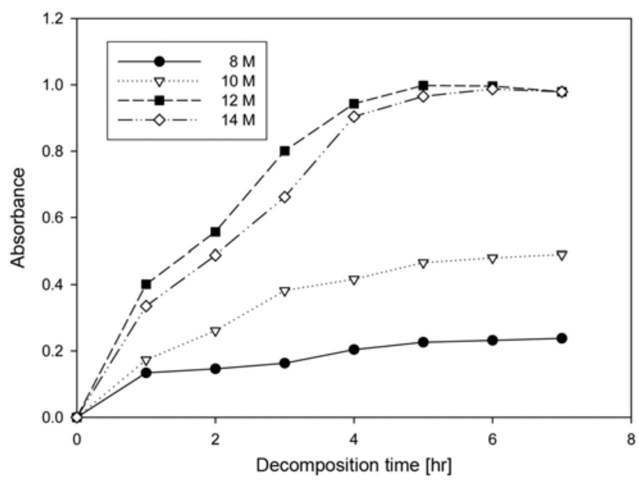


Fig. 3. Time profiles of the absorbance of circulating solutions at different concentrations at 90 °C.

1. Effect of Concentration of Nitric Acid Aqueous Solution

The effects of concentration of nitric acid aqueous solution on the decomposition rate of epoxy matrix and carbon fiber recycling were experimentally examined. The decomposition temperature was fixed at 90 °C. The time profiles of absorbance of the circulating nitric acid aqueous solution at different concentrations are shown in Fig. 3. As the concentration of the solution increased, the absorbance steeply increased and got to higher equilibrium value. The equilibrium values for the 14 M and 12 M did not show significant difference. However, for the lower concentration, equilibrium values dramatically decreased. The equilibrium values represent the extent of decomposition of epoxy matrix.

Equilibrium weight loss of composite specimen after decomposition is an explicit variable for the extent of decomposition of epoxy matrix. The weight loss was precisely measured by precision balance and shown in Fig. 4. Fig. 4 shows that the weight loss increases with concentration of nitric acid aqueous solution. Weight losses for 12 M and 14 M are about 40 wt%. These results mean that epoxy matrix has been completely decomposed at 12 M and 14 M, whereas incompletely decomposed at 8 M and 10 M.

Fig. 5 represents the shapes of recycled carbon fibers at different

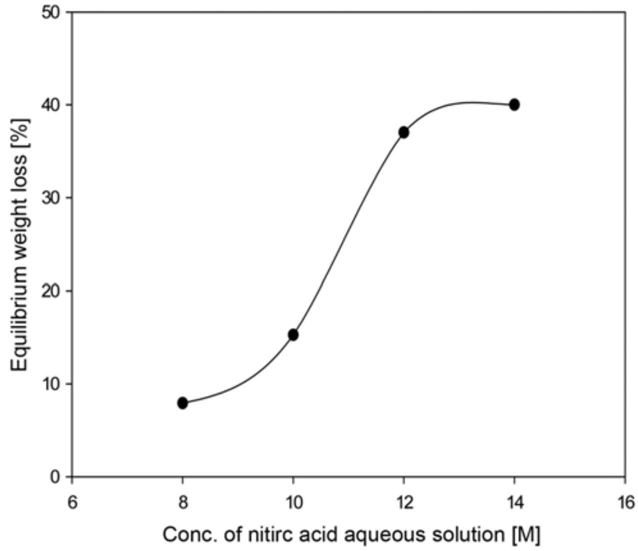
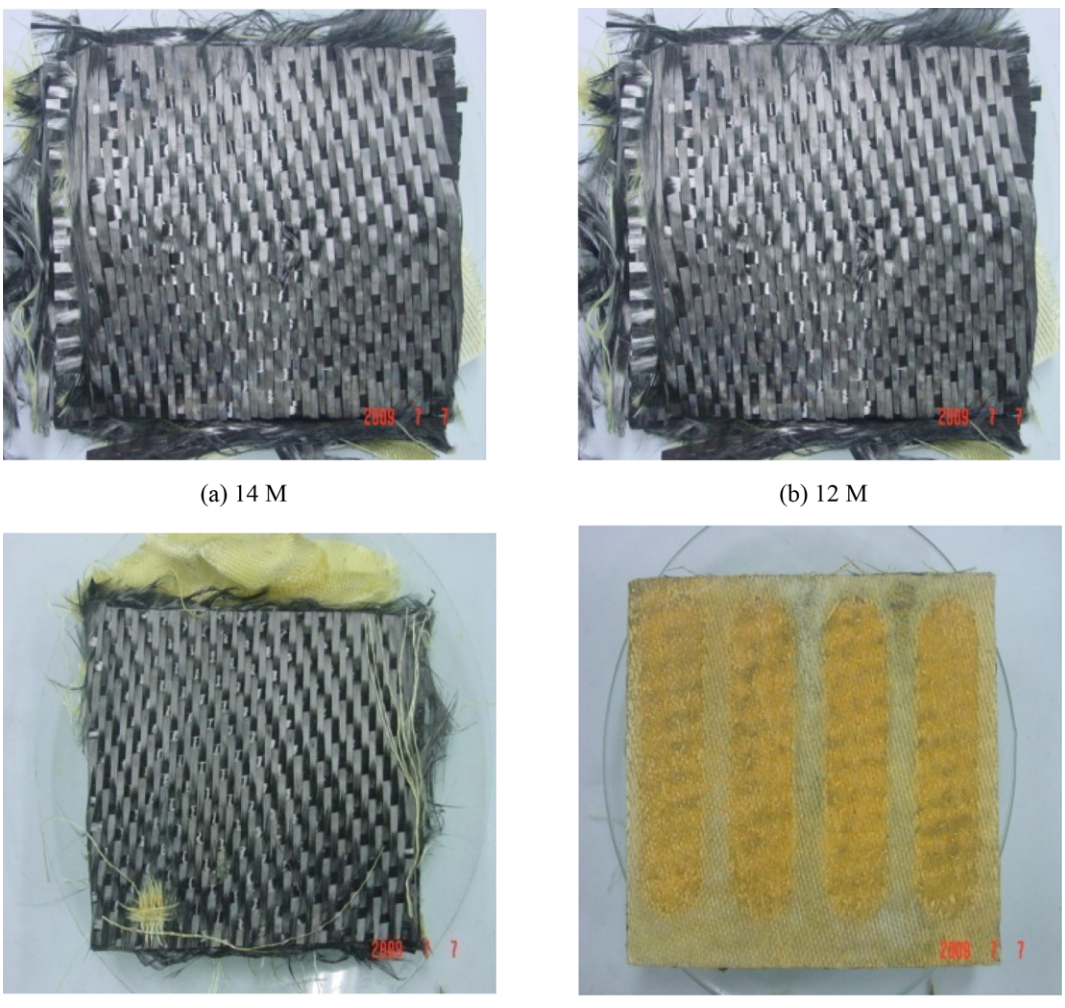


Fig. 4. The effect of the concentration of nitric acid aqueous solution on the equilibrium weight loss of composites specimen at 90 °C.



(a) 14 M (b) 12 M

(c) 10 M (d) 8 M

Fig. 5. Shapes of recycled carbon fiber at different concentrations of circulating solution at 90 °C.

concentrations. In case of 12 M and 14 M, glass fiber was easily removed from solid decomposition product and carbon fiber was recycled. However, glass fiber was hardly removed at 10 M and could not be removed at 8 M. From these results, we could conclude that the minimum concentration of nitric acid aqueous solution for the recycling of carbon fiber via complete decomposition of epoxy matrix was 12 M.

2. Effect of Decomposition Temperature

Decomposition temperature was also an important operating parameter for the recycling process. As expected, decomposition of epoxy matrix was facilitated at higher temperature, as shown in Fig. 6. The concentration of nitric acid aqueous solution was 12 M. Time to get equilibrium absorbance was decreased with decomposition temperature, 4 hours for 100 °C and 6 hours for 80 °C. Equilibrium absorbance for 100 °C and 90 °C did not show significant difference, but that for the 80 °C was less than the others.

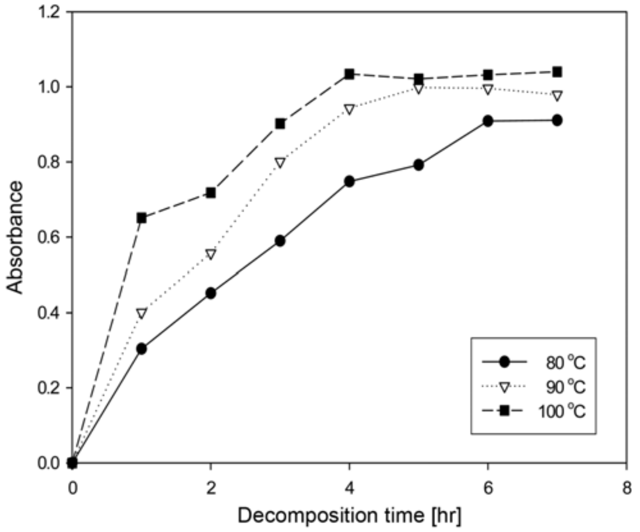


Fig. 6. Time profiles of the absorbance at different decomposition temperatures at 12 M of nitric acid aqueous solution.

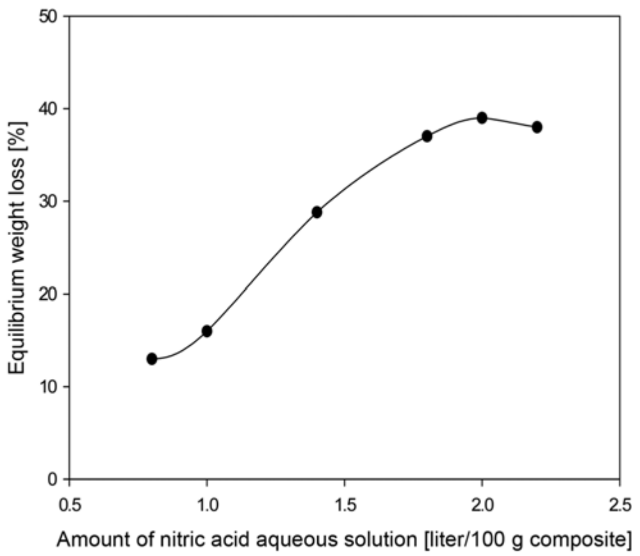


Fig. 7. The effect of the amount of nitric acid aqueous solution on the equilibrium weight loss of composites specimen.

Weight losses of composite specimen after decomposition for 100 °C and 90 °C were about 40 wt% showing complete decomposition of epoxy matrix, but that for 80 °C was only 27.73 wt%. And carbon fiber could be recycled from solid decomposition product at 100 °C and 90 °C. These results show minimum decomposition temperature for recycling carbon fiber is 90 °C.

3. Effect of Amount of Nitric Acid Aqueous Solution

The amount of nitric acid aqueous solution had an effect on the decomposition of epoxy matrix in the composite. As shown in Fig. 7, equilibrium weight loss of the composite specimen was increased with the amount of nitric acid solution. However, positive effect was not significantly observed if the amount of the solution was more than 1.8 liter per 100 g composite. And carbon fiber could not be recycled when less than 1.0 liter per 100 g composite was used.

4. Effect of Linear Flow Rate of Circulating Solution

Linear flow rate of circulating solution through the circulating flow reactor had a minor effect on the decomposition of epoxy matrix. The linear flow rate was calculated from volumetric circulating flow rate divided by effective flow area in the circulating flow reactor. The preferable linear flow rate of the circulating solution was 1.0 cm/sec. Higher linear flow rate of the solution induced more suspending substances, whereas lower linear flow rate resulted in prolonged decomposition time.

5. Recycling of Carbon Fiber in Circulating Flow Reactor

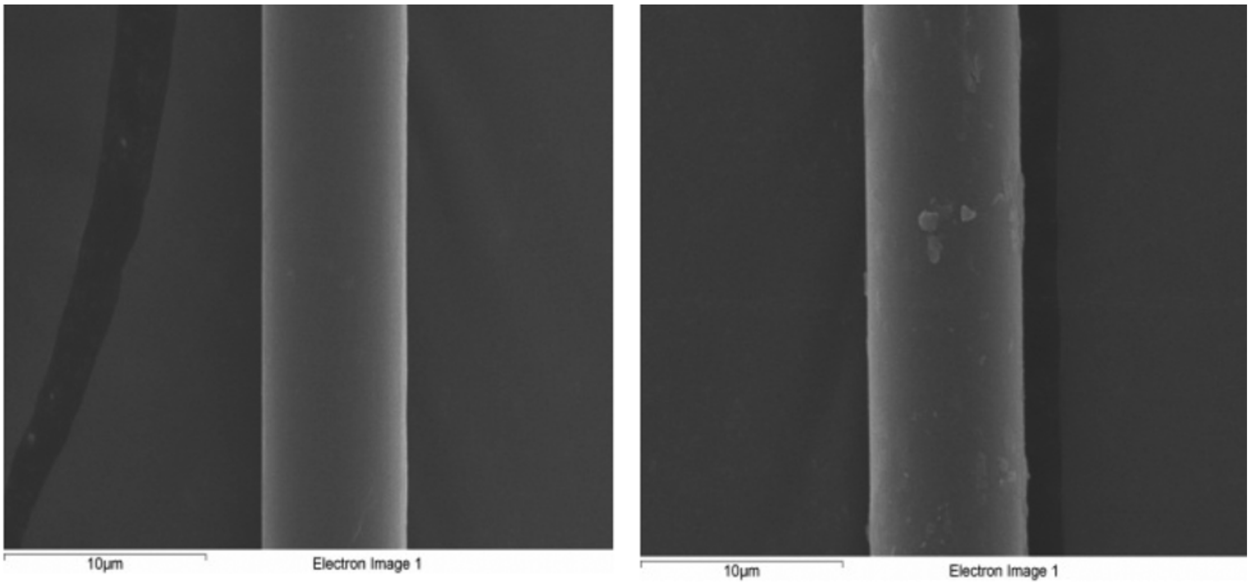
From the results mentioned above, optimum conditions for recycling of carbon fiber from carbon fiber reinforced epoxy composite in circulating flow reactor could be established and listed in Table 1. When the optimum conditions were applied, epoxy matrix in the composite was completely decomposed by nitric acid aqueous solution within 6 hours and undisturbed carbon fibers could be obtained.

For the purpose of examination of surface state of recycled carbon fiber, SEM photos were taken and shown in Fig. 8. The surface of recycled carbon fiber was clean with very little contamination, and we could identify that epoxy matrix was almost completely decomposed and any crack or damage on the surface was not formed during the decomposition process.

Tensile strength of the recycled single-carbon fiber was also examined. Tensile strength of the original single-carbon fiber used for preparation of carbon fiber reinforced epoxy composite was 335.24 kg_f/mm^2. In case of optimum conditions, tensile strength loss of recycled single-carbon fiber was 2.91%. And the loss was increased with decomposition temperature and concentration of circulating solution up to 7%. Liu [14] recycled carbon fiber from epoxy composite in a specially designed glass vessel and reported the tensile strength loss was 1.1-13.4%. Tensile strength loss of 2.91% will not create serious obstacles to reuse of recycled carbon fiber, and we

Table 1. Optimum conditions for the decomposition of epoxy matrix in circulating flow reactor

Operating parameters	Optimum conditions
Conc. of nitric acid solution	12 M
Decomposition temperature	90 °C
Linear circulating flow rate	1.0 cm/sec
Decomposition time	6 hrs



(a) Virgin carbon fiber (b) Recycled carbon fiber

Fig. 8. SEM photos of single carbon fibers.

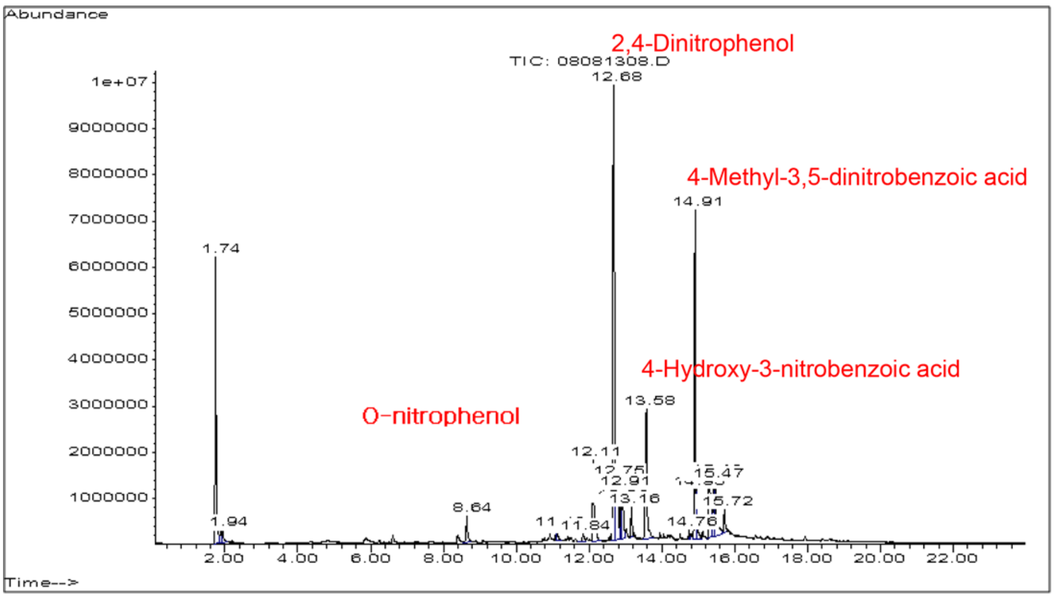


Fig. 9. GC/MS chromatogram of liquid phase decomposition product.

concluded that a circulating flow reactor system effectively recycles carbon fiber from carbon fiber reinforced epoxy composite.

6. Analysis of Liquid Phase Decomposition Products

The liquid phase decomposition product was analyzed by GC/MS and the chromatogram is shown in Fig. 9. The composition of the decomposed compounds was complex and the main components were a mixture with nitrated compounds, including 2,4-dinitrophenol, O-nitrophenol and organic acids. This result showed that epoxy matrix was decomposed into low molecular weight compounds by nitric acid. Alcohols might be formed during the decomposition under nitrogen circumstance and some of them were oxidized to form organic acids.

CONCLUSIONS

A circulating flow reactor system was proposed and adapted to recycling process for carbon fiber from carbon fiber reinforced epoxy composite. Epoxy matrix in the composite was effectively decomposed by nitric acid aqueous solutions in circulating flow reactor, and clean and undisturbed carbon fiber could be recycled. The circulating flow reactor most effectively recycled carbon fiber at 12 M of concentration of nitric acid aqueous solution, 90 °C of decomposition temperature, 1.8 liter of nitric acid aqueous solution per 100 g composite and 1.0 cm/sec of linear flow rate of circulating solution. The liquid phase decomposition product was a mixture with nitrated compounds and the tensile strength loss of the recycled single-carbon fiber at optimized conditions was 2.91%.

ACKNOWLEDGEMENT

This research was financially supported by Korea Railroad Research Institute. The authors gratefully acknowledge the support.

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