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# A novel approach to recycling of glass fibers from nonmetal materials of waste printed circuit boards

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ABSTRACT

The printed circuit boards (PCBs) contain nearly 70% nonmetal materials, which usually are abandoned as an industrial solid-waste byproduct during the recycling of waste PCBs. However those materials have abundant high-value glass fibers. In this study, a novel fluidized bed process technology for recycling glass fibers from nonmetal materials of waste PCBs is studied. The recycled glass fibers (RGF) are analyzed by determination of their purity, morphology and surface chemical composition. This process technology is shown to be effective and robust in treating with nonmetal materials of waste PCBs. The thermoset resins in the nonmetal materials are decomposed in the temperature range from 400 °C to 600 °C. And the glass fibers are collected at high purity and recovery rate by the cyclone separators without violating the environmental regulation. This novel fluidized bed technology for recycling high-value glass fibers from nonmetal materials of waste PCBs represents a promising way for recycling resources and resolving the environmental pollutions during recycling of waste PCBs.



## 1. Introduction

Printed circuit boards (PCBs) are typical and fundamental component for almost all electric and electronic equipment. However with the increase of waste electric and electronic equipment, the amount of waste PCBs is increasing sharply. And they have caused many environmental problems [1–12]. The PCBs contain nearly 70% nonmetal materials. The nonmetal materials, an industrial solid-waste byproduct, are produced in large quantities during the recycling of waste PCBs in the world each year. Traditionally, the nonmetal materials are landfilled or incinerated, which will cause resource waste and potential environment problems [5–7]. With landfill costs increasing and impending legislation to resource recycling, there is an urgent need to develop recycling technologies for nonmetal materials of waste PCBs. A huge source of pollution, they can also be a huge resource. However, one obstacle to recover is the network structure of the thermoset resin matrix.

Traditionally, the recycling technologies are based upon particle recycling, chemical recycling, pyrolysis and combustion [8–19]. But there exist some disadvantages. Particle recycling [8–12] involves grinding the nonmetal materials into fine particles for addition into new composites as fillers. The major disadvantage of this method is that the particles must be clean. However, nonmetal materials from waste PCBs may be heavily contaminated or mixed with other materials. Chemical recycling [13,14] involves converting resin wastes to its original constituent. This process technology tends to be specific to a particular polymer type. However, thermoset resins of nonmetal materials recycled from waste PCBs may contain many resin types such as epoxy resin or phenolic resin, etc. Among the existing technical difficulties, high cost and low quality of products are still main problems. Pyrolysis [15–17] involves the destructive distillation of resin from a range of polymer types and produces hydrocarbon liquids or gases which may be used as fuels. The absence of oxygen in the heating process causes the formation of char and gives the solid product low value. Combustion [6,7] recycles the calorific value of the thermoset resins directly but converts glass fibers to a glassy slag which significantly reduces the combustion efficiency. However, the glass fibers are more valuable than the energy contents of the thermoset resins [18,19]. To our knowledge, there is little published information about recycling glass fibers from nonmetal materials of waste PCBs.

In this paper, a novel fluidized bed process technology in which valuable glass fibers can be recycled from nonmetal materials of waste PCBs is described with the aim to recycle the resources in a more profitable way. In addition, the recycled glass fibers (RGF) are analyzed by determination of their purity, morphology and surface chemical composition. All the results show that the glass fibers can be successfully recycled from nonmetal materials of waste PCBs by fluidized bed process technology without violating the environmental regulation. This novel fluidized bed process technology for recycling high-value glass fibers from nonmetal materials of waste PCBs represents a promising way for recycling resources and

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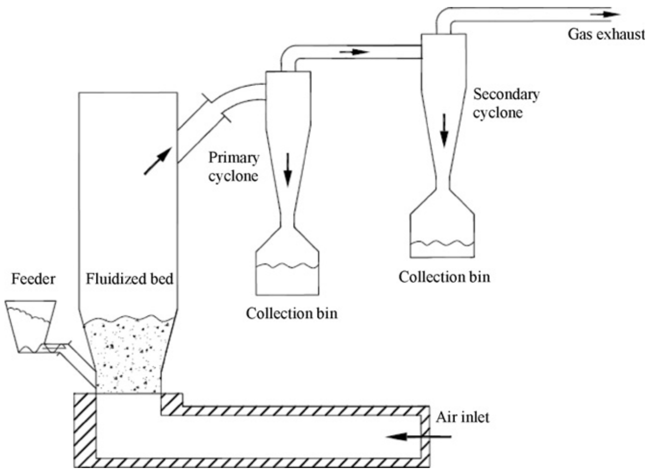


**Fig. 1.** Schematic diagram of the fluidized bed test facility.

resolving the environmental pollutions during recycling of waste PCBs.

## 2. Experimental

### 2.1. Fluidized bed process technology

Fluidized bed is commonly used in many different industrial process technologies because of their ability to achieve good heat transfer between solids and gases, operate at closely controllable temperatures and achieve thorough mixing [18,19]. A fluidized bed test facility in which valuable glass fibers can be recycled from nonmetal materials of waste PCBs is been constructed, as shown in the schematic diagram in Fig. 1. The fluidizing air fed to the bed is preheated by electric heaters and they allow the bed to be operated at controlled temperatures up to 700 °C. The air flow is adjusted manually using a control valve and monitored using an orifice plate. The bed is of silica sands graded probably between 0.5 mm and 1.0 mm, and is 200 mm deep. The nonmetal materials are stored in the feeder and introduced at a point below the hot bed via a feed screw. When nonmetal materials are processed in a fluidized bed operating at high temperature, thermoset resins in the nonmetal materials are broken down and combusted. This releases the glass fibers which are carried out of the bed in the gas stream. The glass fibers are significantly smaller than the silica sands. And the cyclone separators are a common technique employed for the separation of particles based on their size and density in gas stream. Therefore, they can be collected from this gas stream by two stage cyclone separators. Inevitably, the organic constituents existing in gas stream cannot be combusted completely at a low temperature (typically 400 °C or 500 °C). But tail gas treatment technology (secondary combustion, quench and scrubber, etc.) has been very mature [19,20]. Therefore, this process can produce a clean flue gas without violating the environmental regulation.

### 2.2. Preparation of nonmetal materials from waste PCBs

In this study, waste PCBs are from a personal computer PCBs recycling factory. They are end-of-life PCBs and the electronic components were removed from end-of-life PCBs. The nonmetal materials of waste PCBs (non-conductive substrate) consist of a woven fiberglass (modified, 50–70%) mat impregnated with thermoset resins (epoxy resin or phenolic resin, etc., 30–50%). The process technology for preparation nonmetal materials from waste PCBs contains two-step crushing and air separation. The purpose of the crushing is to strip metal from the nonmetal of waste PCBs. The PCBs are firstly pulverized in a process consisting of a coarse-crushing step and a fine-pulverizing step, using a shearing machine and a hammer grinder. The materials of the PCBs are comprised of reinforced resin and metal parts such as copper wires and joints. They have a high hardness and tenacity, so using shearing machine, it is easier to break them under shearing action. But the content of fine particles in discharge is very low. Therefore, the hammer grinder whose main acting force is a shear force is suitable for fine-pulverizing waste PCBs. Then, air classifier is used to separate the nonmetal materials from the metal materials based on their difference in size and density. Air classification is a cleaner separation method that does not use any polluting medium for separation [1]. A vertical air classifier separates nonmetal and metal mixtures by utilizing the difference in the terminal falling velocities in the air. The nonmetal and metal mixtures to be separated is fed into a stream of upward moving air, the nonmetal particles are carried along and the metal particles settle against the air stream with respect to the difference between the superficial air velocity and their settling velocity. After being separated, the nonmetal materials are screened by a vibrating screen. A stack of four sieves with holes of 25, 80 and 150 meshes are selected. Specimens are agitated for 30 min. Then the mass of nonmetals is collected on each sieve. To ensure the recycling efficiency, the nonmetal materials with particle sizes less than 150 meshes are selected for recycling glass fibers in the fluidized bed test facility.

### 2.3. Recycling of the high-value glass fibers

Tests are carried out at the temperature of 400 °C, 500 °C and 600 °C, respectively with the fluidized bed operating at the fluidizing air velocities of 1.0 m/s. This velocity is just sufficient to make the silica sands in the complete fluidization state. It is well known that the higher the fluidized bed temperature, the higher the capability of thermoset resins being broken down. However, processing of glass fibers at elevated temperature is known to reduce their strength significantly [21,22]. And Sakka measured a 50% reduction in the strength of glass fibers after heating at 550 °C for 60 min [22]. Therefore, the highest temperature of 600 °C is selected and operated in the experiment. Meanwhile, it is clear that low temperatures are necessary to maximize residual strength of glass fibers. But in practice, the temperature of 400 °C represents the lowest temperature. Because the rate of resins decomposition is so slow that the throughput is of little practical value below this temperature. Taking the temperatures of 500 °C for example, tests of up to 30 min are carried out, during which time up to 2.000 kg of nonmetal materials of waste PCBs are processed. The amount of the RGF in the collection bin is 1.342 kg by the primary cyclone and is 0.063 kg by the secondary cyclone. In addition, some shorter glass fibers are lost in the gas stream. These will be discussed later in recycling amount of the glass fibers and characterization of the RGF. To close the recycling loop, the application of the RGF will be discussed in the future work.

### 2.4. Measurements

To measure the purity of the glass fibers recycled from the nonmetal materials of waste PCBs, the RGF and nonmetal materials are heated in a muffle furnace at 500 °C for 3 h to volatilize the resins and other organic materials, respectively. The weight contents of resins and glass fibers are then obtained by weighing. The micrographs of the RGF are observed by the scanning electron microscopy (SEM, 1450, LEO Co., Ltd., Germany). The specimens are carbon-sputtered before SEM test. To study the changes of different temperatures on chemical structures of the RGF recycled from the nonmetal materials of waste PCBs, a Fourier transform infrared (FTIR, Excalibur 3100, Varian Inc., Palo Alto, USA) spectroscope is used.

**Table 1**
The amount of the RGF recycled from nonmetal materials of waste PCBs (2.000 kg).

| Specimen | Temperature (°C) | Primary cyclone (kg) | Secondary cyclone (kg) | Total (kg) |
|---|---|---|---|---|
| 1 | 400 | 1.370 | 0.067 | 1.437 |
| 2 | 500 | 1.342 | 0.063 | 1.405 |
| 3 | 600 | 1.317 | 0.066 | 1.383 |

## 3. Results and discussion

### *3.1. Recycling amount of the glass fibers*

The main components of the nonmetal materials of waste PCBs are glass fibers and thermoset resin matrix. The concentration of the glass fibers in the nonmetal materials of waste PCBs are determined by measuring sample weight losses after heating at 500 °C for 3 h in a muffle furnace. The result shows that the concentration of the glass fibers is 71.5 wt%. If the glass fibers in the nonmetal materials are completely recycled without any loss, the amount of the RGF can be about 1.430 kg when up to 2.000 kg of nonmetal materials are processed by the fluidized bed technology. But actually some shorter glass fibers are lost in the gas stream. Table 1 lists recycling amount of glass fibers from 2.000 kg of nonmetal materials of waste PCBs at three different fluidized bed temperatures by two stage cyclone separators. It shows that the most of the glass fibers are collected by the primary cyclone. That is mainly because most of them are long glass fibers with the length/diameter ratio of 8–20 and only a little of them are short glass fibers with the length/diameter ratio of less than 8. The amount of the glass fibers recycled at fluidized bed temperatures of 400 °C, 500 °C and 600 °C by two stage cyclone separators is 1.437 kg, 1.405 kg and 1.383 kg, respectively. The lower the fluidized bed temperature, the larger the amount of the RGF. It is clear that the amount of the glass fibers recycled at 400 °C is a little more than 1.430 kg. But it does not mean that the glass fibers are recycled completely because the RGF may contain a small quantity of organics. Shorter glass fibers lost in the gas stream are ineluctable. These will be discussed later in characterization of the RGF.

### *3.2. Characterization of the RGF*

#### *3.2.1. SEM observation and analysis*

The microstructures of the RGF recycled from the nonmetal materials of waste PCBs at the temperatures of 400 °C, 500 °C, 600 °C by the primary cyclone and at the temperatures of 500 °C by the secondary cyclone are observed by using SEM as shown in Figs. 2 and 3, respectively. As expected, most of them by the primary cyclone are single glass fibers possessing high length diameter ratio (Fig. 2), which indicates that the thermal processing can effectively remove the resins of the nonmetal materials. While the RGF recycled by the secondary cyclone are shorter than that by the primary cyclone (Fig. 3). That is mainly because the cyclone separators are used for the separation of the RGF based on their size and density in gas stream. When the glass fibers are recycled at the temperatures of 400 °C, there is a little glass fiber bundle in the RGF as indicated by the arrow in Fig. 2(a). While there is a little micro-glass bead in the RGF recycled at 600 °C as indicated by the arrow in Fig. 2(c). The glass fiber bundle is the glass fibers impregnated with incomplete decomposition thermoset resin matrix at low temperatures of 400 °C. While at high temperatures of 600 °C, the glass fibers can be thermally damaged and formed micro-glass bead in very hot gas stream. Meanwhile, Fig. 2 shows that the RGF recycled at three different fluidized bed temperatures all have a rough surface but are difference. Therefore, the surface of the RGF recycled at three

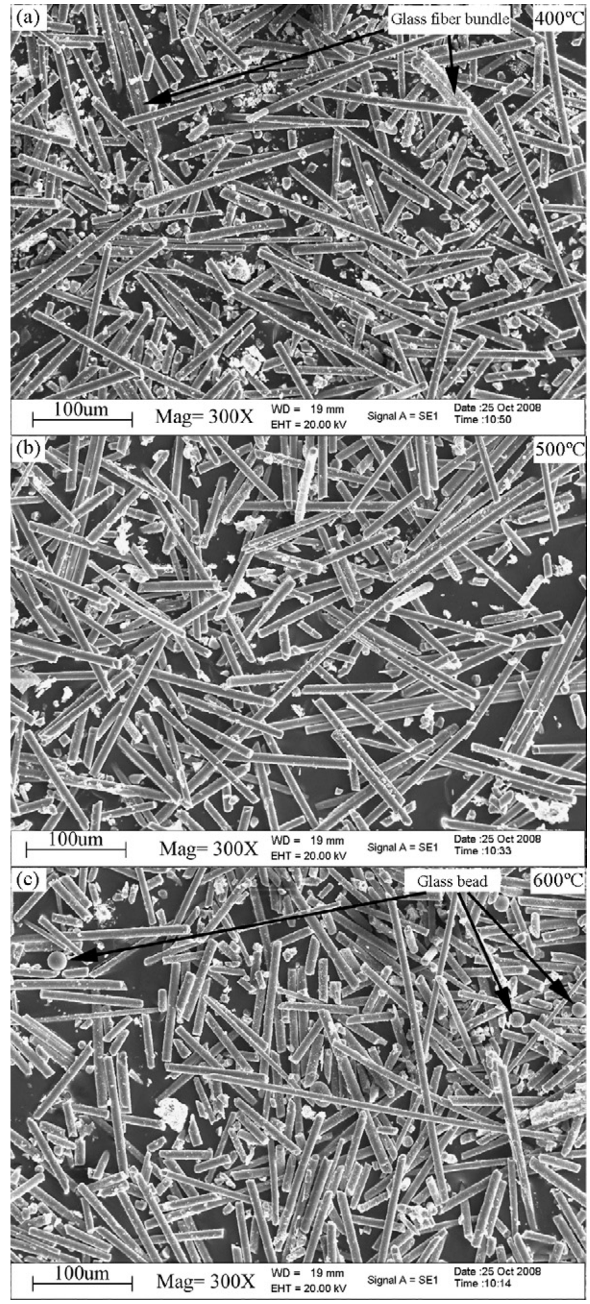


**Fig. 2.** SEM micrograph of the RGF recycled from nonmetal materials of waste PCBs by the primary cyclone (300×): (a) 400 °C, (b) 500 °C and (c) 600 °C.

different fluidized bed temperatures is careful observed on SEM at high magnification.

Fig. 4 shows the microstructures of the RGF recycled at three different fluidized bed temperatures by the primary cyclone at 5.00k× magnification. It is clear seen that all of the RGF recycled at three different temperatures have a rough surface. These indicate that the RGF have a small quantity of organics. The organic component is thought to arise from the silane coated cloth (formed during glass fibers processing) or incomplete decomposition thermoset resin matrix on the surface of the RGF. Meanwhile, there is difference in the surface of the RGF recycled at three different fluidized bed temperatures. The lower the fluidized bed temperature, the higher the uniformity surface of the RGF. In other words, the higher the fluidized bed temperature, the severer destroy to the surface of the RGF. These will be discussed in FTIR analysis of the RGF.

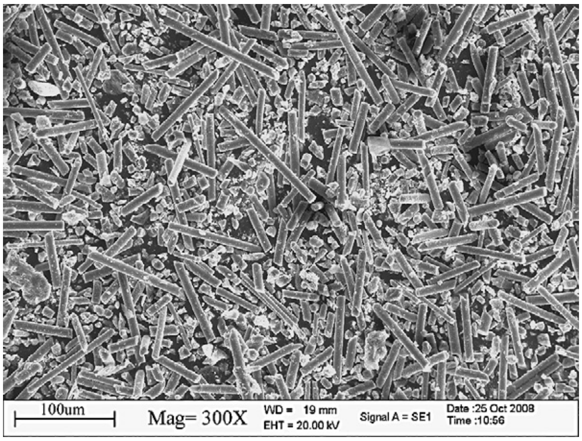


**Fig. 3.** SEM micrograph of the RGF recycled from nonmetal materials of waste PCBs at 500 °C by the secondary cyclone.

The concentrations of organics in the RGF are determined by measuring sample weight losses after heating at 500 °C for 3 h in a muffle furnace. Table 2 lists the purity of the RGF recycled from the nonmetal materials of waste PCBs at three different fluidized bed temperatures. It shows that the concentrations of organics in the RGF recycled at 400 °C, 500 °C and 600 °C are all very low and only 4.6 wt%, 2.8 wt% and 2.0 wt%, respectively. As expected, the higher the fluidized bed temperature, the higher the purity of the RGF. That is mainly because the capability of thermoset resins being broken down is higher when the fluidized bed has a higher temperature. But it does not mean that the higher the purity of the RGF, the more beneficial for their potential practical application. It could be based on comprehensive consideration of the application performance, energy and economy. These will be discussed in the future work.

In addition, based on the amount and purity of the RGF recycled at the fluidized bed temperatures of 400 °C, 500 °C and 600 °C, the concentration of the glass fibers lost in the gas stream is 4.1 wt%, 4.5 wt% and 5.2 wt%, respectively. In other words, the recovery rate of the glass fibers from the nonmetal materials of waste PCBs at the fluidized bed temperatures of 400 °C, 500 °C and 600 °C is 95.9 wt%, 95.5 wt% and 94.8 wt%, respectively. Obviously, the recovery rate of the glass fibers at the fluidized bed temperatures of 600 °C is the lowest. That is mainly because the glass fibers in very hot gas stream can be more easily damaged and formed shorter glass fibers or micro-glass beads which may be lost in the gas stream.

In a word, the high-value glass fibers can be successfully recycled from the nonmetal materials of waste PCBs by a novel fluidized bed process technology and reach a high purity and recovery rate of more than 95.4 wt% and 94.8 wt%, respectively. This novel fluidized bed process technology for recycling high-value glass fibers from the nonmetal materials of waste PCBs represents a promising way for recycling resources and resolving the environmental pollutions during recycling of waste PCBs.

### 3.2.2. *FTIR analysis of the RGF*

The RGF recycled from the nonmetal materials of waste PCBs by fluidized bed process technology have a small quantity of organics. Therefore, the chemical structures of them are measured by using FTIR. FTIR spectra of the samples are recorded in the range of 400–4000 $cm^{-1}$. To clearly compare the difference of the chemical structures, partial FTIR spectra of RGF recycled from nonmetal materials of waste PCBs at three different fluidized bed temperatures by the primary cyclone are shown in Fig. 5. In the spectra of the RGF recycled at the fluidized bed temperatures of 400 °C, there appear the stretching vibrations peaks of N–H at 3518 $cm^{-1}$, 3424 $cm^{-1}$ and bending vibration peaks of C–H at 1451 $cm^{-1}$. In the spectra of the RGF recycled at the fluidized bed temperatures of 500 °C, there appear the stretching vibrations peaks of N–H at 3449 $cm^{-1}$ and bending vibration peaks of C–H at 1466 $cm^{-1}$. The stretching vibrations peaks of N–H is thought to arise from the functional groups of the silane coated cloth on the surface of the glass fibers. And the bending vibration peaks of C–H is thought to arise from the functional groups of the silane coated cloth or incomplete

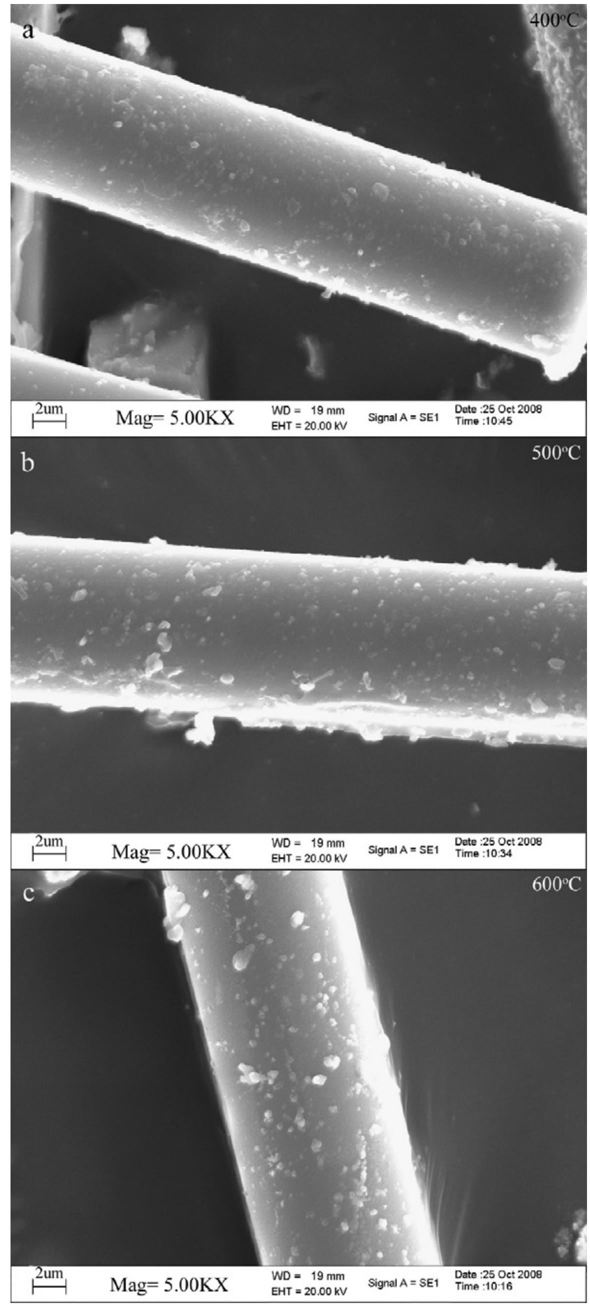


**Fig. 4.** SEM micrograph of the RGF recycled from nonmetal materials of waste PCBs by the primary cyclone (5.00k×): (a) 400 °C, (b) 500 °C and (c) 600 °C.

**Table 2**
The purity of the RGF recycled from nonmetal materials of waste PCBs.

| Specimen | Temperature (°C) | Weight losses (wt%) | Glass fibers purity (wt%) |
|---|---|---|---|
| 1 | 400 | 4.6 | 95.4 |
| 2 | 500 | 2.8 | 97.2 |
| 3 | 600 | 2.0 | 98.0 |

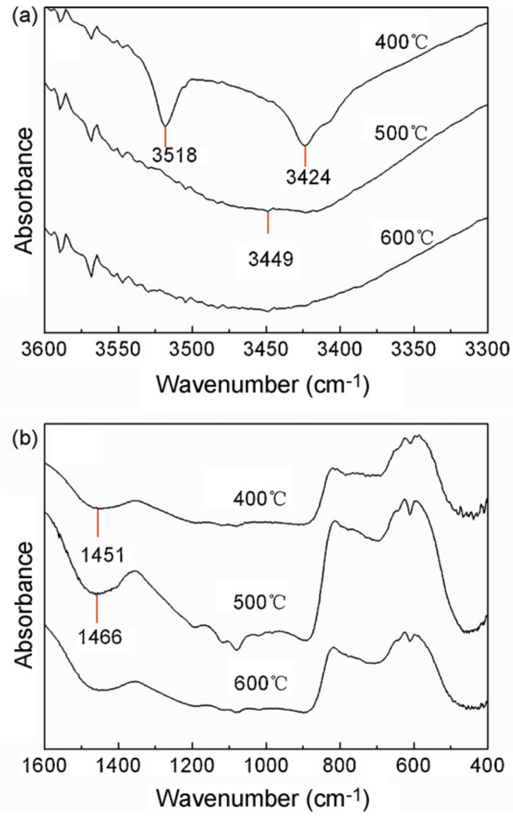


**Fig. 5.** FTIR spectra of the RGF recycled from nonmetal materials of waste PCBs at three different fluidized bed temperatures by the primary cyclone.

decomposition thermoset resin matrix. The silane coated cloth is the protective coating of the glass fibers when they are formed. It is clear that the heat treatment at temperatures of 400 °C and 500 °C cannot damage the protective coating of the glass fibers. It could be particularly beneficial for theirs potential practical application. But in the spectra of the RGF recycled at the fluidized bed temperatures of 600 °C, there do not appear the stretching vibrations peaks of N–H and bending vibration peaks of C–H. These indicate that the heat treatment at temperatures of 600 °C can remove any surface treatment on the glass fibers as well as the thermoset resin matrix. And the glass fibers themselves may be severely weakened. These could be not beneficial for their potential practical application. All of these will be discussed in application of the RGF in the future work.

## 4. Conclusions

The glass fibers can be successfully recycled from nonmetal materials of waste PCBs by a novel fluidized bed process technology. The RGF can reach a high purity and recovery rate of more than 95.4 wt% and 94.8 wt% in the temperature range from 400 °C to 600 °C, respectively. This process can produce a clean flue gas without violating the environmental regulation.

The heat treatment for recycling high-value glass fibers at 400 °C and 500 °C cannot damage the protective coating of the glass fibers. But the RGF recycled at 400 °C contain a little glass fiber bundle. The heat treatment for recycling glass fibers at 600 °C can remove any surface treatment on the glass fibers. Therefore, the glass fibers themselves may be severely weakened.

This novel fluidized bed technology for recycling high-value glass fibers represents a promising way for recycling resources and resolving the environmental pollutions during recycling of waste PCBs.

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