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Recycle Technology for Recovering Resources and Products from Waste Printed Circuit Boards

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The printed circuit board (PCB) contains nearly 28% metals that are abundant non-ferrous metals such as Cu, Al, Sn, etc. The purity of precious metals in PCBs is more than 10 times higher than that of rich-content minerals. Therefore, recycling of PCBs is an important subject not only from the treatment of waste but also from the recovery of valuable materials. Chemical and mechanical methods are two traditional recycling processes for waste PCBs. However, the prospect of chemical methods will be limited since the emission of toxic liquid or gas brings secondary pollution to the environment during the process. Mechanical processes, such as shape separation, jigging, density-based separation, and electrostatic separation have been widely utilized in the recycling industry. But, recycling of waste PCBs is only beginning. In this study, a total of 400 kg of waste PCBs was processed by a recycle technology without negative impact to the environment. The technology contained mechanical two-step crushing, corona electrostatic separating, and recovery. The results indicated that (i) two-step crushing was an effect process to strip metals from base plates completely; (ii) the size of particles between 0.6 and 1.2 mm was suitable for corona electrostatic separating during industrial application; and (iii) the nonmetal of waste PCBs attained 80% weight of a kind of nonmetallic plate that expanded the applying prospect of waste nonmetallic materials.

Introduction

Generally, electronic waste (E-waste) encompasses a broad and growing range of electronic devices ranging from large household appliances such as refrigerators, air conditioners, hand-held cellular phones, personal stereos, and consumer electronics to computers.

The Waste Electrical and Electronic Equipment Regulation provides the official definition of E-waste. The regulations implemented provisions of the European Parliament and Council Directive on waste electrical and electronic equipment (WEEE), applying to all EEE placed on the market falling into any of the 10 product categories (*1*).

Although it is not well-known, WEEE contains over 1000 substances, many of which are toxic (lead, cadmium, mercury, arsenic, hexavalent chromium/chromium VI, etc.), and creates serious pollution upon disposal (*2*). When WEEE is filled or incinerated, it poses significant contamination problems. Landfills leach toxins into groundwater and incinerators emit toxic pollutants into the air, including dioxins (*3*). Likewise, the recycling of WEEE also has serious occupational and environmental implications, especially when the recycling industry aims at profit maximum and would not like to take the necessary precautions to protect the environment and employees' health.

It is necessary for us to develop the WEEE recycling industry not only because WEEE negatively impacts people's lives but also because it is a potential industry with good prospect. Comparing the metals in metal mines to metals in WEEE, it can be easily found that WEEE contains more rare metals and noble metals (*4*). The implication is that WEEE is a rich resource of rare metals, and its proper recycling not only contributes to environmental protection but also to a continuing development with social impacts and economic rewards.

The production of printed circuit boards (PCB) is the basis of the electronic industry as it is the essential part of almost all EEE. In recent years, the average rate of worldwide PCBs manufacture increased by 8.7%, and this figure is much higher in Southeast Asia (10.8%) and mainland China (14.4%). In mainland China, the total production value of the PCBs manufacturing industry has already reached more than $10.83 billion in 2005, only next to Japan, and will reach more than $12 billion in 2006 by anticipating yields (*5*).

PCBs are a mixture of woven glass reinforced resin and multiple kinds of metal. Their special physical and chemical characteristic make it difficult to recycle them. In normal PCBs, plenty of toxic materials including heavy metal, PVC plastic, and brominated flame retardants (BFR) can be easily found. However, just like the two-sided coin, the scrap PCBs contain many kinds of metals, which are a rich mine of wealth. The Rönnskar smelt (*4*) plant of Sweden analyzed the detailed composition of ordinary PCBs used in personal computers.

Chemical and mechanical methods are two traditional recycling processes for waste PCBs. Chemical methods mainly contain pyrolysis, combustion, hydration, and electrolysis. Because of a low cost and easy operation, currently, the majority of waste PCBs is processed in backyards or small workshops using primary methods such as open burning and acid washing (*6*). Even formal pyrometallurgy and combustion can generate atmospheric pollution through the release of dioxins and furans (*3*, *7*). For hydration and electrolysis, large quantities of waste acid liquid are produced during the recycling process, which needs to be carefully disposed. Many researchers have used various mechanical methods to separate metals from PCBs, such as shape separation (*8*), jigging (*9*), and density-based separation (*10*). These tests, however, are time-consuming and expensive and emit waste to the environment.

Corona electrostatic separation has been investigated extensively in the minerals processing industry. Both fundamental and practical aspects concerning the design of the electrode system have been investigated and developed by Iuga et al. (*11*−*14*). The extreme difference in the density and electrical conductivity between metallic and nonmetallic materials provides an excellent condition for the application of a corona electrostatic separation in PCBs recycling. Some industrial applications for the corona electrostatic separation were reported by Botsh et al. (*15*). However, the utilization of corona electrostatic separation in recovery material from waste PCBs is still in its infancy.

In this study, a new process technology without negative impact to the environment for recycling waste PCBs from computers and factory scraps was investigated. The process technology contained mechanical two-step crushing, corona

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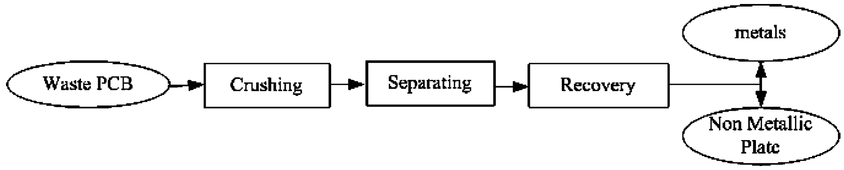

FIGURE 1. Whole process technology of recycling waste PCBs.

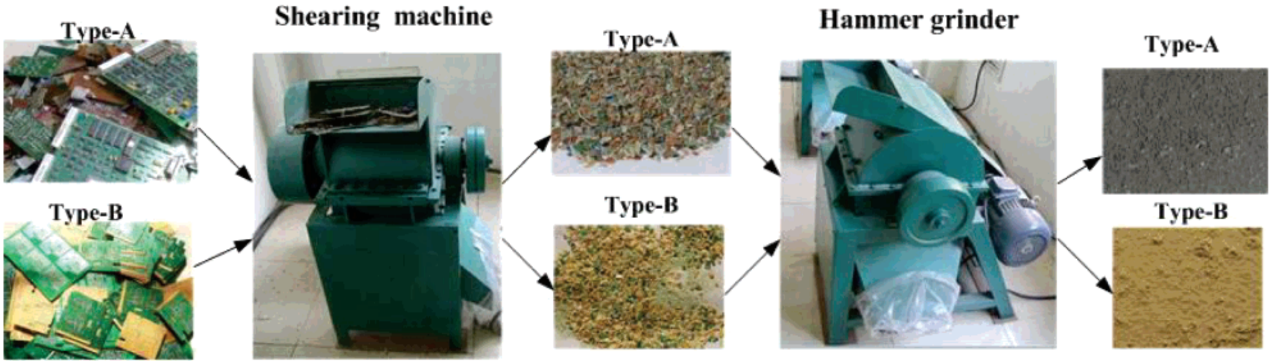

FIGURE 2. Two-step crushing flow chart.

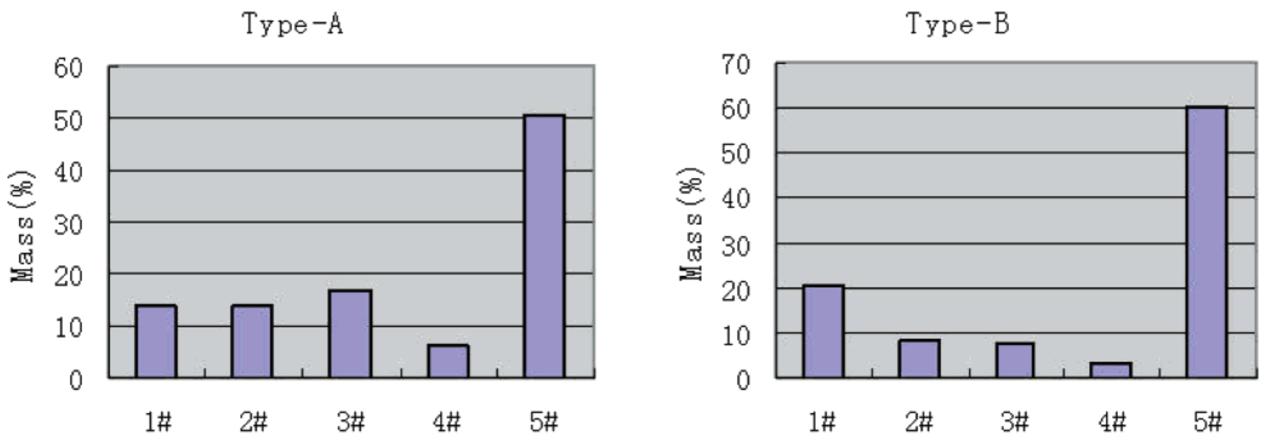

FIGURE 3. Size distributions of two kinds of materials after crushing.

TABLE 1. Comparison of Three Kinds of PCBs Mechanical Treatment Methods

process	environmental implication	power (kw)	productivity (ton/h)
air−current separation	releasing dust	4	0.1−0.5
fluid bed separation	causing wastewater including toxic heavy metals	1.1	0.5−0.8
corona electrostatic separation	none	0.2	0.5−1.0

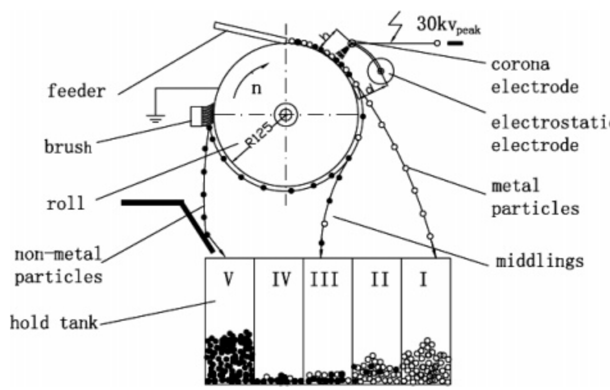

FIGURE 4. Diagram of corona electrostatic separator.

electrostatic separating, and recovery, as shown in Figure 1. The objective of the research was to try to establish a recycle technology to settle the problem of waste PCBs.

Materials and Methods

In 2004 and 2005, a total of 400 kg of waste PCBs was collected from individual collectors, local electronic repair facilities, local household waste collection facilities, and a local PCBs factory. The waste PCBs were separated into two types. Type A (nearly 250 kg) was mainly disassembled from discarded telephones, printers, PCs, and other electrical equipment (with some electronic elements), and type B (nearly 150 kg) was from scraps from a local PCBs factory (without electronic elements), as presented in Figure 2. Type A samples have various metals, and the attachment regimes of materials are complex, such as fastening, inserting, welding, binding, wrapping, coating, etc. (*16*). However, there was only copper coating on the epoxy base plates in the type B sample. The largest size of materials was 250 mm × 200 mm × 20 mm, and the smallest size was 80 mm × 35 mm × 10 mm. The toxic components (relays, switches, capacitors, etc.) were disassembled before crushing.

Two-Step Crushing. The purpose of the crushing was to strip metal from the base plates of waste PCBs. According to the different functions, the crusher machinery mainly contained a crusher (jaw crusher, hammer grinder, cone

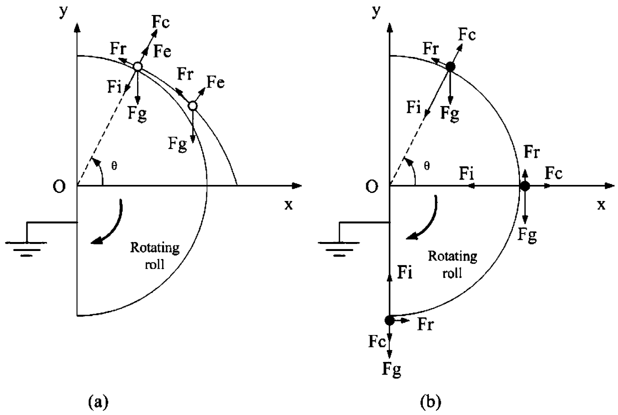

FIGURE 5. Metal (a) and nonmetal (b) particles on the rotating roll, F_r is air friction, F_e is electrostatic force, F_c is centrifugal force, F_g is gravity force, and F_i is electric image force.

crusher, impact crusher, and roll crusher) and a pulverizing mill (globe mill, autogenous tumbling mill, and vibratom). The industrial application type of the crusher machinery depends on the hardness, strength, and caking property of processed materials, the composition of particle size, and the maximum particle size. The materials are comprised of reinforced resin and metal parts such as copper wires and joints. They have a high hardness and tenacity, so using general crushing machines could not provide good metal stripping. In addition, most of base plates contain a fiber structure (glass cloths) that is easier to break under shearing action. Because the content of fine particles in discharge is very low, a normal crusher that depends on extrusion forces to crush does not have a good effect of thorough metal stripping (*17*). Then, the hammer grinder whose main acting force is a shear force is suitable for crushing waste PCBs. According to further analysis of the fragility of materials: (i) the materials with large two-dimensional sizes cannot be crushed by a hammer grinder directly and (ii) the particle size of discharge would be from 0.3 to 3 mm (*18*, *19*). The single crusher cannot satisfy the conditions. So, we use two-step crushing in this capacity, as shown in Figure 2. A high-speed shearing machine was used as the crude crusher. The shearing action generated by the rotor cutters and stator cutters crushed PCB plates to small particles. A hammer grinder specially designed for PCBs was employed as the second crusher. The materials were stroked and milled by high speed hammerheads. The action of hammerheads not only promoted metals to be completely strapped from base plates but also decreased the opportunity of wires wrapping around the tool tips. The diameter of screen holes in the hammer grinder was 1 mm to warrant an excellent grade of metal stripping from the base plates.

The materials coming out of the hammer grinder were screened by an electric shaker. In various sieve layers, the

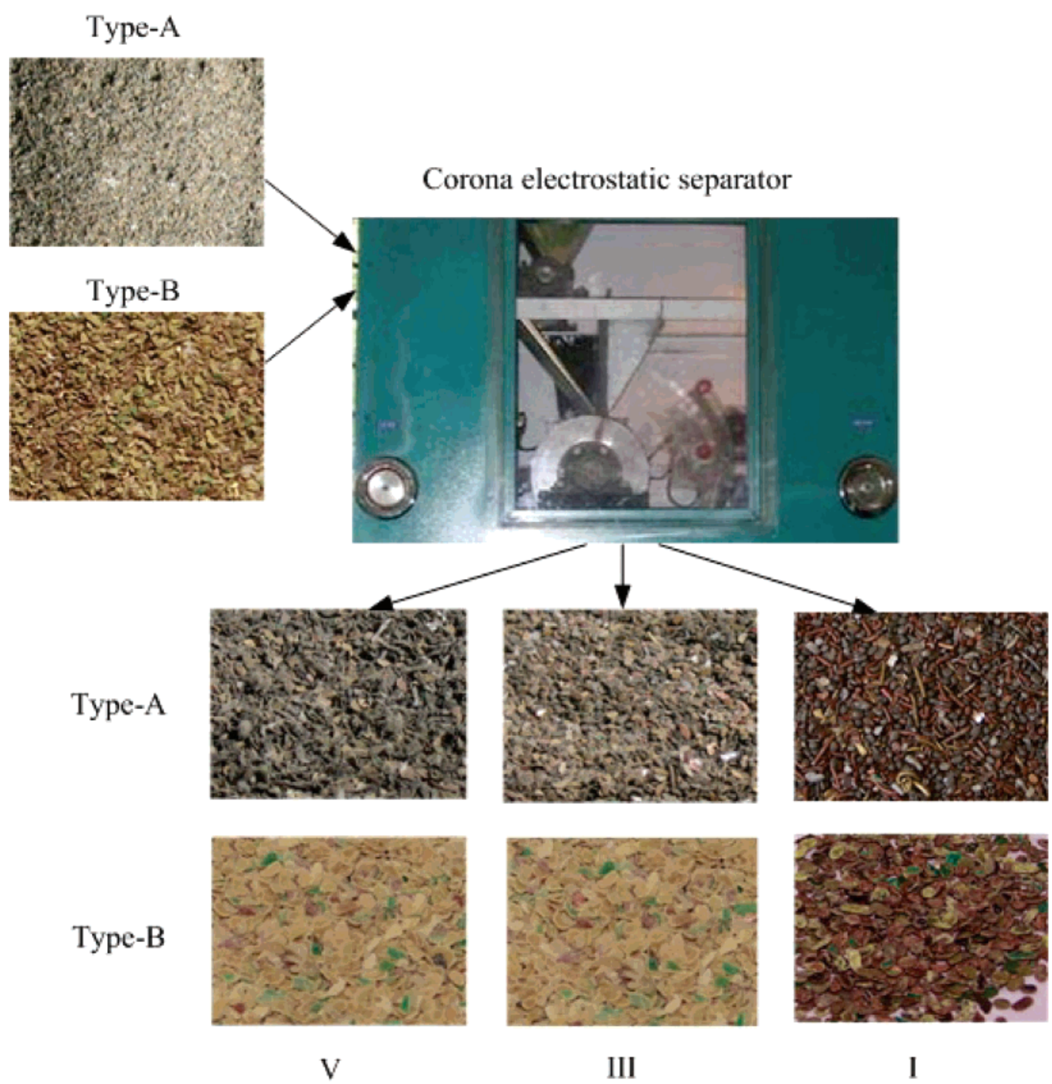

FIGURE 6. Corona electrostatic separating flow chart.

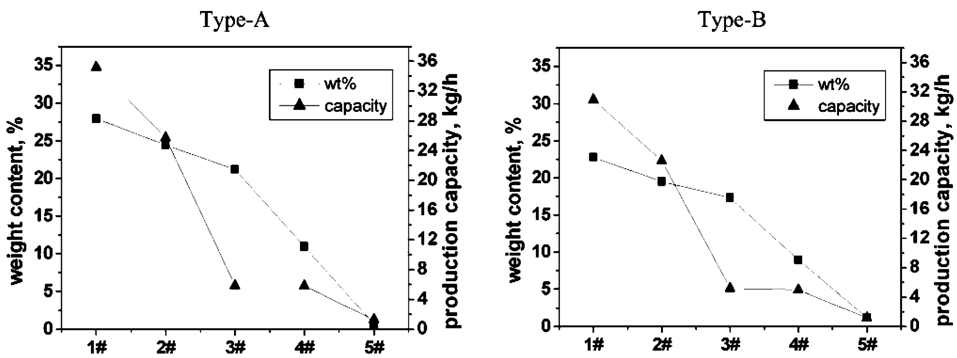

FIGURE 7. Weight content of particles in box I and production capacity of corona electrostatic separator (the parameter of electric shaking feeder is constant) of five samples.

FIGURE 8. Nonmetallic materials recovery flow chart.

delaminated material mix was separated according to size: 1# (0.8 to ~1.2 mm), 2# (0.6 to ~0.8 mm), 3# (0.45 to ~0.6 mm), 4# (0.3 to ~0.45 mm), and 5# (<0.3 mm). All the samples were heated at 100 °C in a drying stove for 3 h to reduce their moisture content to $W \approx 0\%$. The average particle diameter (D) of crushed materials was computed from

$$D = \frac{d_1 G_1 d_2 G_2 + \cdots + d_i G_i + \cdots d_n G_n}{G_1 + G_2 + \cdots G_i + \cdots G_n} \quad (1)$$

where d_1, d_2, d_3, and d_n were the average particle diameters of every grade and G_1, G_2, G_3, and G_n were the mass contents of every grade. After two-step crushing, the average particle diameters of materials were 0.4106 mm (type A) and 0.4007 mm (type B). It was clear that they were close to each other. The mass contents of type A and type B were 16.61 and 7.75% in 3#-grade; type A's 2# and 4# were higher than type B's 2# and 4#, as presented in Figure 3. This suggests that the size distributions of two kinds of materials were very different. The metal stripping degree of type A was nearly 100% under the size of −1.2 mm; however, the stripping degree of type B was only 50% under the size of −1.2 mm + 0.8 mm. Under the size of −0.6 mm, the stripping degree of type B was 100%. The different results between two types can be attributed to the fact that some of the electronic devices such as resistors and chips had a high hardness in type A material and that these components formed bulbous or horny hard particles during crushing and caused a great effect in metal stripping. So, type B should be pulverized finer than type A to strip metals from the base plate completely during industry applications. The experiments have shown that two-step crushing was an effective process to strip metals from base plates completely.

Corona Electrostatic Separating. Corona electrostatic separation is an important technique suitable for separating metals and nonmetals. Compared with other methods, the corona separation had no wastewater or gas during the process, and it had high productivity with a low-energy cost (Table 1). The high-voltage electrostatic field was generated by a corona electrode and electrostatic electrode, as shown in Figure 4. Metal and nonmetal particles entering this field were mainly subjected to electrostatic induction and ion bombardment (corona charge), respectively. The metal particles discharged rapidly to the earthed electrode and detached from the rotating roll until the mechanical and electrical forces exerting on it satisfied the condition (Figure 5a)

$$F_g \sin(\theta) = F_e + F_c - F_i \quad (2)$$

where F_i is the electric image force; F_g is the gravity force of the particle; F_e is the electric force; and F_c is the centrifugal force.

While the charged nonmetal particles are pinned by the electric image force to the rotating roll, the forces that exert on it satisfied the condition (Figure 5b)

$$F_i \geq F_g + F_c \quad (3)$$

The particle will move with the rotating roll and finally fall in the hold tanks. The electric field forces act differently on the two kinds of particles, which achieves the separation goal. The electric vibratory feeder ensures a monolayer of granular material on the surface of the rotating roll (earthed electrode). A set of five collecting boxes allows the study of material distribution on a separation plane. The products contained in boxes II−IV were middling (mixture of metal and nonmetal powders). During the process of separation, the weight component of middling was less than 10%. To obtain the metal parts, the middling can be separated by the separator again. Metal particles fell into box I, and nonmetal particles were collected in box V, as presented in Figure 6.

About 100 kg of type A and 100 kg of type B materials were fed to the electric vibratory feeder, and five size grade (1#–5#) materials were separated individually. Figure 6 shows photographs of sample 2# collected in the hold tanks. Bulbous, strand, and flaky metal particles were concentrated in box I. Nonmetal particles were recovered in boxes IV and V, which were beneath the brush. Figure 7 has shown that the production capacities of the corona electrostatic separator decrease with the size of samples diminished. About 90% of metals of every sample fell into box I via measuring the solution quantity with aqua regia. The production capacity of samples 1# and 2# and their separated metal contents was higher than both the other samples. So, the size of the particles between 0.6 and 1.2 mm is suitable for industrial applications. Then, the adjusted operating parameters of the crushing machines would change the size distribution of the five samples and raise the separating efficiency. But, the effect of aggregation was found during the process of feeding sample 5# and opposed regular production on superfine powders. So, improving the automatic feeding system to decrease electrostatic adherence among fine powders can settle the problem of aggregates (*20*).

Recovery. The materials coming out of separators were metallic and nonmetallic. The type A metals composed of different metals such as copper, aluminum, and lead could be treated with vacuum distilling (*21–25*). The process for type B materials was easy because the metallic part in type B metals was only copper, and it can be sent to the smelting plant directly.

There were about 70% nonmetallic materials after separating. Generally, they were an epoxy resin or phenol formaldehyde resin, glass fiber, and brominated flame retardant. According to the regulations and under the opinion pressure, the storage of these nonmetallic materials is limited. Traditionally, incineration and landfills are currently available to process these materials. However, during the process of incineration, the incomplete combustion leads to producing complex and harmful materials such as hydrogen cyanide and CO; even worse, the brominated flame retardants can produce dibenzo-ρ-dioxins and dibenzo-furans (*3*). How to reuse them in a suitable way is a challenge. Many researchers have performed large quantities of work on recycling thermosetting plastic waste and epoxy resin compounds from waste PCBs (*26–28*). Recently, Mou peng et al. (*29*) published a study of methods for reusing nonmetals reclaimed from waste PCBs. But, in their study, the waste nonmetallic materials were used as filler, and their products did not appear on the market. As discussed previously, nonmetallic materials occupied nearly 70% of waste PCBs and were separated in large quantities. To have suitable disposal and expand the applying prospect of waste nonmetallic materials, we made a kind of nonmetallic plate (abbreviated NMP) whose main component was nonmetallic materials. The NMP was produced by using a hot-press forming technology, as shown in Figure 8. The nonmetal materials were mixed with a few additives and pressed by the hot-press former. The nonmetals of waste PCBs as the main material attained 80% weight of NMP, which expanded the applying prospect of waste nonmetallic materials. The NMP could be used as building materials (tiles, partitions, insulating boards, etc.) (*30*). Additional experimentation using different addition agents, temperature, and pressure is needed to explore the availability of NMP.

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