Recycling and disposal technology for non-metallic materials from waste printed circuit boards (WPCBs) in China

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Abstract

Non-metallic material of waste printed circuit boards (WPCBs) is complicated, which is one of the challenges of electronic waste disposal. Firstly, the source of WPCBs, non-metallic material composition, current major disposal and potential dangers are analyzed in the research. The progress of recycling and disposal technology for non-metallic materials from waste printed circuit board are summarized on the basis of the physical processing technology, pyrolysis processing and chemical processing technology. Future research is also suggested in the paper. Results obtained can provide a reference for the industrial development of regeneration and reuse of WPCBs nonmetallic materials.

Keywords: waste printed circuit boards (WPCBs); non-metallic materials; recycling; disposal

Since the 21st century, the electronic information technology and other high-tech industries have got rapid development, which makes a very positive contribution to the development of human society. However, a large quantity of e-waste is produced at the same time. Currently, with the annual growth rate of 3\%-5\%, the E-waste has become one of the fastest growing types of municipal solid waste. According to the 2010 UNEP data, the production of global e-waste has summed up to 40 million tons per year. China has become the world’s second largest producer of e-waste, only ranked after the United States\textsuperscript{1}. Currently, the recycling of waste printed circuit boards (WPCBs) is mainly focused on precious metals and general metals\textsuperscript{2}, while the recycling research about non-metallic material of WPCBs, which is difficult to dispose and has lower economic benefits, is rather less\textsuperscript{3}. However, with a large number of resources that can be directly reused or recycled, the non-metallic material has its high recycling value. Therefore, this paper summarizes the latest research results of the resource utilization of non-metallic material of WPCBs as...
well as prospects the future research about this topic, aiming to provide some references for the industrialization development of the resource utilization of non-metallic material of the WPCBs.

1. The current situation of disposing non-metallic materials

1.1. The main source and components

The total weight of WPCBs accounts for about 10% of e-waste. With the increase of e-waste, a large amount of WPCBs has been produced. The scrap left during the production of the printed circuit board (PCB) is also an important source of WPCBs, which accounts for about 5% of the PCB. Besides, plenty of imported waste electrical and electronic products is another important source of WPCBs.

Non-metallic material of WPCBs refers to the residue produced by separating the copper and other precious metal materials from the WPCBs through physical and chemical methods. After the valuable copper and other metal components are separated from WPCBs, the non-metallic material accounts for nearly 50%-80% of WPCBs. Non-metallic materials are consisted of 40% organic substance and 60% inorganic substance. The common organic substance is epoxy resin, brominated flame retardants, dicyandiamide curing agent, curing accelerator and so on. However, the common inorganic substance is glass fiber which is made from various oxides dominated by SiO₂, CaO and Al₂O₃.

1.2. Current treatment technology and potential harmfulness

The Landfill treatment is the major way of disposing the non-metallic materials of WPCBs. The environment problem is becoming more and more serious with the increasing number of the WPCBs. The landfill of massive accumulation of great amount of non-metallic WPCBs will cause three serious global problems. Firstly, the landfill will occupy some land, which will cause lots of land resource wasted. Secondly, due to its poor natural degradation performance, the non-metallic material in WPCBs can’t become decayed in a long time after being buried, which will destroy air permeability of soil, reduce the storage capacity of the soil, as well as destroy ecological balance of soil microbial, causing the soil deterioration. Third, the inorganic metallic, heavy metal ion and toxic and harmful substance used in the filler and coloring agent of the non-metallic materials of WPCBs will have an indirect effect on the groundwater quality and plant growth by diffusion and infiltration in the soil. In addition, from the perspective of resource, the synthetic material of non-metallic materials of WPCBs comes from non-renewable petroleum, and it is a kind of chemical synthesis of the monomer refined from the raw petroleum. Therefore, the landfill treatment is also a waste of resource.

Incineration is another method of disposing non-metallic materials of WPCBs. Although part of the heat energy can be recovered by burning, environmental hazard still exists. Under the high temperature and aerobic environment, polymer will thermally cracked and release a lot of toxic gases. The inorganic metal used in the filler and coloring agent of the Non-metallic materials of WPCBs, such as lead and arsenic, will also volatilize into the atmosphere and do harm to the atmospheric environment.

2. Reutilization of non-metallic materials

2.1. Physical processing technology

Physical treatment refers to a method that non-metallic is disposed without any chemical reaction. By mechanical crushing, winnowing, electrostatic separation and other physical and mechanical methods, we can separate the metal and non-metallic from WPCBs, and then process and use the non-metallic. With the major components of glass fiber, thermosetting epoxy resin and various additives, nonmetal powder can be used as filler to produce inorganic material and composite material.

It is an essential way of reclamation to use non-metallic materials of WPCBs as filler to produce the recyclable building materials and paving materials. The nonmetal powder added as additive to concrete, mortar, asphalt and other construction materials significantly enhances the performance of the original material. On the basis of
analyzing the components of nonmetal power of WPCBs, Xie\textsuperscript{7} introduced the idea of adding the nonmetal power as a reinforcing material to concrete and mortar to enhance the intensity of concrete and mortar. The experimental result shows that the nonmetal power of WPCBs can obviously enhance the early intensity of concrete and mortar. Guo\textsuperscript{8} used nonmetal powder separated from WPCBs as a new modifier to improve the performance of asphalt. He also studied how the adding proportion and particle size of nonmetal would have an effect on the product property. When the adding proportion of nonmetal powder is 25\% (by weight), and the particle size is 0.07-0.09 mm, the performance of modified asphalt with nonmetal power will be enhanced significantly in such indexes as standard viscosity, penetration, softening point, etc.

Non-metallic materials of WPCBs are mainly composed by polymers with good thermal stability, which can endure higher thermodynamic test and harsh environmental conditions through a specific chemical processing. With the common properties of filler, the non-metallic material can be used as filler for sound-absorbing material and packing plastic prepared, or as reinforcing material to produce flame retardants and construction materials. Both of them have favorable application prospect. Sun\textsuperscript{9} has used non-metallic material to produce porous sound-absorbing material. Experiment shows that this kind of composite material has good sound absorption property, and its average absorption efficiency is greater than 0.4 within a wide frequency range of 100-6400HZ. As long as the particle size is larger than 2 mm, it will almost have the same performance with the wood fibers and urea formaldehyde foam. The mechanical property tests show it has sufficient intensity to maintain its structure.

In 1995, Japan’s NEC Corp has proposed a recycling program of use glass fiber epoxy powder as epoxy filler instead of calcium carbonate, silica powder, and t alcum powder\textsuperscript{10}. They used epoxy fiberglass powder of three different average particle sizes (0.013mm, 0.020mm, 0.044mm) as filler in the experiment. When the epoxy fiberglass powder accounting for 30\% of the whole weight of the resin was added into a new epoxy resin system, they found that after solidifying, the mechanical strength and thermal expansion property of the resin are better than the resin filled by calcium carbonate, silica powder and t alc, while the bond strength is not changed too much, but the viscosity of the resin is enhanced rather larger. Epoxy powder/polyvinyl chloride (PVC) composite material produced can be cut into fixed-scale as required in order to produce freight trays with different specifications\textsuperscript{11}. The test on the freight tray with the specification of 1100mm×1100mm shows that this kind of freight tray has the dynamic load of 1000kg and static load of 2000kg, without deforming at 100 °C high temperature, or being corroded by concentrated sulfuric acid with the mass fraction of 98\%, which meets the basic requirements for the freight tray of container transportation in the market.

At present, physical methods of recycling non-metallic material of WPCBs is a research highlight, some of which have already been applied in industrialization. The recycling technology with physical methods doesn’t need to change the state of non-metallic materials, and can be handled simply with the low cost and high-usage. But because the components of non-metallic material of WPCBs are not identical, their properties are different from each other, which, to some extent, will affect the performance of the renewable product. Recycled non-metallic materials usually can only be added to other materials or similar new materials with limited using range and quantity, instead of being used alone. Non-metallic materials of WPCBs contain a certain amount of toxic heavy metal, and fire retardant that is not removed, so the range of products application is also limited. If these products are discarded again without any identification, the improper handling will cause environmental pollution. Therefore, we should take priority to solve the problems of routinization of the current physical recovery method.

2.2. Pyrolysis processing technology

The so-called pyrolysis, namely dry distillation used in industry, refers to a chemical process that the organic substance is decomposed into gases, liquids and solids by heating in the oxygen-free or anoxic environment. In the pyrolysis process, non-metallic materials of WPCBs are decomposed into oily hydrocarbon compounds, which can be used as fuel or chemical feedstocks. Pyrolysis residue of inorganic components such as glass fibers, silicic acid and other recyclable solid products can be recycled to prepare composite material, while the pyrolysis gas has certain calorific value, so its heat can be recycled and used as a heat source in the pyrolysis process.

Zhan\textsuperscript{12} found non-metallic material of WPCBs could prepare 21 kinds of organic compounds after pyrolysis, of which the carbon atom number is between 3 and 20, and the relative molecular mass is 58-240. The
pyrolysis oil has the key components of phenol, isopropyl phenol and bisphenol A, etc, the mass fraction of more than 80%, and the calorific value of 24.5-27.5MJ/kg. If these chemical monomers can be extracted from pyrolysis oil, it will not only create greater economic value than being simply used as fuel, but also improve the economical efficiency of the whole pyrolysis process. As for the re-use of pyrolysis oil, Peng\textsuperscript{13} used pyrolysis technique to turn the resin in waste circuit board into phenol-riched pyrolysis oil with the existence of calcium carbonate, and then directly added the formaldehyde solution to react and prepare the pyrolysis oil phenolic resin, achieving the regeneration of resin in waste circuit board. Its performance structure is similar to ammonia-catalyzed phenolic resin. The experimental results show that when the molar ratio of n (formaldehyde) : n (pyrolysis oil) is 1.8–2.1, the nitrogen in resin can be converted to catalyst NH\textsubscript{3} and NH\textsubscript{4}+ for preparing phenolic resin and the extra-catalyst will not be needed. pyrolysis oil phenolic resin, which is prepared by respectively reacting 30min under the temperature of 60°C, 80°C, and 90°C, has the best performance and can meet the relevant standards. In addition, Quan\textsuperscript{14} used pyrolysis oil as raw material to prepare carbon nano tubes and porous functional materials.

After pyrolysis, about 60% residues will be left\textsuperscript{15}, and these residues are mainly composed of coke and other substance from the pyrolysis of glass fiber, metal and resin. The coke formed after pyrolysis will become brittle and can easily separate the metal and fiberglass, thus remove the carbon black from glass cloth. The white glass fiber cloth obtained by this method can be recycled. In contrast\textsuperscript{16}, the fiberglass will be crushed when we adopt mechanical crushing method to dispose WPCBs, so it can’t be recycled. Liang\textsuperscript{17} has used glass fiber recycled from the vacuum pyrolysis residue of WPCBs as filler material to prepare glass fiber/PP (GF/PP) composites, finding that the mechanical properties and heat-resistant quality of the composite material will achieve the best, when the GF content accounts for about 30%. Cunliffe\textsuperscript{18} used recycled glass fiber for the preparation of bulk molding plastic, and found that when the added amount of recycled glass fiber is 20%, the composite material will have similar performance to the new fiber reinforced composite material. With a series work of molding, crushing, carbonizing at 800 °C, and 3hours’ vapor activating at 850°C, Ke\textsuperscript{19} used carbon residue pyrolyzed at 600°C as raw material, and coal tar pitch as binder to prepare granular activated carbon with specific surface area of 1019 m\textsuperscript{2}/g and pore volume of 1.1cm\textsuperscript{3}/g. But when using carbon residue pyrolyzed at 600°C as raw material, adding KOH and activating 2 hours at 900 °C, he prepared the powdered activated carbon with specific surface area of 3112 m\textsuperscript{2}/g and pore volume of 1.13 cm\textsuperscript{3}/g.

By test, Quan\textsuperscript{20} found the main components of pyrolysis gas product are H\textsubscript{2} and CO\textsubscript{2}, and the volume fraction of H\textsubscript{2} can reach the maximum of 55%.With the final pyrolysis temperature increasing, this volume fraction will first increase then decrease; the volum fraction of CO\textsubscript{2} can reach the maximum of 45%, while the volume fraction of CO in pyrolysis gas remains about 7%. Volume fraction of CH\textsubscript{4} will increase with the final pyrolysis temperature rising. Volume fraction of C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8} in pyrolysis is lower, basically remaining below 1%.

Pyrolysis can significantly reduce the number of non-metallic materials of WPCBs and has better recycling result. It can not only recycle energy but also achieve the solid by-product regeneration. But at the same time, with the requirement of high-tech equipment, high investment, and existence of high risk, this method can create its economical benefits only when a large amount of non-metallic material of WPCBs is collected. Furthermore, some hazardous substance will be prepared if the pyrolysis process is controlled improperly. The study found that\textsuperscript{21} the brominated flame retardants composite in WPCBs will generate “three lead” dioxins, furans and other toxic substances at 500-600°C and in the oxygen-free or oxygen-deficit conditions.

2.3. Chemical processing technology

The so-called chemical method refers to using organic or inorganic solvent to cleave the macromolecular reticulate structure of thermosetting epoxy resin in WPCBs. The generated organic compounds can be re-synthesized as the epoxy composites, and generated inorganic compounds (with the major component of glass fiber) can be used to prepare filler.

Dang\textsuperscript{22} used nitric acid to decompose the thermosetting epoxy resin of amine cross-linking agent into linear low molecular weight organic compounds, and the recycled organic compounds will be used for the preparation of new thermosetting epoxy resin. Zhang\textsuperscript{23} used heteropolyacids, phosphotungstic acid, tungsten acid, molybdenum...
phosphoric acid as catalyst, and used water as decomposition fluid to decompose the waste resin composite materials at 250-370°C without using organic solvent. 30-120 min later, decomposed products will become oligomer or monomeric substance which is insoluble in liquid and easy to separate. This method can protect the environment well with low-cost and non-polluting. Through solvent method, Liu24 recycled glass fiber from glass fiber / epoxy composite. After reacting 12h in 8 mol/L nitric acid, at 90°C, the epoxy resin matrix in composite is decomposed into low molecular weight organic compounds containing benzene ring. The recovered glass fiber is clean under microscope and the fiber’s mono filament tensile strength just loses 5.2%, so it is totally recyclable. Zhu25 studied the method of using dimethyl sulfoxide (DMSO) to dispose WPCBs. The experimental results show that when it is disposed with DMSO, the dissolved concentration of bromine epoxy resin will be affected by the change of various parameters, such as solid-to-liquid ratio, temperature, the size of WPCBs and processing time. DMSO Vacuum distillation can obtain the regenerated DMSO and dissolved bromine epoxy resin. Tai26 invented a thermosetting plastic recycling method, which is divided into two steps: The first step is decrosslinking the thermosetting plastic and the second step is crosslinking and solidifying the decomposition product again. If we stir epoxy resin particles of the mass ratio of 1:1 with benzene dimethylamine for 45 min at 150°C, we can obtain liquid decomposition, and then by adding a suitable amount of pre-bisphenol A epoxy resin into the obtained liquid decomposition and curing it at room temperature for 30 min, the renewable curing material will be obtained.

In addition, some other people have also studied how to use mixed solvent composed of tetrabutyl titanate and diethylene glycol27, naphthalene, decahydronaphthalene or cyclohexanol to recycle epoxy resin. More than 40% of phenol and isopropyl phenol monomers can be recycled by this way.

Under the influence of certain pressure and catalyst, the chemical decomposed resin can obtain a higher liquid product. Because the recycled glass fiber cloth is unaffected by high temperature, it can still maintain better mechanical property and has higher recovery value. But a particular type of solvent can only handle few kinds of thermosetting plastics. There still exists lots of problems during this process such as large amount of solvent usage, slow dissolution rate, long processing period.

3. Conclusions

Methods for treating non-metallic material of a large number of WPCBs still remain being tested and fail to achieve industrialization very well. We have not yet found the right way to dispose and use these resources with harmlessness. With the rapid development of electronic information industry, harmless use of non-metallic materials of WPCBs has become a hot spot of society. The recycling of non-metallic WPCBs has great environmental and economic effect.

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References