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Hydrothermal modification and recycling of nonmetallic particles from waste print circuit boards

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ABSTRACT

Nonmetallic particles recycled from waste print circuit boards (NPRPs) were modified by a hydrothermal treatment method and the catalysts, solvents, temperature and time were investigated, which affected the modification effect of NPRPs. The mild hydrothermal treatment method does not need high temperature, and would not cause secondary pollution. Further, the modified NPRPs were used as the raw materials for the epoxy resin and glass fibers/epoxy resin composites, which were prepared by pouring and hot-pressing method. The mechanical properties and morphology of the composites were discussed. The results showed that relative intensity of the hydroxyl bonds on the surface of NPRPs increased 58.9% after modification. The mechanical tests revealed that both flexural and impact properties of the composites can be significantly improved by adding the modified NPRPs. Particularly, the maximum increment of flexural strength, flexural modulus and impact strength of the epoxy matrix composites with 30% modified NPRPs is 40.1%, 80.0% and 79.0%, respectively. Hydrothermal treatment can modify surface of NPRPs successfully and modified NPRPs can not only improve the properties of the composites, but also reduce the production cost of the composites and environmental pollution. Thus, we develop a new way to recycle nonmetallic materials of waste print circuit boards and the highest level of waste material recycling with the raw materials-products-raw materials closed cycle can be realized through the hydrothermal modification and reuse of NPRPs.

1. Introduction

With extensive application of electronic products and rapid development of electronic industry, the number of waste electronic products is increasing gradually. According to estimates of the EU, the growth rate of electronic waste in the past 6 years is maintained at about 11%, which is 4 times of ordinary garbage (Liu et al., 2014; Cucchiella et al., 2015). In 2014, nearly 54 million tons of electronic waste was produced worldwide, and electronic waste production would reach 72 million tons in the end of 2017 (Zeng et al., 2016; Balde et al., 2015). Particularly, waste printed circuit boards (WPCBs) accounts for about 8 wt% of whole electronic waste, and the average rate of worldwide printed circuit boards (PCBs) production has increased with the technological advancement, in developing countries such as China and South Asia its reported increase is by 14.4% and 10.8%, respectively (Wu and Zhang, 2010; Ogunseitan, 2013; Zeng et al., 2015). Considering the use of renewable resources and environmental protection, recycling of WPCBs receives wide concern as the amount of WPCBs increases dramatically. However, the recovery technology for WPCBs in China is still immature. Currently, the recycling of WPCBs is mainly focused on metals, while the recycling research about non-metallic material of WPCBs is rather less because of difficulty to dispose and low economic benefits, (Yadav, 2015; Zhang et al., 2017). After separated from metals in WPCBs, the nonmetallic materials are often burned or landfilled, which not only leads to resource loss but also brings serious environmental problems (Ruj et al., 2015; Fujita et al., 2014; Zhao et al., 2014). Nonmetals in PCBs are reported to be 70% by weight, giving a huge opportunity to recycle (Huang et al., 2009). Non-metallic material of WPCBs refers to the residue produced by separating metal materials from the WPCBs through physical and chemical methods, and its main components are thermosetting resin and fiberglass along with some reinforcing materials, which possess good mechanical properties (Muniyandi et al., 2014). If these materials can be reused synthetically as raw material, a higher level of waste recycling can be achieved. Thus, the recycling of the nonmetallic material of WPCBs has become a pressing environmental issue in the world.

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There are three main types of recovery technology of nonmetallic materials from WPCBs: pyrolysis, physical method and chemical method. Pyrolysis can significantly reduce the number of non-metallic materials of WPCBs but requires high investments. Physical method doesn't need to change the state of non-metallic materials, which is a research highlight and some of results have already been applied in industrialization (Guanghan Song et al., 2016; Hadi et al., 2015; Wang et al., 2014). The nonmetallic part separated from WPCBs has found various uses such as fillers in the polymer composites, strength enhancer in concrete, and temperature resistance of viscoelastic materials (Ghosh et al., 2015; Guo and Xu, 2009; Guo et al., 2008). Wang et al. reported the use of crushed nonmetallic materials as reinforcing fillers in the polyvinylchloride (PVC) matrix. Nonmetallic particles of different sizes were used to improve the physical and thermal properties of PVC (Wang et al., 2010). Xie et al. introduced an idea of adding nonmetallic power as a reinforcing fillers to concrete and mortar to enhance their intensity. The experimental results showed that the nonmetal power of WPCBs can obviously enhance early intensity of the concrete and mortar (Xie et al., 2014). But the composition of nonmetallic materials of WPCBs are not identical, their properties are different from each other, which would affect the properties of renewable composites to some extent (Zhang et al., 2016). The chemical method refers to using solvent to cleave the macromolecular reticulate structure of thermosetting epoxy resin in WPCBs and the generated produce can be used to prepare new material. This method is not simple to use the nonmetallic materials as fillers, but do a further treatment on their surface, which is beneficial to reuse as raw materials. In recent years, there are some reports about modified nonmetallic material of WPCBs. Liu Luyan et al. used silane coupling agent (KH550) to modify nonmetallic parts of WPCBs (NWPCB) and added maleic anhydride grafted polypropylene (PP-g-MAH) as compatibilizers at the same time, the results showed that the mechanical properties of PP/NWPCB composite had been improved significantly after modification (Liu et al., 2013) Muniyandi et al. used maleated polyethylene (MAPE) treated nonmetallic materials as reinforcing fillers in recycled high density polyethylene (rHDPE) (Muniyandi et al., 2013). Xu et al. used modified NWPCB (treated with calcium pimelate) compounded with β-PP through melt blending method at relatively high temperatures to enhance tensile, flexural and impact properties (Xu et al., 2016). But there are few reports on studying the application of hydrothermal method in the recycling of nonmetallic materials from WPCBs. As a kind of chemical method, hydrothermal method is preferred because hydrothermal method is efficient and environmentally friendly and nonmetallic parts of WPCBs can be modified effectively through a simple process with optimized reaction parameters. For example, Yan Liu et al. reported synergistic reaction of potassium hydroxide and phenol in recycling carbon fiber reinforced resin composites under hydrothermal condition (Liu et al., 2012); Jacob G. Dickinson et al. studied the catalytic deoxygenation of 2,3-benzofuran under hydrothermal conditions (Dickinson et al., 2012).

Therefore, it is of great significance to modify the nonmetallic materials of WPCBs with a mild hydrothermal treatment, decompose and produce small molecular organic compounds or monomers, and use them as raw materials to prepare superior products. Compared to other methods, hydrothermal methods is milder and does not need high temperature. Meanwhile, little waste water is generated owing to its reuse of modifier solution, and the modifier solution was centralized treatment after a certain period of time, which would not cause secondary pollution. Therefore we believe that hydrothermal modification is a green and effective method to modify nonmetallic materials of WPCBs. More importantly, the price of recycled plastic is relatively low, using recycled plastic as raw material to produce new composite can save production cost. Hence this method can reduce cost and improve the performance of the composites simultaneously, realizing the recycling of nonmetallic materials from WPCBs, Which can not only have a great economic value but also a social significance.

In this paper, we adopt a mild hydrothermal method using NaOH as a catalyst and water as solvent to modify the NPRPs, and reuse the modified NPRPs as raw materials to prepare composites. The results show that the mild hydrothermal method can interrupt the ether bond of NPRP and make —OH grafted on its surface at the same time. In addition, the modified NPRPs can significantly improve both flexural and impact properties of the glass fibers/epoxy resin composites. Therefore, our work opens up a new way to recycle the nonmetals of WPCBs, and the reuse of the modified NPRPs as raw material in the composites realizes the raw materials – product – raw materials closed cycle, completes the highest level of waste materials recycling.

2. Experimental

2.1. Materials

Waste print circuit boards were industrial solid-waste byproducts and in the form of plate from Shanghai Shenhua Materials Recycling Limited Company (China); epoxy resin (E-51, transparent liquid) was supplied by Shanghai Resin Factory Limited Company (China); 4,4-diaminodiphenyl methane(DDM, analytical grade) was purchased from Honghu Xinlei Resin Material Limited Company (China); glass fiber cloth (7268) was provided by Shanghai Bunt insulation materials Co. Ltd., China; silane coupling agent KH-550 (analytical grade, transparent liquid) was bought from Nanjing Shuguang Chemical groups Co. Ltd., China. Phenol (C_6H_5OH), nitric acid(HNO_3), ethanol (C_2H_5OH), sodium hydroxide (NaOH) and concentrated sulfuric acid were purchased from Sinopharm chemical reagent Co. Ltd., China. All the chemicals were used as-received without any further treatment.

2.2. Hydrothermal modification of nonmetallic particles recycled from print circuit boards (NPRPs)

Print circuit boards were put into the 50% NaOH solution for 30 min, soaked in dilute nitric acid for 180 min to remove surface protective lacquer and metal materials, then washed to neutral and dried. The NPRPs were prepared by using a small impactor to make the circuit boards into small particles with 5 mm in diameter.

The NPRPs, solution (water, ethanol or phenol) and catalyst (NaOH or concentrated sulfuric acid) were added into a beaker according to the experimental proportions and stirred for 20 min. After that the mixture was sealed in a Teflon-lined autoclave and maintained at 100–180 °C for 2 or 4 h to finish the hydrothermal treatment. To make a further modification, the NPRPs were modified with 1.0 wt% content of silane coupling agent KH-550 stirred for 30 min under 80 °C.

2.3. Preparation of composites

NPRP-EP composites: the modified NPRPs, epoxy resin and curing agent DDM were put into a beaker at the same time, stirred and mixed for 30 min. The content of modified NPRPs, epoxy resin and curing agent DDM was 70%, 24% and 6%, respectively. Then the NPRPs/EP/DDM blends were poured into a standard mold and this mold was put into an oven to cure for 2 h at 80 °C and 4 h at 150 °C.

Glass fibers/NPRP-EP composites: the NPRPs/EP/DDM blends prepared according to the above mentioned steps were uniformly spread on the glass fiber clothes using a small shovel. And then the glass fiber clothes were put into an oven to procure for 40

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