MICROWAVE-BASED CHEMICAL RECYCLING TECHNOLOGY RESEARCH FOR WASTE PCB

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Abstract: Because epoxy condensate can be completely decomposed in nitric acid solution, the glass fiber and epoxy resin in PCB can be fully recycled through this way and much more value can be obtained from the waste PCB. However, the decomposition efficiency is low, and several resultants are very toxic to human 0 . To solve this problem, this paper studied the decomposition efficiency of the non-metallic powder from PCB and the resultants by using microwave as an assistant tool. First of all, through a series of experiments, find the best reaction conditions without the assistant of microwave. Then, study the acidolysis of the non-metallic powder with the assistant of microwave through the orthogonal experiments. An analysis on the composition of reaction resultants was done, the result showed that the assistant of microwave changed the chemical reaction of degradation, and also improved the reaction efficiency.

Key words: PCB; recycle; microwave

1. Introduction

With the rapid development of electronic technology, the upgrading of products becomes more frequent. Almost all the electronic products have some PCBs. After the separation of electronic components and solders, the PCB is smashed into powder, and then copper, tin, lead and other metal components in the powder would be seperated 00^0 . Finally, the non-metal remains, which mainly contained epoxy resin and glass fiber, and the main treatment of this non-metal can be classified as physical method and chemical method 0. Among these treatment methods, the solvent chemical method is the most completed one. This experiment used microwave's high digestion capacity, to adjust the reaction kinetics of system and improve the reaction efficiency at last 0.

The Green Manufacturing Department of Changhong Engineering Technology Center has done some research on chemical decomposition of epoxy condensate from the waste TV's PCB. The study shows that in the decomposition reaction of epoxy condensate, microwave can greatly accelerate the reaction speed, and change the reaction process. In this way, it solves the issues of low efficiency, high energy consumption as well as large environmental hazard, etc.

2. Experiments

2.1 Experiment materials

The main materials required by this experiment include: self-made non-metallic powder of PCB, nitric acid, sodium hydroxide, acetone and so on.

2.2 Experiment process

According to a special proportion, put the non-metallic powder and a certain concentration of nitric acid into a tree-neck flask with a reflux condenser. Heat it with the assistant of microwave, in different temperature, power, and time duration. Then, take out reaction products from the flask. After the filtration and washing, place them into a drying oven in 80 ^{o}C. Then, calculate the decomposition rate by weighting. Finally, The Scanning Electron Microscopy (SEM) analysis was carried out on the reaction resultants, test and characterize the reaction solution by Gel Permeation Chrommatograph and Gas Chromatography-Mass Spectrum.

2.2.1 The experimental situation in different material ratios without the microwave

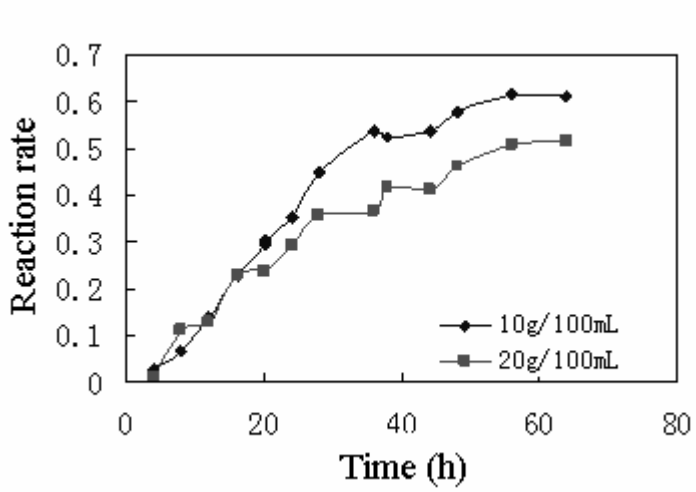

Fig. 1 The data of complete reaction in different material ratios (80°C / 40%)

Fig. 1 shows: the reaction temperature is 80 °C; nitrate acid concentration is 40%; material ratio is 10 g/100 ml, 20 g/100 ml respectively. In these conditions, the reaction rate increases gradually with the reaction time until 56h, when the reaction fully done, then followed by a gradual equilibrium. Meanwhile, Fig.1 also shows that the reaction effect of 10 g/100 ml is better than that of 20 g/100 ml, and the reaction rate is 61.69%. This result is almost consistent with the study results of Liu Yuyan[0] and others (reach a reaction equilibrium at 50 h).

2.2.2 The effect of material ratio on the microwave-assisted nitric acid decomposition of the non-metallic powder

Tab.1 shows the influence of different material ratios on the decomposition rate of the nonmetallic powder, when the reaction temperature is 80 °C, the microwave power is 800 w, and reaction time is 8 h.

Tab. 1 The effect of different material ratios on the decomposition rate of the nonmetallic powder

Material Ratio / g/100 mL	3.3	10	15	20
Decomposition rate / %	68.00	64.47	51.20	35.01

Tab. 1 also shows that: with the increase of material ratio, the decomposition rate of the non-metallic powder declines rapidly within the specified time. According to a preliminary analysis, it is due to the reducing of effective contact area between the non-metallic powder and nitric acid, while the material ratio is increasing.

2.2.3 The orthogonal experiment of microwave-assisted decomposition of the nonmetallic Powder

Fixing the material ratio at 10 g/100 ml and the reaction time at 8 h, considering the effect of 3 factors on the microwave-assisted decomposition rate of the onmetallic powder: microwave power, temperature, and acid concentration.

2.2.4 Analysis of the composition of the reaction resultants

2.2.4.1 Analysis of High-Performance Gel Chromatography

Neutralizing the reaction solution with sodium hydroxide, and using the gel chromatography (AGILENT HP1100, US) to test the molecular weight distribution of the resultants. The mobile phase is tetrahydrofuran; the flow rate is 1 $mL \cdot min^{-1}$; the standard substance is polystyrene; the chromatographic column is plgel①5 min*104 A, plgel②5 min*100 A; the detector temperature is 35 °C. The results are shown in Tab.2.

Tab. 2 The molecular weight distribution of the neutralized resultants

No.	Mn/ $g \cdot mol^{-1}$	Mω/$g \cdot mol^{-1}$	Mz/$g \cdot mol^{-1}$	Mv/ $g \cdot mol^{-1}$	D
1	172.94	256.26	371.45	256.26	1.4817
2	169.84	259.56	399.79	259.56	1.5283

Tab. 2 shows that after the neutralization of sodium hydroxide, the molecular weight distribution of the resultants is in a range from 100 to 1000 $g \cdot mol^{-1}$, which means that with the

assistant of microwave, the high molecular polymer in the nonmetallic powder has been fully degraded to low molecular weight compounds.

2.2.4.2 Analysis of Gas Chromatography-Mass Spectrum (GC-MS)

Making the neutralized resultans dissolved in acetone solution, and using the GC-MS analyzer (VARIAN 3900-Saturn 2100T, US) to analyze the components. The chromatographic column: VF-5MS (30 m×0.25 mm×0.25μm) fused silica capillary column; the column flow rate is 0.5 mL·min-1; the column temperature rises from 100℃ to 200℃ at a speed of 20 °C·min^{-1}; the injection mode: split stream with a ratio 1:10; the carrier gas: He; GC-MS interface temperature: 250 °C; EI source: 70 eV; the scan range: 40-650. Fig.2 shows the corresponding gas chromatography.

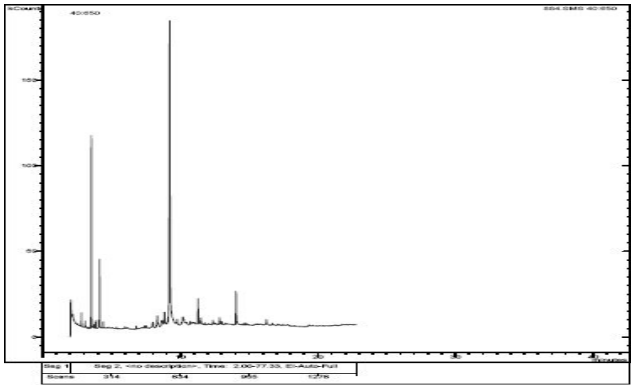

Fig. 2 The gas chromatography of the resultants (800W / 80°C / 40%)

According to Fig. 2., the major resultants include: 2- hexylamine, dcpd dioxide, 1,1,3,3-tetramethyl -1,3- diphenyl disiloxane, butyl cyclohexyl phthalate, etc. Almost all of them are low or no toxic products. On the contrary, LIU Yuyan and others used water bath as the heating medium of nitric acid decomposition reaction. The main resultants are the compounds like 2, 4-dinitrophenol and 2-nitro-4-carboxy-phenol, which are fairly toxic and harmful to the environment.

3. Conclusion

(1) Assisted by microwave, the decomposition rate of the PCB nonmetallic powder grows with the increase of microwave power and acting time. The microwave power can only change the proportion of the resultants' compounds.

(2) The best material ratio is 10 g/100 ml, while the decomposition rate is 64.47%. Through orthogonal experiment, the best reaction conditions are: microwave power 800 w, microwave temperature 80 °C, acid concentration 40%.

(3) In this microwave-assisted decomposition experiment for the PCB nonmetallic powder, the molecular weight distribution of the resultants was within 100-1000 g·mol-1, which proves that the microwave-assisted decomposition of the powder works well.

(4) The major resultants through the process of microwave-assisted decomposition include: 2- hexylamine, dcpd dioxide, 1,1,3,3- tetramethyl -1,3- diphenyl disiloxane, butyl cyclohexyl phthalate, etc. Almost all of them are low or no toxic. It implies that the chemical reactions in the microwave-assisted decomposition are totally different with the ones in other ways.

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