NSC93-2214-E-164-001-

93 08 01 94 07 31

94 10 30

Resource Recovery and Uses on the Catalytic Decomposition of Electronic Molding Resin Materials

ABSTRACT

Electronic molding resin materials including the wastes are produced form electronic packaging process. Its main component is organic matter and silica, and is a potential and economical source of the manufacture of fine ceramic and carbon materials. The purpose of the study is to investigate the effect of catalyst on the thermal decomposition of molding resin material by a thermal gravimetric analysis technique. The physical and chemical characteristics of products are also tested. Experimental results showed the thermal decomposition properties of samples are obviously affected by the addition of catalyst, especially for the kind and loading of catalyst. The decomposed products can be used to prepare the nano-silica and carbon of high surface area. The results of the study can provide the important information on the resource recovery and uses of molding resin materials, and also for the other IC electronic wastes.

Keywords   Electronic molding resin material, Catalyst, Thermal decomposition, Resource recovery and uses, Characteristic analysis

1. INTRODUCTION

Over the past two decades, the electronic packaging industry has grown very rapidly worldwide. Electronic packaging materials are widely used in the encapsulation of electrical devices such as integrated circuits (IC). Electronic packaging uses resin materials with high silica content (60-80 wt%), and residual resins generated during the IC packaging process comprise about 30 - 50 wt % of the total resin compounds. The composition of a typical material used for the IC packaging is epoxy resin, phenol resin, silica and additives. The electronic packaging material is manufactured by melting mixed resins, silica, and additives, after which it is blended, cooled, crushed, and formed into a tablet. Semiconductor chips are sealed with the tablet. The tablet is molded into IC packaging using a conventional transfer molding machine under appropriate condition of curing [1]. The packaging residues of the molding resin are recovered.

Because the waste has been cured with a cross-linking reaction between epoxy resin and hardener in the electronic packaging process. It is hard to melt and decompose, so land-fill is the main method to solve the disposal problem. However, because plastic materials are essentially non-biodegradable, land-fill is currently impracticable. Accordingly, thermal treatment of these materials by pyrolysis or incineration is becoming attractive. In recent years, with the rapid growth of IC packaging, pyrolysis-based technology has been considered as a useful approach to solve the growing quantity of waste. Few studies have been conducted on catalytic pyrolysis of resin compounds containing silica, such as electronic packaging material. This research investigates the effect of catalysts on the pyrolysis of electronic packaging material [2-4].

A resource recovery and uses of molding resin materials is also developed for the experimental results. The decomposed products can be used to prepare the nano-silica and carbon of high surface area. These results should be useful for the pyrolysis or incineration, and recovery uses in which plastic waste from electronic components are involved [5-8].

2. EXPERIMENTAL

2.1 Materials

The samples of electronic packaging material used in the study were supplied by an electronic packaging mill (Siliconware Precision Co., Taiwan). High-purity (99.99 %) nitrogen and air gas were used as the purge and reaction gas. The catalysts used were CuO, Fe_2O_3, Ni_2O_3 and ZSM-5. Analytical grade hydrochloric and sodium chloride were used. H_3PO_4 and $ZnCl_2$ are used as chemical activating agents.

2.2 Experimental procedures

The experiments on the pyrolysis reaction were carried out using a thermogravimetric analysis technique (Perkin-Elmer TGA7) in a nitrogen atmosphere [4]. All samples were in powder form, and the known weight of sample including resin and catalyst is well mixed.

All experiments were performed under non-isothermal conditions. The component of outlet gas during pyrolysis is detected by TG-Mass.

Preparation of nano-silica from molding resin wastes, after pyrolysis the resin, the residual matter and NaOH were boiled in a flask with constant stirring. The solution was filtered and the carbon residue was washed with boiling water. The filtrate is titrated with HCl. The pH of the solution was monitored. After aging, the gel was washed with distilled water repeatedly, and then dried in a vacuum oven.

To prepare the carbon of high surface area from molding resin wastes, the pyrolyzed and base-washed resin is collected. The known amount resin residues were mixed, by stirring with a solution that contained the activating agent (H_3PO_4 or $ZnCl_2$). The carbonization was carried out in a horizontal furnace. The pyrolyzed samples were washed repeated with distilled water, and then were dried at 110 ^{o}C for 24 hr.

3. RESULTS AND DISCUSSION

3.1 Analysis of physical properties

Fig. 1 is electronic micrographs of products obtained by heating catalytic sample in nitrogen. Some pores have been formed when the pyrolysis reaction is completed. The spherical shape of product is the molding filler of silica. The same structural features had been reported by Iwasa et al. [9].

The results of XRD analysis of electronic molding resin before and after pyrolysis are presented in Fig. 2. Fig. 2(a) shows no

characteristic peaks. However, Fig.2(b) has maximum at 2 =22.5 ^{o}C, which is characteristic of silica.
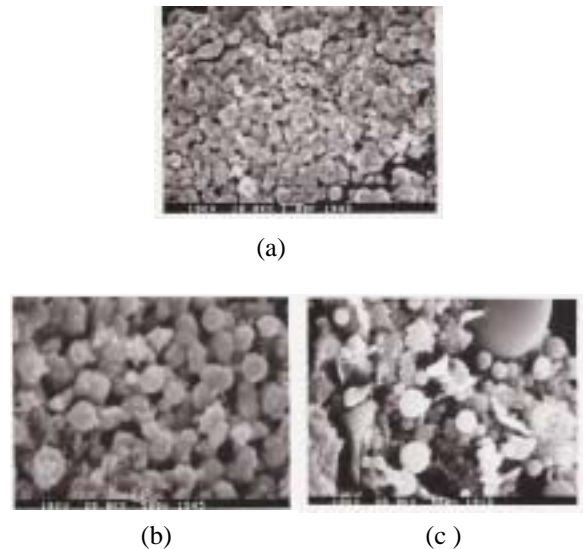

(a)

(b)   (c)

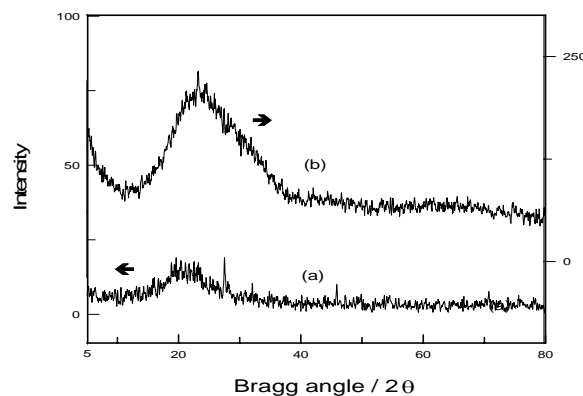Figure 1 Scanning electronic micrographs of specimens.

Figure 2 X-ray diffractogram of electronic packaging materials.

3.2 Effect of catalyst type on the pyrolysis reaction

3.2.1 Effect of cooper oxide catalyst

Fig. 3 shows the effect of cooper oxide catalyst on the pyrolysis of specimen. Experimental results show that pyrolysis temperature is decreased with increasing CuO loading. When the sample loading is 1.0 m mol, the reaction temperature is reached minimally. In addition, the final

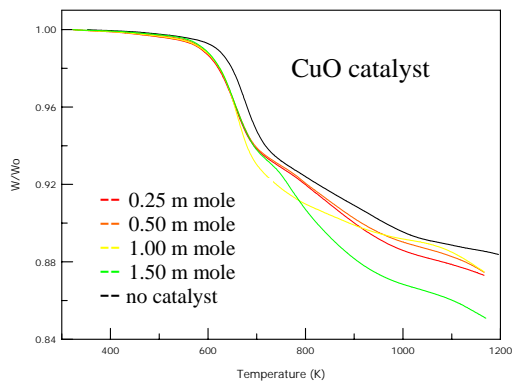residual amounts of sample are decreased with increasing catalyst loading [10].

Figure 3 The effect of cooper oxide catalyst on the pyrolysis properties of molding resin materials.

3.2.2 Effect of ferric oxide catalyst

Fig. 4 shows the effect of ferric oxide catalyst on the pyrolysis of specimen. Experimental results show that, in the first stage, the pyrolysis temperature is increased with increasing Fe_2O_3 loading. However, in the second stage, the effect of catalyst loading on the pyrolysis temperature is not regular. When the sample loadings are 0.25 and 1.0 m mol, the final pyrolysis temperature is reached minimally [11].
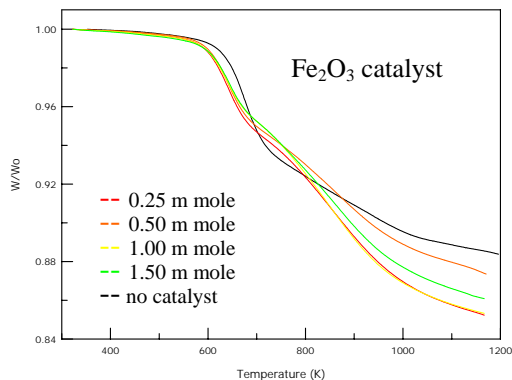

Figure 4 The effect of ferric oxide catalyst on the pyrolysis properties of molding resin materials.

3.2.3 Effect of nickelic oxide catalyst

Fig. 5 shows the effect of nickelic oxide catalyst on the pyrolysis of specimen. Experimental results show that the pyrolysis temperature is increased with increasing Ni_2O_3 loading. When the sample loadings are 0.50 m mol, the final pyrolysis temperature is reached minimally.
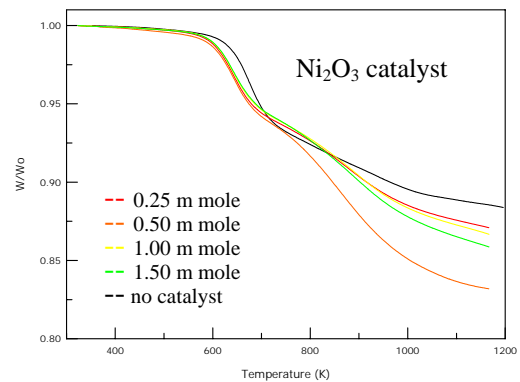

Figure 5 The effect of nickelic oxide catalyst on the pyrolysis properties of molding resin materials.

3.2.4 Effect of ZSM-5 catalyst

Fig. 6 shows the effect of ZSM-5 catalyst on the pyrolysis of specimen. Experimental results show that in the first stage, the pyrolysis temperature is decreased with increasing ZSM-5 loading. However, in the second stage, the effect of catalyst loading on the pyrolysis temperature is not regular. When the sample loadings are 10.0
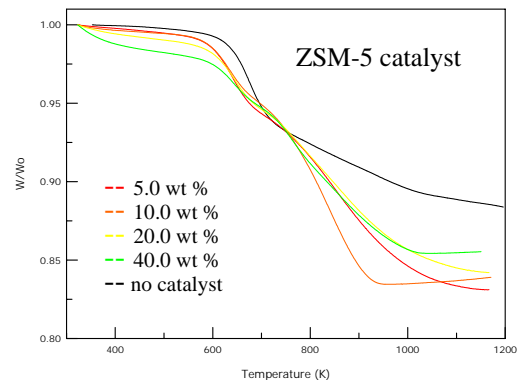

Figure 6 The effect of ZSM-5 catalyst on the pyrolysis properties of molding resin materials.

wt %, the final pyrolysis temperature is reached minimally [12-13].

3.2.5 Analysis of outlet gas during pyrolysis by TG-Mass

Fig. 7 shows the result of outlet gas during pyrolysis by TG-Mass. The main gases produced during pyrolysis include H_2O, CO, CO_2, etc. However, outlet gas of higher molecular weight and few amounts, which beyond 100 a.m.u., are also found.
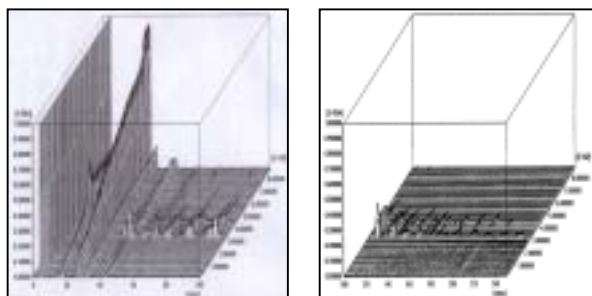

Figure 7 The component of outlet gas during pyrolysis by TG-Mass.

3.3 Preparation of silica ceramic materials for nanometer grade

The nitrogen adsorption-desorption isotherms for silica sample prepared by burning-only and sol-gel technique, are shown in Fig. 8. Fig. 8 (a) shows no obvious hysteresis loop for the burning-only silica sample. Fig. 8(b) shows a hysteresis loop, indicating that the nano-silica product is a porous material. For burning-only silica sample, the specific surface area of is 2.7 m^2/g, the total pore volume is 0.0062 ml/g, and the average pore diameter is 9.1 nm. However, for nano-silica sample, the specific surface area of is 600 m^2/g, the total pore volume is 0.62 ml/g, the average pore diameter is 5 nm, and the powder size is 60 –

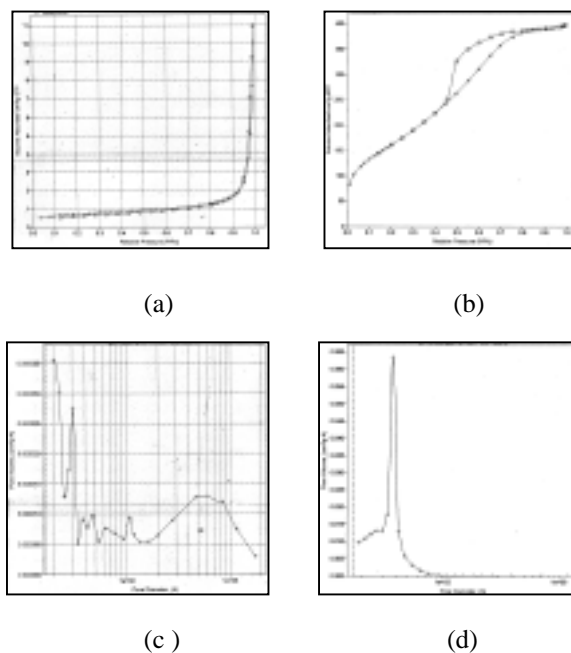100 nm[14-15].

| (a) | (b) |
| (c) | (d) |

Figure 8 The adsorption-desorption isotherms and differential pore size distribution of burning-only silica and nano-silica.

3.4 Preparation of carbon materials for high surface area and high porosity

The nitrogen adsorption-desorption isotherms for carbon sample prepared by $ZnCl_2$ and H_3PO_4 activation, are shown in Fig. 9. The H_3PO_4 activation isotherm displays a sharp knee and a narrow loop, while the $ZnCl_2$ activation sample reveals a broad knee and a more obvious loop. For $ZnCl_2$ activation sample, the specific surface area of is 1250 m^2/g, the total pore volume is 0.8732 ml/g, and the average pore diameter is 2.6 nm. However, for H_3PO_4 activation sample, the specific surface area of is 430 m^2/g, the total pore volume is 0.25 ml/g, the average pore diameter is 2.4 nm [16-18].

4. CONCLUSIONS

Catalytic pyrolysis of electronic

(a)   (b)
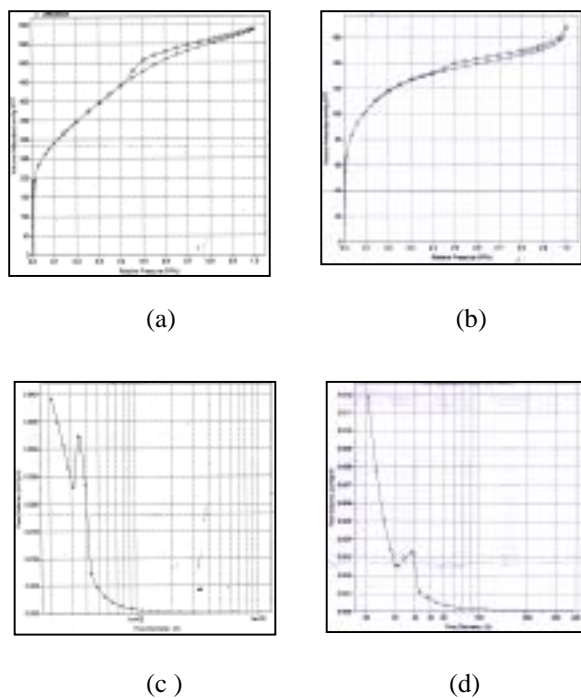

(c)   (d)

Figure 9 The adsorption-desorption isotherms and differential pore size distribution of carbon prepared from ZnCl$_2$ and H$_3$PO$_4$ activation.

packaging material in a nitrogen atmosphere is described. Experimental results showed that catalyst plays a key role in the decomposition of electronic molding resin materials. The advantages include to enhance the reaction rate, reduce the reaction temperature, etc. It has been a potential and economical source of the manufacture of fine ceramics and carbon materials. The results thus obtained may be provided as some of the basic design information needed for the treatment of molding resin waste. In addition, the study is also useful for the resource recovery and uses of plastic waste from electronic components, thus helping to solve the disposal and pollution problems.

REFERENCES

[1]Arai, K., Tomikichi, K. Shiohara, T. Expoy resin composition with good flowability, storage stability, and curability and semiconductor device sealed with it, Patent JP 11263826 A2, 1999.

[2]Iji, M., Ikuta, Y. Pyrolysis-based material recovery from molding resin for electronic parts, J. Environ. Eng. 124, 821,1998.

[3]Liou, T. H., Kinetics study of thermal decomposition of electronic packaging material. Chem. Eng. J., 98(1-2), 39, 2004.

[4]Liou, T. H., Pyrolysis kinetics of electronic packaging material in a nitrogen atmosphere. J. Hazar. Mater., 103(1-2), 107, 2003.

[5]Jesionowski, T., Characterization of silicas precipitated from solution of sodium metasilicate and hydrochloric acid in emulsion medium. Powder Technology. 127, 56, 2002.

[6]Teng, H., Wang, S. C., Preparation of porous carbons from phenol-formaldehyde resins with chemical and physical activation. Carbon. 38, 817, 2000.

[7]Chen, K. S., Yeh, R. Z., Wu, C. H., Kinetics of thermal decomposition of epoxy resin in nitrogen-oxygen atmosphere, J. of Environ. Eng. 123, 1041, 1997.

[8]Budrugeac, P. Non-isothermal degra-dation kinetics of glass-reinforced epoxy resin, Thermochimi. Acta. 221,229, 1993.

[9]Iwasa, M., Yamamoto, K., Takahashi, K., Jpn. Pat. JP 08245214 ,1996.

[10]Juang, R. S., Lee, T. S., Oxidation pyrolysis of organic ion exchange resin

in the presence of metal oxide catalysts. J. Hazar. Mater., B92, 301, 2002.

[11]Brebu, M. Bhaskar, T., Murai, K., Muto, A., Sakata, Y., Uddin, M. A., Thermal degradation of PE and PS mixed with ABS-Br and debromination of pyrolysis oil by Fe- and Ca-based catalysts. Polymer Degradation and Stability, 84, 459, 2004.

[12]Marcilla, A., etc., Catalytic cracking of ethylene-vinyl acetate copolymer: comparision of different zeolites. J. Anal. Appl. Pyrolysis, 68-69, 495, 2003.

[13]Vasile, C., Hooshang, P., Brebu, M., Petru, O., Darie, H., Ciocalteu, S., Thermal and catalytic decomposition of mixed plastics. J. Anal. Appl. Pyrolysis,57, 287, 2001.

[14]Sierra, L., Lopez, B., Guth, J. L., Preparation of mesoporous silica particles with controlled morphology from sodium silicate solutions and a non-ionic surfactant at pH values between 2 and 6. Micro. Meso. Mater., 39, 519, 2000.

[15]Wang, Z., Yang, H., Wang, L., Zhao, M., Mater. Sci. Eng., B48, 211, 1997.

[16]Liou, T. H., Evolution of chemistry and morphology during the carbonization and combustion of rice husk. Carbon, 42(4), 785, 2004.

[17]Hayashi, J., etc., Carbon, 38(13), 1873, 2000.

[18]Danny, C. K., David, H. K., Tsang, J. F., Gordon, M., Applications of multipore model for the mechanism identification during the adsorption of dye on activated carbon and bagasse pith. Langmuir, 19, 722, 2003.

IC