Chemical Engineering Journal 98 (2004) 39–51

Chemical Engineering Journal
www.elsevier.com/locate/cej

Kinetics study of thermal decomposition of electronic packaging material

Tzong-Horng Liou*

Department of Chemical Engineering, Hsiuping Institute of Technology, Taichung 412, Taiwan, ROC

Received 17 April 2003; accepted 9 June 2003

Abstract

A high-purity silica was obtained from thermal decomposition of molding resin used as electronic packaging materials. The reaction was performed at high temperature and in oxidizing atmosphere. The product was suitable for reuse as inorganic filler in the production of semiconductor devices, as well as the starting materials in the manufacture of silicon materials. Thermal decomposition kinetics of the electronic packaging material were investigated under various reaction parameters including gas flow rate, sample loading, grain size, oxygen concentration and heating rate by using a thermogravimetric analysis (TGA) technique. The results indicated that thermal degradation of electronic packaging material consisted of two distinct reaction stages. The corresponding kinetic parameters including the activation energy, pre-exponential factor, and reaction order in the chemical reaction-controlled region are presented. A mechanism of thermal decomposition was proposed, which is in good agreement with the experimental results.

Keywords: Electronic packaging material; Thermal decomposition; Kinetics; Mechanism; Silica

1. Introduction

The technology of semiconductor microelectronic materials manufacturing has progressed at an astonishing rate during the past decade. This is true especially for electronic packaging materials, which affect the quality and useful life of the semiconductor products. Because of good insulating, adhesive, and heat-resistant properties, the electronic packaging materials are mainly used in the packaging of electronic devices such as integrated circuits (ICs).

Packaging residues generated in the IC encapsulating process comprise 30–50 wt.% of the total resin compounds, and the recent increased production of electronic compounds has resulted in a rapid increase in the amounts of such waste produced. Because most methods of disposal or land-fill are currently impracticable. Therefore, thermal decomposition of the packaging residue is becoming an attractive solution to the pollution problem.

Thermo-oxidative decomposition of electronic packaging materials is an important industrial process since large quantities of valuable silica (SiO_2) can be obtained by removing volatile constituents during thermal decomposition of electronic packaging materials in an oxidizing atmosphere. This process has attracted much attention to for recovering and reducing the severity of the total waste problem. Iji and Ikuta [1] reported that the recovered silica from the combustion of electronic packaging material can be used as inorganic filler for cast-insulating materials and for molding resin used in electronic components. The electronic and mechanical properties of the compound using the recovered silica were superior than those of the compound with the original silica.

The major constituents of electronic packaging material are resins, silica, and additives. The resins consist of epoxy resin (thermosetting resin, used as adhesive, waterproof, insulated agent) and phenol resin (used as hardener). Ash, amounting to approximately 80 wt.%, is obtained on burning the electronic packaging material in air. This ash contains 80–90 mass% silica with a small proportion of metallic elements. The silica is used to minimize the shrinkage during resin curing, improve mechanical properties, and reduce the cost of the material. The additives contain a flame retardant composed of organic bromine compounds and antimony oxide. 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 [2]. The packaging residues of the molding resin are recovered.

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* Tel.: +886-4-24961198; fax: +886-4-24961185.
E-mail address: liouth@mail.hit.edu.tw (T.-H. Liou).

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doi:10.1016/S1385-8947(03)00181-5

Nomenclature

A	pre-exponential factor (min^{-1})
C	char
E	activation energy (kJ/mol)
f	function of conversion
I	intermediates during thermal decomposition of resins
k	thermal decomposition rate constant (min^{-1})
M	epoxy resin
n	reaction order
P	phenol resin
R	gas constant = 8.314 (kJ/kmol K)
t	thermal decomposition time (min)
T	thermal decomposition temperature (K)
V_1, V_2, V_3	volatiles
W	weight of sample at time t (mg)
W_0	initial weight of sample (mg)
W_∞	final weight of sample (mg)
X	conversion of electronic packaging material
Greek letters	
β	heating rate (K/min)

The temperature of thermal decomposition may affect the nature of the product (silica) and consequently the quality of recycled electronic material. A lower heating temperature yields the products incompletely decomposed, but a higher heating temperature requires more energy resources. Therefore, it is preferable to treat electronic packaging material with an optimal thermal decomposition procedure, so as to obtain highly purity silica powder.

In the previous literature, the manufacturing procedure of electronic packaging materials is extensively reported. However, few studies have been conducted on recovering useful materials from electronic packaging residues, such as silica. Similar research has been performed on the pyrolysis or burning of thermosetting materials such as epoxy resin or novolac resin [3–8]. Iji and Ikuta [1] observed that combustion exhaust gas containing bromine compounds is generated during the thermal decomposition of electronic packaging material. Budrugeac [9] observed that the major loss of mass during thermal decomposition of glass-reinforced epoxy resin was attributed to formation of volatile products. In addition, the total thermal degradation process is an exothermic reaction.

Previous authors focused on thermal decomposition pretreatment of electronic packaging materials. However, the kinetics of thermal decomposition of electronic packaging materials has received little attention. This research investigates the effect of thermal treatment on the decomposition of electronic packaging materials in order to produce a high-purity silica. The thermal decomposition kinetics of electronic packaging materials are investigated by thermogravimetric analysis (TGA) technique. The kinetic parameters and effect of operating variables on the overall reaction rate are extensively investigated. A mechanism is also developed to account for the experimental results.

The method proposed in this study not only has the benefit of recovering silica used in electronic packaging components, but also may be a potentially attractive method to produce the other silicon materials, such as silicon nitride powder [10,11], and silicon carbide [12], as well as for use as a source of silicon in metallurgical and semiconductor grades. Simultaneously, it solves problems of disposal and pollution created during burning of packaging waste in which thermosetting plastic wastes are involved.

2. Materials and methods

2.1. Material used and sample preparation

The raw material was electronic packaging material obtained from an electronic packaging mill (Siliconware Precision, Taiwan), consisting of epoxy resin, phenol resin, silica and additives. The samples were washed thoroughly with distilled water to remove dust or dirt, and then dried in air at 373 K in an oven.

The water-rinsed samples were pulverized, and then were ground and screened through an ASTM standard sieve to obtain the desired grain sizes. High-purity (99.99%) air (San-Fu Chem.) was used as the reaction gas. Oxygen concentration in the flow gases was measured to be 21 vol.%. For some experiments, high-purity (99.99%) nitrogen (San-Fu Chem.) was used to regulate the concentration of the reaction gas.

2.2. Apparatus and procedures of thermal decomposition

The preparation of silica was carried out using a combustion reaction in a tubular reactor made of quartz. A weighted amount of sample was packed into the reactor, and highly purified air was used as reaction gas. The reactor was inserted into a furnace and heated at the desired rates.

A Perkin-Elmer TGA7 thermogravimetric analyzer was used for the thermal decomposition measurement, as shown in Fig. 1. A known weight of sample was placed in a platinum sample pan. The reaction gas passed through the furnace tube was first introduced at a large rate of flow to purge residual impurities within the system, and then adjusted to the desired rate of flow. When the experimental runs were begun, the computer continuously recorded the mass and temperature for the entire period. The samples were heated up to 1000 K at the desired rates. The various reaction parameters selected in the present study include gas flow rate,

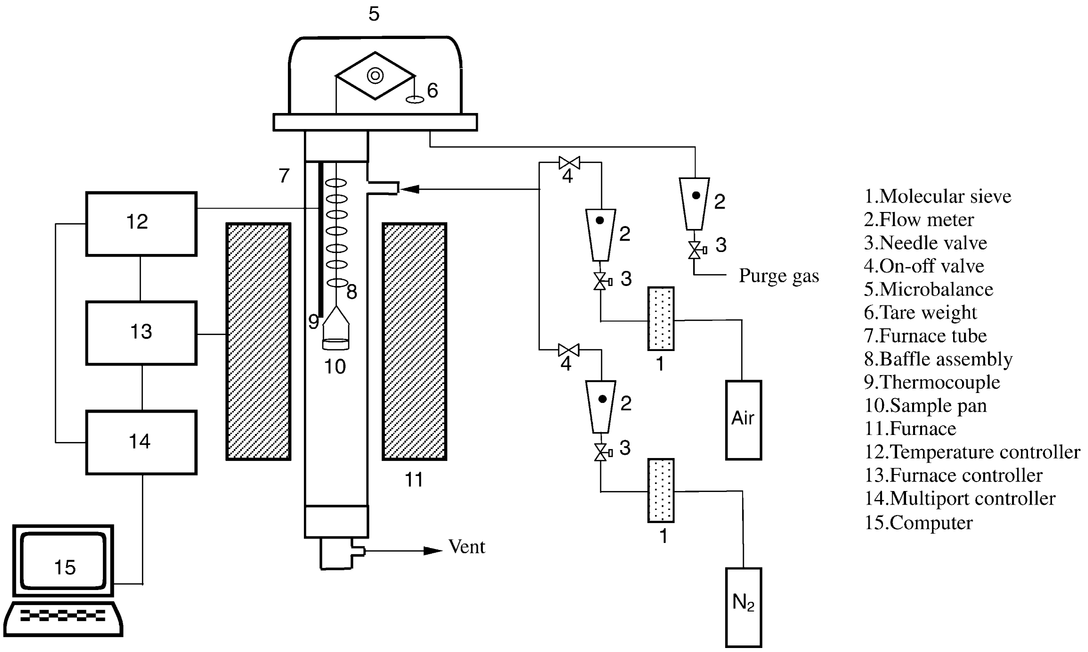


Fig. 1. Schematic diagram of the experimental apparatus for thermal decomposition of electronic packaging material.

sample loading, powder grain size, oxygen concentration and heating rate. Several tests were performed to ensure that the sampling technique employed was valid. Experimental accuracy was also confirmed by examining the mixing condition effect on the oxidation reaction. The W_0 and W are defined as initial and instantaneous masses of sample, respectively. Once the two masses had been read from TGA, the remaining amount (W/W_0) was readily obtained according to a simple calculation.

After thermal decomposition, the samples were purified, following the technique of previous studies [13,14]. HCl used for acidic treatment was all of laboratory grade (Merck). The ash produced after thermal decomposition was refluxed with an acidic solution. It was then filtered and washed repeatedly with distilled water until the filtrate was free from acid. The leached sample was then dried at 373 K for 24 h.

2.3. Analysis of metallic impurities and organic elements

The metallic impurities of unreacted, reacted and purified samples were determined with an inductively coupled plasma-mass spectrometer (Kontron Plasmakon, model S-35). Before analysis, the samples were dissolved in a solution of HNO_3 and HF, and then heated at 453 K for 6 h. To determine the amount of fundamental organic element contained in the samples, elemental analysis was conducted with an Heraeus elemental analyzer. The dried sample was powdered to 325 mesh size (ASTM), and this powder was employed in the analysis.

2.4. Analysis of physical properties

X-ray diffraction (XRD) analysis was undertaken with an X-ray diffractometer (Siemens, model D-500) using Cu Kα radiation. Electron micrographs were obtained with a scanning electron microscope (Topcon, model ABT-150S). The surface area and pore structure of the sample were measured with a nitrogen adsorption apparatus (Micrometric, model ASAP 2000). Infrared spectra of unreacted, and reacted as well as purified samples in the region of 400–4000 cm^{-1} were recorded with an infrared spectrometer (Shimadzu, model FTIR-8300).

3. Results and discussion

3.1. Analysis of metallic impurities and organic elements

The results of analysis of metallic ingredients in water-rinsed, thermally decomposed, and acid-leached samples appear in Table 1. The main metallic impurities present in samples are antimony, iron, sodium, aluminum and chromium; of which the concentration of antimony is greater than the others. The metals were effectively removed to a substantially decreased concentration on burning electronic packaging material with air. The proportions of residual metal elements in the samples treated with HCl are clearly lower than those treated with only burning. The decreased impurities may result from chemical reactions between acid and metals, after which the reacted metals are leached from

Table 1
Amount of metallic ingredients in the electronic packaging material

	Metallic ingredients as oxides (ppm)										
	Sb	K	P	Au	Fe	Na	Mg	Al	Cr	Ag	Total
Water-rinsed	11800	<8	96	<8	5780	240	53	3140	1580	<8	22713
Thermally decomposed[a]	6100	<8	75	<8	91.5	87	101	501	8.7	<8	6988.2
Acid-leached[b]	1400	<8	50	<8	35	15	82	53	<8	<8	1667

[a] Heated at 5 K/min in air.
[b] Heated at 5 K/min in air and leached by HCl.

the acidic solution during filtration. About 93% of impurities were extracted after treatment of sample with HCl.

The fundamental components of electronic packaging materials by element analysis are listed in Table 2, as treated with different processes. The major elements are carbon 15.95 wt.%, hydrogen 1.98 wt.%, oxygen 1.68 wt.%, and nitrogen 0.17 wt.%. The remaining consists of ash at 80.22 wt.%. After thermal decomposition or purification, the percentage of organic matters is clearly decreased. Table 2 also shows that the percentage of ash in the burnt samples is increased from 80.22 to 98.70 wt.%.

When electronic packaging material was heated at 5 K/min in air, and then treated with acid-leached process, a high-purity of SiO_2 was obtained. This resulting material is suitable for use as starting material in the preparation of inorganic filler used as electronic packaging process, as well as in the manufacture of the silicon materials.

3.2. *Analysis of physical properties*

In order to quantify the effect of starting grain sizes on reaction rate, various grain size of samples were used, as listed in Table 3. The table indicates that the various grain sizes of the electronic packaging material have clear effect on the total specific surface area, with finer powder having larger specific surface area. According to the observation of adsorption isotherms (plot of volume adsorbed vs. relative pressure (P/P_0)) of the samples, no hysteresis loop which would be associated with capillary condensation, is observed. This indicates that the pore structures of the reactants are all nonporous or macroporous. In the coarse grain sample, the total cumulative pore volume is smaller than that of the fine grain sample. However, the average pore diameter in the coarse grain sample is larger than that of the fine grain sample. We can conclude that the mechanical treatment will have large effect on the specific area and pore structure. After thermal decomposition of the sample, higher specific area (2.72 m^2/g) and total cumulative pore volume (0.0062 ml/g) are observed, indicating that the burnt product is a porous material.

The results of XRD analysis of electronic packaging material treated with various processes are presented in Fig. 2, showing no characteristic peaks. This indicates that the original, thermally decomposed or purified samples are all in completely amorphous form. However, the thermally decomposed and purified samples (Fig. 2(b) and (c)) have a maximum at $2\theta = 22.5^\circ$, which is characteristic of silica. Iji and Ikuta [1] reported the XRD patterns of burnt electronic packaging material showed that only silica was observed after heating at 1473 K. The result is consistent with this present study.

FTIR spectra of the unreacted sample, and residue obtained from heating and purifying the sample are shown in Fig. 3. There is a slight change in the FTIR spectrum before and after thermal decomposition. Comparison of Fig. 3(a) and (b), the disappearance of the absorption bands at $\sim$1200 and $\sim$1250 cm^{-1}, as well as the increase in intensity of the bands at $\sim$475, $\sim$805, and $\sim$1115 cm^{-1}, are indications of the completion of decomposition of the organic constituents. The purified ash sample has a spectrum similar to that of silica in a commercial grade. It can be concluded that the residue obtained from thermal-oxidative and acid-leached electronic packaging material is a high quality of silica powder.

Table 2
Elemental composition of the electronic packaging material

	Composition (wt.%)				
	C	H	O	N	Ash
Water-rinsed	15.95	1.98	1.68	0.17	80.22
Thermally decomposed[a]	1.18	0.32	0.00	0.04	98.46
Acid-leached[b]	0.97	0.30	0.00	0.03	98.70

[a] Heated at 5 K/min in air.
[b] Heated at 5 K/min in air and leached by HCl.

Table 3
Surface area and pore characteristic of the electronic packaging material

	BET surface area (m^2/g)	Total pore volume (ml/g)	Average pore diameter, Å (4V/A)
<32 μm[a]	1.3781	0.003935	100.3476
32–38 μm[a]	1.1345	0.003067	102.9836
38–45 μm[a]	1.0933	0.002822	103.2638
45–53 μm[a]	0.7050	0.001522	108.3501
53–63 μm[a]	0.4086	0.001135	111.1061
Thermally decomposed[b]	2.7162	0.006226	91.6900

[a] Sample was ground and unreacted.
[b] Sample was ground to 325 mesh size (ASTM) and heated at 5 K/min in air.

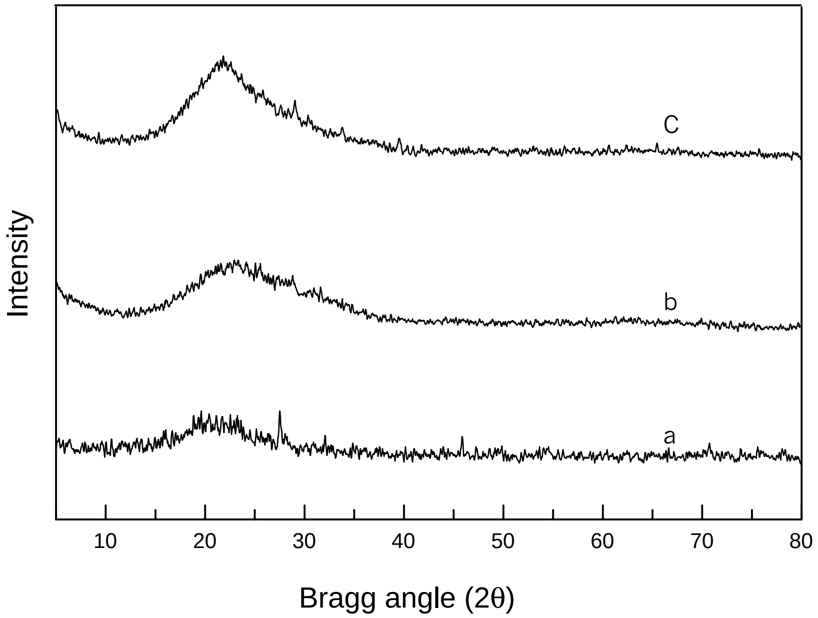


Fig. 2. X-ray diffractogram of electronic packaging material: (a) unreacted specimen; (b) reacted specimen at 5 K/min in air; (c) reacted specimen at 5 K/min in air and leached by HCl.

Typical scanning electron micrographs illustrating the morphological variation of electronic packaging material samples and thermal decomposition products are shown in Fig. 4. Fig. 4(a) shows the apparent surface of original material is smooth and nonporous, which is consistent with the results of pore structure measurement, as indicated in Table 3. Fig. 4(b) shows that the parts of spherical silica having average grain diameter of 0.42 μm are distributed within specimen. The spherical morphology is also pointed out by Arai et al. [2]. After thermal decomposition, Fig. 4(c) indicates that some small pores have been formed for the partially reacted specimen. The same observation is verified by pore structure measurement (Table 3). Fig. 4(d) indicates that the greater part of silica produced is in the form of irregular grains. However, a small part of the silica is produced in spherical structures.

3.3. Effect of gas flow rate

For a gas–solid reaction system, increasing the gas flow rate would favor on increased thermal decomposition rate, and the resistance of external mass transfer may be neglected.

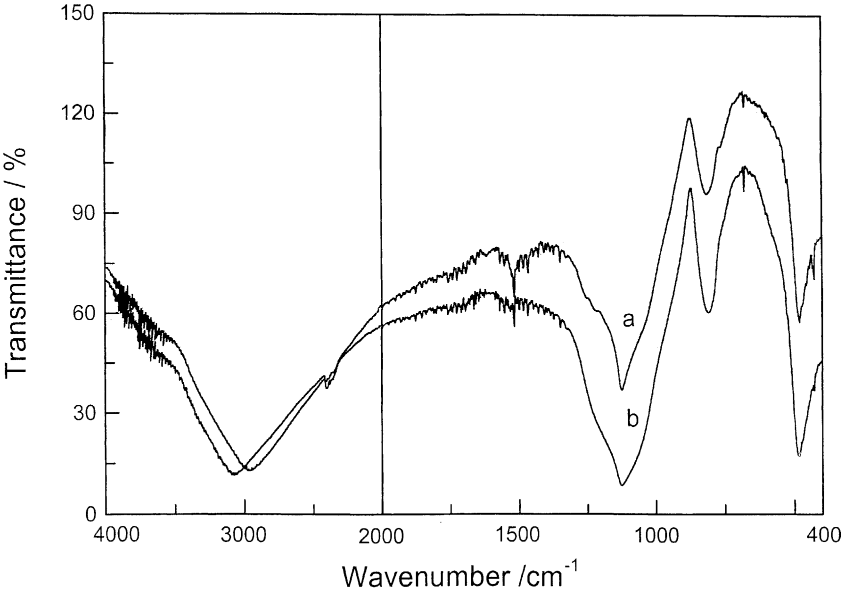


Fig. 3. FTIR spectrogram of electronic packaging material: (a) unreacted specimen; (b) reacted specimen at 5 K/min in air and leached by HCl.

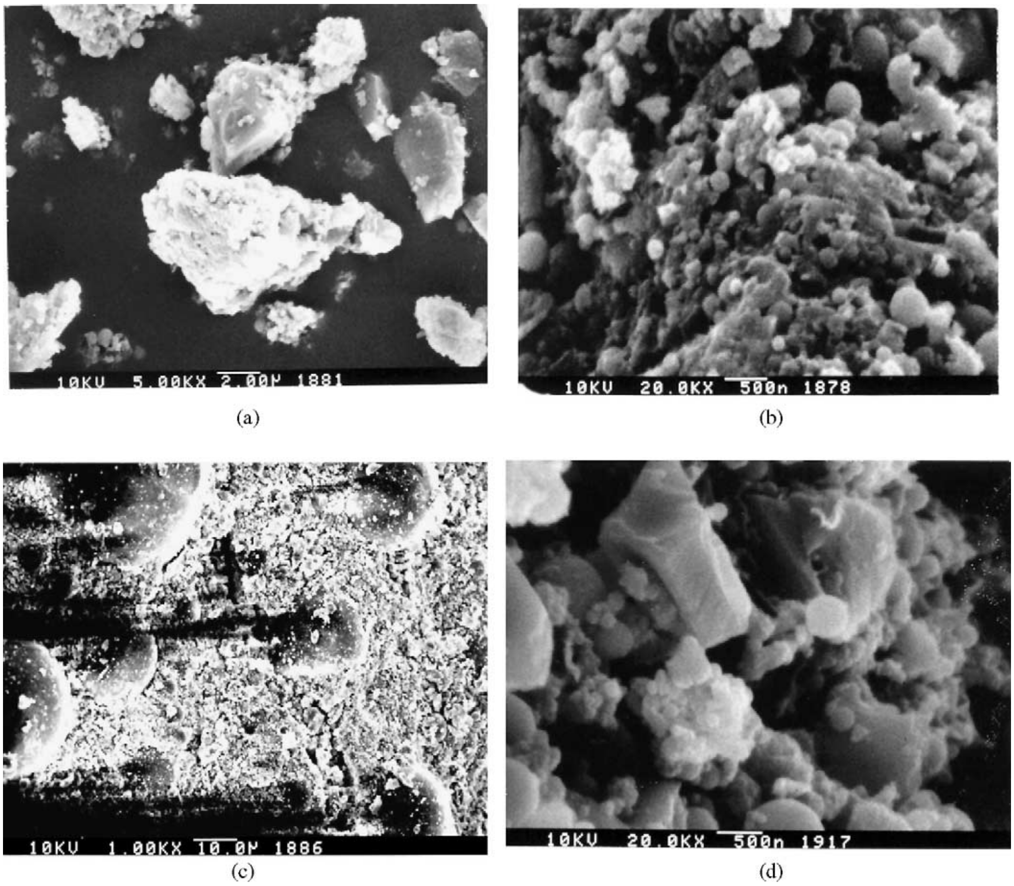


Fig. 4. Scanning electron micrographs of electronic packaging material: (a) powder of unreacted specimen (5000×); (b) inner surface of unreacted specimen (20,000×); (c) reacted specimen at 5 K/min in air (1000×); (d) inner surface of reacted specimen at 5 K/min in air (20,000×).

Fig. 5 shows the remaining amount of reactant plotted as a function of temperature under various gas flow rates. The change of gas flow rate has no effect on the remaining amounts when the gas flow rate is increased to 100 ml/min. The result indicates that the external mass transfer through gas film resistance of the powder can be neglected under the gas flow rate used. Vogt [15] reported that a large number of volatile compounds are formed during thermal degradation of epoxy resin. In order to increase the rate of thermal decomposition, the gas volatiles (such as alkane and alkene compounds) must be removed as soon as possible. Hence, a higher flow rate of air would be favorable in maintaining a low gas products concentration and would also provide a more efficient reaction of reactant and oxygen to silica. Experimental results show that the yield of silica is about 83 wt.%.

3.4. Effect of sample loading

For an intrinsic chemical reaction system, reducing the sample loading would be favorable for the reaction to take place uniformly around the specimen.

Fig. 6 shows that the reaction rate increases with decreasing sample loading. When the sample loading is smaller than 40 mg, the reaction rate is unaffected. This indicates that the effect of resistance to thermal and mass transfer on thermal decomposition is eliminated on placing small amounts of specimen into the sample pan. For a larger loading of sample, air cannot easily flow throughout the sample, reducing the reaction rate. In addition, Budrugeac [9] previously reported that the thermal decomposition of resin is highly exothermal. Hence, increasing the sample loading not only adversely releases the reaction heat, but also may result in a large temperature gradient around the sample during thermal decomposition. The result will affect the equilibrium of thermal decomposition, and reduce the reaction rate.

3.5. Effect of grain size of reactant

Fig. 7 shows that the reaction rate is significantly increased with smaller grain size. It is observed that the yield of silica for heating temperatures up to 825 K ranges from 79.0 to 86.5 wt.%, increasing with increasing grain size. The results indicate that sample segregation takes place during grinding. It is probable that fines produced have a higher resin content than the coarse particles, and therefore result in higher yield is observed for the coarse particles.

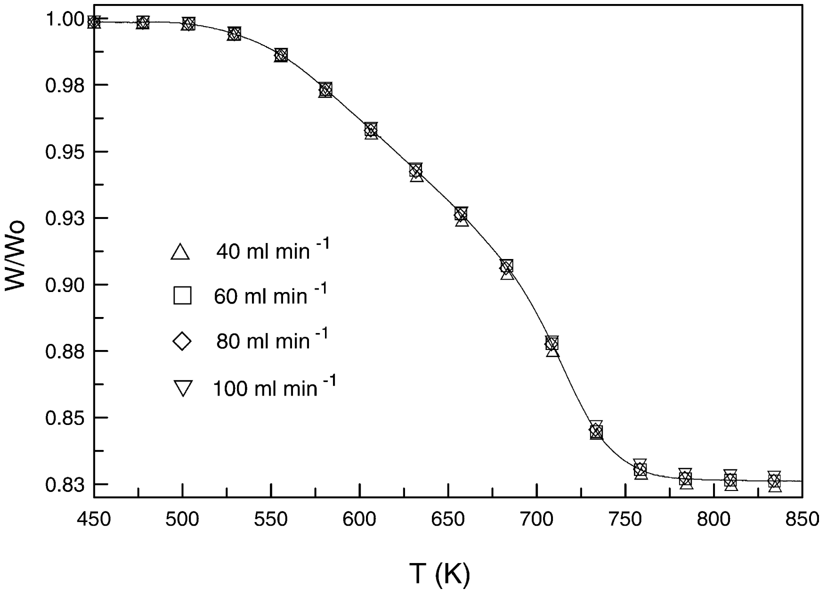


Fig. 5. Effect of gas flow rate on the thermal decomposition of the specimen. Initial conditions: sample loading, 10 mg; initial grain size, 38–45 μm; oxygen concentration, 21 vol.%; heating rate, 5 K/min.

3.6. Effect of oxygen concentration

The present investigation used air as reaction gas, and the nitrogen was used to regulate the concentration of the reaction gas. Fig. 8 illustrates the relationship between oxygen concentration and the amount of residues remaining during heating at 5 K/min. The rate of thermal decomposition in low oxygen concentration is much slower than that of in high oxygen concentration. However, the final temperature of thermal decomposition in low oxygen concentration is higher than that of in high oxygen concentration. This is because nitrogen acts an inert gas to dilute the oxygen concentration, which will decrease the probability of collision between oxygen and reactant, thus slowing down the rate of thermal decomposition. The same tendency is also observed by Chen et al. [16] for the thermal decomposition of epoxy resin in an oxidizing system.

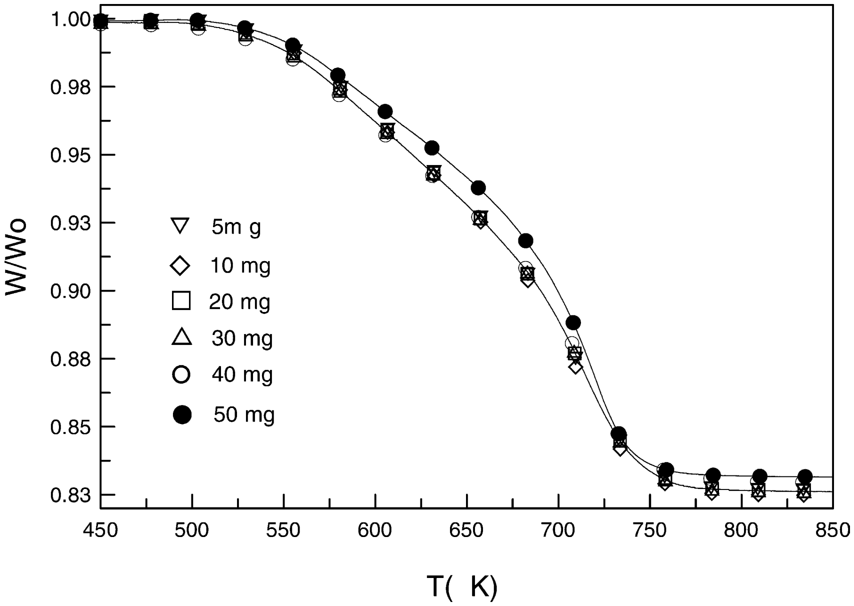


Fig. 6. Effect of sample loading on the thermal decomposition of the specimen. Initial conditions: gas flow rate, 60 ml/min; initial grain size, 38–45 μm; oxygen concentration, 21 vol.%; heating rate, 5 K/min.

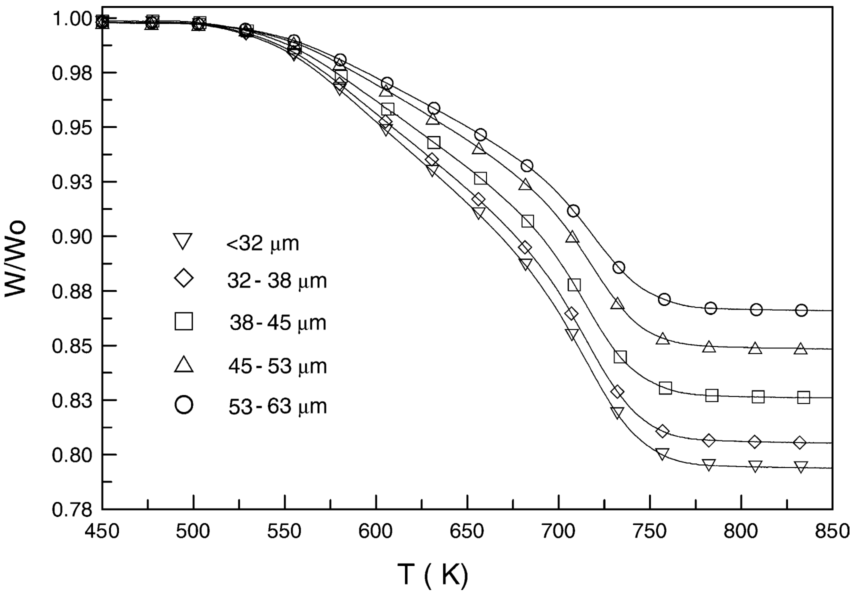


Fig. 7. Effect of grain size on the thermal decomposition of the specimen. Initial conditions: gas flow rate, 60 ml/min; sample loading, 10 mg; oxygen concentration, 21 vol.%; heating rate, 5 K/min.

4. Kinetics analysis

4.1. Effect of temperature on thermal decomposition

When the gas flow rate exceeds 40 ml/min and the sample loading is smaller than 40 mg, the resistance due to mass transfer is negligible, and the overall rate of thermal decomposition reaction-controlled by chemical kinetics can be obtained. The degree of conversion of electronic packaging material, X, is defined here as

$$X = \frac{W_0 - W}{W_0 - W_\infty} \qquad (1)$$

where W_0, W and W_∞ represent initial, instantaneous and final masses of sample, respectively.

Fig. 9 presents plots of conversion vs. temperature of electronic packaging material decomposed in air at a heating rate of 2, 5 or 10 K/min. The total temperature range of thermal decomposition is within 500–825 K. The conversion increased because of loss in mass during thermal decomposition, representing the mass of volatile matter removed. For all three heating rates, a single inflection point is observed during the reaction, indicating that there are two principal stages of reaction distinguished by two significant and distinct variations of conversion. For a given

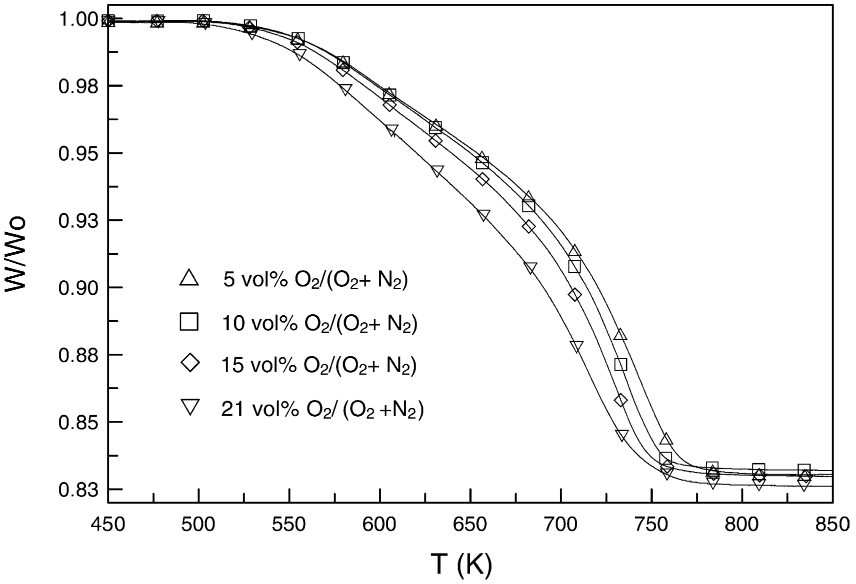


Fig. 8. Effect of oxygen concentration on the thermal decomposition of the specimen. Initial conditions: gas flow rate, 60 ml/min; sample loading, 10 mg; initial grain size, 38–45 μm; heating rate, 5 K/min.

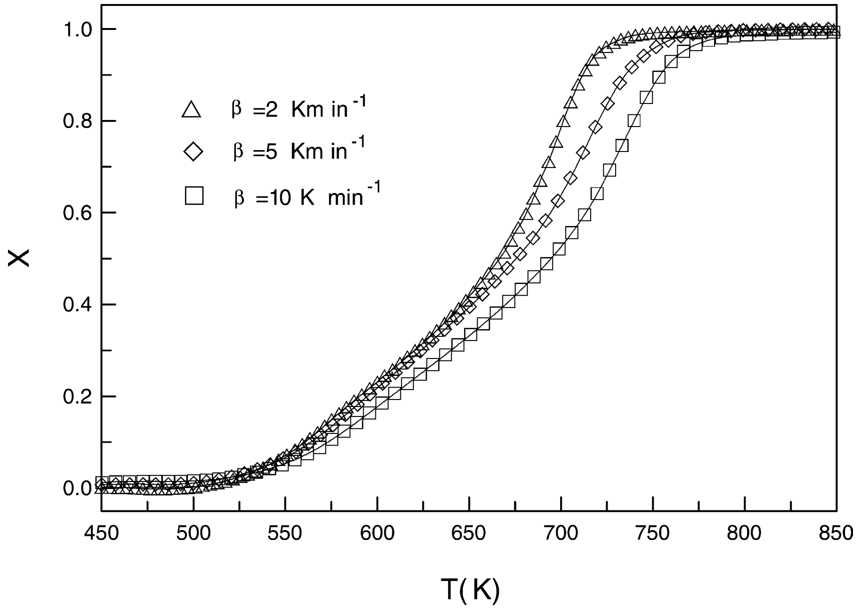


Fig. 9. Effect of heating rate on the thermal decomposition of the specimen. Initial conditions: gas flow rate, 60 ml/min; sample loading, 10 mg; initial grain size, 38–45 μm; oxygen concentration, 21 vol.%.

conversion, the corresponding temperature for thermal decomposition at a small rate of heating is less than that at a large rate of heating. The reason for this phenomenon is that as the heating rate increases, the time interval during which the sample is exposed at a given temperature decreases. The same tendency was also observed by Iji and Ikuta [1].

During the thermal decomposition, it can be clearly observed that the volatilization of gas products is accompanied by the formation of tar. From the variation of conversion shown in Fig. 9, about 55% of conversion is observed in first stage, when the temperature varied from 500 to 675 K for all three heating rates. The increase of conversion in the first stage may be due to evolution of volatile matter. This phenomenon may result from breakdown or depolymerization of the original resin constituents that are further decomposed to yield volatiles and char. The second stage, when the temperature varied from 675 to 825 K, is mainly attributed to dehydration or oxidation of residual resin components (or char) that decompose to yield gases and the other char. The slope of the heating curves in the second stage is slightly larger than in the first stage, indicating that part of the reactant is not easily decomposed in the beginning stage. When the temperature exceeded 825 K, the electronic packaging materials were almost completely decomposed, and a higher reaction temperature did not affect the loss of mass.

4.2. Rate of reaction

Fig. 10 shows the variations in rate of conversion ($\mathrm{d}X/\mathrm{d}t$) during thermal decomposition of electronic packaging material with respect to temperature. There are two distinct peak rates in each heating rate, for which two stages of thermal degradation are involved under air. The reaction zone shifts to a greater range of temperature when the heating rate is increased, and the peak height also increases. A similar observation was also reported by Chen et al. [16]. It may be that with increased heating rate, the duration of retention is shorter, and therefore the temperature required for resin matter to decompose is also higher. This causes the maximum rate curve to shift to the right. Furthermore, with a larger rate of heating, a larger instantaneous thermal energy is provided in the system, which also results in a larger instantaneous rate. Liou et al. [14] reported the pyrolysis kinetics of husk in nitrogen atmosphere, and also obtained the same conclusion. According to the results in Fig. 10, the maximum decomposition rate occurs from 560 to 600 K in the first stage, and 695–730 K in the second stage for the three rates of heating.

4.3. Activation energy

In a previous report, Liou et al. [14] used the Friedman method [17] to evaluate the apparent kinetic parameters E, A, and n of pyrolyzed husk from the TG data. The derivation of kinetic data in the present work follows that of the previous investigation, and also refers to other related theory [18–21].

The overall thermal decomposition rate of electronic packaging material, as written in an Arrhenius-type equation can be represented as follows:

$$\frac{\mathrm{d}X}{\mathrm{d}t} = kf(X) = A\exp\left(\frac{-E}{RT}\right)f(X) \tag{2}$$

where k is the rate constant, A the pre-exponential factor, E the activation energy, and T the reaction temperature,

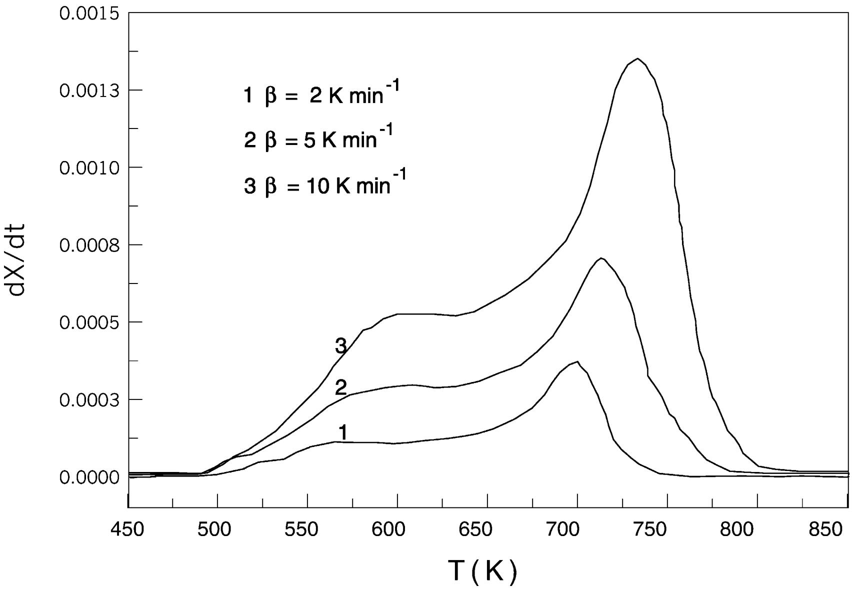


Fig. 10. Variation of the instantaneous reaction rate with temperature at different heating rates for thermal decomposition of the specimen.

respectively. A function of conversion independent of temperature, $f(X)$, is expressed as

$$f(X) = (1 - X)^n \tag{3}$$

Substituting Eq. (3) into Eq. (2) and taking a natural logarithm yields

$$\ln\left(\frac{\mathrm{d}X}{\mathrm{d}t}\right) = \ln[A(1 - X)^n] - \frac{E}{R}\frac{1}{T} \tag{4}$$

Based on Eq. (4), by using the method of least-squares, a plot of instantaneous rates (ln(dX/dt)) vs. temperature (1/T) from Fig. 11, the activation energy (E) corresponding to the selected conversion (X) is thus obtained. For various heating conditions, Fig. 12 shows the plot of $\ln(A(1 - X)^n)$ against $\ln(1 - X)$. A least-squares straight line is yielded, the slope is n and the intercept is ln[A]. Then, the reaction order (n) and pre-exponential factor (A) are also obtained.

Table 4 lists values of the kinetic parameters for the thermo-oxidation of electronic packaging material. The apparent activation energies for thermal decomposition of electronic packaging material may be divided into three groups over the whole range of conversion degree. The

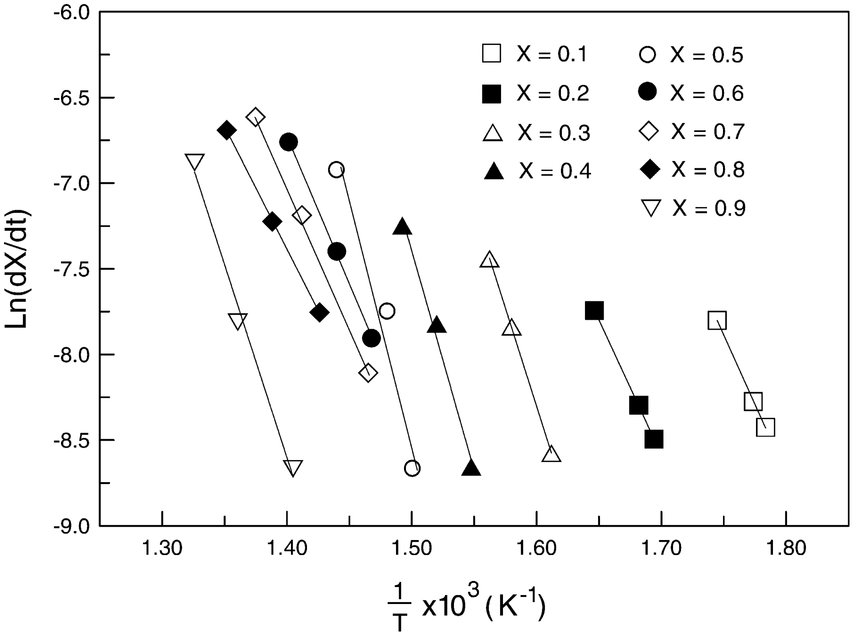


Fig. 11. ln(dX/dt) vs. 1/T for thermal decomposition of the specimen.

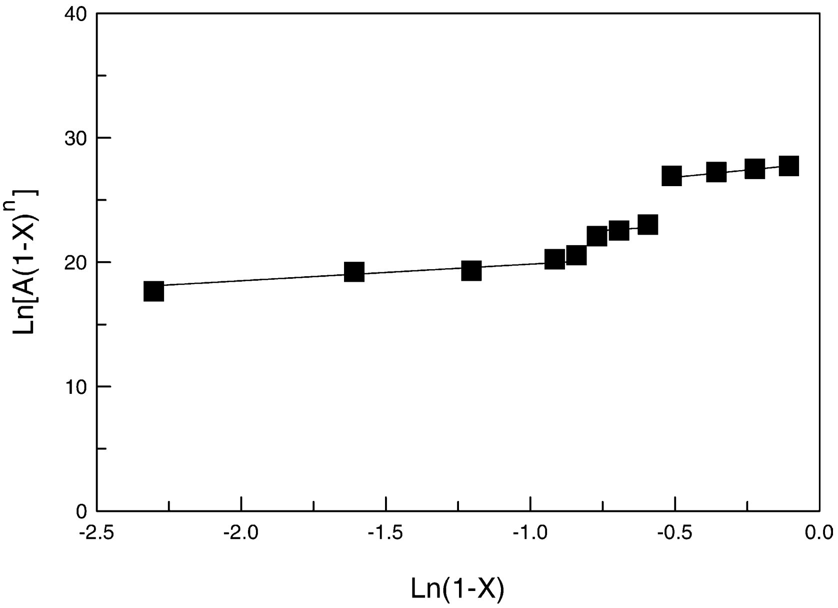


Fig. 12. $\ln(A(1-X)^n)$ vs. $\ln(1-X)$ for thermal decomposition of the specimen.

average activation energy values are $E = 154 \pm 10$ kJ/mol for $X = 0$–0.4; $E = 171 \pm 5$ kJ/mol for $X = 0.4$–0.55 and $E = 139 \pm 10$ kJ/mol for $X = 0.55$–1.0.

The activation energies obtained by Chen et al. [16] for the thermal decomposition of epoxy resin in 20% O_2–80% N_2 atmosphere are 129.52 ± 9.1 kJ/mol for the first-stage reaction, and 103.02 ± 7.7 kJ/mol for the second-stage reaction. These values are lower than those obtained in the present study. One possible reason for this is that the activation energy contributed by thermal decomposition of phenol resin in electronic packaging material is higher than that of pure epoxy resin.

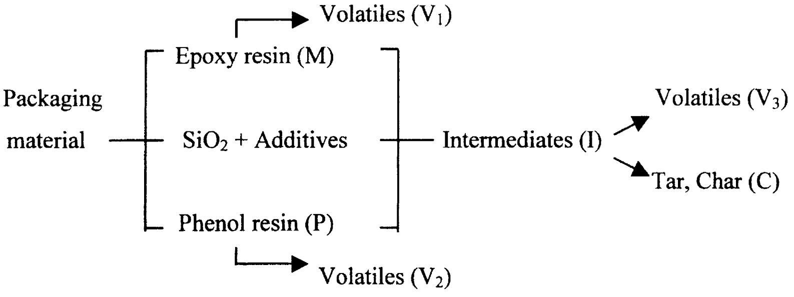
4.4. Thermal decomposition mechanism

According to the calculation of activation energy, three groups of values are obtained, which indicates that the degradation process of electronic packaging material is much more complex than a single resin component. In the present investigation, the average activation energies in the first-stage reaction (conversion 0–0.55) can be divided into two groups. Hence the mechanism of thermal decomposition of electronic packaging material in the first stage must be composed of more than one reaction. There are two components of resin material (mainly epoxy resin and phenol resin) present in the first stage, indicating that the two average activation energies are attributed to the thermal decomposition of the two resin materials. The conversion range from 0.4 to 0.55 corresponds to a transition from the first stage to the second one. In the second stage (conversion 0.55–1.0), there is only one activation energy observed, indicating that thermal decomposition in the second stage may be regarded as being further decomposition of intermediates (noted as residual resin matter from the first stage).

Table 4
Kinetic parameters of thermal decomposition of electronic packaging material

	First stage		Second stage
	$X = 0$–0.4	$X = 0.4$–0.55	$X = 0.55$–1.0
E (kJ/mol)	154 ± 10	171 ± 5	139 ± 10
A (min^{-1})	1.39×10^{12}	1.76×10^{10}	2.47×10^{9}
n	2.0	1.5	1.5

A reasonable mechanism for the steps of thermal degradation of electronic packaging material might be simply described by the following scheme:



In this scheme, the original constituents of packaging resin are epoxy resin and phenol resin. This fact further reveals that there are two different components of resins participate in the thermal decomposition reaction. The first stage of thermal degradation mainly proceeds via destruction of epoxy resin (M) and phenol resin (P) into the intermediates (I). The chemical products produced by the thermal decomposition of epoxy resin or phenol resin have been analyzed extensively and summarized by previous authors [8,22,23]. These observations indicate that the aromatic–aliphatic compounds are the intermediate results of thermal decomposition in the first stage. Then, both gaseous volatiles (V_1 and V_2) were released from individual thermal decomposition reactants (M and P). The gaseous volatiles (V_1 and V_2) have a low molecular weight, and may be alkane or alkene derivatives. As the phenol resin is more difficult to decompose than epoxy resin, a greater activation energy is observed in the later period of the first stage. When the reaction proceeds in the second stage, the intermediates (I) continue to further oxidize or decompose to form other volatile species (V_3), tar and char (C). The final char is composed of a solid product of silica. The volatile species (V_3) could be attributed to oxidation or dehydration of intermediates, and further forms the CO, CO_2, H_2O or the other carbohydrate compounds of smaller molecular mass. From the above observation, we can conclusion that the mechanism consists of two competitive reactions: the thermal decomposition of epoxy resin and phenol resin to form intermediates, and further decomposition to yield SiO_2, tar and gas volatiles.

A theory with degradation in one or two stages for decomposition of plastic materials such as epoxy resin or polyvinyl chloride (PVC) has been proposed by other researchers [16,22,24], with a consistent conclusion that the major loss of mass during degradation is attributed to evolution of volatile matter, with further decomposition to char or tar. Because the major constituent of electronic packaging materials is more than one resin component, the thermal decomposition reaction is complicated, with more than one pathway of chemical decomposition observed in the present work.

5. Conclusions

Using a recycling technology based on thermal decomposition, high-purity silica has been recovered for the epoxy resin compounds used in electronic packaging materials. The thermal decomposition process is performed with thermogravimetric measurement in an oxidizing atmosphere under various reaction conditions. The decomposition rate of packaging resin in air could be increased by reducing in sample loading, grain size or heating rate, as well as by increasing oxygen concentration. A reaction temperature above 825 K is conducive to complete decomposition of resin matter into silica. The activation energy for the reaction process is divided into three groups, and a two-stage degradation mechanism is proposed as one possible way of thermal decomposition. This mechanism can be assumed to occur via two competitive reactions (degradation of epoxy and phenol resins), and yielding intermediates, with the intermediates then further decomposing to form silica. This thermal decomposition process has the benefit not only of recovering silica which can be used as the filler for electronic packaging material, but also of producing valuable materials such as Si_3N_4, SiC and Si. In addition, the results are useful in solving the disposal and pollution problems, and in developing pyrolysis or burning systems for other plastic wastes.

Acknowledgements

The author expresses thanks to the National Science Council of Taiwan for its financial support under Project no. NSC 90-2214-E164-001.

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