Full Length Research Paper

Pyrolysis of Diglycidyl ether of Tetrabromobisphenol A (DGETBA) using molten salt and its reaction kinetics

Ching-Lin Ho[1], Kuo-Ching Chang[2], Sheau-Ming Chen[3]*, Yun-Hwei Shen[4], Wen-Cheng Wu[4] and Kun-Liao Chen[4]

[1]Open University of Kaohsiung, Siaogang District, Kaohsiung City 812, Taiwan.
[2]Department of Environmental Engineering and Science, National Pingtung University of Science and Technology, Pingtung 907, Taiwan.
[3]Kainan University, No.1 Kainan Road, Luzhu, Taoyuan 338, Taiwan.
[4]Department of Resources Engineering, National Cheng Kung University, Tainan 701, Taiwan.

Diglycidyl ether of Tetrabromobisphenol A (DGETBA) is mainly for making copper clad laminate (CCL), which is the base of printed circuit board (PCB) in Taiwan. If not properly treated and disposed, waste printed circuit board would make the already polluted environment worse. The objective of this study is to pursue the chemical reaction kinetics for pyrolysis of DGETBA by molten salt. The molten salt used in this study composed of Sodium-nitrate ($NaNO_3$) and Sodium-nitrite ($NaNO_2$) with the ratio of 4:1. The following reaction rate equation has been obtained: $dC/dt = -kC^{0.7}$, where k is the reaction rate constant, C is the reactant concentration, t is the reaction time, and which can further be obtained as follows: $k = AT^b exp(-E/RT) = 33.9 \times T^{0.00034} exp(-2118/1.987T)$, where A is a frequency factor (1/s), b is a empirical parameter temperature function, E is the activation energy (cal/mol), R is universal gas constant (1.987 cal/mol K), and T is the reaction temperature (K).

Key words: Diglycidyl ether of tetrabromobisphenol A (DGETBA), printed circuit board (PCB), kinetics, pyrolysis, molten salt.

INTRODUCTION

Diglycidyl ether of Tetrabromobisphenol A (DGETBA) is a key material which has wide applications in electronic, electric appliance, and coating industries packing, adhesion, and coating (ITRI, 1996). USA-based Camper's set up its production bines in Taiwan in 1969 and opened up the development of the industry of printed circuit board (PCB) or printed wiring board (PWB) in Taiwan. Having survived several global recessions, the local PCB industry managed to turn in a smart achievement. A report of been ranked the third largest makers of PCB either in total production value or quantity (Chatterjee and Kumar, 2009). Domestic PCB industry has done a significant contribution to the economic development for Taiwan, according to Republic of China R.O.C) statistics monthly published by Directorate General of Budget Accounting and Statistics, Executive Yuan, the total PCB production in Taiwan by 1998 has been over NT$109.3 B.

Electronic-based products once junked would pollute the environment. Surging awareness of environmental protection and ever getting stricter environmental law have been causing a grave problem for the PCB industry. Moreover, a questionnaire survey conducted revealed that most of the PCB manufacturers had ranked the issue of environmental protection as the greatest problem confronting their operation (Tseng et al., 1995). Furthermore, the introduction of ISO-14000 certification has pushed the PCB makers to the corner that they just have to take serious looks at environmental issues (Ekmekçi, 2011). An investigation conducted by Liu (1995) indicated that the three primary refuse currently

---

*Corresponding author. E-mail: sheaumingchen@yahoo.com.tw or n4893117@yam.com.

generated by the PCB industry were liquid waste, wastewater sludge, and waste board strips. The first two wastes had been treated and disposed satisfactorily while the last one remained as a serious problem due to the lack of economically viable and technically feasible solution. The DGETBA contained in 60% of the waste board strips presented an annoying air pollution problem when copper is recovered by thermal treatment (Rao, 1989).

As estimated by the Industry Pollution Control Service Group in 1995, the waste board strips generated from the domestic PCB industry amounted up to 8,400 tons each year. Accordingly, given an annual expansion rate of approximately 25% in average, the annual tonnage of waste board strips should be over 16,000 tons by 1998. Whereas waste board strips are classified as the hazardous industrial waste and there is the absence of any proper technologies available to treat the waste board strips from local sources, the greater majority of the waste board strips have been stored in plant while only a small portion has been shredded and treated by the solidification method by external contractor.

The waste printed circuit boards including waste semi-products, rejected products and cutting strips, contains large portion of organics, therefore, according to Wang et al. (1993), the acid bath method, the erosion method, the rocker floatation method, the crashing method, the solidification method, the incineration method, or the oxide-free pyrolysis method of the existing treatment technology is not economic viable, nor capable of preventing the secondary pollution (Dambrot, 1992). The difficulties in providing the final disposal would eventually render all those methods not applicable in the future given the ever getting stricter environmental law enacted in Taiwan.

In coping with the flaws found with the existing treatment technologies for the waste printed circuit boards, Lee (2000) and Huang (2000) had developed a package of feasible recycling method by having the molten salt as the thermal treatment environment for the pyrolysis of waste printed circuit boards to complete the processes including pyrolysis, separation, and scum removal in one run within the reaction kiln. They had created a set of complete laboratory treatment process for reference by subsequent efforts in mass treatment and design of the reactor (Gibbins et al., 1990; Wen et al., 2005; Li et al., 2007; Zhou et al., 2007; Park and Fray, 2009; Siddiqui and Redhwi, 2009).

By referring to the method developed by Lee and Huang for the recycled PCBs using pyrolysis, and for exploring into the chemical kinetic behavior of the DGETBA cements inside PCBs, this study used DGETBA as the subject for the experiment of molten salt pyrolysis method (Upadhye et al., 1992; Gay et al., 1993; Rudolph, 1995; Chien et al., 2000a; Chien et al., 2000b) to simplify the treatment environment, reduce interferences from those factors that prevent easy control, and focus on the core reaction mechanism of DGETBA pyrolysis.

MATERIALS AND METHODS

(1) DGETBA: containing 10% acetone.
(2) Extraction solvent: LC-grade Dichloromethane is used to absorb bromoalkanes from the non-reduced gaseous products resulted from the condensed waste gas after the pyrolysis process.
(3) Molten salt: mixture of industrial sodium-nitrate and sodium-nitrite.
(4) Dilution solvent: LC grade methanol is used to dilute the condensed liquid.
(5) Absorption solution: 1M Sodium hydroxide (NaOH) water solution is used to absorb hydrobromine.
(6) TVA1000 Standard Gas: 100 ppm methane, zero-point air.
(7) GC/FID Standard Items: as listed in Table 1.
(8) Calibration: Blank samples were clean with pure Nitrogen gas 3 times in the sampling bags then test by GC/FID to make sure no impurities. The calibration in this study is tested 5 (or more) different standard concentrations of diluted methanol to draw an investigation basis for unknown samples.

Pyrolysis furnace: made of SUS 316, with internal capacity approximately 4 L, operating with direct feeding method by batch, that is, DGETBA was fed into the furnace to undergo the pyrolysis reaction at the temperature up to 850°C, with temperature indicator and controller.
    Pyrolysis furnace: an air-tight furnace, made of SUS 316, with internal capacity approximately 300 ml., operating with direct feeding method by batch, that is, DGETBA was fed into the furnace to undergo the pyrolysis reaction a, also containing temperature display, controller, and pressure display.
    Pyrolysis furnace: made of glass, with internal capacity approximately 120 ml, operating on direct feeding method by batch, that is, DGETBA is fed into the furnace to undergo the pyrolysis reaction, adapted with TVA1000 for the detection of total VOCs concentration.

Gas collection system

Waste gases produced from the first Pyrolysis furnace in the pyrolysis process at temperature of 450, 500, and 550°C respectively were analyzed in this experiment (Table 2). The gas collection system is comprised of a connected network of gas filter, condensation device (13 to 15°C, containing pump, condensation pipe and liquid collection flask), gas absorption flask, and vacuum pump. Gases produced from pyrolysis (at a temperature approximately at 200°C), was pumped at the tail end of the system, followed with filtration, condensation, and absorption to collect carbon slag and tar one by one (Peltonen, 1986; Nakagawa and Tsuge, 1987).
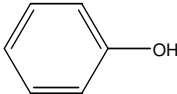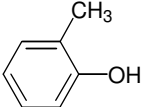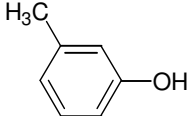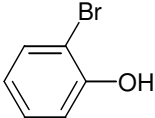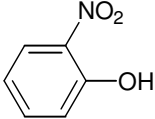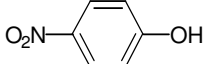
Detection of total VOCs

DGETBA was fed into the third Pyrolysis furnace at different working temperature. Resultant total VOCs concentration of waste gases generated from pyrolysis were at various reaction time detected by TVA1000 and documented to retrieve the parameters of reaction kinetics.

Process flow

This paper attempted to find a set of reaction kinetics parameters by using molten salt as the treatment environment for the pyrolysis of DGETBA and to complete the pyrolysis procedure in a single run inside the reaction furnace in Table 3. Therefore, the piloting program was to build up process-related basic operating conditions and analytical data in terms of operating temperature, reaction times, resultant pressure, and changing total VOCs concentrations

Table 1. GC/FID standard items used in the experiment.

Designation	Structural formula	Concentration	Grade
Phenol (94.11 g/mol)		99.5% purity	Merck standard
o-cresol (108.14 g/mol)		5000 ppm in MeOH	Accu standard
m-cresol (108.14 g/mol)		5000 ppm in MeOH	Accu standard
o-Bromophenol (173.01 g/mol)		2000 ppm in MeOH	Accu standard
o-Nitrophenol (139.11 g/mol)		500 ppm in MeOH	Accu standard
p-Nitrophenol (139.11 g/mol)		500 ppm in MeOH	Accu standard

Table 2. Filling pillar of HP 6850 series GC gas chromatograph.

Type of pillar	HP-5
Filler	5% Phenyl Methyl Siloxane
Polarity	Non-polarity
Scope of application	Phenols, amines, hydrocarbons, sulfur compounds, pesticides, PCBs
Compatibility	DB-5, BP-5, SPB-5, GB-5
Upper temperature limit	325℃
Length	30 cm
I.D.	0.25 mm
Film thickness	0.25μm

for the reference by the subsequent production on commercial scale.

RESULTS AND DISCUSSION
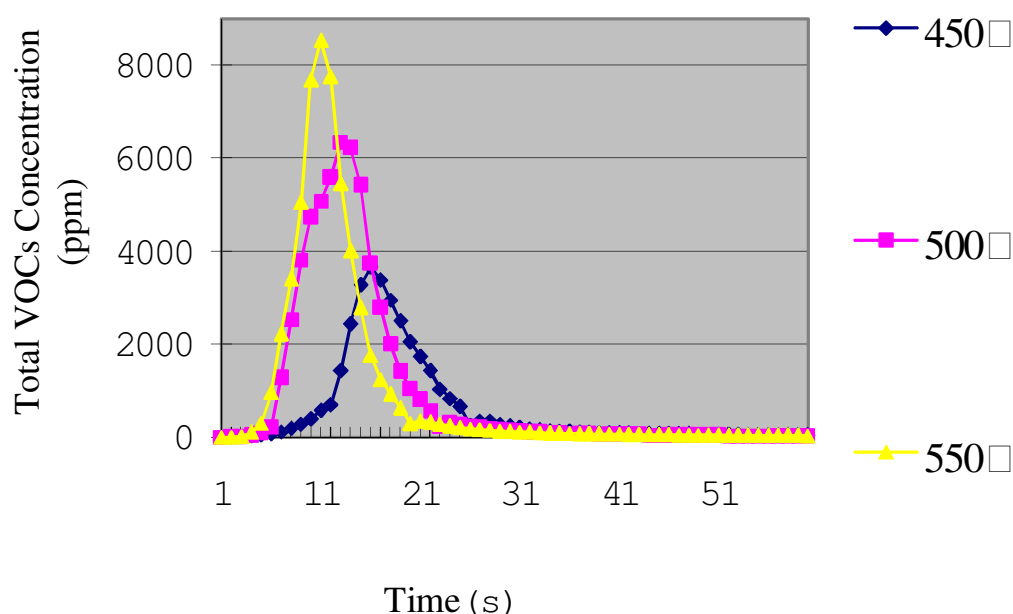
Gases changed during DGETBA pyrolysis

Massive smokes were generated several seconds after the feeding of DGETBA during the pyrolysis accompanied with occasional sparks, since DGETBA would generate significant portion of volatile organic compounds (VOCs) when heated. TVA1000 was used for measurement with the results illustrated in Figure 1.

Figure 1 shows the VOCs generated from DGETBA vary with the reaction time sequence during pyrolysis; wherein, when 60 mg of DGETBA were fed at the temperature of 450, 500, and 550°C respectively, violent pyrolysis and massive smokes were observed within 5 s indicating logarithmic increase as the reaction progress, and the entire process was completed and balanced

Table 3. Operating conditions of HP 6850 Series GC gas chromatograph.

Initial temperature	40℃
Initial time	2 min
Rate	10℃/min
Final temperature	250℃
Final time	0 min
Inject temperature	275℃
Detector temperature	280℃
Carry gas flow rate	1.2 ml/min
Purge valve on time	0.5 min
Purge valve off time	2 min

Figure 1. DGETBA Gases generated in Pyrolysis at different temperature and progressive reaction time.
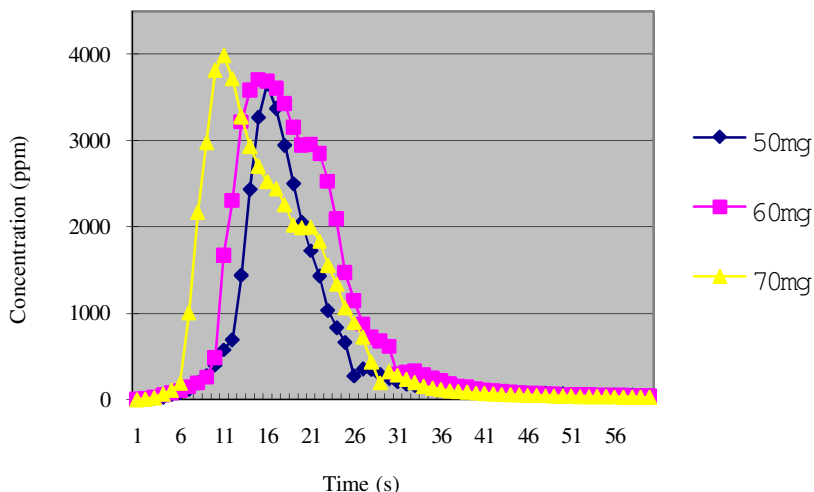
within 30 s. When operated at 450, 500, and 550°C respectively, the highest total VOCs concentrations were measured at the 17 s, 3373 ppm; the 13 s, 6352 ppm; and the 11 s, 8533 ppm.

In comparing the same amount of 60 mg DGETBA fed at three different operating temperature, the time for the presence of the highest amount of products at the higher temperature is shorter, indicating that the faster the pyrolysis gets, the more amount of the resultant smaller molecules is; on the contrary, the lower the reaction temperature gets, the slower the pyrolysis is, and the less amount of the resultant smaller molecules is. Furthermore, when various amount, namely, 50, 60, and 70 mg of DGETBA were fed in the pyrolysis at 450°C, the changed total VOCs was not significant as illustrated in Figure 2.
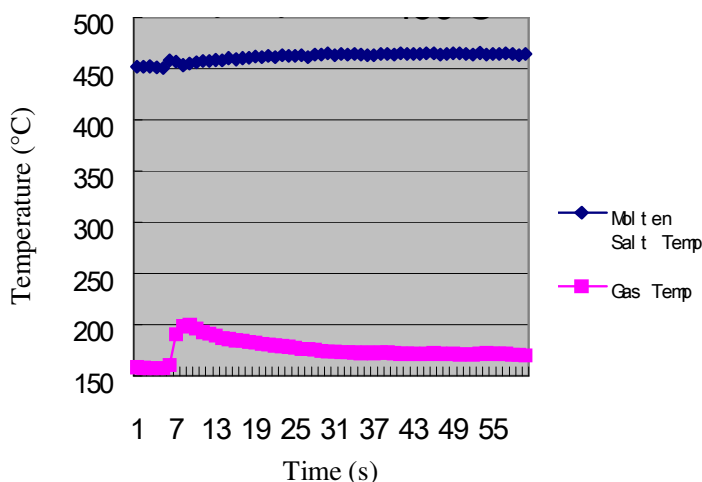
Resultant total VOCs vs reaction time of various feeding at 450°C

Changed gas temperature of DGETBA during pyrolysis at 450°C is illustrated in Figure 3. Figure 3 shows the changed gas temperature variation at the operating temperature of 450°C when 60 mg of DGETBA is fed to the second pyrolysis furnaces, which is connected to labview digit retrieve software. As observed, the gas temperature is 168°C at 8 s; later with a significant rise up to 195°C at 16 s and balanced at approximately 170°C at the 40 s.

It appears that as illustrated in Figure 3, massive energy released during gas pyrolysis could be accompanied by sparks, resulting in rapid rise in ambient temperature before dropped down to the final steady state,

Figure 2. The VOCs outcomes of three reagents pyrolysis within 60 min at 450°C.

Figure 3. The VOCs outcome of 60 mg reagent pyrolysis within 60 min at 450°C.

the completion of the pyrolysis can be confirmed at the same time. The similar profile was observed at the operating temperature of 500 and 550°C, respectively.

Retrieval of empirical kinetic parameters

Reaction order n

It takes sixty (60) seconds to complete the pyrolysis in this experiment and the reaction is assumed to be a power law function as most researchers did with the data of the operating temperature vs. the time concentration of the resultant total VOCs having the vacuum flow

rate controlled at 100 L/h (CH_4 to represent the total VOCs concentration). The profile of the time of reaction half-life vs. the initial concentration was achieved by first having the concentration unit changed from ppm to $\mu g/m^3$, and then logarithm was taken to solve the parameters respectively at 400, 500, and 550°C using the least square method (Chen et al., 1999).

As solved, C_{AO} at 450°C are 14,941,344; 14,327,016 and 17,333,360 respectively with the time of reaction half-life at 17.3, 14.8 and 16.6 s, respectively; C_{AO} at 500°C are 27,172,840; 28,123,480 and 26,648,160 respectively with the time of reaction half-life at 13.6, 12.8 and 13.2 s, respectively; and C_{AO} at 550°C are 24,980,120; 23,696,200 and 25,270,520 respectively with
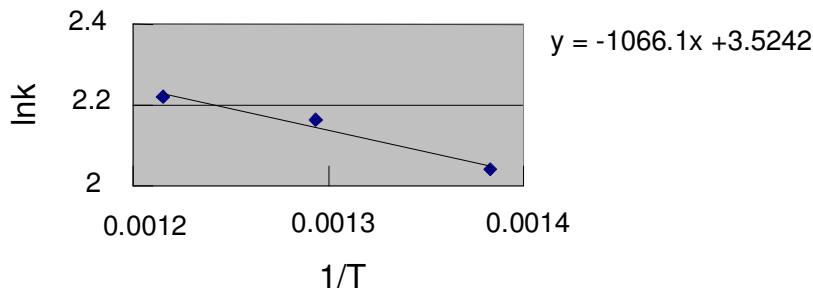
Figure 4. The relationship between rate constant k and $1/T$.

the time of reaction half-life respectively at 11.1, 11.2 and 11.3 s, respectively. With log C_{AO} as X-axis and the logarithm of the time of reaction half-life as Y-axis, the reaction progression is solved as 0.7 from the conditions of having the mean value of n = 0.7 from slope = 1-n, slope $_{(450°C)}$ = 0.0247, slope $_{(500°C)}$ = 0.0124, and slope $_{(550°C)}$ = 0.8732.

Reaction rate constant K

The n in the equation $dC/dt = -kC^n$ was substituted with n = 0.7 and integrated, and then the integral result of −3.33 ($C_{AO}^{0.3} - C_A^{0.3}$) and the reaction time t are plotted to obtain the mean value of reaction rate constant, k, at three different temperature respectively, $k_{(450°C)}$ = 7.7; $k_{5\ (500°C)}$ = 8.7; and $k_{(550°C)}$ = 9.2.

Activation energy E

The logarithm of reaction rate constants; and the reciprocal of the temperature T are plotted as illustrated in Figure 4. The slope is at −1066.1, that is, −E/R, therefore, E=2118 cal/mol.

Frequency factor A

The Arrhenius equation $k = A \exp(-E/RT)$ was used to obtain the mean frequency factor A = 33.9 from $A_{(450°C)}$ = 33.7, $A_{(500°C)}$ = 34.5, and $A_{(550°C)}$ = 33.6, respectively. As the temperature varies, temperature modification is required, the equation of $k = AT^b \exp(-E/RT)$ was used to obtain the temperature modification factor $b_{(450°C)}$ =-0.00057, $b_{(500°C)}$ =0.0027, and $b_{(550°C)}$ =-0.0014, and the mean b is 0.00034. Therefore, the final equation for the entire reaction kinetics is obtained as follows: $dC/dt = -kC^{0.7}$, where, $k = 33.9 \times T^{0.00034} \times \exp(-2118/1.987T)$.

Conclusions

Based on the results of the experiment described earlier, the following conclusions for the lab treatment process of pyrolysis of DGETBA with molten salt can be drawn:

1. Reaction temperature affects the reaction completion and has time inverse relationship the pressure inside the furnace, is directly proportional to the amount of feeding each other;
2. Waste gases from the pyrolysis process can be easily condensed into the form of tar. Therefore, only a condensation system is required to reclaim the tar. The residual non-condensed gases do not contain any element of bromine, thus can be treated with an ordinary air pollution control method and then discharged into the atmosphere without causing the problems of the secondary pollution;
3. Insignificant temperature variation is observed with the molten salt in the pyrolysis behavior, but a temperature surge did occur in the gas phase of pyrolysis.

A total reaction equation of $dC/dt = -kC^{0.7}$ has been obtained from this experiment where the rate constant $k = 33.9 \times T^{0.00034} \times \exp(-2118/1.987T)$.

REFERENCES

Chatterjee S, Kumar K (2009). Effective electronic waste management and recycling process involving formal and non-formal sectors. Int. J. Phys. Sci., 4(13): 893-905.
Chen KS, Chen HC, Wu CH, Chou YM (1999). Kinetics of Thermal and Oxidative Decomposition of Printed Circuit Boards. J. Environ. Eng. (ASCE), 125(3): 277-283.
Chien YC, Wang HP, Lin KS, Huang YJ, Yang YW (2000a). Fate of bromine in pyrolysis of printed circuit board wastes. Chemosphere, 40: 383-387.
Chien YC, Wang HP, Lin KS, Yang YW (2000b). Oxidation of printed circuit board wastes in supercritical water. Wat. Res., 34(17): 4279-4283.
Dambrot SM (1992). NEC Develops New Printed Circuit Board Recycling Process. Electronics, 65(17): 2-5.
Ekmekçi AK (2011). The value of environmental management and green product design within sustainable development and competitive strategies of the companies: An examination of the energy industry. Afr. J. Agric. Res., 6(1): 51-59.
Gay RL, Navratil JD, Newman C (1993). Molten Salt Oxidation of Mixed Waste. Proceeding of the 1993 International Conference on Nuclear Waste Management and Environmental Remediation. Prague, Czech Republic.

Gibbins JR, Khogali K, Kandiyoti R (1990). Relationship between results from conventional proximate analyses and pyrolysis yields under rapid-heating conditions. Fuel Process. Technol., 24(1): 3-9.

Huang KC (2000). Analysis of solid products in treatment of waste printed circuit boards by molten salt (Chinese version). unpublished thesis, National Pingtung University of Science and Technology, Taiwan.

Industrial Technology Research Institute (1996). PCB Supply-and-Demand Status Quo and Trends Analysis (Chinese version). Industrial Technology Research Institute, Taiwan.

Lee WH (2000). Analysis of gaseous products in treatment and recovery of waste printed circuit boards by molten salt (Chinese version). unpublished thesis, National Pingtung University of Science and Technology, Taiwan.

Li J, Lu H, Guo J, Xu Z, Zhou Y (2007). Recycle Technology for Recovering Resources and Products from Waste Printed Circuit Boards. Environ. Sci. Technol., 41: 1995-2000.

Liu TY (1995). Reclaim and Treatment of PCB Industrial Refuses (Chinese version). Ind. Pollut. Prevention Control, 85(8): 1-3.

Nakagawa H, Tsuge S (1987). Studies on Thermal Degradation of Epoxy Resins by High-Resolution Pyrolysis-Gas Chromatography. J. Anal. Appl. Pyrolysis, 12(2): 97-113.

Park YJ, Fray DJ (2009). Recovery of high purity precious metals from printed circuit boards. J. Hazard. Mater., 164(2-3): 1152-1158.

Peltonen K (1986). Gas Chromatographic-Mass Spectrometric Determination of Phenols and Heterocyclic Nitrogen Compounds in the Thermal Degradation Products of Epoxy Powder Paint. J. Anal. Appl. Pyrolysis, 10(1): 51-57.

Rao BS (1989). Norbornene end capped bisimide resins via epoxy-carboxy addition reaction. J. Polym. Sci. Part C: Polym. Lett., 27(4): 133-140.

Rudolph JC (1995). Molten Salt Oxidation of Chloro-organic Compounds: Experimental Results for Product Gas Compositions and Final Forms Studies. Oak Ridge National Laboratory, TN, USA.

Siddiqui MN, Redhwi HH (2009). Pyrolysis of mixed plastics for the recovery of useful products. Fuel Process. Technol., 90(4): 545-552.

Tseng DH, Chang MB, Wu TN, Lee HM (1995). Study of Low Pollution Industrial Process and Pollution Control Technology - PCB Industry (Chinese version). Department of Environmental Protection, Taiwan Province, Taiwan.

Upadhye RS, Brummond WA, Pruneda CO (1992). Destruction of High Explosives and Wastes Containing High Explosives Using the Molten Salt Destruction Process. Lawrence Livermore National Laboratory, CA, USA.

Wang WY, Liu BC, Wu MH, Yang CC (1993). Waste PCB and Engraving Waste Liquid Reclaim and Treatment Technologies (Chinese version). The Third Industrial Waste Reduction Technologies and Strategies Seminar, Taipei, Taiwan.

Wen X, Zhao Y, Duan C, Zhou X, Jiao H, Song S (2005). Study on metals recovery from discarded printed circuit boards by physical methods. Electronics and the Environment. Proc. IEEE Int. Symp., pp. 121-128.

Zhou G, Luo Z, Zhai X (2007). Experimental study on metal recycling from waste PCB. Proc. Int. Confer. Sustain. Solid Waste Manage., 5-7: 155-162.