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Flame-Retarding and Recycling Technologies for Plastics Used in Electronic Products

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Chapter 1

General Background

1-1 Environmental issues of current plastics for electronic products

The current remarkable progress of electronic industry produces a large volume of discarded electronic products. The safe treatment and recycling of these wastes are important to decrease their stress on the environment. Generally, the electronic products consist of various materials, and in particular, plastics are largely used in housings and electronic components because of their good characteristics, including electronic, mechanical and molding properties, as well as their low cost. In most electronics products, thermoplastics such as polycarbonate and polystyrene are used in housings, and thermosetting plastics, mainly epoxy resin compounds, are used as insulating materials in electronic components. They are chosen for each purpose according to their useful properties (see Figure 1-1).

However, compared with other main materials such as metal and glass used in these products, plastics have been far more difficult to treat safely and recycle effectively. This difficulty has prevented progress in environmental countermeasures for electronic products. Mainly, two technical problems have caused these environmental issues. The first is the inclusion of halogen compounds as a flame-retarding additive. These compounds generate harmful substances such as dioxin when burned. This problem has limited thermal treatment of plastic wastes and their reuse for other purposes. The second is the use of thermosetting plastics for electronic components. These plastics are difficult to remelted because of their cross-linking structures and are rarely reused for their original purposes. Therefore, in order to promote safe treatment and recycling of electronic products, overcoming these problems with the current plastics is absolutely necessary. The details of these problems and previous countermeasures are described below.

1-1-1 Current flame-retarding technologies using toxic substances

In order to prevent fire from originating in electronics products, current plastics in these products contain flame-retarding additives, most commonly in form of halogen compounds, such as organic bromine compounds. These compounds decompose along with the plastics during burning and then retard their combustion by trapping radicals generated from the plastics, as well as by forming gas-phase-barriers against oxygen (1). There is a serious problem with such halogen compounds, however. During burning the compounds generate toxic substances, such as dioxin and halogen derivatives, which can injure people and contaminate the environment (2, 3). Furthermore, antimony oxide is usually used together with the halogen compounds to increase their flame-retarding effectiveness, but the oxide itself is toxic. In addition to fire related dangers, the treatment of the plastic wastes and their reuse for other purposes are therefore extremely difficult.

Attempts have begun to replace these halogen compounds with phosphorus compounds such as red phosphorus and phosphoric esters, which form flame-retarding glass-like barriers (4, 5). However, red phosphorus can generate toxic substances such as phosphine when burned, and phosphoric esters are somewhat toxic and can cause a wide range of biological damage after disposal, including that on human (6, 7). Furthermore, most phosphorus compounds have the disadvantage of reducing useful characteristics of the plastics, such as water resistance and heat resistance.

Metal hydroxides (those of aluminum, magnesium, etc) have also been suggested as replacement for halogen compounds (1). By absorbing heat during combustion, they are able to retard flames, but they must be added in extremely large amounts, and this adversely affects the molding and electronic properties of plastics. Therefore, safer and more practical flame-retarding technologies are required for the plastics in electronic products.

1-1-2 Difficulty in recycling of thermosetting plastics

Thermosetting plastics, especially epoxy resin compounds, are mainly used as insulating material in electronic components such as integrated circuit (IC) packages and printed wiring boards (PWBs) because they show excellent insulating, thermal, and adhesive characteristics. However, until now, the recycling of the compounds' wastes has been difficult because in addition to the inclusion of toxic halogen-type flame-retarding additives as discussed above, the compounds cannot be re-melted after the molding process due to their cross-linking structures. Therefore, most of the wastes have been disposed of in landfill dumps.

Reuse of pulverized thermosetting plastics such as polyester, polyurethane, and phenol resin by blending them with the original plastics has been studied (8-11). These studies indicated that the resulting products, composed of these powdered cured plastics and the original plastics, have sufficient basic properties at a limited low-recycling ratio. However, few studies have been made on the recycling of epoxy resin compounds (12, 13, 14). Particularly, study of their application to practical products such as electronic components has been extremely insufficient.

On the other hand, recovery of valuable material included in large amounts, such as silica particle filler, from epoxy resin compounds by using pyrolysis can be useful. While many studies have been made of using pyrolysis of thermoplastics to recover their raw materials (15, 16), few have been conducted on recovering useful materials (inorganic filler, additives, etc) from thermosetting plastics such as epoxy resin compounds (17, 18). Furthermore, to be practical, these recovery methods would require better quality control of the recovered material and stricter treatment of the toxic exhaust gases, especially when the epoxy resin compounds contain halogen-type flame-retarding additives. Yet, to the author's knowledge, there has been no study taking them into consideration.

1-2 Outline and scope of this study

In this thesis, the author describes new environment technologies of plastics used in electronic products, regarding safer flame retardation without using halogen compounds and other toxic substances, and effective recycling for thermosetting plastics, especially epoxy resin compounds. These technologies will significantly promote countermeasures to the environmental problems caused by the electronic products containing plastics.

The outline of this study is shown in Figure 1-2. Composition of this thesis is as follows.

First, the author described safely flame-retarding technologies using highly safe specific silicone derivatives and self-extinguishing resins and their application to plastics used in main parts in electronic products, including housings and electronic components such as IC packages and PWBs.

Chapter two discussed new silicone derivatives as highly safe flame-retarding additives and their application to flame-resistant polycarbonate (PC) for housings. The flame-retarding effectiveness of silicones containing phenyl group was evaluated and the most effective structure of the silicones (a branched chain structure with methyl and phenyl groups) for use as flame-retarding additives in PC and its derivatives was demonstrated. The flame-retarding mechanism of the silicone, which is the formation of a flame-resistant layer on resin surface during ignition, was revealed. Finally, the characteristics of the PC with the silicone used as a practical housing material were evaluated. It had high flame resistance and other good properties, including strength, heat resistance, moldability and recyclability.

In chapter three, new self-extinguishing epoxy resin compounds and their application to molding compounds for electronic parts such as IC

packages were descried. The high flame resistance of epoxy resin compounds containing novolac derivatives with specific aromatic moiety (phenol aralkyl-type epoxy resin compounds) was demonstrated. Their unique self-extinguishing mechanism, which is the formation of a stable foam layer retarding the transfer of heat to the inside during ignition, was reported. Based on the self-extinguishing epoxy resin compounds, an environmentally friendly molding compound with no inclusion of any flame-retarding additives was developed. The characteristics of the molding compound were evaluated and compared with those of conventional molding compounds containing halogen-type flame-retarding additives. The compound showed excellent characteristics including flame resistance, water resistance and package reliability.

Chapter four reported an environmentally friendly glass epoxy laminate-type PWB with no inclusion of toxic flame-retarding additives. The PWB contains the phenol aralkyl-type epoxy resin compounds mentioned above and a limited amount of metal hydroxide. The synergistic effectiveness of the resin compounds and metal hydroxides on flame resistance of the PWB was described. Also, the characteristics of the PWB were evaluated and compared with those of current PWBs containing halogen-type and phosphorus-type flame-retarding additives. It had high flame resistance and other good characteristics, including electronic properties and resistance to solder heating and chemical agents in processing.

Next, the author discussed useful recycling technologies for thermosetting plastics used in electronic components, in particular, epoxy resin compounds used as molding compounds in IC packages and glass-epoxy laminates in PWBs. Their wastes are mainly generated as by-products (mold residues) of molding compounds at fabrication processes of IC packages and as PWBs with mounted electronic parts including IC packages after disposal of electronic products.

Chapter five described recycling technologies of molding compounds for electronic parts such as IC packages, regarding reuse after grinding and recovery of valuable materials by using pyrolysis. The basic properties of the ground mold residues of molding compounds (molding compound powder), such as chemical structure and surface reactivity, were reported. Next, the reuse of the molding compound powder into original molding compounds, the other epoxy resin products, and other plastics products was tested. The resulting products with the powder at limited recycling ratios had good characteristics for each purpose.

Further, a pyrolysis-based technology for recovering high-purity silica filler from the mold residues of the molding compounds was discussed. Both basic tests performed to determine appropriate pyrolysis conditions and practical tests conducted by using a roller kiln-type furnace were reported. The recovered silica was sufficiently pure to be employed as an inorganic filler in epoxy resin compounds used as cast-insulating materials and original molding compounds. An exhaust gas treatment process consisting of secondary combustion, dry recovery and wet recovery was tested. It successfully treated the exhaust gas containing toxic substances originated from halogen compounds and antimony oxide as flame-retarding additives.

Chapter six reported a recycling technology of PWBs with mounted electronic parts for the purpose of easily disassembling the boards, effectively recovering valuable materials, and reusing these materials. Electronic parts and solder were removed from the boards by heating and impacting. A glass fiber-resin mixture powder (glass fiber-resin powder) and copper-rich powder were recovered from the boards by pulverizing them and separating the powders. The reuse of the recovered materials was studied. The parts, solder, and copper-rich powder were reused as valuable metal resources. The glass fiber-resin powder was also reused as a useful filler to improve the characteristics of the other epoxy resin products and other plastic products.

In chapter 7, conclusions and future planning were summarized.

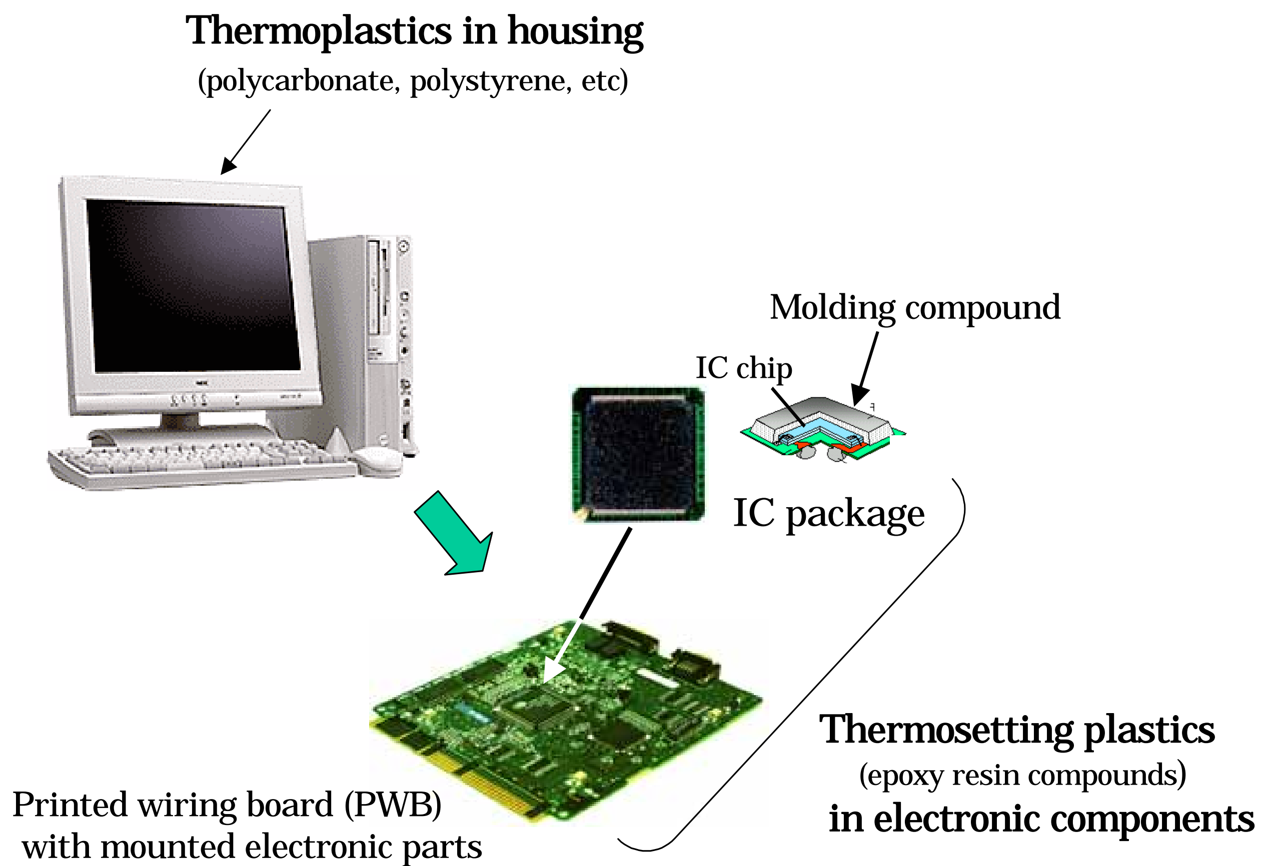

Fig. 1-1 Main plastics used in electronic products

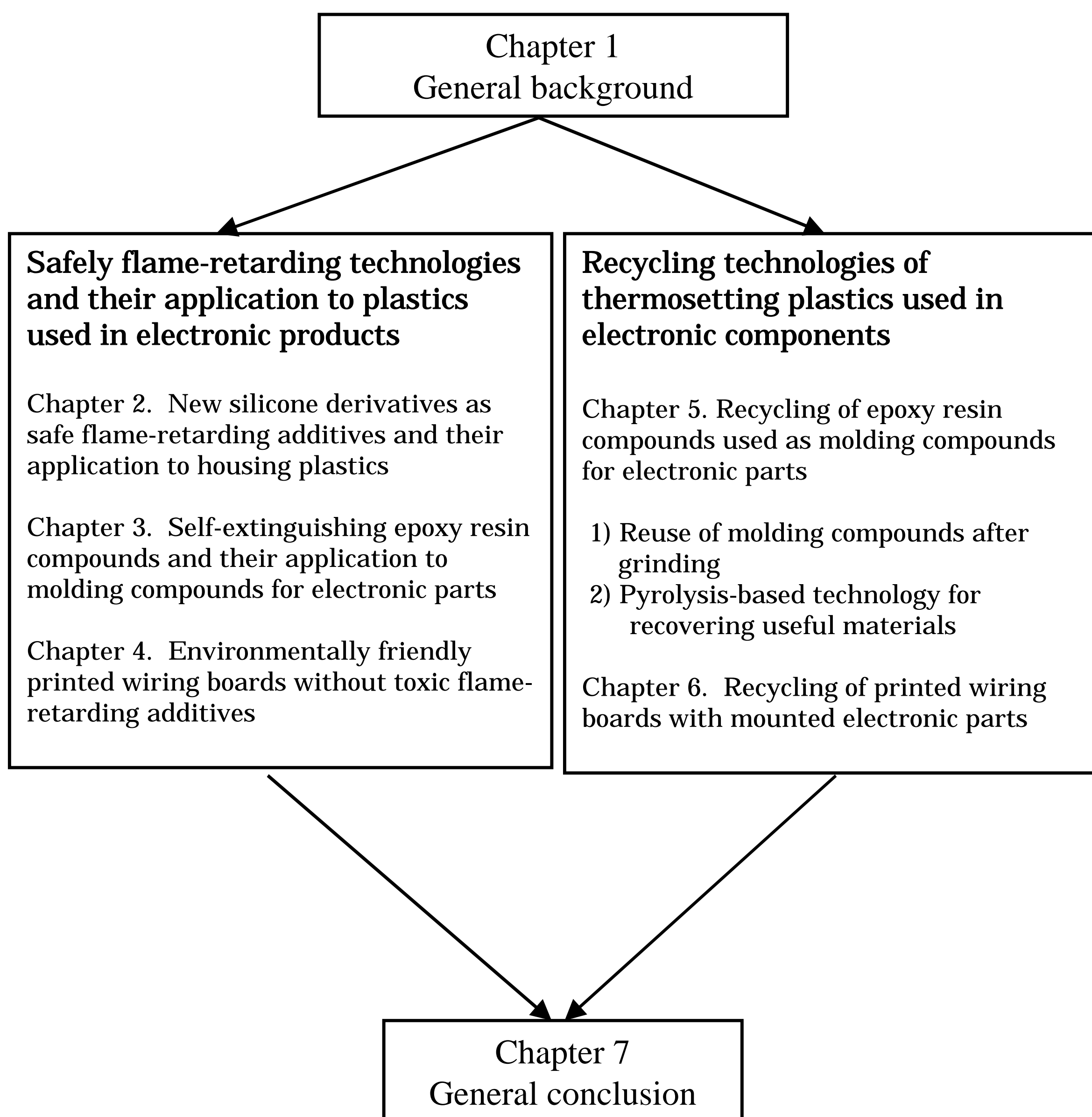

Figure 1-2 Outline of this dissertation

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Chapter 2

New Silicone Derivatives as Safe Flame-Retarding Additives and Their Application to Housing Plastics

2-1. Introduction

Most electronics products currently contain thermoplastics in their housings. Thermoplastics containing aromatic moiety, which mainly include polycarbonate (PC), PC and acrylonitrile-butadien-styrene copolymer (ABS) alloy, ABS, and polystyrene (PS), are used for their high heat-resistance, strength, and moldability. In order to prevent fire from originating in the electronics products, these plastics contain flame-retarding additives, most commonly in form of halogen compounds. As previously mentioned, during burning, these compounds generate toxic substances. While attempts have begun to replace these halogen compounds with phosphorus compounds, the compounds themselves are somewhat toxic and frequently have the disadvantage of reducing the characteristics of the thermoplastics.

In response to this problem, the use of silicone derivatives as flame-retarding additives has been looked to because of their high heat resistance, non-toxicity, and non-generation of toxic gases during combustion. Previous attempts at using silicone derivatives as flame-retarding additives included studies of polydimethylsiloxanes (linear type) mixed with PC, PS, poly (methyl methacrylate), and other plastics (1), but none has suggested sufficient flame-retarding characteristics, and all experienced difficulty in mixing with thermoplastics because of the poor solubility of the silicone derivatives in the plastics.

While mixing polydimethylsiloxans containing reactive functional groups (alcohoxy, vinyl, etc) with organic metal compounds (magnesium stearate, etc) improved flame resistance to a degree (2, 3), the most effective mixture proposed, that with organic lead compounds (4), obviously defeats the purpose of a search for an environmentally safer substitute.

Further, cross-linked polydimethylsiloxians were found to be effective in preventing many thermoplastics from dripping during combustion (5). However, they have to be used together with other flame-retarding additives because their flame-retarding properties are insufficient in

themselves.

Rather than the silicone derivatives containing methyl groups (methyl silicones) that were the subject of the studies cited above, silicone derivatives containing phenyl groups (phenyl silicones) might be likely candidates as flame-retarding additives for the aromatic thermoplastics such as PC, because such derivatives are highly heat resistant and highly soluble in these plastics. Also, they are expected to form an effective char on the surface of the aromatic thermoplastics synergistically during combustion. There have been few studies of such phenyl silicones, however, and while they have shown some potential flame-retarding qualities (4), to the author's knowledge, no study has yet appeared reporting which particular phenyl silicone's structure might be best for use as a flame-retarding additive.

In this chapter, new silicone derivatives as highly safe flame-retarding additives and their application to flame-resistant PC for housing were described. The flame-retarding effectiveness of phenyl silicones was studied and the most effective structure of the silicones was determined for use as flame-retarding additives in PC and PC alloys. The flame-retarding mechanism of the silicone was investigated. Finally, the characteristics of the PC with the silicone as a practical housing material were evaluated and compared with those of conventional flame-resistant PC with halogen-type and phosphorus-type flame-retarding additives.

2-2 Experimental

2-2-1 Materials

Silicone derivatives to be tested were produced as follows: chlorinated silane compounds containing organo functional groups (either methyl, phenyl, vinyl, methoxy or a mixture of two of them) were mixed with methoxy silane compounds containing these functional groups. They were mixed in a solvent (toluene), and then water was added for hydrolysis. After the hydrolysis reaction, the resulting silicone derivatives were separated by water-solvent extraction and then dried (see Table2-1 for a list of the tested silicone derivatives and their respective compositions and Figure 2-1 for their representative structure). As thermoplastics, PC (Calibre 301-10, Sumitomo Dow Co.), PC/ABS alloy (H-270, Sumitomo Dow Co.), ABS (GA-701, Sumitomo Dow Co.), and PS (H-65, Nippon Steal Chemical Co.) were used. Silicone derivatives were mixed with these plastics using a screw type mixer (KCK80×2-35VE×5, KCK Co.). Mixing temperatures were 280℃ for PC, 260℃ for PC/ABS, 260℃ for ABS, and 220℃ for PS. For references, PC containing an organic bromine compound (tetrabromobisphenol A) (Calibre 801-10, Sumitomo Dow Co.) and PC containing a condensed aromatic phosphorus ester (a test sample, Sumitomo Dow Co.) were also tested.

2-2-2 Method

Thermoplastics to be used as samples in oxygen index measurements were molded with a press-type molding machine at 270℃, and those for determination of other properties were molded with an injection-type molding machine at 290℃.

The flame resistance of the molded plastics was determined by the oxygen index method (JIS K 7201, ASTM D2863). It measures the oxygen concentration in a mixture of oxygen and nitrogen needed to support combustion. The UL94V method, which is regulated by Underwriters

Laboratories Inc. and determines the burning time and dripping of plastics after ignition, was also used. In the method a sample of molded plastics is held vertically and ignited with the flame of a gas burner applied to the bottom twice for ten seconds. The flame resistance of the materials is classified according to how long it burns and whether or not particles that ignite surgical cotton placed under the specimen fall from it. The range of burning time for a total of five samples classified flame resistant extend form V-0 (total time is less than fifty seconds) to V-1 (total time is less than 250 seconds). If the cotton is ignited, the material is classified V-2 ; otherwise it is classified Not V-2. Most electronics devices require a rating of V-0 for molded samples with a thickness of 1.6mm.

The strength of the molded plastics with respect to impact and flex were tested using methods specified in ASTM D256 and D792 respectively. Their Rockwell hardness was measured by the method specified in ASTM D785. The heat distortion temperature was measured as specified in ASTM D648. The moldability was tested in terms of melt flow rate (heating at 300℃, load of 1.2kgf), measured by the method specified in ASTM D1238.

The dispersion of silicone derivatives in thermoplastics samples was observed with a microscope (Optiphot, Nikon Co.). The concentration of silicone derivatives (mol ratio of silicon to carbon) on the surface of plastics was measured by means of X-ray photoelectron spectroscopy (XPS), using a spectrometer (S-Probe ESCA Model 2803, Surface Science Instruments Co.). The thermal degradation of silicone derivatives was evaluated at a heating rate of 10℃/min (in air) with a thermogravimetric analyzer (TGA40, Shimazu Co,).

The structures of silicone derivatives before and after ignition (oxygen index testing) were determined by means of Fourier-transform infrared spectra (FT-IR), using a spectrophotometer (FTS-15E/D, Perkin Elmer Co.).

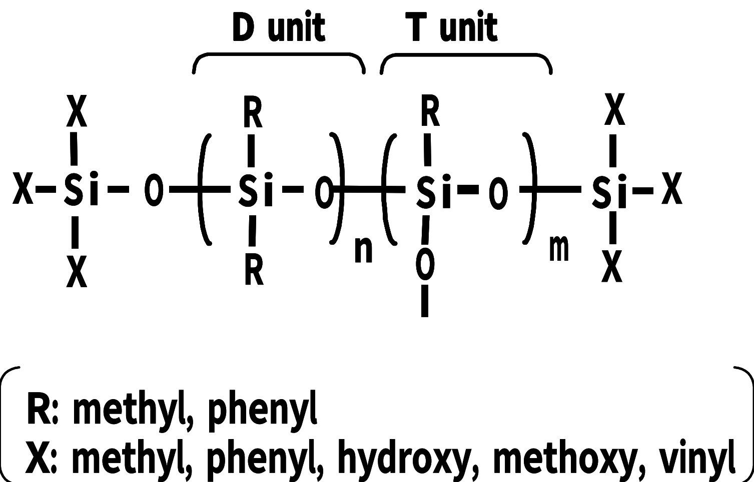


Fig. 2-1 Structure of silicone derivatives

Table 2-1 Structures of tested silicone derivatives

Sample NO	D/T* (mol %)	Methyl/Phenyl ** in chain (mol %)	Terminal functional group	Mean molecular weight [Mw]
S1	70/30	56/44	Methyl	160,000
S2	20/80	40/60	Methyl	16,000
S3	20/80	40/60	Methyl	36,000
S4	20/80	40/60	Methyl	110,000
S5	20/80	30/70	Methyl	11,000
S6	20/80	20/80	Methyl	11,000
S7	20/80	0/100	Phenyl	15.000
S8	20/80	40/60	Hydroxy	16,000
S9	0/100	100/0	Methyl	15,000
S10	0/100	100/0	Vinyl, Methoxy	23,000
S11	0/100	100/0	Methoxy	25,000
S12	100/0	100/0	Methyl	60,000
S13	100/0	100/0	Methyl	86,000

* Ratio of D unit ($R_2SiO_{1.0}$) to T unit ($RSiO_{1.5}$)
** S1-S6, S8 : T unit has phenyl group

2-3 Results and Discussion

2-3-1 Flame-retarding effects of silicone derivatives

The flame-retarding effects on PC of various silicone derivatives, in particular on that of phenyl silicone were studied. The structure variables were the chain structure (linear-type, branch-type), the functional group in the chain (methyl, phenyl, mixture of them), and the functional group in terminals of the chain (methyl, phenyl, hydroxy, methoxy, vinyl).

As shown in Figure 2-2, the flame-retarding effects of branched chain-type silicone derivatives (branch silicones) were superior to those of linear-chain-type silicone derivatives (linear silicones). Branch silicones containing a mixture of methyl group and phenyl group in the chains were more effective than those containing either only methyl group or only phenyl group. Branch silicones containing non-reactive functional groups (methyl, phenyl) in the chain-terminals were also more effective than those containing reactive functional groups (hydroxy, methoxy, vinyl), whether phenyl group was contained in the chains or not. That is to say, branch silicone derivatives containing a mixture of methyl group and phenyl group in the chains and containing methyl group in the chain-terminals were the most effective. Hereafter these derivatives are referred to as “branch silicone with methyl and phenyl”.

Also, the influence of the amount of phenyl group in the chain and of the mean molecular weight for the branch silicone with methyl and phenyl was studied. As shown in Figure 2-3, the silicone with phenyl group at 60-80 mol % in the chain was most suitable. Lowering the average molecular weight of the silicone increased the flame resistance of PC, though the silicone with a mean molecular weight of less than about 10,000 was badly suited for mixing with PC because of its extremely low viscosity.

The branch silicone with methyl and phenyl (here, the phenyl content was 60 mol%, the mean molecular weights were 36,000 and 110,000) was applied to PC/ABS alloy, ABS, and PS used as housing materials in electronics products.

Figure 2-4 shows the relationship between the concentrations of the silicone and its flame-retarding effectiveness of these thermoplastics, with PC as a reference. The silicone's flame-retarding effect for these plastics was good as well, and particularly so for the PC/ABS alloy. Also, other silicone derivatives showed insufficient effectiveness.

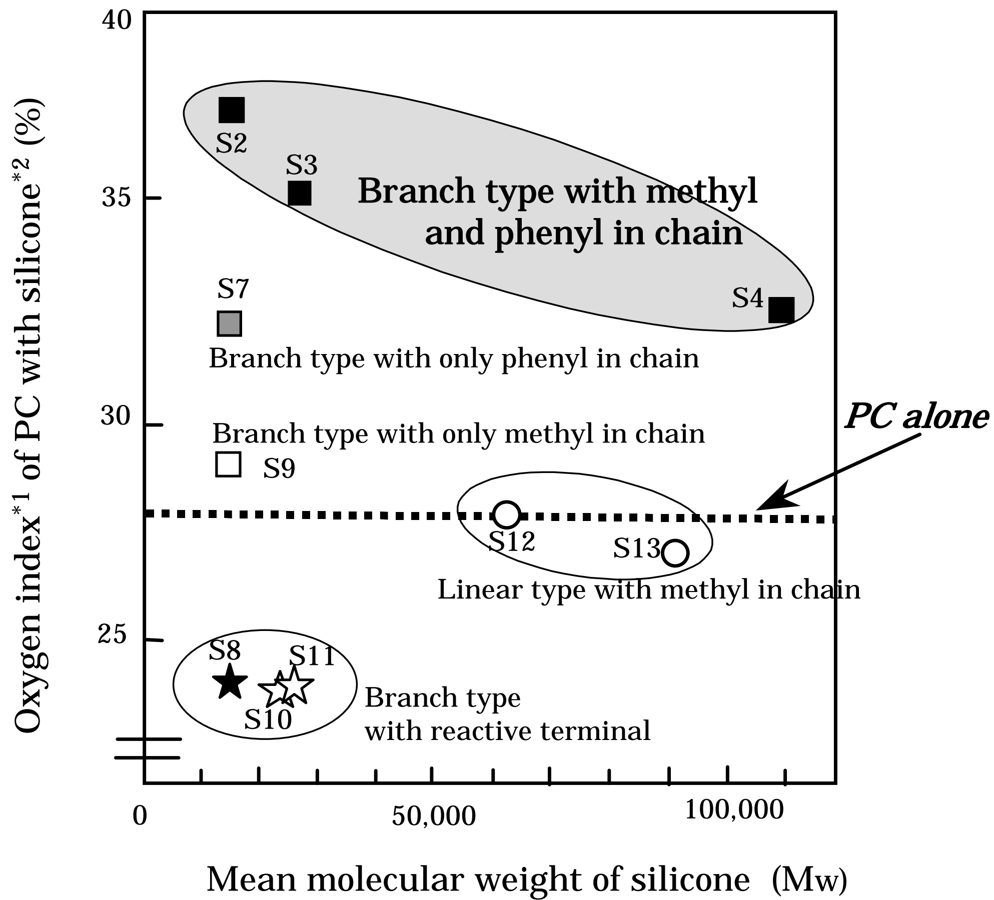


Fig. 2-2 Flame-retarding effectiveness of silicone derivatives for PC (*1: Oxygen concentration in a mixture of oxygen and nitrogen needed to support combustion, *2: Silicone concentration in PC : 5phr)

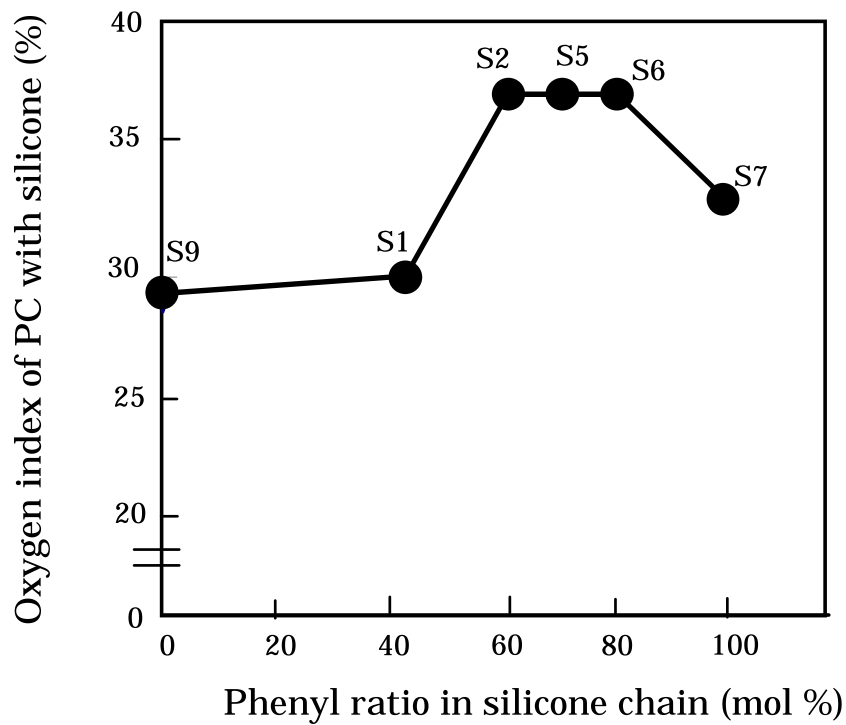


Fig. 2-3 Relationship between phenyl group ratio in chain of branch silicone and flame-retarding effectiveness for PC (Silicone concentration in PC : 5phr)

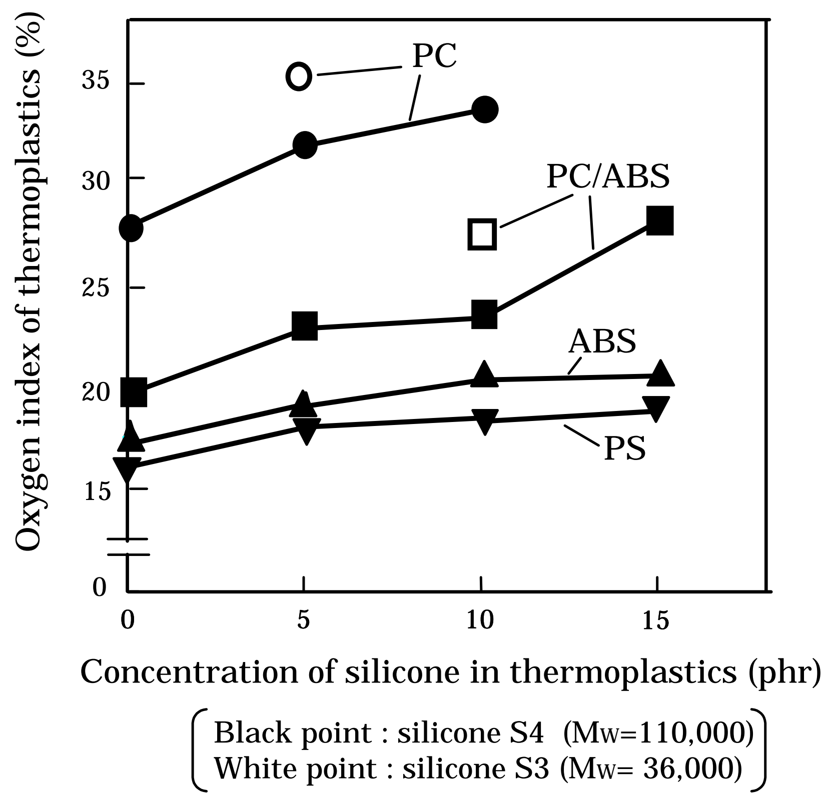


Fig.2-4 Flame-retarding effectiveness of new silicone

2-3-2 Flame-retarding mechanism of new silicone

To clarify the flame-retarding mechanism of the branch silicone with methyl and phenyl, its dispersion in PC, its movement to the surface of molded PC during ignition, and the flame resistance of itself were investigated, which the author regards as newly required properties of silicone derivatives for retarding the flaming of PC. Further, these results were compared with those of other silicone derivatives whose flame-retarding effects were less pronounced.

As shown in Figure 2-5, in PC, dispersion of the branch silicone with methyl and phenyl was extremely fine, and particularly so for the derivatives with increased phenyl group in the chains. This can be mainly credited to their high solubility with PC, which results from the phenyl group in the chain. Dispersion of other silicone derivatives was inferior to the silicone. Silicone derivatives with only methyl group in the chains (branch-type and linear-type) showed low solubility with PC due to lack of phenyl group. Branch silicone derivatives with reactive groups in the terminals, whether containing phenyl group in the chains or not, showed poor dispersion because of their gelation during mixing with PC (The gelation was confirmed by solubility tests in chloroform.).

Figure 2-6 and Table 2-2 indicate the concentration (the mol ratio of Si to C) of silicone derivatives at the surface of molded PC before and after ignition. It shows movement of the branch silicone with methyl and phenyl to the PC surface during ignition. Silicone derivatives with only methyl group in the chain (branch-type and linear-type) moved more than that of the branch silicone with methyl and phenyl due to their lower solubility with PC. When reactive functional groups were contained in the chain terminals of branch silicones (with methyl and phenyl, and with only methyl in the chains), the movement of the silicone derivatives during ignition decreased because of their gelation during mixing with PC. Also, the initial concentrations of the silicone derivatives on the PC surface (before ignition) decreased due to decreased

movement during molding.

The flame resistance of the branch silicone with methyl and phenyl itself was far higher than that of PC alone and also that of branch silicone with only methyl (see Figure 2-7). Also, branch silicone derivatives containing reactive functional groups in the terminals themselves showed good flame resistance, whether they contained phenyl group or not. The flame resistance of linear silicone derivatives themselves could not be measured by oxygen index method because they were liquid, but thermogravimetric analysis indicated that they had far less heat resistance than the branch silicone with methyl and phenyl (see Figure 2-8).

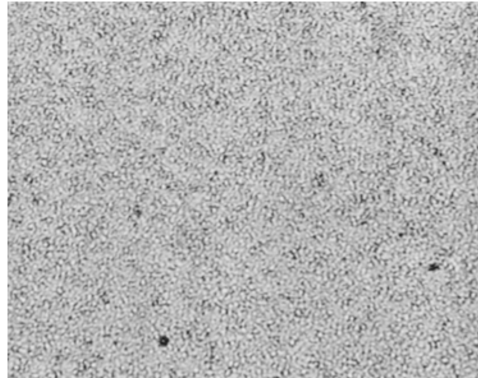
From these results, it was clear that the branch silicone with methyl and phenyl was the only silicone derivative that can satisfy all of the required properties (dispersion in PC, movement to PC surface, flame-resistance of itself). That is, the silicone finely dispersed in PC and moved to the PC surface during ignition, and then could formed a uniform and highly flame-resistant barrier on the surface (see Figure 2-9). Other silicone derivatives could not satisfy all of these properties, in particular dispersion in PC and flame resistance of themselves, and hence these derivatives seemed to fail uniform and effective barrier for retarding the flaming of PC.

To study the structure of the barrier formed with the branch silicone with methyl and phenyl on PC during ignition, the silicone before and after ignition (oxygen index testing) was analyzed by means of FT-IR. As a result, it was found that condensed aromatic compounds (see Figure 2-10) formed from phenyl groups in the silicone during ignition (770 cm^{-1}: condensed aromatic bond appears, 2970-3080 cm^{-1}: aromatic hydrogen bonds decrease). These condensed aromatic compounds are known as precursors to highly flame-resistant char (carbonaceous substances) (6). PC alone can form similar compounds on the surface during ignition, and ultimately a limited amount of char (7, 8, 9). Therefore, there was a strong possibility that during ignition, the branch silicone with methyl and phenyl and PC synergistically formed a highly

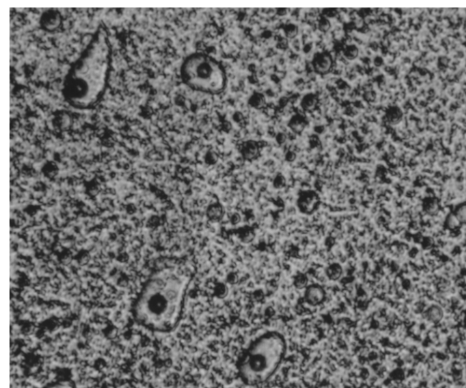
flame-resistant complex substance consisting of polysiloxane and condensed aromatic compounds on the PC surface. This substance might be structured as shown in Figure 2-11. The particular flame-retarding effects of the silicone for PC and its derivative (PC/ABS alloy) seemed to result mainly from the formation of the complex substances like this.

The fact that lowering the molecular weight of the branch silicone with methyl and phenyl improved the flame-retarding effect appeared to be due to its accelerated movement to PC surface as a result of its lower viscosity. The improved flame-retarding effect resulting from increasing the phenyl group ratio to about 60 mol% was credited to the better solubility with PC and the higher flame resistance of the silicone itself. Perhaps the limit of about 60% represents the point at which the advantage of solubility was offset by a resulting decreased in movement to the surface.

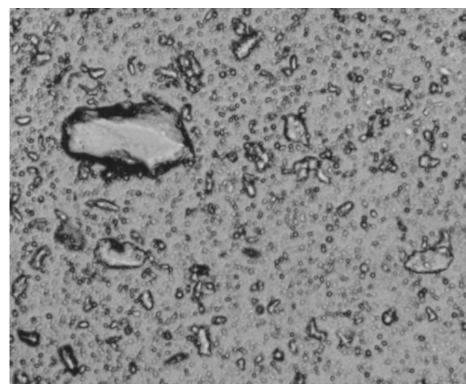
a) Branch silicone with methyl and phenyl in chain and methyl terminal (non reactive) (S2)



b) Linear silicone with only methyl in chain and methyl terminal (non reactive) (S12)



c) Branch silicone with only methyl in chain and methoxy terminal (reactive) (S11)



50 μm

Fig. 2-5. Dispersion of silicone derivatives in PC

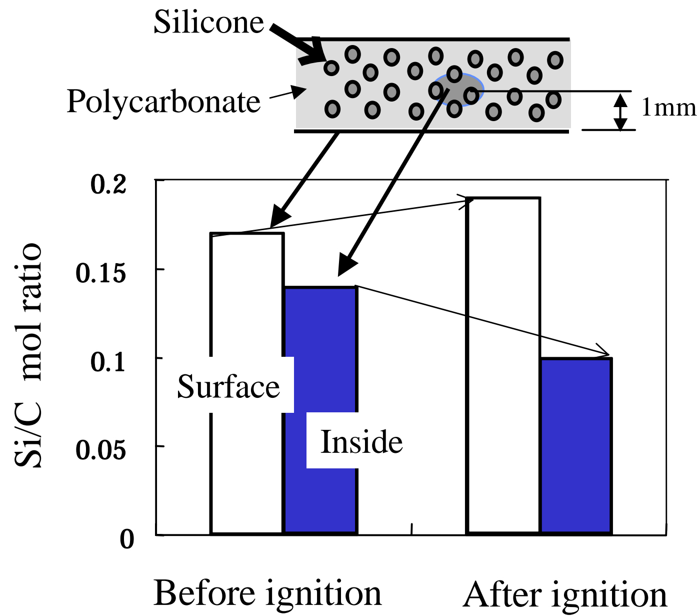


Fig.2-6 Concentration of new silicone (S4) in polycarbonate before and after ignition

Table 2-2 Concentration of silicone in polycarbonate (PC) before and after ignition

Sample NO	Structure of silicone derivatives*	Si／C in surface of PC (mol ratio)	
		Before ignition	After ignition**
S2	Branch type with methyl and phenyl and with methyl terminal	0.21	0.27
S8	↑ with hydroxy terminal	0.16	0.17
S9	Branch type with methyl and with methyl terminal	0.21	0.86
S11	↑ with methoxyl terminal	0.18	0.46
S12	Linear type with methyl and with methyl terminal	0.35	0.47

* Initial concentration of silicone in PC : 5phr
** After ignition by UL method for 15 seconds

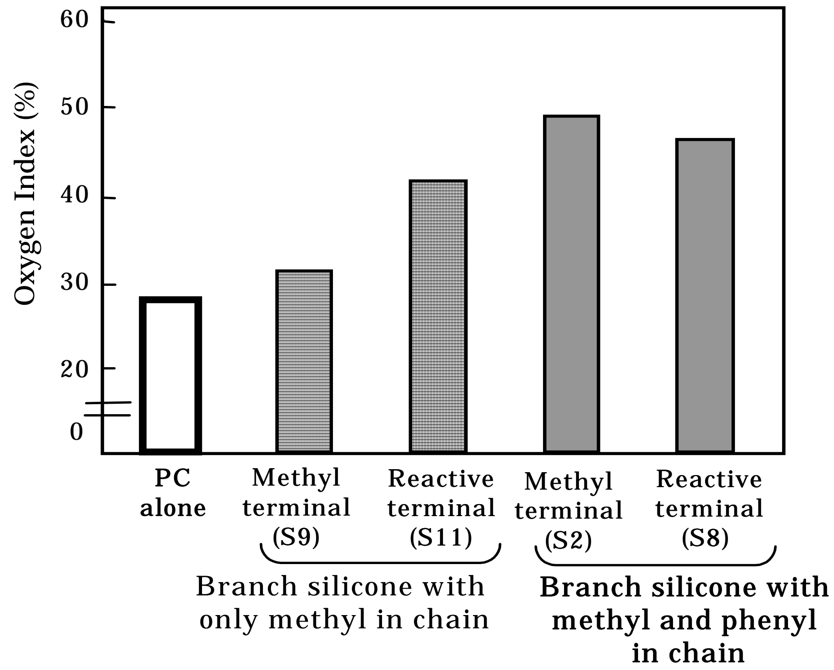


Fig. 2-7　Flame resistance of silicone derivatives themselves

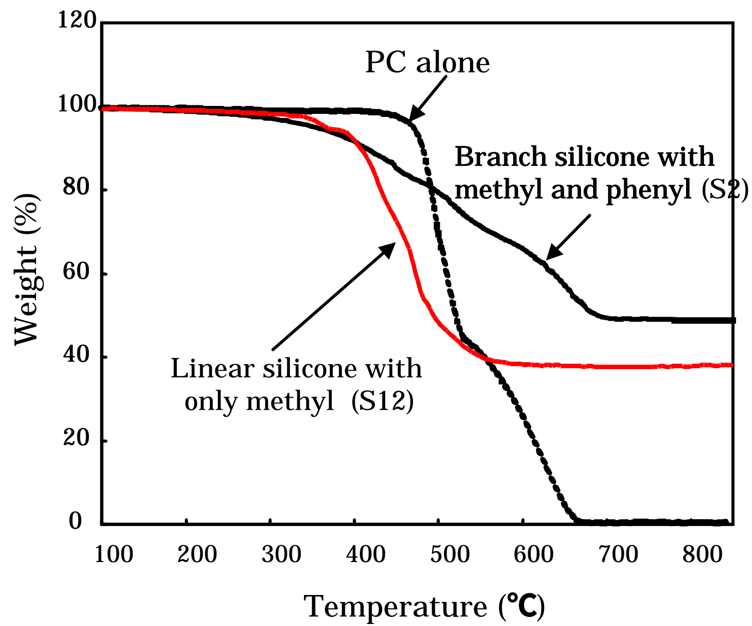


Fig. 2-8　Thermogravimetric analysis of silicone derivatives

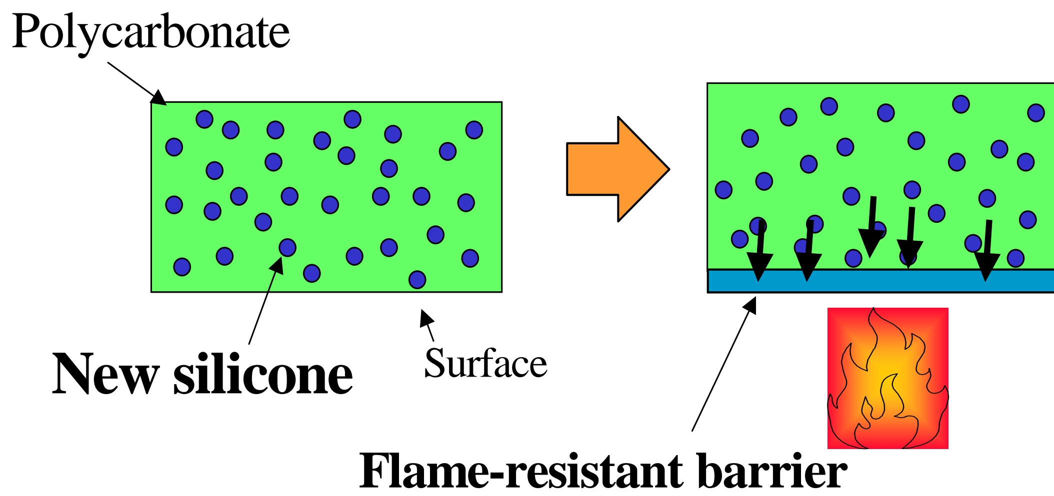


Fig. 2-9　Flame-retarding mechanism of new silicone

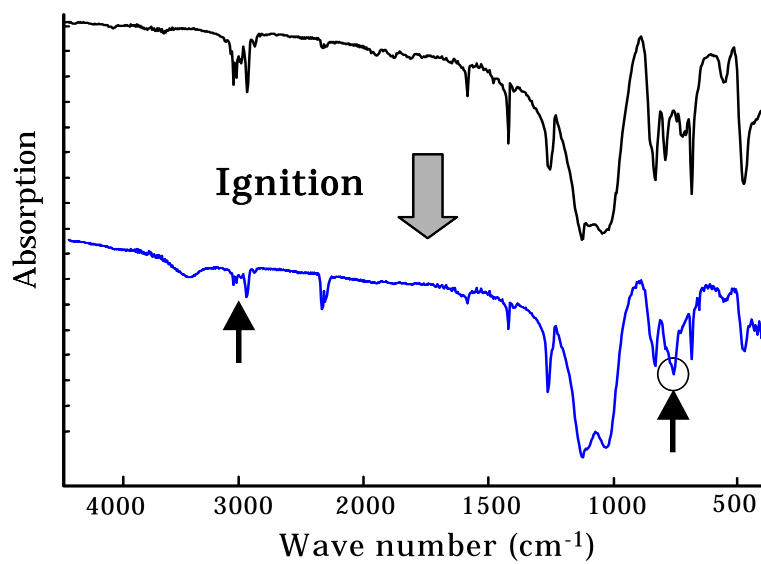


Fig. 2-10 FT-IR spectrum of branch silicone with methyl and phenyl (S2) before and after combustion

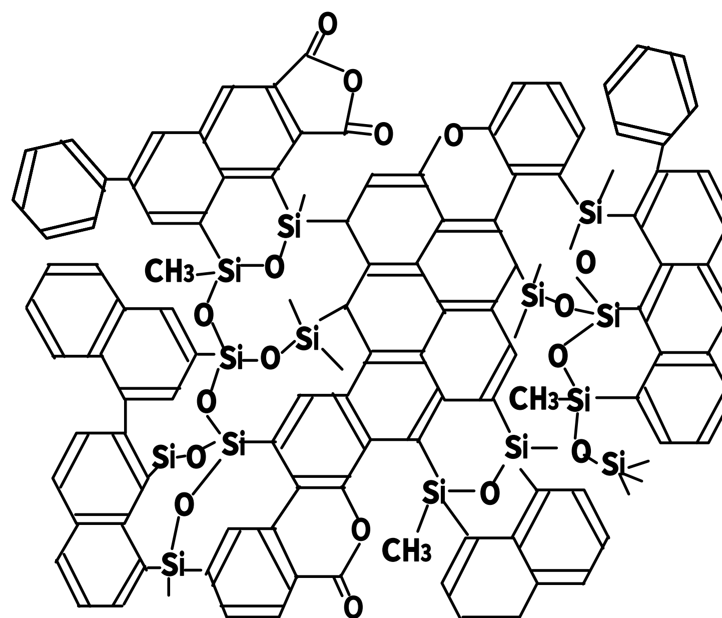


Fig. 2- 11 Imagined structure of complex substance consisting of branch silicone with methyl and phenyl and PC after combustion

2-3-3 Characteristics of flame-resistant polycarbonate containing new silicone

As listed in Table 2-3, adding the new silicone derivative (branch silicone with methyl and phenyl) sufficiently improved PC's flame resistance and did not adversely affect its other important properties, such as strength, moldability (melt flow rate), surface hardness, and heat resistance. The fame-retarding effectiveness of the silicone was almost the same as that of a bromine-type flame-retarding additive (TBBA).

The flame resistant PC containing the new silicone was completed as a practical housing material by adjusting the silicone and the other components. The new flame-resistant PC achieved higher safety when burned and when disposed of than current plastics containing toxic halogen or phosphorus type flame-retarding additives. Table 2-4 shows the properties of the PC containing the new silicone. The PC met a high flame-retarding standard (UL 94 V-0) and had other good important properties, such as strength, moldability (no contamination of mold and PC surface, good melt flow characteristic in mold), surface hardness, and heat resistance. In particular, the impact strength was several times higher than that of PCs containing a bromine compound and a phosphorus compound because the silicone worked as a shock absorbent. Furthermore, these characteristics were maintained at good levels when recycled (re-pelletized and re-molded). Especially, the flame resistance was highly kept comparing with the reference flame-resistance PCs due to the silicone's higher resistance to degradation than that of halogen and phosphorus compounds during re-pelletizing and re-molding.

The new flame resistant PC with the silicone is now commercially available and widely used in housings of electronic products such as monitors, projectors, and personal computers, and also in electronic parts such as battery packs for computers.

Table 2-3 Properties of PC and PCs with flame-retarding additives including new silicone and bromine compound

Properties	PC alone	PC with bromine compound*1	PC with new silicone*2
Flexural strength (kgf/mm^2)	9.6	9.7	9.3
Flexural modulus (kgf/mm^2)	230	230	220
Impact strength (kgf・cm/cm)	97.3	44.7	79.9
HDT (ºC)	138	137	134
Rockwell hardness	62.5	66.1	60.0
Melt flow (g/min)	10.4	10.7	11.8
Flame resistance (UL-94, 1/16 in.)	V-2	V-0	V-0

*1: TBBA: 10phr
*2: Branch type with methyl and phenyl (S3) : 10 phr

Table 2-4 Properties of PC, practical product of PC with new silicone, and conventional flame-resistant PCs

Properties		PC	PC with bromine compound*1		PC with phosphorus compound*2		**PC with new silicone *3**	
Flexural strength	(kgf/mm^2)	9.2	9.8	(9.8) *4	11	(11) *4	9.2	(9.3) *4
Flexural modulus	(kgf/mm^2)	230	232	(234)	270	(266)	228	(228)
Izot impact strength	(kgf･cm/cm)	75	12	(11)	4	(4)	45	(38)
HDT *5	(℃)	134	134	(136)	106	(107)	133	(133)
Melt flow	(g/10min)	22	22	(23)	47	(48)	22	(22)
Flame resistance	(UL94, 1.6 mmt)	V-2	V-0	(V-1)	V-0	(V-0)	V-0	(V-0)

*1: TBBA, *2: Condensed aromatic phosphoric ester, *3: PC with new silicone as a practical product,
*4: The values in parentheses are the results when recycled once at a reuse rate of 100%,
*5: Heat distortion temperature

2-4 Summary

A new silicone derivative was developed for use as a highly safe flame-retarding additive in aromatic thermoplastics, especially polycarbonate (PC) and its derivatives used as housing materials in electronics products. A special silicone with a branched chain structure, with a phenyl-rich mixture of phenyl and methyl groups in the chain, and with methyl groups at the chain terminals, was found to be effective in retarding the combustion of these plastics, and particularly so for PC. The superior flame-retarding effect of the silicone was credited to its excellent dispersion in PC and its movement to the surface of PC during ignition, and then its formation of the highly flame-resistant char barrier in combination with PC. The PC containing the silicone had high flame resistance with no inclusion any toxic flame-retarding additives such as halogen compounds, which made it highly environmentally safe when burned, disposed of, and reused for other purpose. Further, the PC had good other properties, such as strength, moldability, and heat resistance as housing materials; impact strength was in fact better than that of PCs containing halogen-type and phosphorus-type flame-retarding additives. These characteristics were maintained at good levels when recycled.

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Chapter 3

Self-Extinguishing Epoxy Resin Compounds and Their Application to Molding Compounds for Electronic Parts

3-1. Introduction

Epoxy resin compounds, usually composed of epoxy resin, hardener, filler and additives, are widely used as molding compounds for electronic parts such as integrated circuit (IC) packages because of good heat resistance, insulating, adhesive, and strength properties (1, 2). Novolac resin (polymer consisting of phenol derivatives linked with methylene) as hardener and novolac-type epoxy resin (glycidylized novolac resin) are frequently used in molding compounds because these resins have good resistance to heat and humidity. High-fluidity epoxy resins, such as biphenyl-type epoxy resin have begun to be used in high-quality molding compounds for current thin-type and large-type IC packages that require higher moldability at high filler contents of their molding compounds.

As a fire-prevention measure, epoxy resin compounds used in electronic parts generally contain flame-retarding additives, most commonly in the form of halogen compounds as well as other plastics. However, during burning, such halogen compounds generate toxic substances as mentioned in chapter one. Attempts have been made to replace the halogen compounds with phosphorus compounds. But these compounds themselves are somewhat toxic and often degrade the resistance of epoxy resin compounds to heat and humidity.

Further, there have been attempts to produce flame-resistant epoxy resin compounds without using such flame-retarding additives, mainly by restraining the movement of the molecular segments in epoxy resin-hardener networks at high temperatures in order to increase heat resistance for the compounds. One way that has been done is by increasing cross-link densities in the networks to reduce free volumes and to tie-up the molecular segments through the use of multi-functional epoxy resins and hardeners (3-7). Another way that has been tried is to insert bulky substituents into the networks, such as condensed aromatic groups including fluorene derivatives and anthrone derivatives (8, 9) and also

branched structured groups including t-butyl (3). These measures have increased the heat resistance of the resin compounds, as indicated by their higher glass transition temperatures, but they have not produced sufficiently flame resistant compounds. As far as the author knows, there have been no studies of ways to make the flame-resistant epoxy resin compounds other than by increasing the heat resistance of the compounds.

To enable high flame resistance of epoxy resin compounds used as molding compounds without adding flame-retarding additives, there was an attempt to use the above-mentioned high- fluidity epoxy resin in conjunction with a large increase in silica filler content (>90 wt%). This improved flame resistance as well as thermally mechanical properties of the compounds (e.g., decrease in thermal expansion), but did not render the high flow properties required in the molding process of current thin-type and large-type IC packages.

In this chapter, highly flame-resistant epoxy resin compounds that can extinguish themselves without using any flame-retarding additives and their application to molding compounds for electronic parts, especially IC packages, were reported. The high flame resistance of epoxy resin compounds containing novolac derivatives with specific aromatic moiety such as phenylene and biphenylene (phenol aralkyl-type epoxy resin compounds) was shown. Their unique self-extinguishing mechanism, which is the formation of a stable foam layer retarding the transfer of heat to the inside during ignition, was discussed. Improving general properties by locally increasing cross-link density was investigated. The synergistic effectiveness of the silica filler and the epoxy resin compounds for flame resistance were also studied. Based on the self-extinguishing phenol aralkyl-type epoxy resin compounds, the development of an environmentally friendly molding compound with no inclusion of any toxic flame-retarding additives for electronic parts was described. The characteristics of the molding compound were evaluated and compared with those of conventional

molding compounds containing halogen-type flame-retarding additives.

3-2 Experimental

3-2-1 Materials

The sample epoxy resin compounds consisted of epoxy resin, phenol novolac resin derivative as a hardener, fused silica powder as a filler, (70wt%, average particle size 15 μm, crashed shape type, Denkikagaku Kougyo Co.), triphenylphosphine as a curing promoter (0.20wt%, Kantou Kagaku Co.), and carnauba wax as a releasing agent (0.25wt%, Nikkou Fine Products Co.).

In molding compounds to be practically used for IC packages, carbon black as coloring agent (0.3wt% in molding compounds) and an epoxy-type silane coupling agent as surface treatment agent for the silica filler (0.6 wt% in molding compounds) were added as additional additives. In the compounds, only the spherical shape-type silica filler described above was used (84.7wt% in molding compounds). Flame-retarding additives including brominated epoxy resin (tetrabromobisphenol A-type, bromine content was 50 wt%, 1.5 wt% in molding compounds) and diantimony trioxide (1.0 wt% in molding compounds) were also added. These materials were supplied from Sumitomo Bakelite Co.

The reference epoxy resins included a mixture (equal parts by weight) of 4, 4'-diglycidyl (3, 5, 3', 5' tetramethyl-biphenyl) ether and 4, 4'-diglycidyl-biphenyl ether) (biphenyl-type epoxy resin, melting temperature : 111℃, epoxy equivalent : 170, Yuka Shell Co.), phenol novolac-type epoxy resin (softening temperature: 65℃, epoxy equivalent: 176, Sumitomo Chemical Co.), *o*-cresol novolac-type epoxy resin (softening temperature: 68℃, epoxy equivalent: 194, Sumitomo Chemical Co.), tetrakis(glycidyloxyphenyl)-ethane (four-functional-type epoxy resin, softening temperature: 92℃, epoxy equivalent: 203, Yuka Shell Co.) and phenol dicyclopentadiene-type epoxy resin (softening temperature: 56℃,

epoxy equivalent: 241, Nippon Kayaku Co.). As phenol aralkyl-type epoxy resins, phenol *p*-xylene-type epoxy resin (softening temperature.: 55℃, epoxy equivalent: 238, Mitui Chemical Co.) and phenol 4, 4’-dimethylbiphenylene-type epoxy resin (phenol biphenylene-type epoxy resin, softening temperature: 57℃, epoxy equivalent: 270, Nippon Kayaku Co.) were tested. The structures of these resins are shown in Table 3-1.

The reference phenol novolac derivative hardeners included phenol novolac resin (softening temperature: 106℃, hydroxyl equivalent: 106, Showa Koubunshi Co.) and phenol dicyclopentadiene resin (softening temperature: 92℃, hydroxyl equivalent: 170, Nippon Kayaku Co.). As phenol aralkyl resin hardeners, phenol *p*-xylene resin (softening temperature: 83℃, hydroxyl equivalent: 175, Meiwa Kasei Co.) and phenol 4, 4’-dimethylbiphenylene resin (phenol biphenylene resin, softening temperature: 120℃, hydroxyl equivalent: 203, Meiwa Kasei Co.) were tested. The structures of these resins are also shown in Table 3-1.

The epoxy resin compounds were produced by blending the above components in a roll blender heated to 110-115℃, and molding them in a metal mold by using a conventional transfer molding machine under a curing condition of 170℃ for five minutes and then post-curing them at 170℃ for six hours.

3-2-2 Methods

The flame resistance in the molded epoxy resin compounds was determined by the limited oxygen index (LOI) method specified in ASTM D2863 and the UL94V method, which is regulated by Underwriters Laboratories Inc. These methods’ details were shown in the chapter two.

Furthermore, the combustion properties such as heat release rate and time to ignition of the compounds was evaluated by using a cone calorimeter (Fire Testing Technology Co.) under a heat flux of 50 kW/m^2. The method is

specified in ASTM E 1354.

The heat transfer to the inside of molded compound specimens (13mm wide, 30 mm long, 3.2 mm thick) being ignited was determined by measuring the increase of the temperature of the inside of the specimens (10 mm apart from the ignited surface) using a thermocouple (Nihon Netudenki Seisakusho Co.) and a temperature detector (NR-250, Keyence Co.). In this method, a sample held vertically was ignited to the bottom for sixty seconds with a flame as in the UL 94 method.

The cross sections of the molded epoxy resin compounds (13 mm wide, 50 mm long, 1.6 mm thick) after being ignited with a flame for 10 seconds (as in the UL94V method) were observed by using a microscope (MH90, Nippon Kougaku Co.).

The glass transition temperatures and thermal expansion ratios of the molded compounds were measured, at a heating rate of 5℃/min, by thermal mechanical analysis using the method specified in JIS K 7197. The insulation and strength of the molded compounds were measured by the method specified in JIS K 6911, and the water absorption ratios were measured by putting samples in boiling water for 24hours. The degradation products obtained by heating the epoxy resin compounds (700℃, in helium) were analyzed by gas chromatography-mass spectrometry analysis (GC-MS, QP-5050, Shimazu Co.). The thermal degradation of molded compounds was measured by thermogravimetric analysis (TG/DTA6200, Seiko Instruments Co.) in air at a heating rate of 200℃/min.

To determine the moldability of the molding compounds in the molding process, the spiral flow as their flow properties in a metal mold and the barcol hardness as their curing properties were measured as specified in the EMMI normalization and JIS K 6911, respectively. These tests were performed under a curing condition of 175℃ for two minutes

The reliability of IC packages encapsulated with the molding compounds was tested in terms of the packages' resistance to solder heating

after absorption of moisture, humidity, thermal impact, and storage at high temperatures. Silicon test chips with mounted aluminum test circuit (width of 10 μm and interval of 10 μm) were adhered to lead frames made of a nickel-iron alloy (42 Alloy) by using an epoxy resin adhesive containing silver powder and were wire-bonded with gold wires. The bonded chips were molded into the packages encapsulated with the molding compounds by using a conventional transfer molding machine under a curing condition of 175 ℃ for 90 seconds, and then the packages were post-cured at 175 ℃ for six hours.

The solder heating resistance was determined by measuring the ratio of packages that incurred defects after they were soldered with infrared-ray reflow at 240℃ for ten seconds (three times) after a moisture treatment (85 ℃, 85 RH%). Defective packages were detected by observing inner cracks and delaminated interfaces between the chips (9.0 mm wide, 9.0 mm long, 0.35 mm thick) and the resins by using a scanning acoustic tomograph (AT5000, Hitachi Co.). The tested IC packages (20 mm wide, 14 mm long, 2.0 mm thick) were quad flat-type with eighty pins. The number of packages tested was six. The humidity absorption of the packages was determined by measuring the increase in the weight of the packages after the moisture treatment.

The humidity resistance was determined by a pressure-cooker test under a bias voltage (PCTB). In this test, the ratio of packages that incurred open-circuit defects during steaming at 125℃ under 100 RH% and under an electrical condition at a bias voltage of 20 V (DC) between the circuits on the chip (3.0 mm wide, 3.5 mm long, 0.35 mm thick) was measured. The tested IC packages (19 mm wide, 5.0 mm long, 4.0mm thick) were dual in-line type with sixteen pins. The number of the packages tested was fifteen.

The thermal impact resistance was determined by a temperature cycling test. The ratio of packages that incurred outer-crack defects after being subjected to temperature cycles ranging from −65℃ to +150℃ at a

frequency of 3 cycles/hour was measured. The silicon chips and the packages tested were the same type as those used in the solder-heating-resistance test. The number of the packages was twelve.

The resistance to high-temperature storage was estimated by measuring the ratio of defective packages, in which the circuits on the chip had an increase in the resistance of more than twenty percent after high-temperature storage (175℃, 185℃). The tested silicon chips and the packages were the same type as those used in the humidity-resistance test. The number of the packages was ten.

Table 3-1 Chemical structure of tested resins

Kind of Resin	Chemical Structure
Phenol novolac-type epoxy resin (PN-type epoxy resin)	O, OCH2CHCH2, CH2, m
o-Cresol novolac-type epoxy resin (CN-type epoxy resin)	O, OCH2CHCH2, CH3, CH2, n
A mixture of 4, 4'-diglycidyl (3, 5, 3', 5' tetra-methyl-biphenyl) ether and 4, 4'-diglycidyl-biphenyl ether (50+50wt%) (Biphenyl-type epoxy resin)	O, CH2CHCH2O, CH3, CH3, CH3, CH3, OCH2CHCH2, O + O, CH2CHCH2O, OCH2CHCH2, O
Phenol *p*-xylene-type epoxy resin (PX-type epoxy resin)	O, OCH2CHCH2, CH2, CH2, o
4, 4'-dimethylbiphenylene-type epoxy resin {Phenol biphenylene-type (PB-type) epoxy resin}	O, OCH2CHCH2, CH2, CH2, p
Phenol dicyclopentadiene-type epoxy resin	O, OCH2CHCH2, q
Tetrakis(glycidyloxyphenyl) ethane (Four-functional-type epoxy resin)	O, CH2CHCH2O, OCH2CHCH2, O, CHCH, O, CH2CHCH2O, OCH2CHCH2, O
Phenol novolac resin (PN resin)	OH, CH2, r
Phenol *p*-xylene resin (PX resin)	OH, CH2, CH2, s
Phenol 4, 4'-dimethylbiphenylene resin (Phenol biphenylene resin: PB resin)	OH, CH2, CH2, t
Phenol dicyclopentadiene resin	OH, u

3-3 Results and Discussion

3-3-1 Structure of self-extinguishing epoxy resin compounds

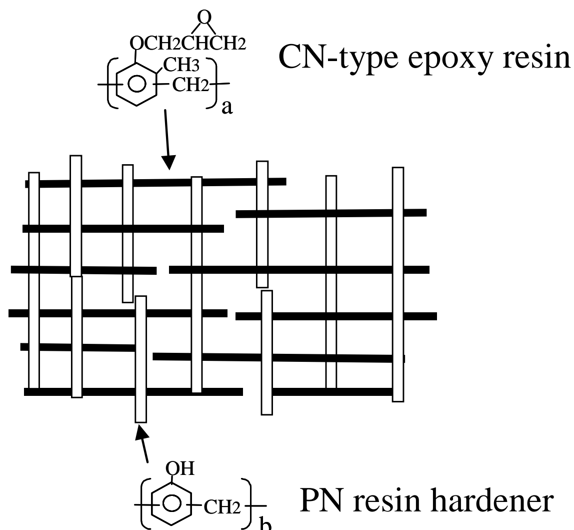
Epoxy resin compounds containing phenol aralkyl-type epoxy resin and the same-type resin hardener, both of which include aromatic moiety such as phenylene and biphenylene in novolac resin structure (phenol aralkyl-type epoxy resin compounds) showed high flame resistance and extinguished themselves even though the compounds did not have any flame-retarding additives and a large contents of silica filler. In particular, a combination of phenol biphenylene (PB)-type epoxy resin and phenol biphenylene (PB) resin hardener, both of which contain biphenylene moiety, resulted in an extremely highly flame-resistant epoxy resin compound. An example of the network structures obtained is schematically shown in Figure 3-1.

The results obtained by the limited oxygen index (LOI) method and the UL method are listed in Table 3-2, and also the results measured using the cone calorimeter are shown in Figure 3-2 and listed in Table 3-3. The phenol aralkyl-type epoxy resin compounds displayed higher flame resistance than that of conventional epoxy resin compounds without such aromatic moiety in novolac resin structure, including *o*-cresol novolac (CN)-type and biphenyl-type epoxy resins and phenol novolac (PN) resin hardener. Of the two aromatic moieties in novolac structure, biphenylene was more effective than phenylene. On the other hand, the inclusion of a non aromatic moiety (dicyclopentadiene) in novolac structure had no flame-retarding effect (Table 3-2).

Furthermore, the flame resistance of phenol-aralkyl epoxy resin compounds was further improved by adding excess hardeners to epoxy resins so as to obtain non stoichiometric compositions. Figure 3-3 indicates the relation between flame resistance and the ratios of phenol derivative hardeners to epoxy resins (H/E ratios) in PB-type epoxy resin compounds containing novolac derivatives with biphenylene moiety. The calculation of

these ratios was based on the stoichiometric reaction ratios (molecular ratios of hydroxy groups in hardener to glycidyloxy groups in epoxy resin). The flame resistance of phenol biphenylen-type epoxy resin compounds was highly improved by the addition of excess hardener. The phenol p-xylene-type (PX) epoxy resin compounds with phenylene moiety showed similar improvement. But the compounds without these aromatic compounds showed limited improvement.

a) Conventional epoxy resin-hardener network



b) New flame-resistant epoxy resin-hardener network

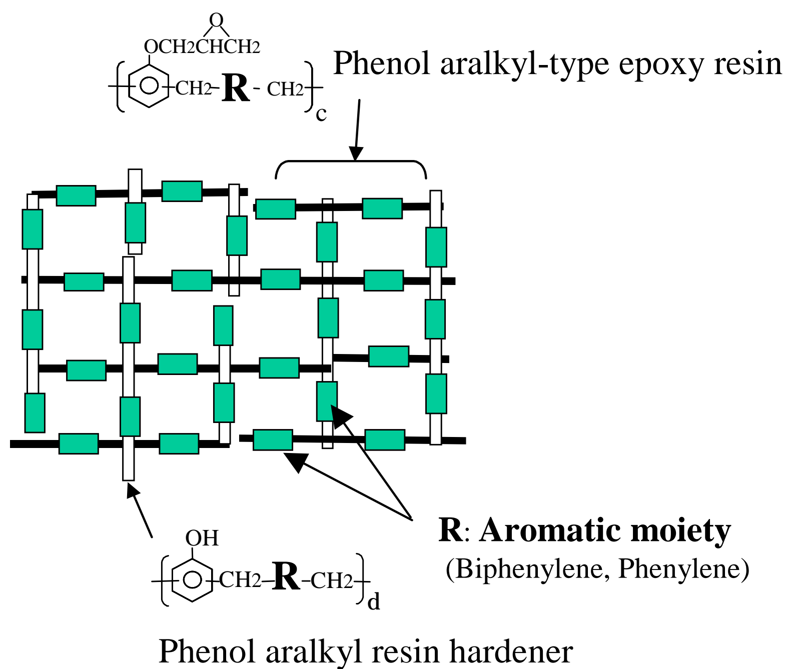


Fig.3-1 Schematic of network structures formed with epoxy resins and hardeners in epoxy resin compounds

Table 3-2 Flame resistance of epoxy resin compounds* containing novolac derivatives

Aromatic moiety inserted in novolac structure	Epoxy resin / Hardener	Limited oxygen index (%)	UL Test
—	Biphenyl-type / PN resin	38.3	V-1
Phenylene	Biphenyl-type / PX resin	48.6	V-1
Biphenylene	Biphenyl-type / PB resin	64.9	V-0
—	Four-functional-type / PN resin	39.5	–
Biphenylene	Four-functional-type / PB resin	62.9	V-0
—	PN- type / PN resin	30.4	V-2
—	CN-type / PN resin	30.2	V-2
Phenylene	PX-type / PX resin	55.9	V-0
Biphenylene	PB-type / PB resin	73.0	V-0
Dicyclopentadiene**	Phenol dicyclopentadiene-type / Phenol dicyclopentadiene resin	28.4	V-2

* Molecular ratio of hydroxy groups in hardeners to glycidyloxy groups in epoxy resins (H/E) is 1.0. ** Non aromatic moiety

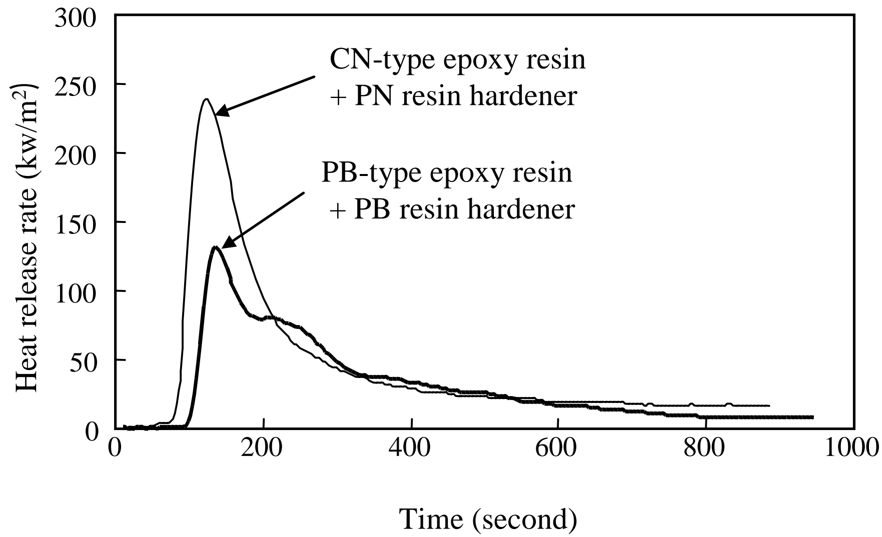
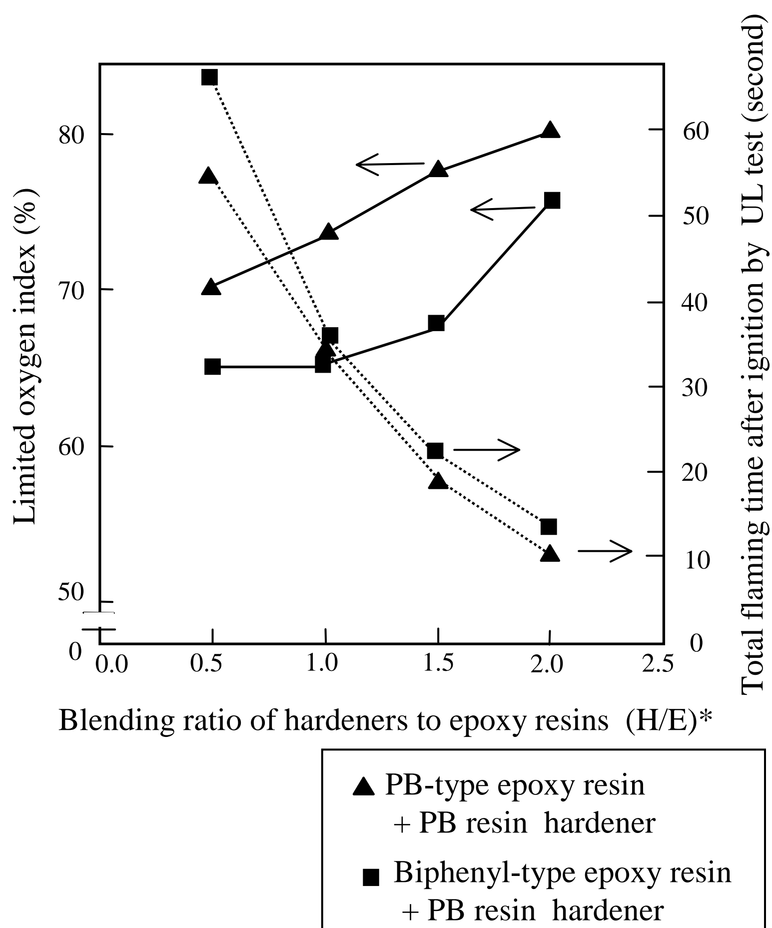


Fig.3-2 Heat release rates of epoxy resin compounds measured with cone calorimeter

Table 3-3 Combustion properties of epoxy resin compounds* measured w

Test items	CN-type epoxy resin + PN resin hardener	PB-type epoxy resin + PB resin hardener
Time to ignition (seconds)	70	83
Maximum heat release rate (kw/m^2)	242	140
Total heat release amount (MJ/m^2)	36	27
Amount of generated CO (g)**	0.53	0.33
Amount of generated CO_2(g)**	4.44	3.79

* H/E=1.0, **Generation amount from epoxy resin compound of 54.0g



Relationship between flame resistance of epoxy resin compounds containing novolac derivative with biphenylene group and ratios of hardeners to epoxy resins. (*Molecular ratio of hydroxy groups in hardener to glycidyloxy groups in epoxy resin)

3-3-2 Self-extinguishing mechanism

It was observed that after ignition, the molded phenol aralkyl-type epoxy resin compounds containing the novolac derivatives with these specific aromatic moieties immediately formed stable foam layers on their surfaces (intumescent phenomena, see Figure 3-4, 3-5). The layers consisted mainly of the resin compounds, chars, and volatile materials generated by the degradation of the compounds. By measuring the heat transfer to the inside of the molded compounds during ignition, it was confirmed that these foam layers effectively retarded the heat transfer as shown in Figure 3-6. Therefore, these improvements in flame resistance were mainly the result of the formation of the stable foam layers during ignition.

These highly flame-resistant epoxy resin compounds had low elasticity at high temperatures because of lower cross-link densities due to the network structures including the aromatic moiety (see Figure 3-1). The low elasticity was confirmed by their lower glass transition temperatures (Tg) and lower elastic modulus at a high temperature (240℃) as listed in Table 3-4, both of which were further decreased by adding excess hardener. Because of the low elasticity of the compounds at high temperatures, the volatile materials (mainly hydrocarbons and carbon oxides) generated from the insides of the compounds by thermal degradation changed the surface layers of the compounds into foam layers.

The epoxy resin compounds containing biphenylene moiety in the novolac structure were more effective in retarding flames than the compounds containing phenylene moiety because as listed in Table 3-2, the former's longer molecular units in the network resulted in lower cross-link densities and lower_elasticity that can facilitate to form foam layers.

The high cross-link density of the epoxy resin compounds without these aromatic moiety made the network structures too rigid to produce foam layers during combustion. The samples of these compounds instead cracked and continued flaming until the flame was extinguished (see Figure 3-5).

Furthermore, as shown in Figure 3-7, the phenol aralkyl-type epoxy resin compounds showed relatively high pyrolysis resistance while having lower cross-link densities. Although the pyrolysis resistance of the compounds slightly decreased by the addition of excess hardener, it was maintained at a good level even (Figure 3-8). This high pyrolysis resistance appears to have made an important contribution to the stability of the foam layers during combustion.

As previously noted, the epoxy resin compound with inclusion of a non aromatic moiety (dicyclopentadiene) in the novolac structure failed to form any flame-retarding foam layers in spite of the low cross-link density of the epoxy resin compound. This must have been due to the lower pyrolysis resistance of the compound with the non aromatic compound (Figure 3-7).

It was also found that the addition of excess phenol derivative hardener not only facilitated the formation of the foam layers by decreasing the cross-link densities but also reduced the amount of flammable substances generated from the epoxy resin compounds during ignition. Among these substances, the most dramatic decreases resulting from the addition of excess hardener were seen in the amount of allylalcohol from glycidyloxy groups in the epoxy resins and in the amount of phenol from the phenol-derivative hardeners.

When the epoxy compounds consisting of phenol biphenylene-type (PB-type) epoxy resin and phenol biphenylene resin (PB resin) hardener with various hardener/epoxy resin (H/E) ratios were heated at 700℃ in helium, the total amount of main hydrocarbon derivatives (flammable substances) generated from the compounds decreased as the H/E ratio increased (see Figure 3-9). The amount of allylalcohol was greatly decreased by the addition of excess hardener. The decrease in allylalcohol appears to have been due to the smaller amounts of the epoxy resin in the compounds with $H/E \geqq 1$. The amount of phenol initially increased when the phenol derivative hardener was added ($H/E>1$), but it decreased with the addition

of excess hardener. The fact that the phenol decreased in spite of the excess phenol derivative hardener in the compound seemed to be due to the formation of condensed phenol compounds with low volatility. (The formation of condensed phenol compounds derived from phenol novolac resin at a high temperature was reported (10)). Such condensed phenol compounds can also contribute to the stability of the foam layer. While epoxy resin compounds with excess epoxy resin (H/E<1) had low elasticity at high temperature (see Table 3-5) because of their low cross-link densities and formed foam layers, they showed lower flame resistance due to the larger amounts of flammable substances such as allylalcohol, which were produced during ignition.

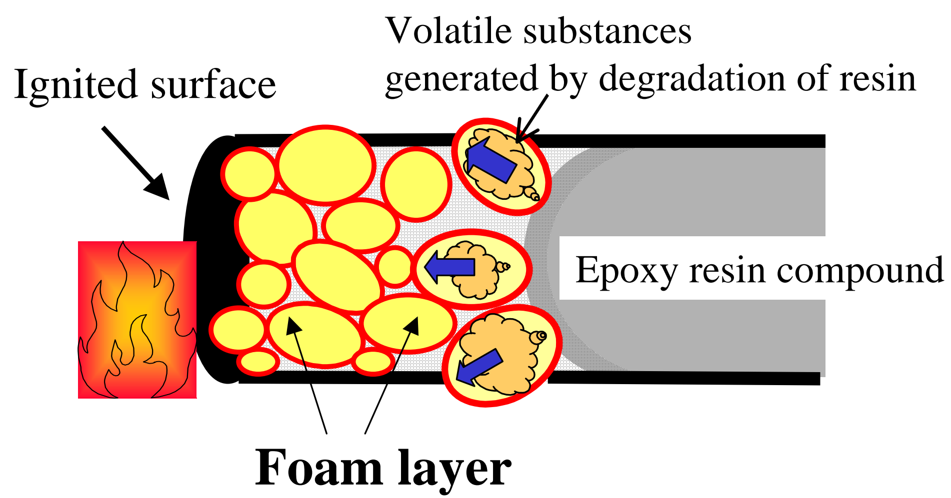
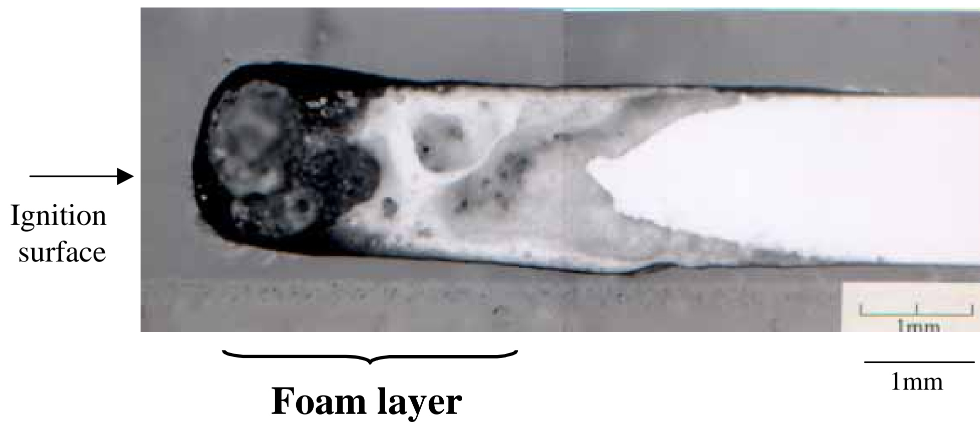


Fig. 3-4 Schematic representation of formation of foam layer on new epoxy resin compounds (phenol aralkyl-type) during ignition

(a) PB-type epoxy resin +PB resin hardener



(b) CN-type epoxy resin + PN resin hardener

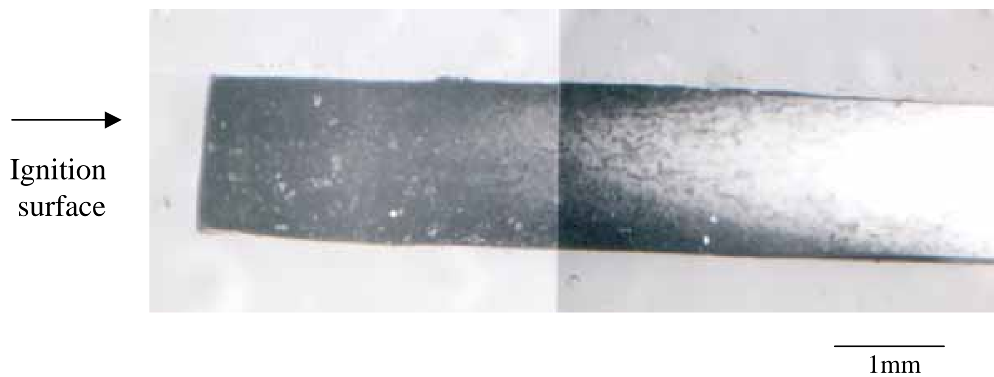


Fig. 3-5 Cross sections of molded epoxy resin compounds after ignition (*1: H/E=1.0. The flame self-extinguished within three seconds. *2: H/E=1.0. The flame self-extinguished within five seconds.)

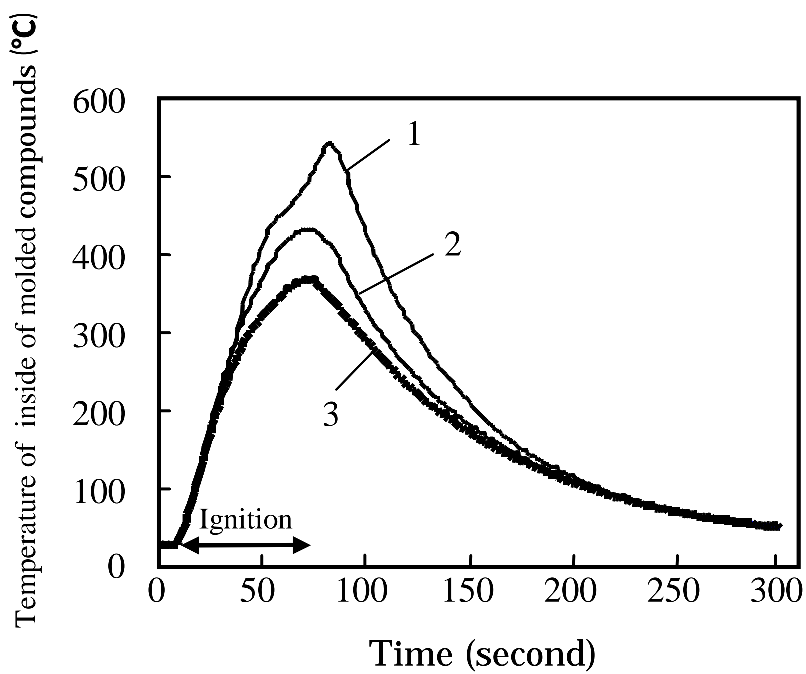


Fig. 3-6 Heat transfer to inside of molded epoxy resin compounds during ignition (*1: H/E= 1.0. No foam layer formed, *2: H/E=1.0. A foam layer formed, *3: H/E=1.0. A foam layer effectively formed.)

Table 3-4 Characteristics of epoxy resin compounds containing novolac derivatives*

Aromatic moiety inserted in novolac structure	Epoxy resin / Hardener	TMA** Tg (℃)	TMA** α_1 ($\times 10^{-5}$)	TMA** α_2 ($\times 10^{-5}$)	Water absorption ratio (wt%)	Flexural strength at room temp. (kgf/mm^2)	Flexural modulus at room temp. (kgf/mm^2)	Flexural strength at 240℃ (kgf/mm^2)	Flexural modulus at 240℃ (kgf/mm^2)	Volume resistance at 150℃ (Ωcm)
—	Biphenyl-type / PN resin	140	2.3	4.8	0.38	14.2	1330	0.97	61.7	2.6×10^{12}
Phenylene	Biphenyl-type / PX resin	126	2.1	5.3	0.40	15.1	1310	0.99	42.1	–
Bipenylene	Biphenyl-type / PB resin	120	2.1	5.4	0.37	13.8	1240	1.09	33.5	2.0×10^{12}
Bipenylene	Four-functional-type / PB resin	165	2.4	4.6	0.44	13.4	1320	1.29	54.3	2.0×10^{13}
—	CN-type / PN resin	178	2.2	4.1	0.31	11.6	1310	1.38	103.0	1.2×10^{13}
Bipenylene	PB-type / PB resin	118	2.1	5.4	0.30	13.2	1300	0.68	28.2	4.6×10^{12}

* H/E=1.0 ** Thermal mechanical analysis

Table 3-5 Characteristics of epoxy resin compounds with various blending ratios of hardener to epoxy resin

Epoxy resin / Hardener	H/E*	TMA Tg (℃)	TMA α_1 ($\times 10^{-5}$)	TMA α_2 ($\times 10^{-5}$)	Water absorption ratio (wt%)	Flexural strength at room temp. (kgf/mm²)	Flexural modulus at room temp. (kgf/mm²)	Flexural strength at 240℃ (kgf/mm²)	Flexural modulus at 240℃ (kgf/mm²)	Volume resistance at 150℃ (Ωcm)
PB -type / PB resin	0.5	75	2.2	5.9	0.38	10.5	1410	0.21	5.0	—
	1.0	118	2.1	5.4	0.30	13.2	1300	0.68	28.2	4.6×10^{12}
	1.5	105	2.0	5.5	0.34	13.2	1350	0.37	11.3	1.4×10^{12}
	2.0	95	1.8	5.1	0.44	10.4	1390	0.19	3.7	—
Biphenyl-type / PB resin	0.5	96	2.2	5.3	0.46	12.1	1370	0.64	12.4	—
	1.0	120	2.1	5.4	0.37	13.8	1240	1.09	33.5	2.0×10^{12}
	1.5	101	1.8	4.5	0.49	10.0	1350	0.34	6.2	5.8×10^{11}

* Molecular ratio of hydroxy groups in hardener to glycidyloxy groups in epoxy resin

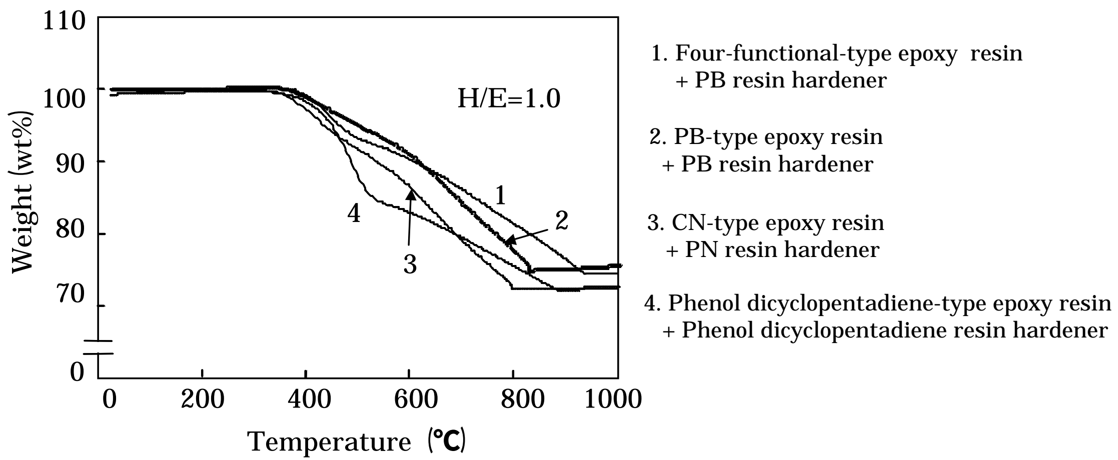


Fig. 3-7 Thermogravimetric analysis of various epoxy resin compounds* containing novolac resin derivatives.

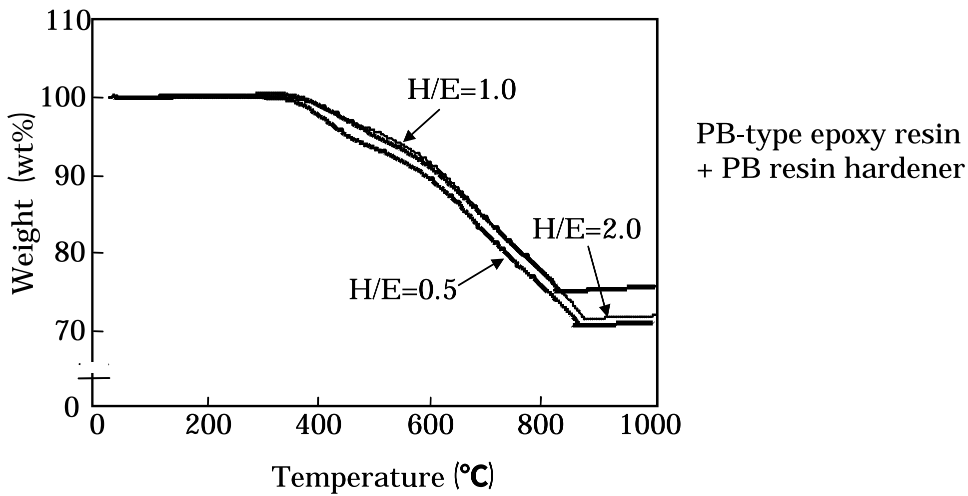


Fig. 3-8 Thermogravimetric analysis of epoxy resin compounds containing PB-type epoxy resin and PB resin hardener with various blending ratios (H/E)

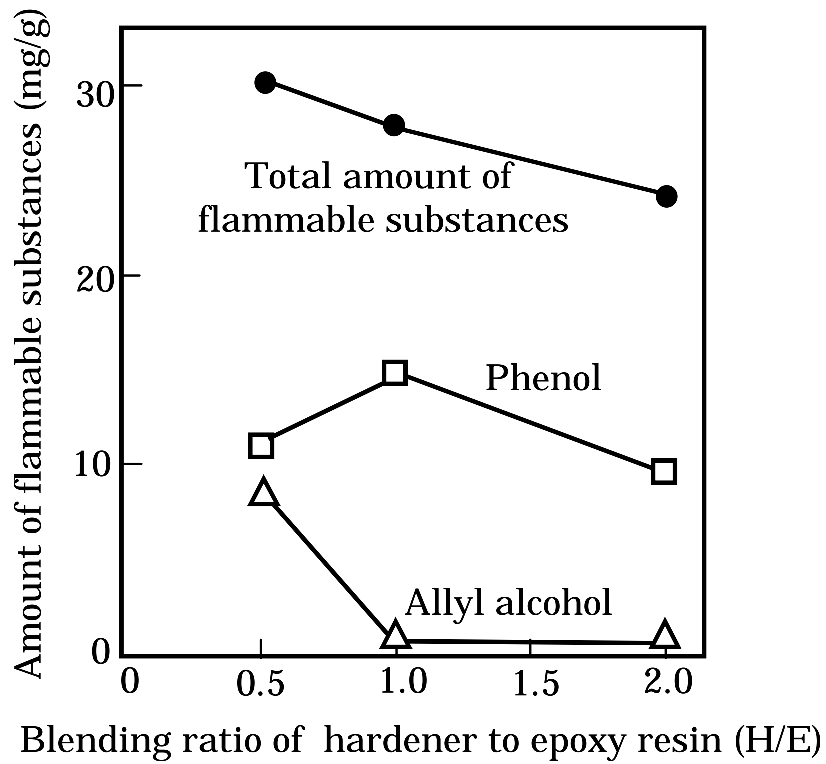


Fig. 3-9 Relation between blending ratio of hardener to epoxy resin and amount of flammable substances generated from PB-type epoxy resin compounds by heating (700℃)

3-3-3 Improving general properties by locally increasing cross-link density

These self-extinguishing phenol aralkyl-type epoxy resin compounds obtained showed good other characteristics such as mechanical properties, water resistance, and insulating properties (Table 3-5). However, the compounds came at the expense of a decrease in heat resistance indicated by the lower Tg values and strength at high temperature, because of the lower cross-link densities in the networks. Particularly, too excess addition of the hardener caused the decrease.

The use of a multi functional epoxy resin with four glycidyloxy groups [tetrakis-(glycidyloxyphenyl)ethane, see Table 3-1] in these epoxy resin compounds improved these properties while still maintaining excellent flame resistance (see Figure 3-10 and Table 3-6). As shown schematically in Figure 3-11, this combination of results was attributed to a purely local increase in cross-link density within the network by using the epoxy resin. Although the overall elasticity slightly increased, it remained low enough for foam layer formation. Furthermore, as shown in Figure 3-7, the improvement of pyrolysis resistance contributed to flame resistance by increasing the stability of the foam layers.

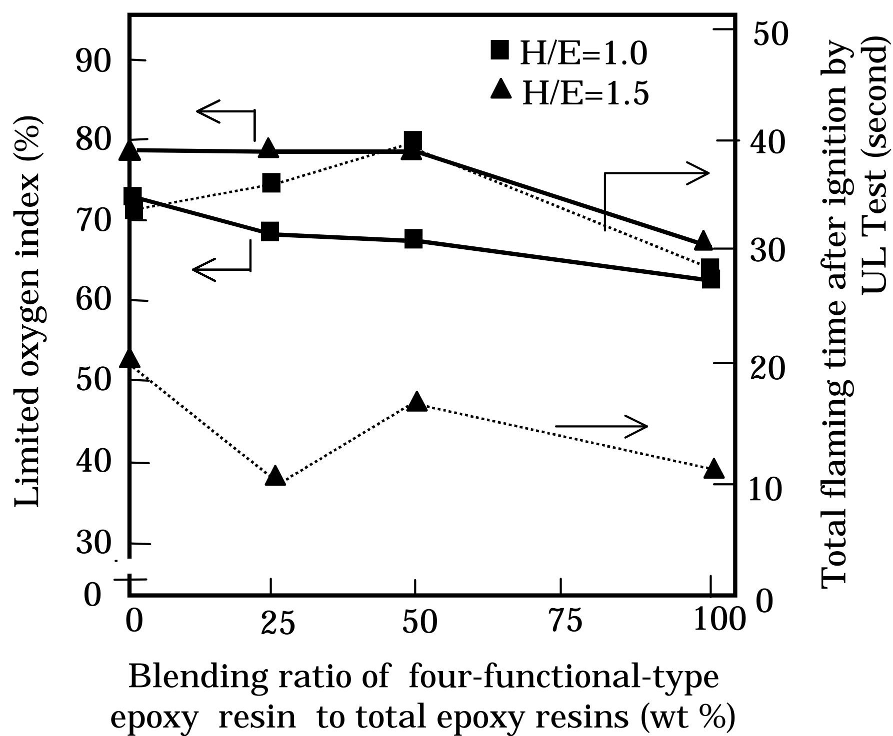


Fig. 3-10 Relation between flame resistance of epoxy resin compounds* and blending ratio of four-functional-type epoxy resin to total epoxy resins.
(* PB-type and four-functional-type epoxy resin + PB resin hardener)

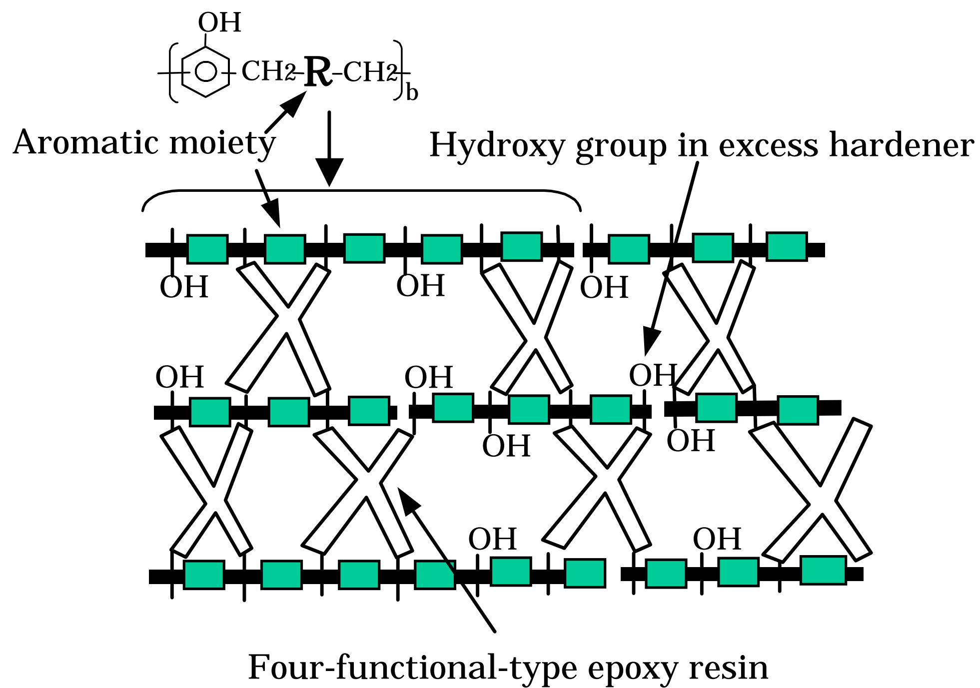


Fig. 3-11 Schematic representation of network structure in epoxy resin compound comprising four-functional-type epoxy resin and excess phenol aralkyl resin hardener

Table 3-6 Characteristics of epoxy resin compounds* with various blending ratios of four-functional-type epoxy resin to total epoxy resins

Ratio of four-functional-type epoxy resin in total epoxy resin (wt%)	H/E	TMA			Water absorption ratio (wt%)	Flexural strength at room temp. (kgf/mm²)	Flexural modulus at room temp. (kgf/mm²)	Flexural strength at 240℃ (kgf/mm²)	Flexural modulus at 240℃ (kgf/mm²)	Volume resistance at 150℃ (Ωcm)
		Tg (℃)	α_1 ($\times 10^{-5}$)	α_2 ($\times 10^{-5}$)						
0	1.0	118	2.1	5.4	0.30	13.2	1300	0.68	28.2	4.6×10^{12}
25	1.0	129	2.0	5.1	0.30	14.1	1260	1.76	35.0	-
50	1.0	143	2.1	4.8	0.35	13.4	1260	1.99	41.8	-
100	1.0	165	2.4	4.6	0.44	13.4	1320	1.29	54.3	2.0×10^{13}
0	1.5	105	2.0	5.5	0.34	13.2	1350	0.37	11.3	1.4×10^{12}
25	1.5	110	1.9	5.2	0.33	13.8	1300	0.67	25.6	-
50	1.5	118	1.9	5.2	0.35	13.3	1310	0.77	35.6	-
100	1.5	125	2.0	5.1	0.38	13.9	1510	0.73	29.2	4.9×10^{12}

*The compounds contain PB-type and four-functional-type epoxy resins and PB resin hardener

3-3-4 Effectiveness of silica filler in flame resistance

Among the additives in epoxy resin compounds as molding compounds for IC packages, silica-particle filler is added in the largest amounts (more than 70 wt%) and affects flame resistance of the compounds as well as their other important characteristics, such as mechanical properties and moldability. It was found that the self-extinguishing phenol-aralkyl-type epoxy resin compounds had a highly synergistic effectiveness of silica filler for their flame resistance.

Figure 3-12 shows the effects of silica-filler content on flame resistance of epoxy resin compounds. The phenol aralkyl-type (PB-type) epoxy resin compound showed much higher flame resistance than the conventional epoxy resin compounds in terms of the overall content of silica filler. Its flame-resistance effectiveness increased as the filler content increased. These results showed that, in addition to the flame-retarding effectiveness of the silica filler as an incombustible material, the synergistic action between the silica filler and the resin part in the compound significantly increased its flame resistance. Based on the observation during the combustion, it appeared that the silica filler in the compound worked to increase the stability of the foam layer formed with the compound when it was ignited. At a low silica content, the foam layer was easily broken because of the low strength of the compound. As the silica filler content was increased, the foam layer became more stable due to the higher strength of the compound (Table 3-7). The compound showed excellent flame resistance when it had a silica filler content of more than 70 wt%, but much larger amounts (more than 90wt%) of the silica retarded the formation of the foam layer due to an excess increase in the modulus and a decrease in the elongation of the compound.

In contrast, the conventional epoxy resin compounds used as references showed only limited improvement of their flame resistance when the silica content was increased. In particular, the epoxy resin compound containing

CN-type epoxy resin and PN resin hardener showed no improvement. This was because the foam layer formation at ignition was difficult when the network structures had high cross-link densities, described above.

3-3-5 Development of an environmentally friendly molding compound for electronic parts

An environmentally friendly molding compound has been developed for electronic parts, especially IC packages by using PB-type epoxy resin and PB resin hardener, and by adjusting the contents of silica filler and other additives. For the reference purposes, the new compound was compared with a model of high-quality epoxy molding compounds currently used. The compound contains biphenyl-type epoxy resin, PX resin hardener, and flame-retarding additives consisted of a bromine compound and diantimony trioxide. Also, another model compound containing the epoxy resin, the hardener, and no flame-retarding additives was tested.

The new epoxy molding compound had excellent characteristics as a high-quality encapsulating material for current IC packages, as can be seen in Table 3-8. The compound achieved the high flame-resistance standard (UL94V-0) required even though it had no flame-retarding additives. This means that it can be burned and disposed of much more safely compared with current molding compounds including halogen compounds. It also showed high water resistance (low water absorption) due to its hydrophobic characteristics resulting from the inclusion of a large amount of aromatic moiety (biphenylene) in the resin structures. Other general properties, including strength, insulation, and moldability, such as flow properties and curing properties at molding process, were good enough to enable practical use of this compound for current IC packages. Though its glass transition temperature was a little lower than those of the reference compounds due to its lower cross-link density, it did not pose any problems in using this compound.

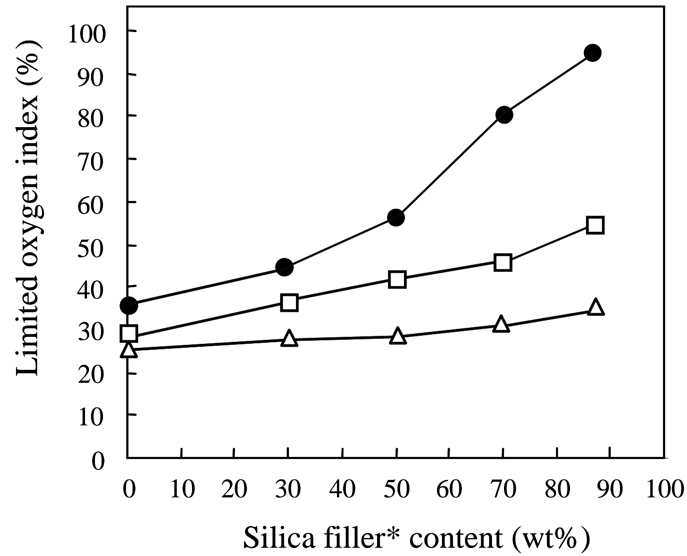
The reliability of IC packages encapsulated with this new molding compound was higher than that of the packages with reference molding compounds (Table 3-9). In particular, its solder-heating resistance after humidity absorption was superior to that of the reference compounds. It is well known that explosive evaporation of absorbed water results in cracks in IC packages and delaminates the interfaces between IC chips and molding compounds during soldering (11,12). The higher resistance of the new molding compound to solder heating was mainly attributed to the lower moisture absorption in the packages (Figure 3-13) due to the hydrophobic characteristics of the compound as above-mentioned. In addition, the lower elastic modulus of the compound at high temperatures could improve the resistance to delamination of the interface between the chips and the compound because the lower modulus of epoxy molding compounds was reported to be closely related to their ability to adhere strongly to chips during soldering (13).

The new molding compound showed higher humidity resistance than that of reference molding compounds due to the hydrophobic property of the compound. It also resulted from the lack of flame-retarding additives of bromine compounds and antimony oxide, both of which generate corroding substances that damage ICs during steaming.

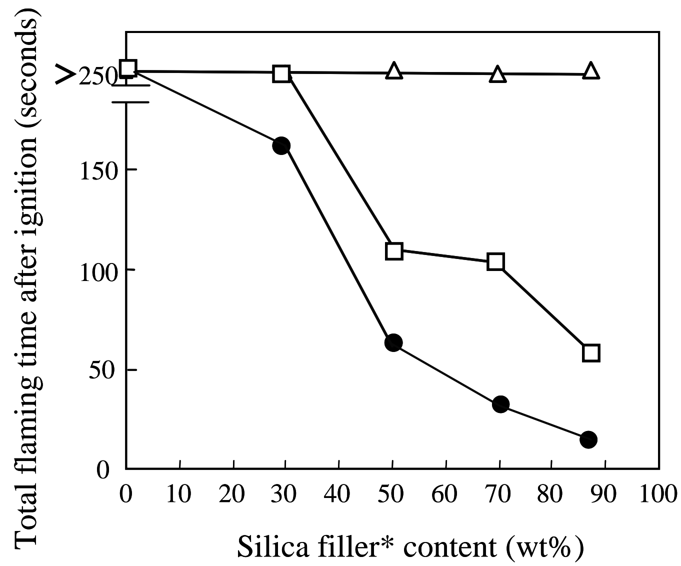
The resistance of the new molding compound to high-temperature storage was much higher than that of the reference compounds (Figure 3-14). This was because of the higher pyrolysis resistance of the compound and the lack of these flame-retarding additives, which also generate corroding substances at high temperatures. The thermal-cycle resistance of the compound was on the same level as that of the reference compounds.

These excellent characteristics of the new molding compound should enable its use as a high-quality encapsulating material with using no toxic flame-retarding additives, which makes it highly environmentally safe when burned, disposed of, and reused to other purpose.

a) Limited oxygen index method



b) UL test method



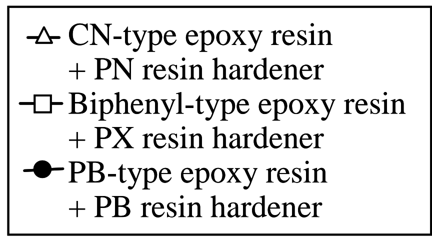


Fig. 3-12 Relation between flame resistance and silica filler* content in epoxy resin compounds (*Spherical shape-type)

Table 3-7　Strength properties at high temperature (240℃) of molding compounds.

Strength properties	Silica filler* content (wt%)	Epoxy resin / Hardener		
		PB-type / PB resin	CN-type / PN resin	Biphenyl-type / PX resin
Flexural strength (kgf/mm^2)	30	0.39	0.51	0.24
	50	0.40	0.62	0.45
	70	0.78	1.42	0.79
	87	1.92	2.80	2.36
Flexural modulus (kgf/mm^2)	30	3.75	14.4	2.94
	50	4.76	21.2	6.53
	70	11.1	65.4	15.6
	87	58.4	253	84.3
Elongation (mm/mm)	30	0.104	0.035	0.082
	50	0.084	0.029	0.069
	70	0.070	0.022	0.051
	87	0.033	0.011	0.028

* Spherical shape-type

Table 3-8 Characteristics of molding compounds for practical use

		New molding Compound*	Reference molding Compounds* (1)	Reference molding Compounds* (2)
Epoxy resin/ Hardener		PB-type/ PB resin	Biphenyl-type/ PX resin	←
Flame-retarding additive		non	Bromine compound and Sb_2O_3	non
Specific gravity	(g/cm^3)	1.96	1.95	1.99
Water resistance	Water absorption ratio (%) (Boiling for 24hrs)	0.17	0.25	0.21
Strength property	Flexural strength at room temperature (kgf/mm^2)	17.2	16.1	17.7
	Flexural modulus at room temperature (kgf/mm^2)	2140	2160	2340
	Flexural strength at 240°C (kgf/mm^2)	1.59	1.48	1.88
	Flexural modulus at 240°C (kgf/mm^2)	48.1	56.1	64.2
Heat resistance	Glass transition temperature (°C)	124	134	132
Thermal expansion	α_1 ($x10^{-5}$)	1.3	1.1	1.1
	α_2 ($x10^{-5}$)	5.0	4.8	5.1
Insulating property	Volume resistance ($x10^{11}\Omega cm$) at 150 °C	86	89	91
Moldability	Spiral flow length (cm)	106	115	130
	Barcol hardness	> 80	> 80	> 80
Flame resistance	UL94 test (1.6mmt)	V-0	V-0	Not V-2

* Spherical shape- type silica filler of 84.7wt% is contained

Table 3-9 Package reliability of molding compounds

			New molding compound	Reference molding compounds (1)	Reference molding compounds (2)
Flame-retarding additive			non	Bromine compound and Sb_2O_3	non
Solder heating Resistance	Humidity treatment time before soldering	96 hrs	0/6[*1] (0/6)[*2]	0/6 (6/6)	0/6 (6/6)
		168 hrs	0 (S6)	6 (6)	0 (6)
Humidity resistance (Pressure cooker bias test)	Humidity treatment time	120 hrs	0/15[*3]	2/15	2/15
		140 hrs	0	3	2
		180 hrs	0	13	14
		240 hrs	1	–	–
Thermal cycle resistance	Thermal cycle number	1000cycles	0/12[*4]	0/12	0/12

*1: Inner cracked package ratio after soldering (85°C/85RH% → 240°C)
*2: Failure package ratio with delaminated interface between chip and resin (S shows small delaminated interface)
*3: Failure package ratio with opened circuit (125°C/100RH%, 20V)
*4: Outer cracked package ratio after thermal cycle (150～-65 °C)

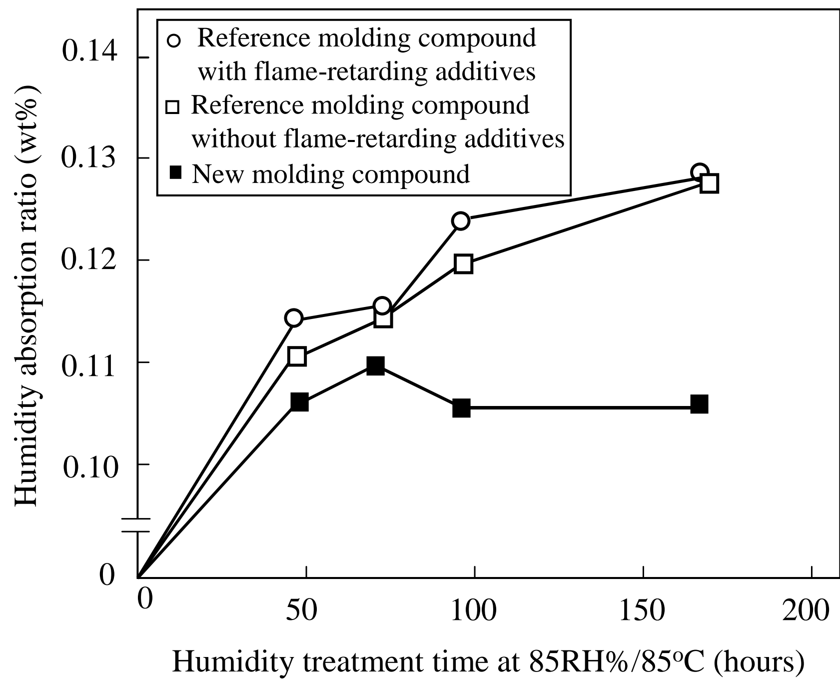
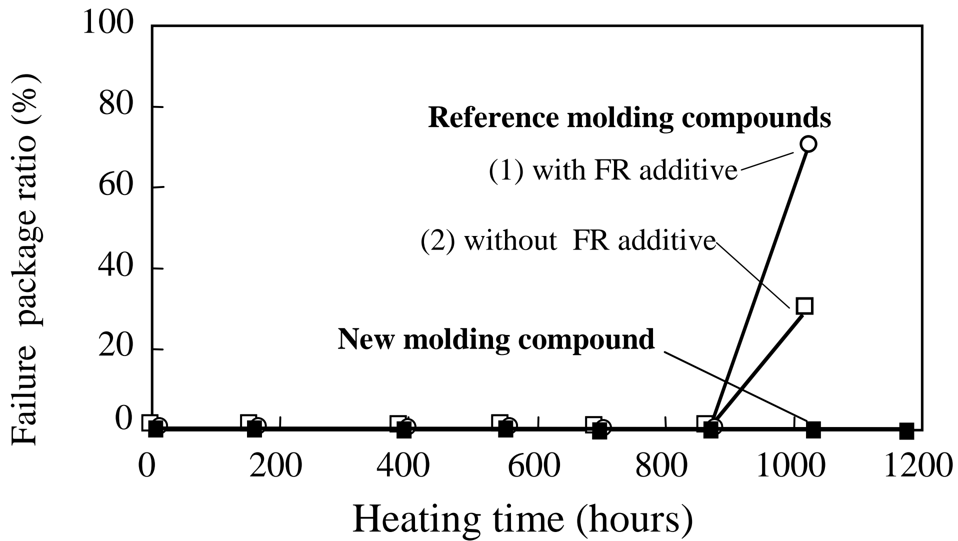


Fig. 3-13 Humidity absorption of IC packages* molded with molding compounds (* Quad flat-type packages used in the test of solder-heating resistance)

a)175℃



b) 185℃

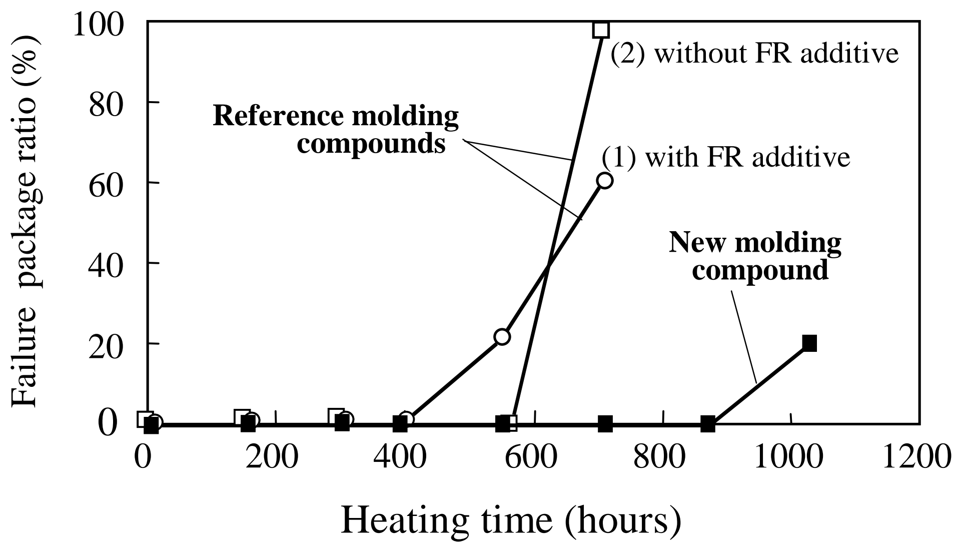


Fig. 3-14 Resistance to high temperature storage of IC packages encapsulated with molding compounds

Self-extinguishing epoxy resin compounds with no inclusion of toxic flame-retarding additives such as halogen compounds and their application to molding compounds for electronic parts were studied. Phenol aralkyl-type epoxy resin compounds containing novolac derivatives with specific

aromatic moieties such as biphenylene had high flame resistance and extinguished themselves after ignition. The compounds formed stable foam layers on the resin surfaces during the ignition due to low elasticity at high temperatures (low cross-link densities) of the compounds after curing and their high pyrolysis resistance. The foam layers effectively retarded the transfer of heat to the insides during the ignition. A purely local increase in the cross-link densities within the network structures of the cured compounds by using an epoxy resin with four glycidyloxy groups improved heat resistance and strength at high temperatures of the compounds while maintaining flame resistance. Adding silica filler to the epoxy resin compounds resulted in the synergistic effectiveness of the compounds for flame resistance because it increased the foam-layer stability during ignition. Based on the phenol aralkyl-type epoxy resin compounds, especially phenol biphenylene-type epoxy resin compound, an environmentally friendly molding compound was developed. It had highly flame resistance with no inclusion of any toxic flame-retarding additives, which made it highly environmentally safe when burned and disposed of. The compound showed other excellent characteristics including water resistance and package reliability such as solder-heating resistance and high temperature storage resistance, which enabled its use as a high quality encapsulating material.

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Chapter 4

Environmentally Friendly Printed Wiring Boards without Toxic Flame-Retarding Additives

4-1 Introduction

Printed wiring boards (PWBs), which are frequently laminates consisting of glass-fiber fabric and epoxy resin compounds (glass-epoxy laminates), are used as a principal electronic component to mount electronic parts such as IC packages. The boards usually include halogen compounds as a flame-retarding additive to provide them with high flame resistance required of the components. The use of halogen compounds, however, raises environmental concerns, as mentioned in the previous chapters. Therefore, in addition to fire related dangers, the treatment of the PWB wastes and their reuse for other purposes are also made extremely difficult.

These halogen compounds are being replaced with phosphorus compounds. However, these compounds themselves are somewhat toxic and adversely affect the characteristics of PWBs, including humidity resistance and heat resistance. Moreover, metal hydroxides such as aluminum hydroxide and magnesium hydroxide have been suggested as replacements for the halogen compounds. These hydroxides retard flames by absorbing the heat during ignition, but they must be added in large amounts, and this adversely affects important characteristics of PWBs, such as chemical resistance, electronic properties, and moldability.

The chapter three reported self-extinguishing phenol aralkyl-type epoxy resin compounds including no flame-retarding additives. In this chapter, the development of an environmentally friendly glass-epoxy laminate-type PWB by using the phenol aralkyl-type epoxy resin compounds and a limited amount of harmless metal hydroxides was described. The synergistic effectiveness of the phenol aralkyl-type epoxy resin compounds and metal hydroxides in improving the flame resistance of the PWB was demonstrated. Also, the characteristics of the PWB were evaluated and compared with those of current PWBs containing halogen or phosphorus-type flame-retarding additives (1, 2, 3). Finally, the safety of the PWB when it was thermally treated, disposed of, and recycled was discussed.

4-2 Experimental

4-2-1 Materials

The tested reference epoxy resin was bisphenol A-type epoxy resin (epoxy equivalent: 473, Japan Epoxy Resin Co.). Phenol aralkyl-type epoxy resins tested were phenol *p*-xylene-type (PX-type) epoxy resin (softening temperature: 55 ℃, epoxy equivalent: 238, Mitui Chemicals Co.) and phenol biphenylene-type (PB-type) epoxy resin (softening temperature: 57 ℃, epoxy equivalent: 270, Nippon Kayaku Co.). The reference hardeners tested included phenol novolac resin (softening temperature: 106℃, hydroxyl equivalent: 107, Meiwa Plastics Industries Co.) and dyciandiamide (active hydrogen equivalent: 21, Air Products Japan Co.). As phenol aralkyl resin hardeners, phenol *p*-xylene resin (PX resin, softening temperature: 83 ℃, hydroxyl equivalent: 175, Meiwa Plastics Industries Co.) and phenol biphenylene resin (PB resin, softening temperature: 120 ℃, hydroxyl equivalent: 203, Meiwa Plastics Industries Co.) were tested. These hardeners were added to the epoxy resins at their equivalent ratios. These phenol aralkyl resins' structures are shown in Table 3-1 in chapter three.

The tested metal hydroxide powders were aluminum hydroxide (BW103, Nippon Keikinzoku Co.) and magnesium hydroxide (Fine Magu MO、TMG Co.).

Prepregs consisting of half-cured epoxy resin compounds and glass-fiber woven fabrics (E-glass, 0.18mm thick, Nittobou Co.) were produced by impregnating the fabric with a solution containing resins and additives, drying the fabric at room temperature for ten minutes, and half-curing them at 120 ℃ for one hour. The solution consisted of the above-mentioned epoxy resin and hardener, an amine-type curing promoter (2E4MZ, Shikoku Kasei Co.), a silane coupling agent (KBM 403, Sin-Etsu Chemical Co.), and a suitable solvent (methylethylketone).

Glass-epoxy laminate-type printed wiring boards (PWBs) were prepared by pressing (2-4 MPa) the prepregs (seven layers) under curing conditions at

180 ℃ for one hour and then post-cured at 175 ℃ for six hours. Double-sided copper-clad laminates consisting of seven layers of the prepregs between two sheets of 18 μm-thick copper foil were prepared by hot-pressing and post-curing as described above.

Epoxy resin composites used as molding compounds consisted of phenol aralkyl-type epoxy resins, phenol aralkyl resins as a hardener, fused silica powder as a filler, (crushed- shape-type: average particle size: 20 μm, Denkikagaku Kougyo Co.), triphenylphosphine as a curing promoter (0.66 wt% in resin part except for filler, Kantou Kagaku Co.), and carnauba wax as a releasing agent (0.75 wt% in the resin part, Nikkou Fine Products Co.). The epoxy resin composites were produced by blending the above components in a roll blender heated to 105-115 ℃. The composites were molded in a metal mold by using a conventional transfer molding machine under curing conditions at 175 ℃ for three minutes, and then post-cured at 175 ℃ for six hours.

4-2-2 Methods

The flame resistance of PWBs and epoxy resin composites was determined by using the UL94V method, as mentioned in the chapter two.

Cross sections of the PWBs and the molded composites (13 mm wide, 50 mm long, 1.6 mm thick) were observed by using a reflective fluorescent microscope (BH-2, Olympus Optical Co.) after being ignited with a flame for ten seconds (as prescribed in the UL94V method).

The thermal degradation and thermal release behavior of the PWBs were analyzed using a thermogravimetric analyzer (TG/DTA6200, Seiko Instruments Co.) in the air at a heating rate of 200 ℃ /min.

The chemical resistance was evaluated by weighing the PWBs after dipping them for four hours in various acid and alkali solutions used to form copper circuits on PWBs. The water resistance of the PWBs was determined by weighing the PWBs after dipping them in boiling water and in water at

room temperature.

The glass transition temperature (Tg) and thermal expansion ratio of the PWBs at a heating rate of 5 ℃ /min were determined by a thermal mechanical analysis using a method specified in JIS K 7197. The solder-heating resistance of the PWBs was determined by observing the incurred defects, such as delamination and swelling of the boards, after they had been soldered in solder bath at 260 ℃ after humidity treatment (121℃, 100RH%, 2atm) for three hours. The solder-heating resistance of the PWBs without the humidity treatment was also measured. The insulation and dielectronic properties of the PWBs and their copper-peel strength were measured by a method specified in JIS C 6481.

The processability of the PWBs in their practical fabrication was evaluated using double-sided copper-clad laminates shaped according to the specifications of the Institute for Interconnecting and Packaging Electronic Circuits (IPC). After circuit-formation that includes plating and wet-etching, in which various chemicals such as acids and alkalis were used, the boards were weighed. After hole drilling (0.9 mm in diameter) and cupper plating, the roughness of the inside of the hole was measured.

The resistance to thermal stress and humidity of the PWBs was determined by a method specified in JIS C 5012. The change in the insulation resistance between the comb-circuits (width and space width were both 165 μm) on the PWBs regulated by the IPC was measured after the PWBs had been subjected to temperature cycles ranging from 25 to 65 ℃ at humidity concentrations between 90 and 95 %. The heating profile of one cycle is shown in Figure 4-8.

The degradation substances generated from the pulverized PWBs (0.3 g, under 80μm in diameter) in a tube-type electric furnace during heating at 850 ℃ for thirty minutes in the air (0.3 L/min) were measured by using methods specified in JIS K 7217. Hydrogen cyanide in the exhaust gases was absorbed in a solution containing sodium hydroxide (2.0 wt%), and then

its concentration was measured by using an absorptionmetry analyzer (UV-1200, Shimazu Co.). Hydrogen bromide and phosphoric acid in the exhaust gases were absorbed in a solution containing hydrogen peroxide (0.1 vol%), and their concentrations were measured by using an ion chromatography analyzer (HIC-10A, Sumazu Co.). Carbon oxides (CO, CO_2) in the exhaust gases were collected in a gas bag, and their concentrations were determined by using a gas chromatography mass spectrometer (QP-5050A, Shimazu Co.). These concentrations were compared with those of polyethylene, including no additives (Niporon hard 1000, Tosoh Co.).

4-3 Results and Discussion

4-3-1 Flame resistance

The flame resistance of the new glass-epoxy laminate-type PWBs fabricated with phenol aralkyl-type epoxy resin compounds, consisting of phenol aralkyl-type epoxy resins and phenol aralkyl resin hardeners, was investigated. The PWBs were found to have higher flame resistance than reference PWBs with conventional epoxy resin compounds, consisting of bisphenol A-type epoxy resin, and dicyandiamide or phenol resin as a hardener when these PWBs did not contain flame-retarding additives (see Table 4-1). However, the flame resistance of the new boards did not meet the UL94V-0 standard (i.e., total flaming time after ignition must be within fifty seconds) required of current FR-4-grade PWBs. Their flame resistance was lower than that of the epoxy resin composites as molding compounds, mainly consisting of the phenol aralkyl-type epoxy resin compounds and silica particle filler. As shown in Figure 4-1, the boards did not sufficiently form flame-retardant foam layers such as those formed with the composites because the glass-fiber-woven fabrics in the boards retarded the foam layer formation. This inability of the new boards to form foam layers seems to have caused their insufficient flame resistance. In contrast, the silica particle filler in the composites did not retard the foam layer formation, as mentioned in chapter three.

To improve the flame resistance of the new boards, the combinations of the phenol aralkyl-type epoxy resin compounds and harmless metal hydroxides such as aluminum and magnesium hydroxides, which absorb heat during ignition was studied. As a result, it was found that the boards containing the phenol aralkyl-type epoxy resin compounds were made to meet the UL94V-0 standard by adding the hydroxides in a limited amount (more than 40 wt% in the resin parts except for glass fiber in the boards) (see Figure 4-2). In contrast, the reference boards containing the conventional epoxy resin compounds did not meet the standard even when

the hydroxides were added in much greater amounts.

Figure 4-3 compares the thermal degradation of the new PWBs and the reference PWBs. As can be seen, the new boards containing the phenol aralkyl-type epoxy resin compounds had higher pyrolysis resistance than the reference boards containing the conventional epoxy resin compounds, whether they contained metal hydroxides or not. The resin parts in the new boards, which included the aromatic moiety of the epoxy resin compounds, could easily form pyrolysis-resistant substances when heated, because polymers containing such aromatic moiety are known as precursors that form highly pyrolysis-resistant carbonaceous substances during combustion (4).

Figure 4-4. shows the heat release and absorption during the heating of the new boards. Adding metal hydroxides (aluminum hydroxide) gave these boards high heat absorption, in particular around the ignition temperature (about 500 ℃).

These results showed that the high flame resistance of the new boards containing the phenol aralkyl-type epoxy resin compounds and the metal hydroxides was obtained as a result of the combination of the high pyrolysis resistance of the epoxy resin compounds and the heat absorbance of the metal hydroxides during ignition.

Of the metal hydroxides tested in the new boards, aluminum hydroxide had almost the same flame-resistant effectiveness as magnesium hydroxide. And of the phenol aralykyl-type epoxy resin compounds tested in the boards, phenol p-xylene-type (PX-type) epoxy resin compound had a little higher flame-resistant effectiveness than that of phenol biphenylene-type (PB-type) epoxy resin compound (see Figure 4-2). Therefore, the former compound was chosen for the remaining tests.

Table 4-1 Flame resistance of laminates and composites with epoxy resin compounds

Epoxy resin ／Hardener	Phenol aralkyl type*1) ／Phenol aralkyl resin*1)			BA- type ／Phenol resin	BA-type ／Dicyandiamide
Form	Laminate*2)	Composite*3)		Laminate*2)	Laminate*2)
Filler content(wt%)	50	50	70	50	50
UL94 Class	V-1	V-1	V-0	Not V-2	Not V-2
Flaming time (seconds)	130	55	10	>250	>250

*1: PX-type
*2: Inclusion of glass fiber fabric of seven layers as filler
*3: Inclusion of silica particle as filler

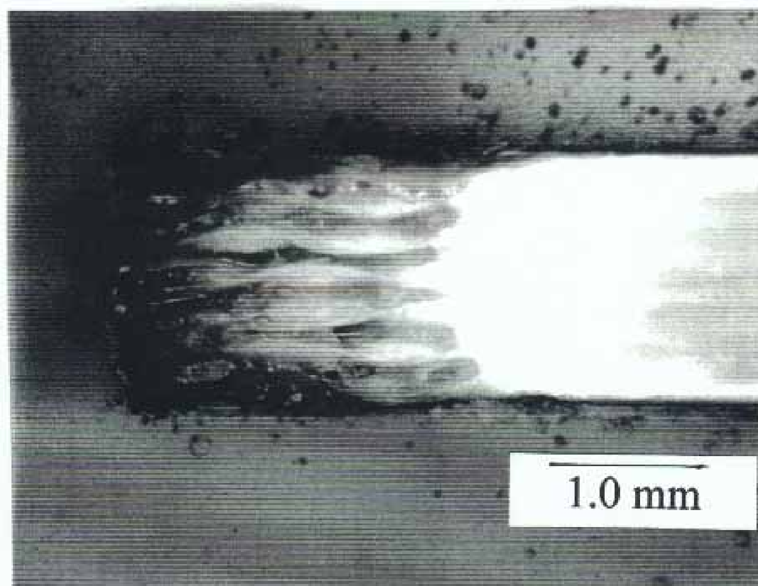


Fig. 4-1 Cross section of PWB containing phenol aralkyl-type (PX-type) epoxy resin compound after ignition

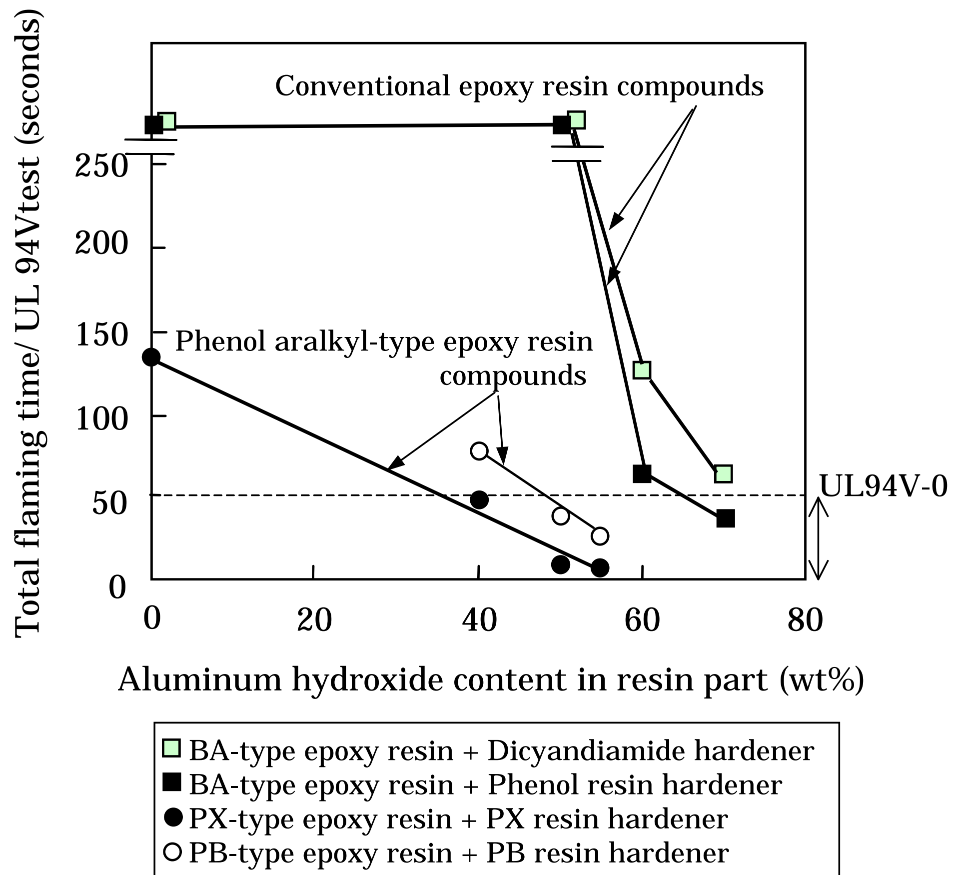
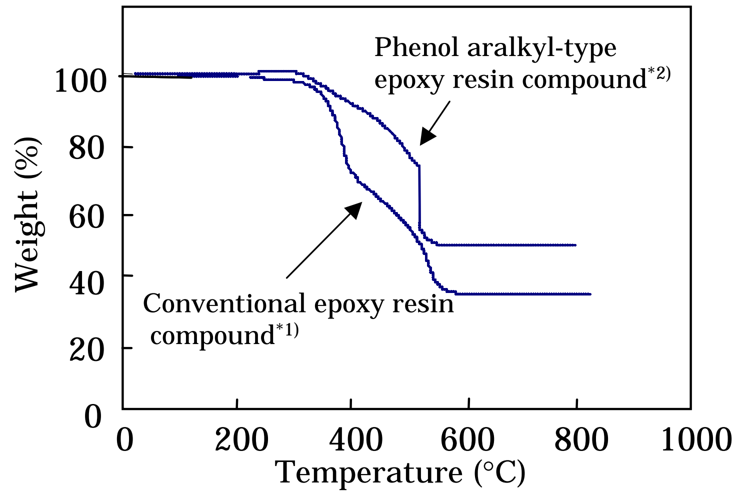


Fig. 4-2 Flame resistance of PWBs containing metal hydroxides

a) PWBs without metal hydroxide



b) PWBs with metal hydroxide

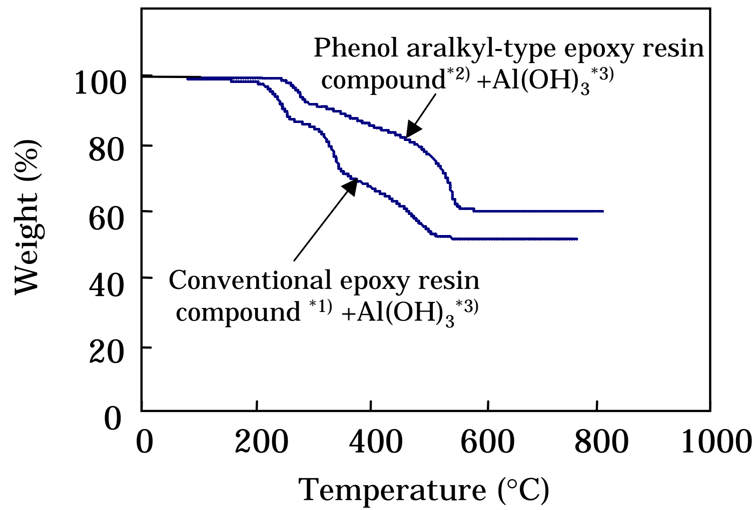


Fig. 4-3 Thermogravimetric analysis of PWBs (*1: BA-type epoxy resin + Dicyandiamide hardener, *2: PX-type epoxy resin + PX resin hardener, *3: 50wt% in resin part)

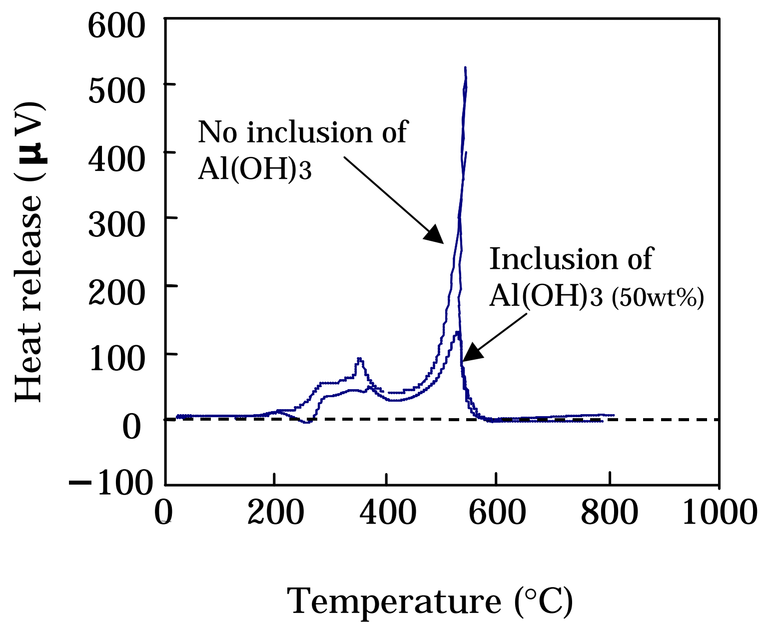


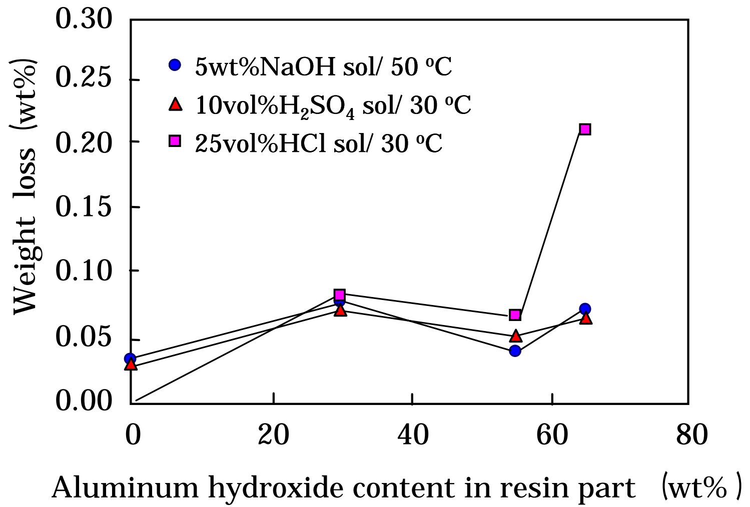
Fig. 4-4 Differential thermal analysis of PWBs with phenol aralkyl-type (PX-type) epoxy resin compound

4-3-2 Chemical resistance

The chemical resistance of the new PWBs with the PX-type epoxy resin compound and the metal hydroxides was evaluated, because various chemicals such as acids and alkalis are used to form copper circuits on PWBs through plating and etching. Figure 4-5 compares the weight loss of the new PWBs and the reference PWBs after these boards were dipped in representative chemicals during the plating and etching processes. When added in large amounts, aluminum hydroxide adversely affected the resistance of these boards. However, the chemical resistance of the new boards was rather good within the amount of aluminum hydroxide (40−50 wt%) added, at which the flame-resistance standard could be met. Also, the resistance of the boards was better than that of the reference boards for the overall amount of the hydroxide added. The superior chemical resistance of the new boards resulted from the hydrophobic properties of the PX-type epoxy resin compound in them as revealed by the lower water absorption of the boards (see Figure 4-6). These hydrophobic properties were a result of the inclusion of the aromatic moiety in the structure of the epoxy resin compound.

As listed in Table 4-2, the boards containing aluminum hydroxide showed higher chemical resistance than that of the boards containing magnesium hydroxide. For the remaining tests, therefore the former boards was used.

a) PWBs with phenol aralkyl-type epoxy resin compound[*1]



b) PWBs with conventional epoxy resin compound[*2]

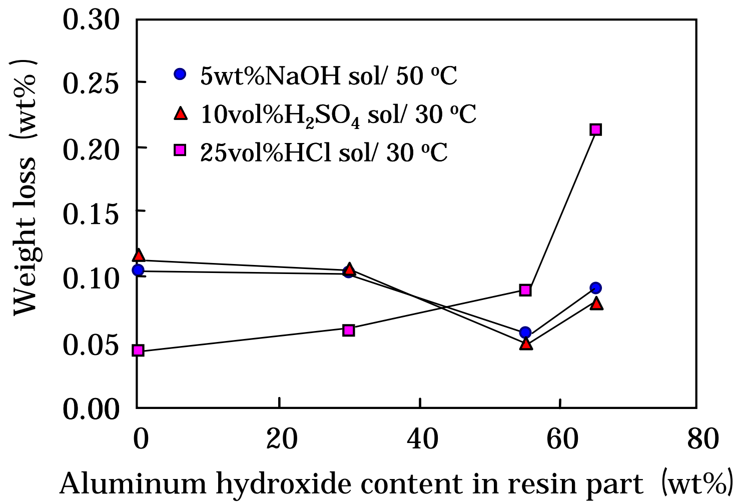


Fig. 4-5 Chemical resistance of PWBs (*1: PX-type epoxy resin + PX resin hardener, *2: BA-type epoxy resin + Dicyandiamide hardener)

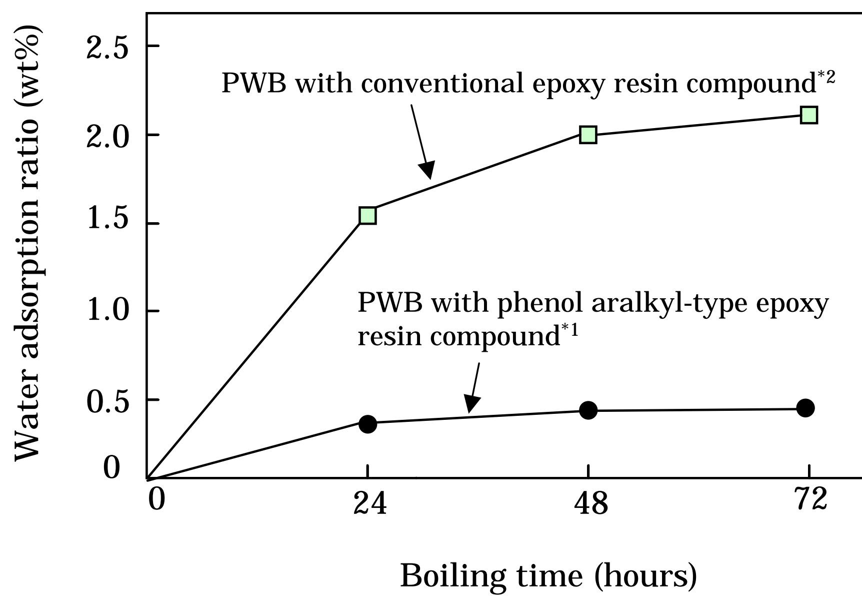


Fig. 4-6 Water resistance of PWBs (*1: PX-type epoxy resin + PX resin hardener, *2: BA-type epoxy resin+Dicyandiamide hardener)

Table 4-2 Chemical resistance of PWBs containing metal hydroxides

Epoxy resin compound	Metal hydroxide	Weight loss of PWBs (wt%)*4)		
		NaOH sol (5wt%, 50ºC)	H_2SO_4 sol (10 vol%, 30ºC)	HCl sol (25vol%, 30ºC)
Conventional-type*1)	None	0.11	0.12	0.046
Phenol aralkyl-type*2)	None	0.083	0.0062	0.028
	Magnesium hydroxide*3)	0.00	0.45	0.81
	Aluminum hydroxide*3)	0.044	0.022	0.034

*1) BA-type epoxy resin+Dicyandiamide hardener
*2) PX-type epoxy resin + PX resin hardener
*3) 40wt% in resin part of PWBs
*4) After four hours in chemicals

4-3-3 Dielectronic properties

The dielectronic properties of the new PWBs, including dielectronic constant and dissipation factor, were evaluated. Figure 4-7 shows these properties of the new PWBs and the reference PWBs. When added in large amounts, aluminum hydroxide adversely affected the properties of these boards. However, the properties of the new boards remained good within the amount of aluminum hydroxide added, at which high flame resistance was retained. Also, these properties were superior to those of the reference boards for the overall amount of the hydroxide added because the PX-type epoxy resin compound in the new boards included a large amount of non-polar aromatic moiety.

4-3-4 Characteristics for practical use

The new PWB was completed by using the PX-type epoxy resin compound and adjusting the amount of aluminum hydroxide (50 wt% in the resin part) based on the experimental results above-mentioned. The characteristics of the PWB were compared with those of current FR-4 -type PWBs containing halogen-type or phosphorus-type flame-retarding additives, which have been reported (1, 2, 3). Table 4-3 lists the results.

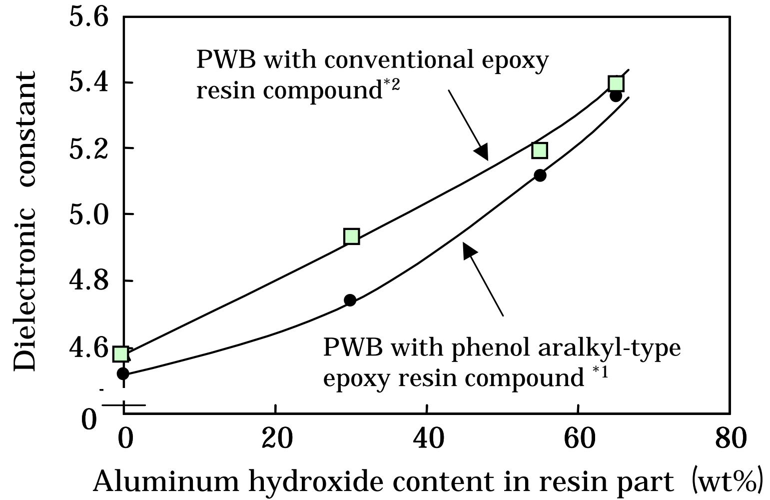
The flame resistance of the new board met the UL94V-0 standard. Its thermal expansion was lower than those of the current boards because of the inclusion of the metal hydroxide. The glass transition temperature was a little lower due to the lower cross-linking density of the epoxy resin-hardener network structure including the aromatic moiety. However, the new board had rather good solder-heating resistance and exhibited no defects, such as delamination and swelling caused by solder heating, ether before or after the humidity treatment. The good solder-heating resistance was most likely due to higher pyrolysis resistance of the PX-type epoxy resin compound in it. The electronic properties of the new board, including

insulation and dielectronic properties, were found to be comparable to those of the current boards. Its water resistance and copper peel strength were satisfactory.

The processability of the new board was also compared to that of the current boards. In the circuit formation process, its behavior during plating and etching was almost the same as that of the current boards. After hole drilling and plating for the new board, the roughness of the inside in the hole was found to be acceptable (within 18.5 μm in depth), which satisfies the requirements for its practical use.

The resistance to thermal stress and humidity of the new board was also found to be good. As shown in Figure 4-8, it retained high volume resistance between the comb circuits on it after thermal cycle under the high humidity condition.

a) Dielectronic constant of PWBs



b) Dissipation factor of PWBs

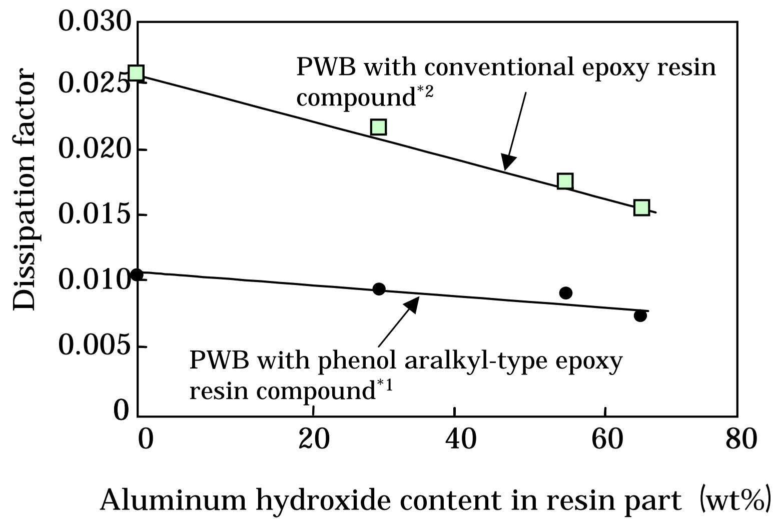
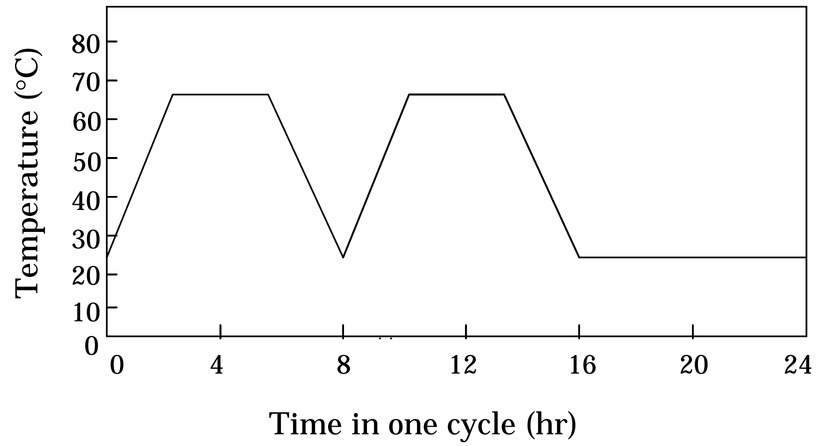


Fig. 4-7 Dielectronic properties of PWBs (*1: PX-type epoxy resin + PX resin hardener, *2: BA-type epoxy resin+Dicyandiamide hardener)

a) Heating profile



b) Insulation

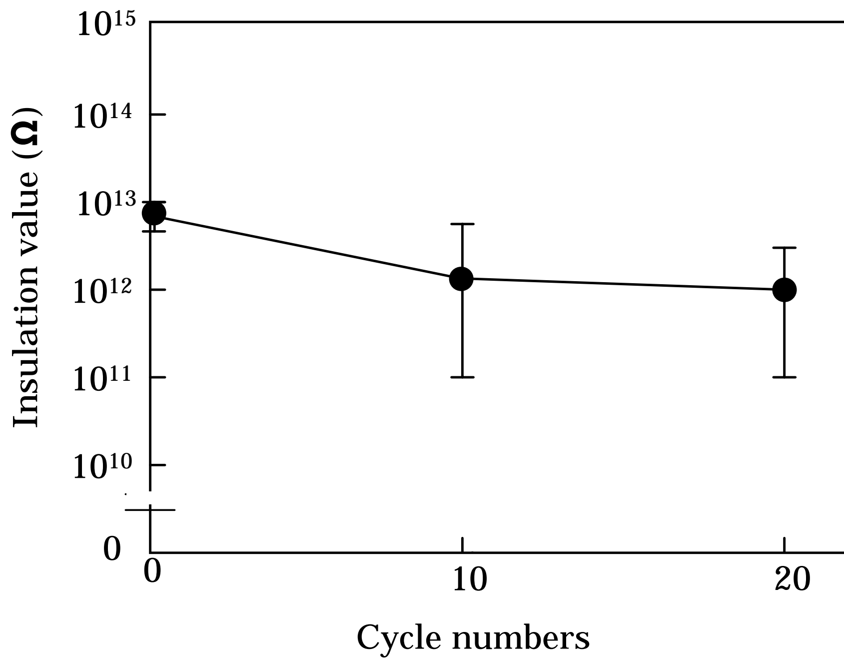


Fig. 4-8 Insulation of the new PWB after cycling of heat and humidity treatment

4-3-5 Safety in waste treatment

The safety of the new PWB during thermal treatment was investigated, and also its safety after disposal and in recycling was discussed. The toxic substances in the exhaust gas generated from the board during heating (850 ^{o}C) were analyzed. As listed in Table 4-4, the exhaust gas generated from the board was at a highly safe level. Hydrogen cyanide, which is frequently generated from nitrogen-containing compounds and polymers, was not detected. Hydrogen bromide generated from bromine-type flame-retarding additives and phosphorus acid generated from phosphorus-type flame-retarding additives were not detected because such additives were not included. The concentration of toxic carbon monoxide was lower than that of polyethylene, which is a representative safe plastic. Therefore, it was concluded that the new PWB waste was highly safe when it was burned to decrease its volume and to recover thermal energy from it. Also, the PWB waste is highly safe after disposal in a landfill dump because it does not contain any toxic substances.

As will be reported in the chapter six on a recycling technology of glass-epoxy laminate-type PWBs (5), the recovered powder consisting of glass fiber and cured epoxy resin (glass fiber-resin powder) from the boards can be reused as a useful filler for various plastic products to improve the mechanical characteristics of these products. However, halogen-type and phosphorus-type flame-retarding additives included in current PWBs adversely affect the safety of these products. In contrast, the recovered glass fiber-resin powder from the new PWB can be safely reused for these products due to the fact it does not include such toxic flame-retarding additives.

Table 4-4 Analysis of exhaust gas generated from new PWB during heating

Substances in exhaust gas	Amount of the substances (mg/g)*	
	New PWB	Polyethylene
HCN	<0.013	—
H_3PO_4	<0.050	—
HBr	<0.015	—
CO	20	65
CO_2	760	610

* Amount of the substance generated from samples by heating at 850 °C

4-4 Summary

A highly flame-resistant glass-epoxy laminate-type printed wiring board (PWB) that does not contain such flame-retarding additives as halogen compounds and phosphorus compounds was developed to overcome environmental problems caused with these flame-retarding additives. The PWB contained a self-extinguishing epoxy resin compound (phenol aralkyl type) and a limited amount of harmless metal hydroxide (aluminum hydroxide). It had high flame resistance with no inclusion of halogen or phosphorus compounds and showed other good characteristics, including resistance to solder heating and chemical agents in processing, electronic properties, and moldability, which made it a practical PWB. These good characteristics were obtained by utilizing of the epoxy resin compound's superior properties with respect to its pyrolysis resistant, hydrophobic, and non-polar properties, and by minimizing of the amount of metal hydroxide. The board was found to be highly safe when burned, disposed of, and reused as a filler after pulverizing because it did not contain any toxic substances.

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(3) H. Murai, Y. Takeda, and N. Takano, Proceedings of *IPC Printed Circuits Expo 2000*, S16-4, 1-6 (2000).

(4) D. W. Van Krevelen, *Polymer*, 16, August, 615-620 (1975).

(5) M. Iji and S. Yokoyama, *Circuit World*, 23, 3, 10-15 (1997).

Chapter 5

Recycling of Epoxy Resin Compounds Used as Molding Compounds for Electronic Parts

5.1 Introduction

Epoxy resin compounds are mainly used as molding compounds in electronic parts such as integrated circuit (IC) packages because of their good insulating, adhesive, and heat-resistant properties. These molding compounds mainly consist of epoxy resin (thermosetting plastics), phenol resin derivative hardener, silica particle filler, flame-retarding additives, usually composed of halogen compounds (organic bromine compounds) and antimony oxide (diantimony trioxide), and other additives. Increased production of electronic parts in recent year greatly increased the amount of the mold residue of molding compounds, which is generated in the molding process of electronic parts (see Figure 5-1). But recycling this residue has been difficult because the epoxy resin in the residue cannot be remelted for its cross-linked (cured) structure formed in the molding process, in addition to the inclusion of these toxic flame-retarding additives as mentioned in the previous chapters. Most of the residue is therefore disposed of at landfill sites.

Material recycling that reuses pulverized waste materials by blending with the original materials or other materials has been studied for thermosetting plastics as a practical method. Studies for general thermosetting plastics such as polyester, polyurethane, and phenol resin indicated that these recycled plastics composed of these cured plastics powders and the original plastics have sufficient strength at a low recycling ratio (1-5). But few studies have been made on recycling epoxy resin compounds. In one study, a cured epoxy resin compound powder consisting of epoxy resin and amine hardener was recycled into the original compound. The strength of resulting material was sustainable at a low recycling ratio (less than 20wt%) (6). However, no study has been reported on the recycling of cured epoxy resin compounds containing silica particle filler and various additives, such as the mold residue of molding compounds.

On the other hand, because the molding compounds contain valuable

pure-silica powder filler in large quantities (70-90 wt %), a pyrolysis-based technology appears to be a useful approach to their recovery, as well as a promising means for reducing the severity of total waste problem. The serious problem to be overcome with pyrolysis, however, is finding an effective means to treat the exhaust gas containing toxic substances generated from conventional flame-retarding additives consisting of halogen compounds (bromine compounds) and antimony oxide during burning.

While many studies have been performed on the pyrolysis of thermoplastic for recovering oil and raw materials from them (7-10), few have been conducted on recovering useful materials (inorganic filler, additives, etc) from thermosetting plastics such as epoxy resin compounds used as molding compounds. The recovery of silica sand from phenol resin compounds by pyrolysis was studied, but the purity of the recovered silica sand was not sufficiently considered (11). Also, it was attempted to recover raw epoxy resins and glass fiber from epoxy resin compounds used in printed wiring boards (12). The resin compounds were subjected to pyrolysis, after which the organic raw materials and halogen compounds generated from the flame-retarding additives in the resin compounds were recovered from the exhaust gas. Glass fiber was also recovered from the residues, but to be practical, this method requires better control of the quality of the recovered glass fiber and stricter treatment of the exhaust gas. To determine optimal heating temperature and oxygen concentration was attempted in a study of the use of pyrolysis to recover glass fiber from polyester composites, but the purity of the recovered glass fiber was insufficient nonetheless, and further treatment with acids was needed (13).

Studies on the treatment of the exhaust gas containing organic bromine compounds generated in the burning of plastics that contain flame-retarding bromine compounds indicated that toxic organic bromine compounds, such as dioxin, can be decomposed by secondary-pyrolysis of the exhaust gas (14, 15). But there have been very few attempts to treat exhaust gas that also

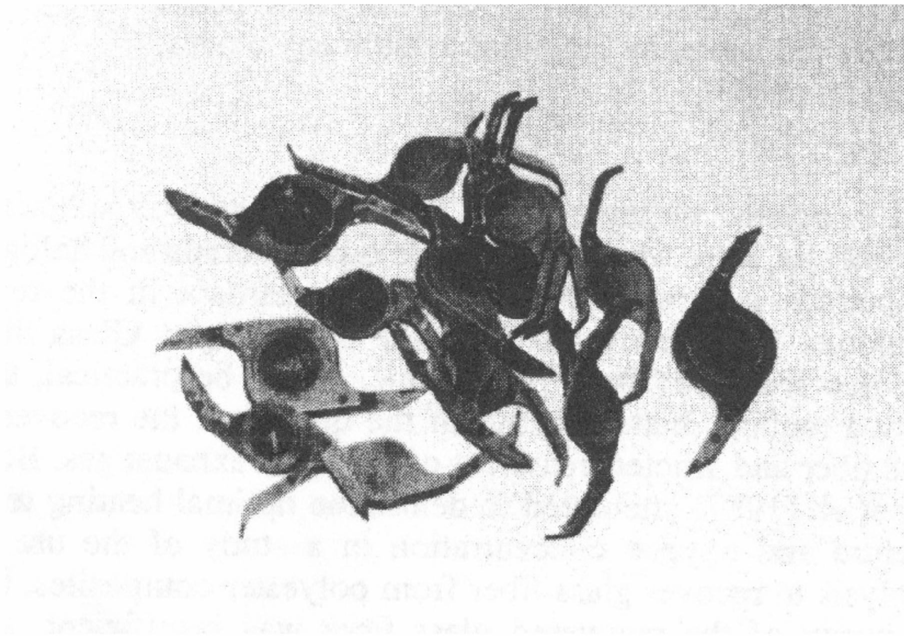
contains antimony compounds. Such compounds generated from flame-retarding additives that contain both bromine compounds and antimony oxide and that have recently come to be used in many plastics for electronic products, such as molding compounds. A possibility that antimony bromides are transformed to antimony oxides in flames was shown (16). The behavior of antimony compounds in the exhaust gas generated was investigated in the burning of the plastics contain these flame-retarding additives (17). However, a practical method was not offered to treat these compounds in such gas safely and to recover them as useful materials.

This chapter reported a newly developed technology for recycling of epoxy resin compounds used as molding compounds for electronic parts, including reuse after grinding and recovery of valuable materials by pyrolysis.

In session 5-1, reuse of mold residue of molding compounds after grinding was described. First, to determine the basic properties of the residue powder (molding compound powder) for recycling, the powder's chemical structures and reactivity toward polar resins such as epoxy resin and phenol resin were investigated. Then the reuse of the molding compound powder into original molding compounds was studied. Moreover, the possibility was examined of using it as a filler for epoxy resin products used as insulating materials, paints, and adhesives, and also as a decorating agent for acrylic resin-type construction materials.

In session 5-2, a pyrolysis-based technology for recovering high-purity silica filler from the mold residue of molding compounds was reported. Both basic tests to determine appropriate pyrolysis conditions and practical tests using a roller kiln-type furnace were performed. The reuse of recovered silica filler to be employed in original molding compounds and the other epoxy resin products was studied. An exhaust gas treatment process consisting of a secondary combustion, a dry recovery, and a wet recovery was attempted for treating the combustion exhaust gas containing organic

bromine compounds and antimony bromide, both of which are originated from flame-retarding additives including organic bromine compounds and antimony oxide. Decreasing the organic bromine compounds to a safe level and converting the antimony bromide to antimony oxide, which can then be collected as a useful raw material, were studied.



1.0cm

Fig. 5-1 Mold residues of molding compounds

5-2 Reuse of molding compounds after grinding

5-2-1 Experimental

(1) Material

Molding compounds

This study used two model-molding compounds for standard compound and low-stress-type compound. The model-standard-molding compound was composed of *o*-cresol novolac-type epoxy resin (melting point: 70℃), phenol novolac resin hardener (melting point : 80℃), fused silica particle filler, curing catalyst (triphenilphosphine), a releasing agent (Carnauba wax), carbon black powder, a silane coupling agent (γ -glycidoxypropyl-trimethoxysilane), and flame-retarding additives (brominated bisphenol A type-epoxy resin and diantimony trioxide). The model-low-stress-type molding compound additionally contained silicone elastomer (polydimethylsiloxanes) as a low-stress agent that decreases the modulus of the compound. The blending ratios of these components in the compounds are listed in Table 5-1, and these components were supplied by Sumitomo Bakelite Co. The molding compounds were produced by premixing the components in a mixer, mixing the resulting pre-mixture by using a roll blender heated to about 100-105℃, and then cooling, crushing, and tabulating. The molding compounds were molded into an IC package (dual inline type package : DIP) with sixteen pins by using a conventional transfer molding machine under the curing condition of five minutes at 170℃. The mold residues of the molding compounds were then recovered and grinded into powders (average particle size: 16 μm) with a roll mill and a ball mill.

These compound powders were mixed with the components of the molding compound, and molded in the same way mentioned above, and then post-cured under the condition of six hours at 170℃.

Epoxy resin products with molding compound powder

Epoxy resin compounds for insulating materials, paints, and adhesives were prepared as epoxy resin product models. The insulating material consisted of the standard molding compound powder as a filler (60 wt%), *o*-cresol novolac epoxy resin (20.8 wt%), phenol novolac resin hardener (12.2 wt%), a releasing agent (0.9 wt%), carbon black powder (0.4 wt%), a curing catalyst (0.3 wt%), brominated epoxy resin (2.7 wt%), and diantimony trioxide (2.7 wt%). Fused silica powder (average particle size: 20 μm, Denki Kagaku Co.) was used as a conventional filler. These components were the same materials as listed in Table 5-1. These were mixed, molded, and post-cured in the same way as above-mentioned. For surface treatment of the molding compound powder, silane coupling agents such as γ -glycidoxypropyl- trimethoxy-silane and aminopropyltriethoxysilane (Shin-Etsu Chemical Co.) were premixed with the molding compound powder in a ball mill at weight ratios of 1.0 : 100 and 0.5 : 100 and were heated to 100℃ for one hour.

The paint consisted of the standard molding compound powder as a filler, bisphenol A-type epoxy resin (Epicoat 828, Yuka Shell Epoxy Co.), a diluting agent (propyleneglycolether : Eponit 028, Asahidenka Co.), a leveling agent (acrylic co-polymer: Polyflow S, Kyoueisha Chemical Co.), fine silica powder (Aerogiru 200, Nippon Aerogiru Co.), a silane coupling agent (γ - glycidoxypropyltrimethoxysilane, Shinetu Chemical Co.), and an amine-type hardener (X-4199, ACR Co.). The blending ratio is listed in Table 5-2. As conventional fillers, talc powder (average particle size: 11μm, Takehara Chemical Co.), calcium carbonate powder (average particle size: 9.2 μm, Shiraishi Karusiumu Co.), and fused silica powder (average particle size: 10 μm, Denki Kagaku Co.) were used. These components were mixed in a mixer and then degassed in a vacuum at room temperature. The compounds were molded in a mold and cured at 23℃ for seven days.

The adhesive consisted of the above-mentioned components for the paint but another amine-type hardener (Tormide245, Fujikasei Co.). The blending ratio is also listed in Table 5-2. These components were mixed and degassed by the same method mentioned above. The resulting compounds were bonded between two ferric boards (SPCC-SB) and cured at 23℃ for seven days.

Construction material with molding compound powder

An acrylic resin compound was prepared as a model construction material. It consisted of acrylic resin and aluminum hydroxide powder (maximum powder size 150 μm) at a weight ratio of 35 : 65. These components were supplied by Tsutsunaka Plastics Co. The standard molding compound powders with maximum particle sizes of 1 mm and 5 mm were added to the components at the weight ratios listed in Table 5-6 and then mixed in a mixer and compression-molded in a mold at 190℃ for 35 minutes.

Table 5-1 Composition of tested epoxy resin compounds for molding compounds

Compositions	Low stress type	Standard type
Epoxy resin (o-cresol novolac)	13.3 (wt%)	15.3 (wt%)
Phenol resin hardener	7.9	9.0
Silica powder	70.0**	70.0*
Curing catalyst	0.2	0.2
Releasing agent (wax)	0.7	0.7
Carbon black powder	0.3	0.3
Silane coupling agent	0.6	0.5
Flame retarding additive		
Brominated epoxy resin	2.0	2.0
Diantimony trioxide	3.0	2.0
Silicone elastomer	2.0	

* Pulverized silica (average 15 μm)

**Pulverized silica (average 15 μm)+Spherical silica (average 22 μm) : 50+50 (wt%)

Table 5-2 Compositions of tested epoxy resin compounds for paints and adhesives

Compositions	Paint	Adhesive
Epoxy resin	39.7 (wt%)	38.8 (wt%)
Diluting agent	7.9	7.8
Leveling agent	0.2	0.2
Fine silica powder	0.2	0.2
Silane coupling agent	0.2	0.2
Filler	31.8	31.0
Amine hardener	20.0	21.9

(2) Measurement methods of properties

Basic properties of molding compound powder

The average particle size and size distribution of powder samples such as molding compound powder and other fillers were measured by using a laser-diffraction-type particle-size-distribution measurement apparatus (SALD-2000, Shimaze Co.). The surface areas of the powders were determined by using a surface area measurement apparatus (Flow-SorbⅡ 2300, Shimaze Co.).

The chemical surface structure of the molding compound powder was determined by means of scanning electron microanalysis (SEM) and electron probe X-ray microanalysis (EPMA), which were obtained with a Shimazu EPMA-8705 analyzer. Fourier-transform infrared spectra (FT-IR) recorded on a FTS-15E/D spectrophotometer (Bio. Rad. Digilab. Co.), and carbon-13 nuclear magnetic resonance spectra (^{13}C-NMR) obtained with a JNM-EX270W spectrometer (Japan Electron Co.) were also used for the chemical analysis of the powder.

The standard molding compound powder's reactivity toward polar resins such as *o*-cresol novolac epoxy resin (ESCN 195 XF, Sumitomo Chemical Co.) and phenol resin (BRG 556, Showa Kobunshi Co.) was measured by a gravimetric method. The molding compound powder (average particle size : 16μm , surface area : 1.9 m^2/g) and the epoxy resin were mixed at the weight ratio of 20 : 1 in a solvent (acetone), dried at room temperature for one day, and then heated at 170℃ for two time periods (2.5 and 5.0 hours). The resulting samples were washed twice with a solvent (mixing a 5g sample with 50ml acetone, stirring, and centrifuging) to remove the unreacted epoxy resin, dried at 120℃ for two hours, and then measured for the resulting weight loss, which is the unreacted epoxy resin's weight. Finally, the reaction ratio of the molding compound powder toward the epoxy resin was obtained by evaluating the ratio of the reacted epoxy resin's weight to the originally added epoxy resin's weight, and was then compared

with that of the fused silica powder (average particle size : 16 μm , surface area : 2.0 m^2/g, Denki Kagaku Co.) toward the epoxy resin treated in the same way mentioned above. The same experiment was also performed using the phenol resin in place of the epoxy resin.

Moldability of molding compound in molding process

To determine the moldability of recycled molding compounds in the molding process of electronic parts, the compounds' flow property in the metal mold (spiral flow) and barcol hardness of the molded compounds were measured at 170℃ for two minutes according to EMMI normalization and JIS K 6911, respectively. Also, The burr, which is penetrating resin in the air vent (depth of about 100 μm) in the metal mold used for a 16-pin DIP-type IC package, was measured for its maximum length. The gelation time for the compounds was determined at 170℃.

Reliability of molding compound

The reliability of the recycled molding compounds was measured in terms of moisture resistance and thermal impact resistance by using a 16-pin DIP-type IC package. A silicon test chip (4.5×9.0 mm) with an aluminum test circuit (width of 10 μm, interval of 10 μm) was mounted on a lead frame made of 42 alloy and molded into the package by using the molding compounds at 170℃ for two minutes. The package was post-cured at 170℃ for six hours. The moisture resistance was determined by using a pressure-cooker test, which measures the ratio of defective packages with opened circuits after boiling at 125℃ under 2.3 atm. The thermal impact resistance was determined by a temperature cycling test, which measures the ratio of defective packages with outside cracks after temperature cycles over a range of -60℃ to +150℃ at a frequency of 3 cycles / hour.

General properties of molding compound

The strength properties of the molded compound samples, such as tensile strength, flexural strength, and charpy impact strength, were measured according to JIS K 7111 and JIS K 7203. Their thermal expansion ratios were tested at a heating rate of 5℃/min. according to JIS K 7197, volume resistance was measured according to JIS K 6911, surface hardness was measured by comparison with pencil hardness, and thermal deformation temperatures were determined according to JIS K 7207. The viscosity of the compound samples before adding the hardener was measured at a rotating rate of 2 rpm by using a BH-7 type viscometer (Tokyo Keiki Co.). The adhesive strength of the compound samples for the ferric board (SPCC-SB) was measured by tearing the specimens according to JIS K 6850.

5-2-2 Results and discussion

(1) Basic properties of molding compound powder

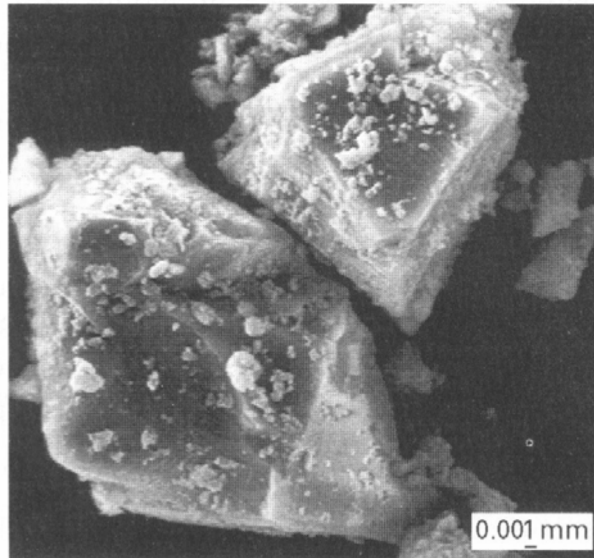
The chemical structure of the ground cured standard molding compound (molding compound powder) was investigated. As shown by the SEM photo and the carbon distribution of the EPMA photo (see Figure 5-2), the molding compound powder consisted mainly of silica powder and cured epoxy resin, and the silica surface was partly covered with the resin. FT-IR spectrum analysis indicated that the molding compound powder had silanol group from the silica in the resin. However, the amount of silanol group was smaller than that in the original silica powder as shown by the difference spectrum between the powder and the original silica powder. Therefore, a part of the silica powder in the molding compound powder was found to react with the epoxy resin. The ^{13}C-NMR spectrum of the molding compound powder indicated that the powder had glycidyloxy group from the epoxy resin unreacted with the phenol resin hardener and also hydroxyl group resulting from the reaction between the epoxy resin and the hardener. From these results, the molding compound powder was proposed to be able to react with polar resins because of its reactive functional groups (glycidyloxy, hydroxyl, silanol).

The reactivity of the molding compound powder toward polar resins such as epoxy resin and phenol resin was measured by the gravimetric method and also compared with that of the fused silica powder toward these polar resins. Figure 5-3 shows the reaction ratios of the molding compound powder and the fused silica powder with the epoxy resin, and also shows the same with the phenol resin. The molding compound powder maintained a good level of reactivity toward the epoxy resin, but was a little less reactive than the original silica powder. This was probably because the molding compound powder had smaller amount of silanol group than original silica powder ; this group effectively reacts with glycidyloxy group in epoxy resin. On the other hand, the molding compound powder was a little more reactive

with the phenol resin than the original silica powder. This was mainly due to the remaining glycidyloxy group in the molding compound powder ; this group shows good reactivity toward hydroxy group in phenol resin.

These results showed that molding compound powders can sufficiently bind to polar resins such as epoxy resin and phenol resin by reacting with them in a similar manner in which silica powder reacts with them.

a) SEM photo



b) EPMA photo

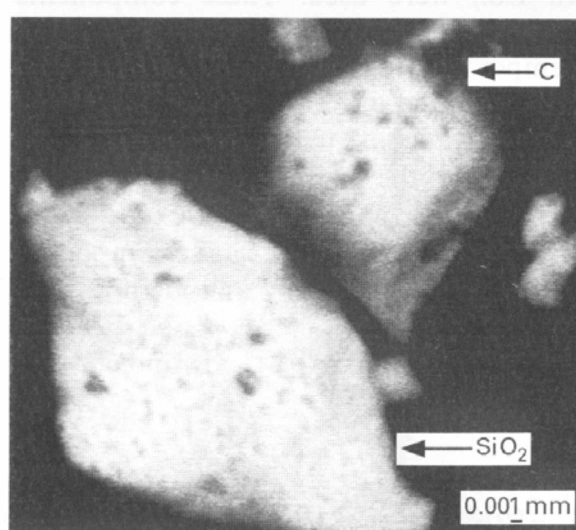
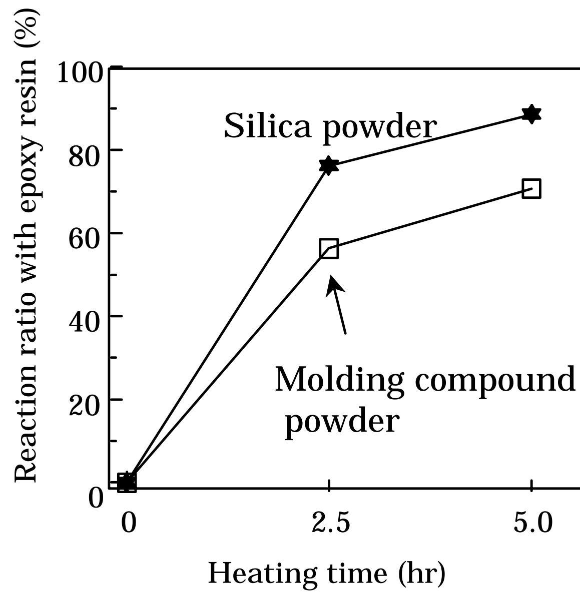


Fig. 5-2 Structure of ground cured molding compound (molding compound powder)

a) Reactivity toward epoxy resin



b) Reactivity toward phenol resin

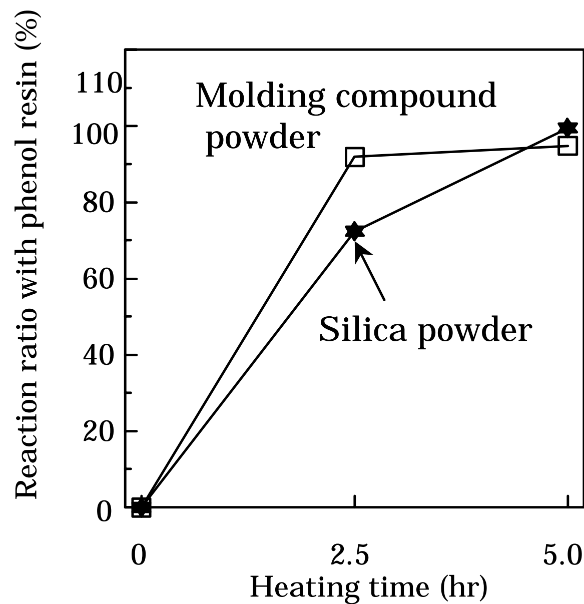


Fig. 5-3 Reactivities of molding compound powder and silica powder toward epoxy resin and phenol resin

(2) Recycling into original molding compounds

Molding compounds are broadly classified into two types: standard compounds used for general IC packages and low-stress-type compounds used for large scale integlated circuit (LSI) packages. The latter compounds contain elastomer represented by silicone derivatives in addition to the components of the standard compounds in order to reduce the stresses, which are generated in the interface between molding compounds and IC chips due to differences in their modulus and thermal expansions. Table 5-3 lists the properties of these model molding compounds and indicates that the thermal impact resistance of low-stress-type compound was better than that of the standard compound. This property is mainly affected with the interface stress.

Table 5-3 also shows the properties of the recycled compounds obtained by recycling these two molding compound powders into the original standard molding compound. When the standard compound powder was recycled into the original standard compound at a recycling ratio of 10 wt%, the flow property of the recycled compound in the molding process was considerably reduced (68 cm → 22 cm). Using an epoxy resin with a melting temperature (55℃) lower than that of the original epoxy resin (70℃) for the recycled molding compound improved the flow property, but the moisture resistance and thermal impact resistance of the recycled molding compound were inferior to those of the original standard compound. This was probably due to insufficient solubility between the resin components and the solid components in the recycled compound by adding the cured molding compound powder.

When the low-stress-type molding compound powder was recycled into the original standard compound, the flow property was also insufficient. By using a spherical silica powder (average powder size of 20μm) which was mixed into the original pulverized silica at 50 wt%, in addition to using the above mentioned epoxy resin with a low melting temperature, the flow

property of the resulting product was improved to a sufficient level up to the recycling ratio of 25 wt% for its practical use. Furthermore, heating the molding compound powder (at 170℃ for 8 hours) improved the flow property. The ^{13}C-NMR spectrums of the low-stress-type molding compound powder before and after heating showed that the amount of glycidyloxy group in the powder was decreased by heating. This heating effect was therefore due to the lowering of the molding compound powder's surface reactivity, which influenced the main factors (viscosity, thixotropy) improving the flow property of the resulting products. Moreover, the thermal impact resistance of the resulting product was found to be far better than that of the original standard compound. This improvement was mainly caused with the silicone elastomer in the low-stress-type compound powder. The compound had other good important properties, which were sufficient for its practical use.

From these results, it was concluded that there was a distinct possibility of using the residue of low-stress-type molding compounds to make a new molding compound that has thermal impact resistance higher than original standard molding compounds and better cost performance.

Table 5-3 Properties of recycled molding compounds

Properties	<Original molding compounds>		<Recycled molding compounds>		
	Standard type	Low stress type	Standard type* with standard-type powder (10wt%)	Standard type** with low-stress-type powder (25wt%)	→ with low-stress-type powder heated at 170 °C for 8 hrs
Moldability					
Flow (cm)	69	73	68	47	61
Barcol hardness	74	58	58	55	62
Burr (mm)	0.6	1.0	1.3	1.3	2.3
Strength property					
Flexural strength (kgf/mm^2)	14.7	14.2	17.3	15.8	14.2
Flexural modulus (kgf/mm^2)	1418	1240	1505	1391	1353
Charpy impact strength (kgf・cm/cm)	2.3	2.3	2.8	3.6	2.7
Thermal mechanical property					
Glass transition temperature (℃)	155	171	139	154	154
Thermal expansion coefficient α_1 / α_2 ($\times 10^{-5}$/℃)	2.0 / 6.5	1.8 / 7.4	2.2 / 6.3	2.0 / 6.6	2.1 / 6.3
Moisture resistance					
(Defected package ratio) 200 hours	0/ 10	0 / 10	0 / 10	0 / 10	0 / 10
120 °C, 2.3 atm 520 hours	1 / 10	0 / 10	4 / 10	0 / 10	0 / 10
Thermal impact resistance					
(Defected package ratio) 100 cycles	3 / 10	0 / 10	7 / 10	0 / 10	0 / 10
150 ℃ ～ -60 ℃ 150 cycles	5 / 10	0 / 10	9 / 10	0 / 10	0 / 10
200 cycles	8 / 10	0 / 10		1 / 10	0 / 10

* An epoxy resin with low melting temperature was used.
** An epoxy resin with low melting temperature and a spherical silica filler (50wt% of total silica) were used.

(3) Use as filler for other epoxy resin products

The present study examined using the standard molding compound powder as a filler for other epoxy resin products, such as insulating materials, paints, and adhesives. Since these products use epoxy resins similar to that in the molding compound powder, strong affinity between the matrix epoxy resin and the molding compound powder was expected.

Filler for insulating materials

The moldability in the molding process, strength, and insulating property of epoxy resin-type insulating material with the molding compound powder were compared with those of the reference material with a fused silica filler. Table 5-4 lists the properties of the resulting material. The flexural strength and insulating property of the molded material with the molding compound powder were almost the same as those of the material with the silica powder. The flow property of the material with the powder in the molding process was not as good as that of the material with the silica powder, but was sufficient for molding. As will be discussed later, this difference was because of higher volume of molding compound powder than that of silica powder.

The effect of treating the molding compound powder's surface on the characteristics of the resulted material was also examined by using silane coupling agents that are usually used for improving and adjusting the surface reactivity of inorganic fillers. The surface treatment of molding compound powder with the coupling agents, especially aminopropyl-triethoxysilane (amino silane) improved the strength and insulating property of the molded material with the powder. This seemed to be caused by the improvement of the interface adhesion between the matrix epoxy resin and the molding resin powder by treating with the silane. Treating the molding resin powder with γ -glycidoxypropyltrimethoxysilane (epoxy silane) had little effect on the strength and insulating property, but

improved the flow property in the molding process of the resulting material. These difference effects of these silanes were mainly attributed to the lower reactivity of the epoxy silane toward the molding compound powder and the matrix resin, and its higher plasticity for the matrix resin.

Filler for paints

The strength and thermal expansion properties of the epoxy resin compound with the molding compound powder were compared with those of compounds with conventional fillers such as calcium carbonate powder, talc powder, and silica powder. Table 5-5 shows the results. The strength of the molded compound with the molding compound powder was comparable to that of the compound with silica powder, and was superior to those of compounds with calcium carbonate powder and talc powder. The thermal expansion of molded compound with the molding compound powder was comparable to that of compounds with these conventional fillers. These results were mainly caused by containing silica filler in the molding compound powder and good binding between the powder and the matrix epoxy resin.

In addition, the viscosity of the compounds with the molding compound powder and the conventional fillers was measured before adding the hardener. As also listed in Table 5-5, the viscosity of compound with the molding compound powder was higher than those of compounds with calcium carbonate powder and silica powder and was lower than that of compound with talc powder. This was mainly due to the difference in filler volumes resulting from difference in specific gravity (talc, 1.8; molding compound, 1.9; silica, 2.2; calcium carbonate, 2.9) and also structure of these fillers. This effect on the viscosity indicated that the molding compound powder was a suitable filler for improving paintability by preventing dripping.

Filler for adhesives

Table 5-5 also shows the adhesive strength of the epoxy resin compounds with the molding compound powder and the above-mentioned conventional fillers for the ferric board. The adhesive strength of the cured compound with the molding compound powder was almost equal to that of the cured compounds with these conventional fillers.

These results showed that the molding compound powder was a usable filler for epoxy resin products such as insulating materials, paints, and adhesives.

(4) Use as decorating additive for construction materials

Since the molding compounds were carbon-blackened, the standard molding compound powder was tested as a decorating additive for an acrylic resin-type construction material.

As shown in Figure 5-4, the molded construction material including 10 wt% of the molding compound powder (maximum particle size of 1 mm) had a good appearance, looking rather like a certain type of marble. The molding compound powder in the molded material also had high stability during cutting the material because of the strong binding between the powder and the matrix acrylic resin. Table 5-6 lists the properties of molded materials with the powders (maximum particle sizes of 1 mm and 5mm). The strength of materials with the powders were not as good as that of the original material, particularly when large-sized powder was used, but they were sufficient for the construction materials to be used according to JIS regulation. The thermal deformation temperature of the materials with the powders was comparable or superior to that of the original material. The surface hardness of the materials with the powders was higher than that of the original material. This improvement was due to the hard silica filler in the molding compound. These showed that the powder was used as a filler, especially a decorating additive for acrylic resin-type construction materials

From these results, it was concluded that the molding compound powder can be a useful filler for other plastic products, including epoxy resin and acrylic resin. However, when the molding compounds contain toxic halogen-type flame-retarding additives, their powders should be limited to the use in the plastics products containing the same-type flame-retarding additives.

Table 5-4 Properties of epoxy resin compounds with molding compound powders for insulating materials

Properties	Silica powder 60 wt%	Molding compound powder 60wt%	→Treated with Amino silane 0.5 wt%	→ Amino silane 1.0 wt%	→ Epoxy silane 1.0 wt%
Moldability					
Flow (cm)	199	76	78	75	89
Gelation time (sec.)	105	72	67	70	68
Burr* (mm)	7.2	1.0	0.8	0.5	0.3
Strength property					
Flexural strength (kgf/mm^2)	14.6	14.8	16.1	16.1	14.0
Flexural modulus (kgf/mm^2)	1057	696	722	742	678
Insulation resistance					
at 150 ℃ ($\times 10^{13}\Omega cm$)	4.0	2.0	24	22	4.0
after boiling at 100 ℃ for 24 hrs ($\times 10^{14}\Omega cm$)	14	15	32	57	16
Glass transition temperature (℃)	141	142	138	143	141
Thermal expansion coefficient					
α_1 / α_2 ($\times 10^{-5}$/℃)	2.8 / 8.6	3.9 / 11	4.1 / 11	4.1 / 11	4.1 / 11

(* Penetrating resin in air vent in metal mold)

Table 5-5 Properties of epoxy resin compounds with molding compound powder and other fillers for paints and adhesives

Properties	Filler				
	None	Molding compound powder	Silica powder	Calcium carbonate powder	Talc powder
Average particle size of filler (μm)	-	16	10	9.2	11
Viscosity (Pas)	2.5	48	14	12	206
Flexural strength (kgf/mm^2)	8.2	8.0	7.9	6.1	5.8
Charpy impact strength (kgf•cm/cm)	2.3	2.4	1.6	2.5	2.5
Tensile strength (kgf/mm^2)	4.4	4.7	4.3	3.4	2.8
Thermal expansion ($\times 10^{-5}$/℃)	13	11	11	14	9.5
Adhesive strength (kgf/mm^2)	1.8	1.6	1.5	1.7	1.4

Table 5-6 Properties of acrylic resin type construction material with molding compound powder

Properties	Acrylic resin + Aluminum hydroxide (65 wt%)	→ + Molding compound powder		
		< 1 mm (10 wt%)	< 1 mm (20 wt%)	< 5mm (10 wt%)
Flexural strength (kgf/mm^2)	5.5	4.5	4.3	3.6
Charpy impact strength (kgf ・cm /cm)	1.5	1.6	1.7	1.6
Tensile strength (kgf/mm^2)	2.7	2.9	2.9	2.3
Thermal deformation temperature (℃)	94	93	93	93
Surface hardness (H)	6	7	8	7

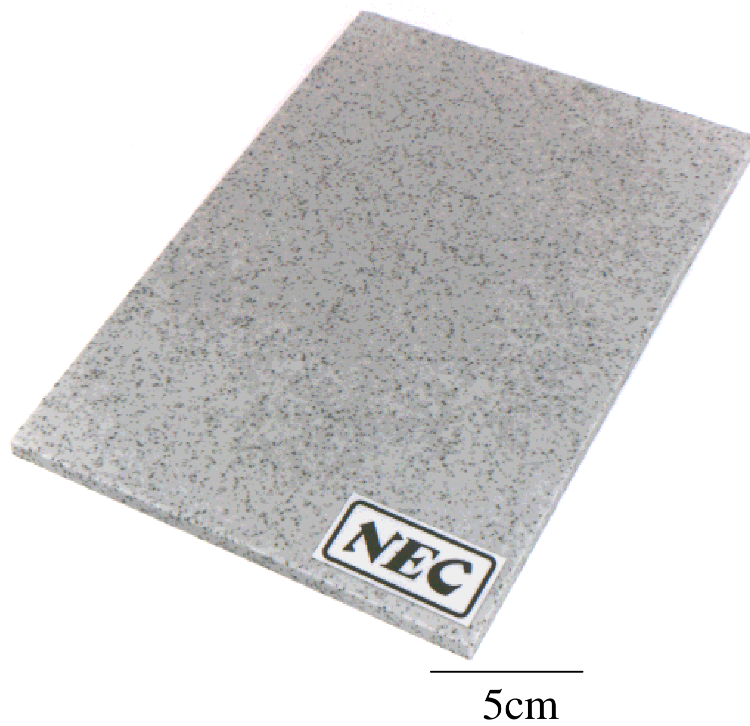


Fig. 5-4 Construction material (acrylic resin) containing molding compound powder

5-3 Pyrolysis-based technology for recovering useful materials from molding compounds

5-3-1 Experimental

(1) Materials

Sample molding compound consisted of fused silica powder filler (a mixture of spherical and pulverized particles, 50+50 wt %, average particle size 15 μm, surface area 0.72 m^2/cm^3), an epoxy resin, a phenol resin hardener, flame-retarding additives (a mixture of brominated epoxy resin and diantimony trioxide), a curing promoter (triphenylphosfine), a silane coupling agent (γ-glycidoxypropyltrimethoxysilane), a coloring agent (carbon black), a releasing agent (carnauba wax), and a low-stress agent (silicone elastomer). The blending ratios of these components are listed as a low-stress-type molding compound in Table 5-1. These materials were supplied by Sumitomo Bakelite Co. The molding compound was produced and molded by the method mentioned in secession 5-1. The mold residues (see Figure 5-1) of the molding compound before post-curing were recovered and used as test samples.

(2) Methods

Pyrolysis of molding compound

Basic pyrolysis of the mold residue of the molding compound was conducted in a tube-type electric furnace. Pulverized samples of the molding compound from 1 to 5 mm in diameter (2.0g) were placed on a quartz board (W 25×L 115×H 10 mm), which was inserted into an open-ended quartz tube (L 1000×D 40 mm). Figure 5-5 shows the basic scheme of the experimental set-up. Oxygen concentration in the flow gases (3000 cm^3 /min.) was monitored with an oxygen meter. The following range of heating conditions was tested: heating temperature (100-1200℃), heating rate (5,

20°C/min.), holding time during heating (15-160 minutes), and oxygen concentration (2-22 vol.%). When the effects of variations in heating temperature were studied, the samples were heated up to a prescribed temperature at 10°C/min. in air and then cooled after no holding time. When the effects of variations in holding time during heating were examined, the samples were placed in the furnace already at 1100°C in air flow and then cooled after prescribed holding times. To study the effects of variations in oxygen concentration, the samples were heated up to 1100°C, at 5 °C/min. and at 20°C/min. and then cooled after no holding time.

A roller kiln-type furnace (F1-L Roller Kiln, Takuma Co.) was used as a prototype for a practical pyrolysis system (see Figures 5-6 and 5-7). In order to avoid any kiln contamination, the mold residues of the molding compound were placed on ceramic boards (W 50×L 50×H 2 cm; made of alumina) in unpulverized form at 1500g/board. The boards were then carried on rollers through three zones (temperature-rise, temperature-hold, and cooling) in the furnace (W 1.3×L 25.2 ×H 1.0 m).

The amount of carbon in the recovered silica was determined using a post-combustion-carbon infrared absorption analyzer (CA-20SM, Kawatetsu Advantech Co.). In order to determine the amount of antimony in the recovered silica, a mixture of hydrofluoric acid, nitric acid and sulfuric acid was added to the silica to dissolve it completely, and then the antimony amount in the solution was measured using an inductively coupled plasma (ICP) emission spectrometer (ICPS-1000, Shimazu Co.). The antimony compounds (metal Sb, Sb_2O_3, and Sb_2O_4) were identified by using an X-ray diffraction analyzer (RU-200, Crigar Co.). For the measurement of amounts of ionic substances in the recovered silica, the silica was held in distilled water (electronic conductivity <0.5 μs/cm) at 125°C for 20 hours in an autoclave, and then the amounts of ionic substances in the solution were determined with an ion chromatography analyzer (IC 7000, Yokokawa Analytical System Co.). The electrical conductivity of the resulting solution

was measured using a conductivity meter (CM-5S, Towa Electronic Wave Co.).

Reuse of recovered silica

Since the recovered silica powder was partially aggregated, it was pulverized by one of either two methods. The first employed a conventional crushing- type mill (ANM-1000, Nitto Kagaku Co.) that used shearing and compression forces and pulverized the recovered silica powder at a rate of 500 g/hr. The second method employed a jet stream collision type mill (jet mill; STJ-200, Seishin Enterprise Co.) that used the impact between particles in a jet stream of nitrogen. The recovered silica powder was supplied into the chamber at a pressure of 1.0 kg/cm^2 and at a rate of 2.0 kg/hr. The particle distribution and average particle size of the resulting silica powder were measured with a particle distribution analyzer (7000s, Seishin Enterprize Co.). The surface area of the silica powder was measured with a surface-area-measurement apparatus (Flow-SorbⅡ 2300, Shimazu Co.).

The resulting silica powder was added to an epoxy resin compound used for cast-insulating electronic parts, which consisted of bisphenol-A type epoxy resin (84 wt%, Epicoat 828, Yuka-Shell Co.) and aliphatic amine-type curing promoter (16 wt%, Epicure T, Yuka-Shell Co.). The silica powder formed 50 wt% of the epoxy resin compound, which was cured in a mold at room temperature for 4 days. The mechanical strength of the molded compound's samples was determined using methods specified in JIS K 7111 and JIS K 7203. Their electric insulating properties were measured as specified in JIS K 6911. The fractured surfaces of the molded samples were observed with a scanning electron microscope (SEM) (EPMA-8705, Shimazu Co.).

Also, the resulting silica powder was added to the original molding compound by the previously mentioned method for producing the molding

compound. The properties of the resulting molding compounds were evaluated by using the methods described in session 5-1.

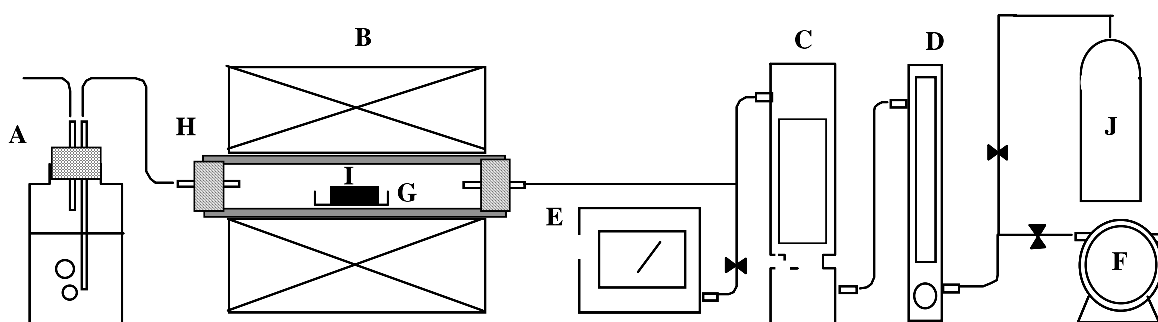
Analysis and treatment of combustion exhaust gas

In the basic pyrolysis test using the tube-type electric furnace, inorganic bromine compounds (HBr and Br_2) and antimony bromide in the combustion gas were collected in an alkaline solution (5mM sodium carbonate + 2mM sodium hydrogen carbonate) and then analyzed by ion-chromatography and ICP as mentioned previously.

Figure 5-6 illustrates the exhaust gas treatment system positioned after the practical pyrolysis system using roller kiln-type furnace. It consisted of a secondary combustion process, a cooling process, a dry recovery process, and a wet recovery process. The exhaust gas generated from the molding compound by heating at 700℃ in the roller kiln-type furnace. A secondary combustion of the exhaust gas was conducted with a tube-type furnace (D 40 × L 100 cm) by heating using LPG burning. The conditions of the secondary combustion were as follows: exhaust-gas flow rate 1.1-1.2 m^3/hour, air flow 12.0-13.2 m^3/min, heating temperature 900-1100℃, and heating holding time 2-3 seconds. After the secondary combustion, the gas was immediately cooled to below 250℃ by the cooling system spraying water. After this, solid particles such as antimony oxide in the gas were collected by the dry recovery process using a bag filter (average pore size 15μm, E-PTFE, Japan Goatex Co.). Finally, soluble materials such as inorganic bromine compounds and the remaining solid particles in the gas were removed by the wet recovery process using a scrubber that sprayed a sodium hydroxide solution (pH 10-11).

For the measurement of the organic bromine compounds in the exhaust gas, the compounds were collected with a resin-type absorbent (Amberite XAD-2, Orugano Co.), and then dissolved with toluene and methanol. Their concentrations were determined with a gas-chromatography analyzer

(Shimazu/Kratos Concept 32 type, Shimazu Co.). The antimony oxide in the gas was collected with a glass filter (pore size 0.3 μm). After the filter was heated at 300℃ for vaporizing antimony bromide collected together with the antimony oxide, the oxide in the filter was dissolved in a hydrogen chloride solution (2.0M), and its concentration was determined by the ICP analysis mentioned previously. The antimony bromide in the gas was collected in an alkaline solution (1.0M sodium hydroxide + 0.2M hydrogen peroxide) and its concentration was determined by the ICP analysis.



A: alkaline solution, B: electric furnace, C: dehydrating tower,
D: gas flow meter, E: oxygen meter, F: air pump, G: quartz board
H: quartz tube, I: sample, J: nitrogen cylinder

Fig. 5-5 Experimental apparatus for pylolysis of molding compounds

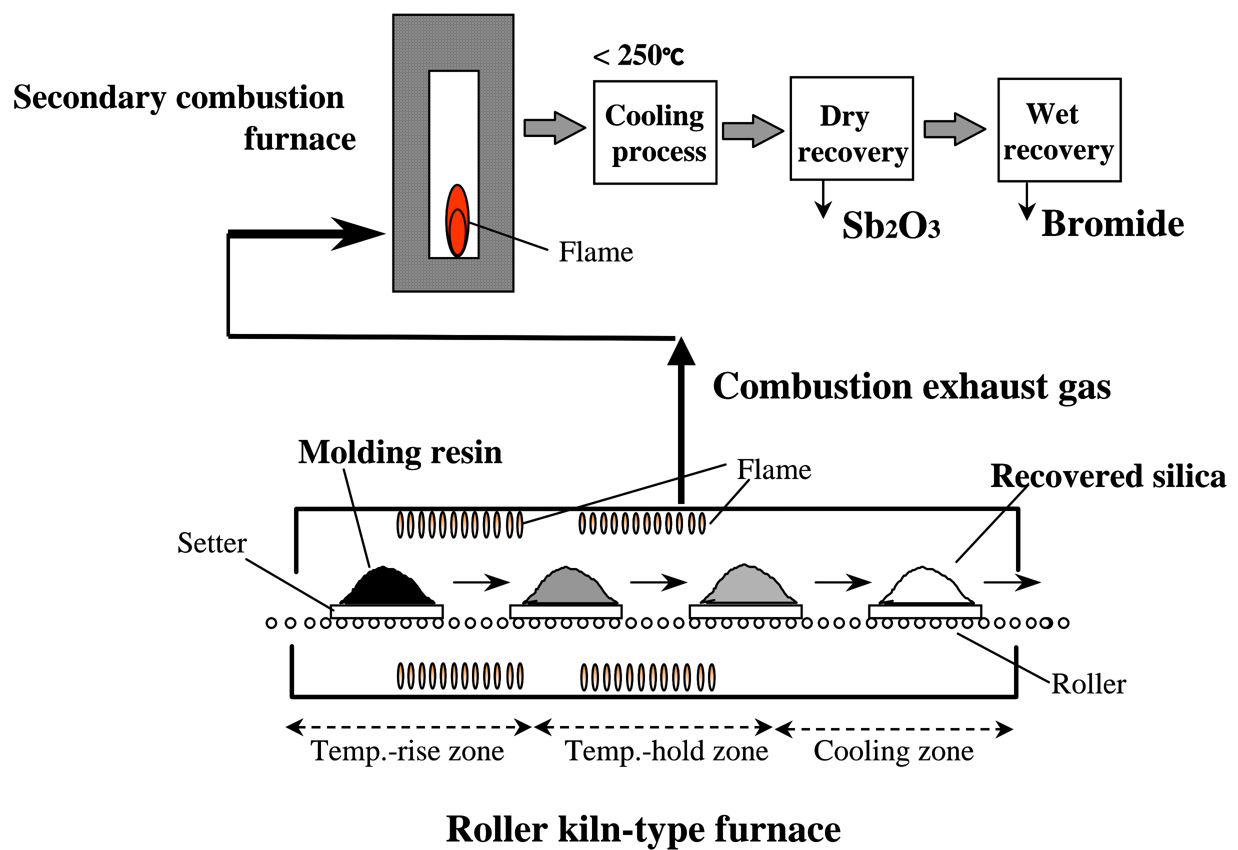


Fig. 5-6　Pyrolysis system for recovering useful materials from molding compounds and exhaust gas treatment system

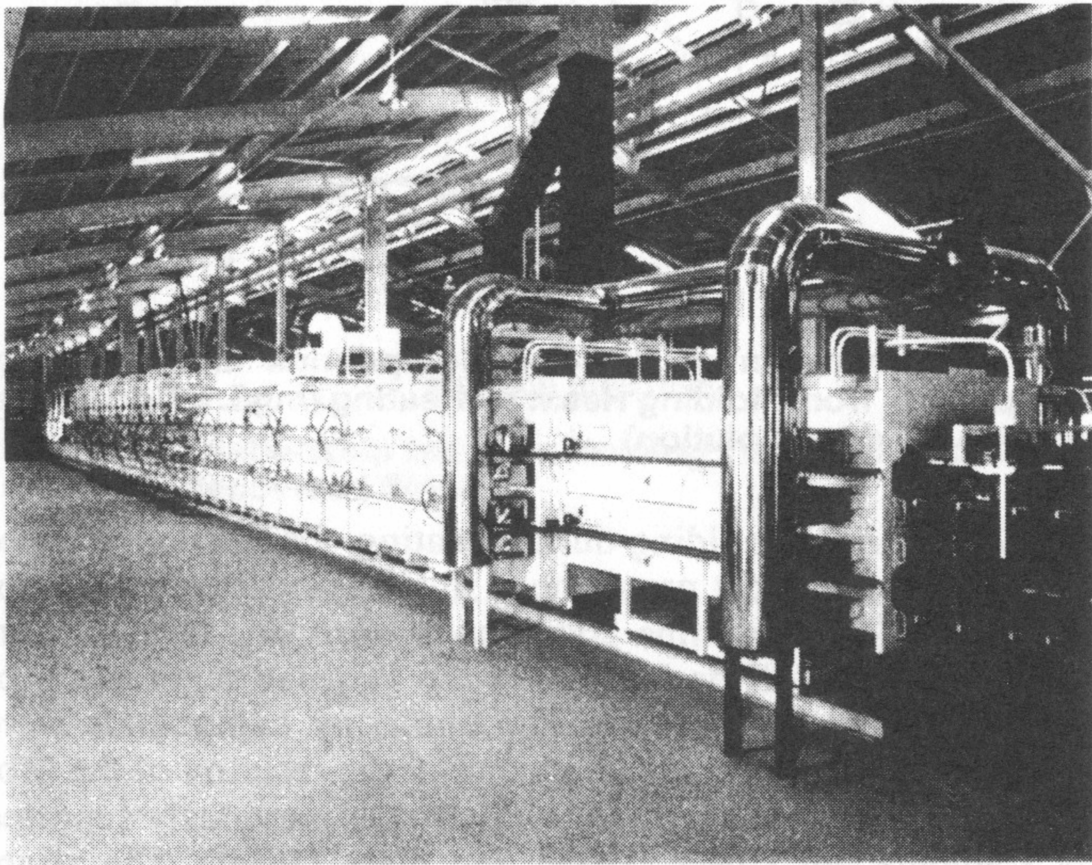


Fig. 5-7 Roller kiln-type furnace

5-3-2. Results and Discussion

(1) Thermal degradation of molding compounds

The thermogravimetric behavior in air of the mold residue of the tested molding compound was studied. Thermal decomposition of the resin part of the molding compound was essentially complete at approximately 600℃, and it progressed little thereafter (see Figure 5-8).

Figure 5-9 illustrates the generation of bromine compounds and antimony compounds from the flame-retarding additives consisting of brominated epoxy resin and diantimony trioxide (Sb_2O_3) in the molding compound during heating. Generation of these compounds was most pronounced in the temperature range of 300-600℃. The bromine compounds were bromine (Br_2), hydrogen bromide (HBr), and organic bromides, all derived from the thermal degradation of the brominated epoxy resin. The antimony compounds were mainly antimony bromide generated in the reaction of the bromine compounds with Sb_2O_3, which reaction was previously reported (18, 19). The slight spurt of activity above 1000℃ seemed to be due to the volatilization of the Sb_2O_3 remaining after the reaction with the bromine compounds.

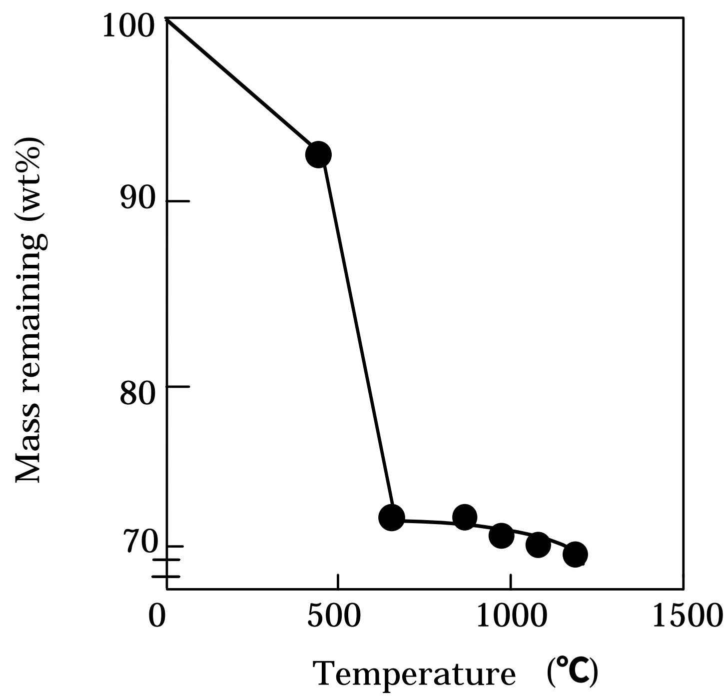


Fig. 5-8 Thermogravimetric analysis of molding compound

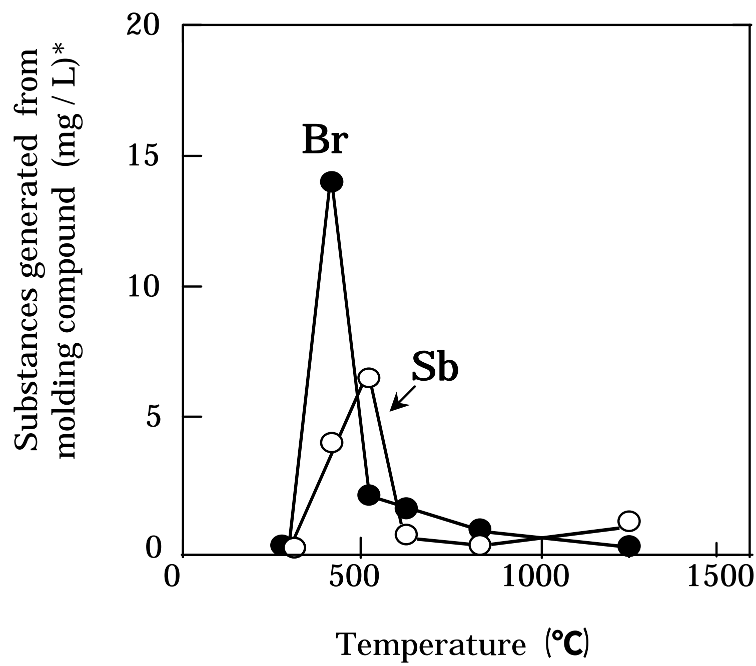


Fig. 5-9 Generation of bromine compounds and antimony compounds from molding compound by heating (* concentration in absorbing solution)

(2) Behavior of remaining impurities in recovered silica filler

The main impurities in the silica powder recovered after pyrolysis of the molding compound were carbon, antimony, and ionic substances. The effects of certain thermal degradation parameters (heating temperature, heating rate, holding time during heating, oxygen concentration) on the amounts of these impurities in the recovered silica powder were studied.

Carbon (C)

Figure 5-10 shows the relationship between heating temperature and the amount of C remaining in the recovered silica powder. The amount of C decreased with increased heating temperature, dramatically so between 600 and 700℃, but changed little thereafter. Figure 5-11 shows the effect of holding time during heating on the amount of C and indicates that this amount decreased with increased holding time. Figure 5-12 illustrates the relationship between oxygen concentration during heating at 1100℃ and the amount of C remaining. The amount of C quickly decreased at first with increased oxygen concentration, but little effect was observed above 10%. A decreased heating rate also produced decreased C. (a carbonaceous substance with non-volatility was formed under the conditions of rapid heating and low oxygen concentration.) In short, the amount of C in the recovered silica was reduced by increase in heating temperature, holding time during heating, and oxygen concentration, as well as by a decreased heating rate.

Antimony (Sb)

Figure 5-13 shows the relationship between heating temperature and the amount of Sb in the recovered silica powder. The amount of Sb decreased with increased heating at temperatures below 500℃ (Figure 5-13-a), but did not decrease in the approximate range of 500-1000℃

(Figure 5-13-b). Above 1000℃, the amount of Sb again decreased to a final level of approximately 0.4 wt%. The first decrease in Sb seemed to be due to the volatilization of $SbBr_3$, which was formed by the reaction of Sb_2O_3 and bromine compounds generated from the brominated epoxy resin, as has been previously noted. In the temperature range of 500-1000℃, a non-volatile antimony compound appeared to form. X-ray diffraction analysis (XRD) was used to determine the structure of this antimony compound in the silica. The XRD pattern (Figure 5-14-a) after heating at 900℃ indicates the formation of diantimony tetraoxide (Sb_2O_4). It is generally known that Sb_2O_4 is remarkably stable below about 1000℃ (20). Furthermore, the decrease in Sb above 1000℃ (Figure 5-13-C) strongly suggests the volatilization of the Sb_2O_3 that was formed by decomposition of Sb_2O_4. Above 1100℃, however, the rate of volatilization of antimony decreased. In this temperature range (1200℃), only fused silica was observed in the XRD pattern (Figure 5-14-b), in spite of the fact that a sufficient amount of Sb_2O_3 (0.4wt%) remained to be detected. This suggested that the remaining Sb_2O_3 (melting temperature 652-656℃) melted into the silica, which would make it very hard to remove.

Figure 5-11 shows the effect of holding time during heating on the amount of Sb remaining in the recovered silica. It indicates that the amount of Sb decreased with increased holding time, but this effect was not dramatic.

Figure 5-15 shows the relationship between oxygen concentration and the amount of Sb remaining in the recovered silica. It was found that the optimum oxygen concentration for reducing the level of Sb was approximately 5-8 vol%. In this range, the oxidation of Sb_2O_3 was extremely slight, which allowed for its greater volatilization. Below this range, however, the increased amount of remaining Sb appeared to be mainly caused by the formation of nearly non-volatile metal antimony (boiling temperature 1640℃) generated as a result of the reaction between Sb_2O_3

and C resulting from insufficient thermal degradation of the resin part at the low oxygen concentrations.

These results indicated that the most effective condition for reducing antimony in the silica was heating at greater than 1100℃ in an atmosphere with a limited oxygen concentration (5-8 %).

Ionic impurities

The ionic impurities formed in the recovered silica powder after pyrolysis of the molding compound included a significant amount of phosphoric acid ion (PO_4^{3-}) and only traces of other ions, such as sodium ion (Na^+). Reducing the amount of PO_4^{3-} , then, is crucial if the recovered silica is reused in insulating materials. This PO_4^{3-} appeared as a decomposition product of the triphenylphosphine added as a curing promoter in the molding compound. Figures 5-16 and 5-17, respectively, show the effects of heating temperature and oxygen concentration on the amount of ionic substances in the recovered silica. This PO_4^{3-} decreased with increased heating temperature and also with increased oxygen concentration. This suggested that the most effective way to reduce PO_4^{3-} in the recovered silica was to heat above 1000℃ and kept oxygen concentration above about 10 vol%. The amounts of other ionic substances, represented here by Na^+ , were little affected by these pyrolysis conditions.

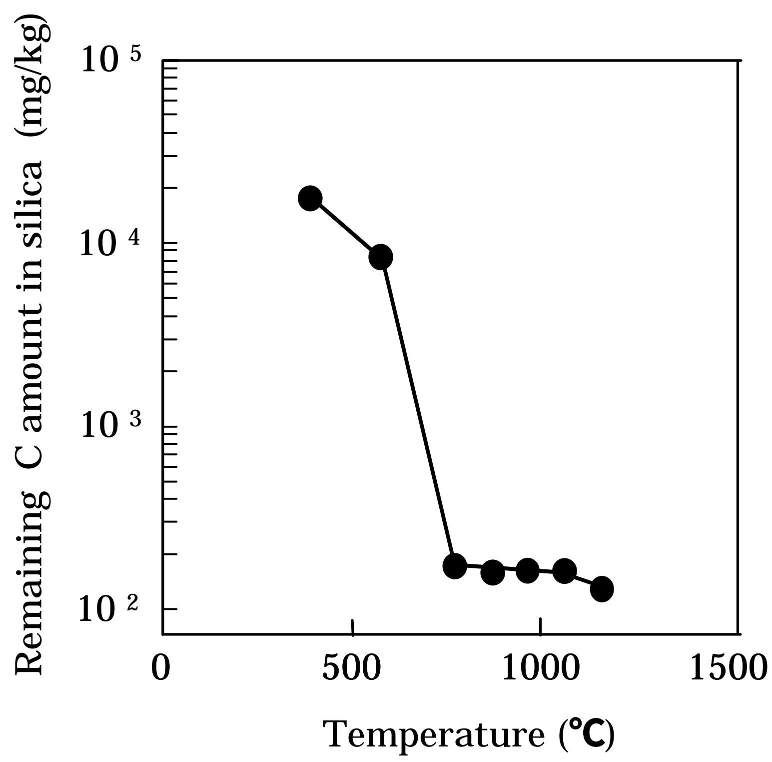


Fig 5-10 Relationship between heating temperature and remaining C in recovered silica

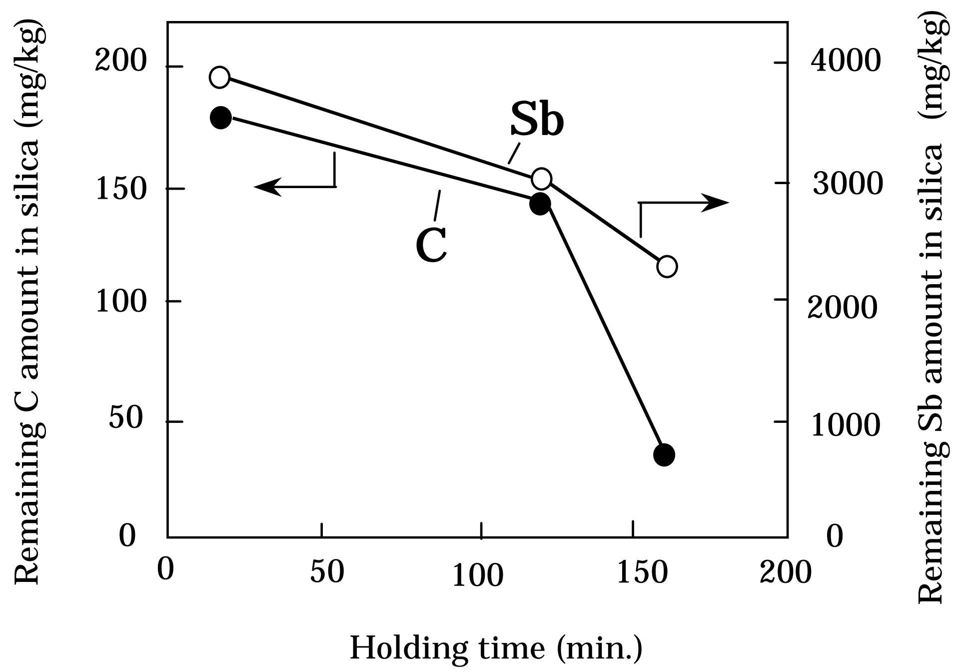


Fig. 5-11 Relationship between holding time and remaining of C and Sb in recovered silica

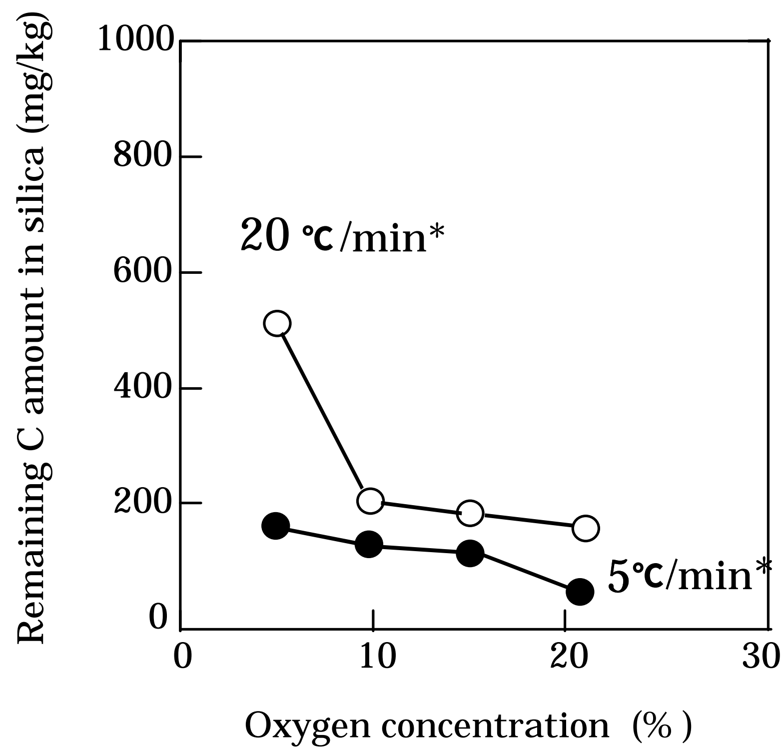


Fig. 5-12 Relationship between oxygen concentration and remaining C in recovered silica (* Heating rate)

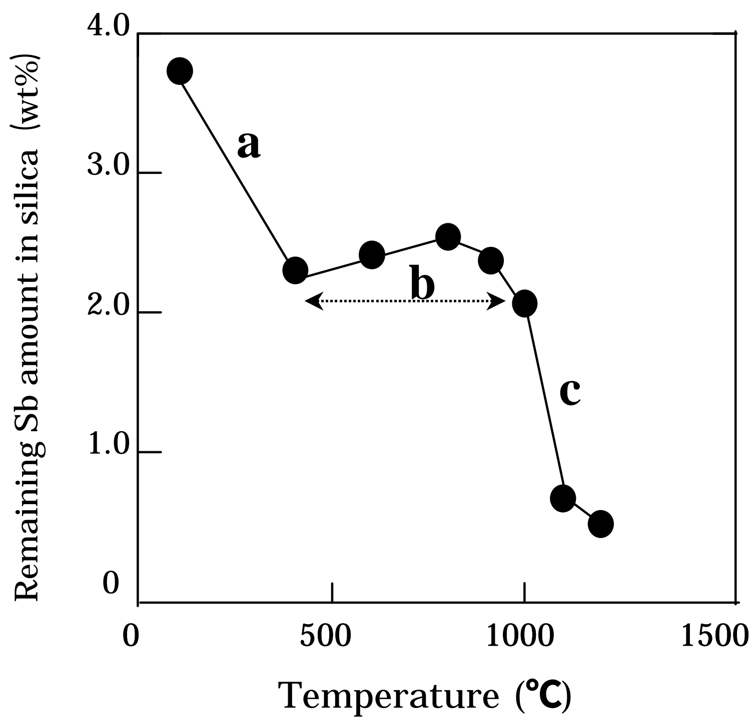


Fig. 5-13 Relationship between heating temperature and remaining Sb in recovered silica

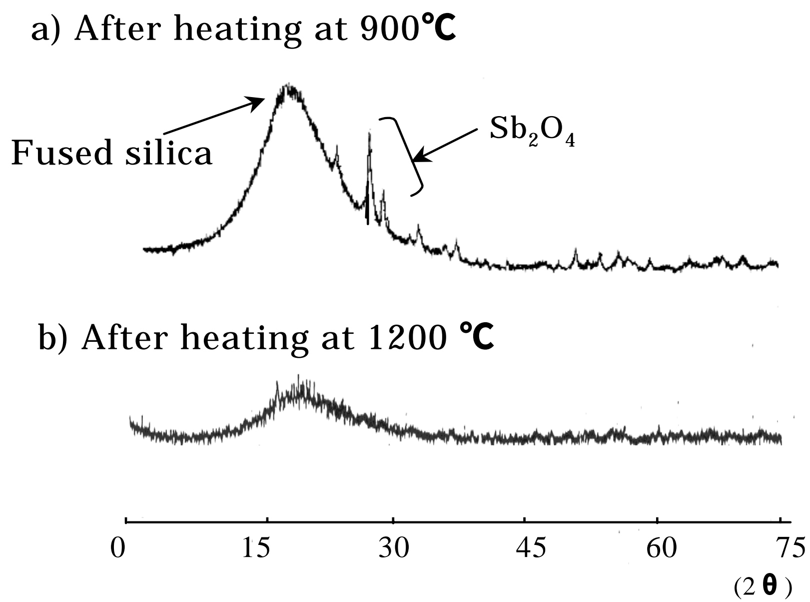


Fig 5-14 X-ray diffraction patterns of recovered silica

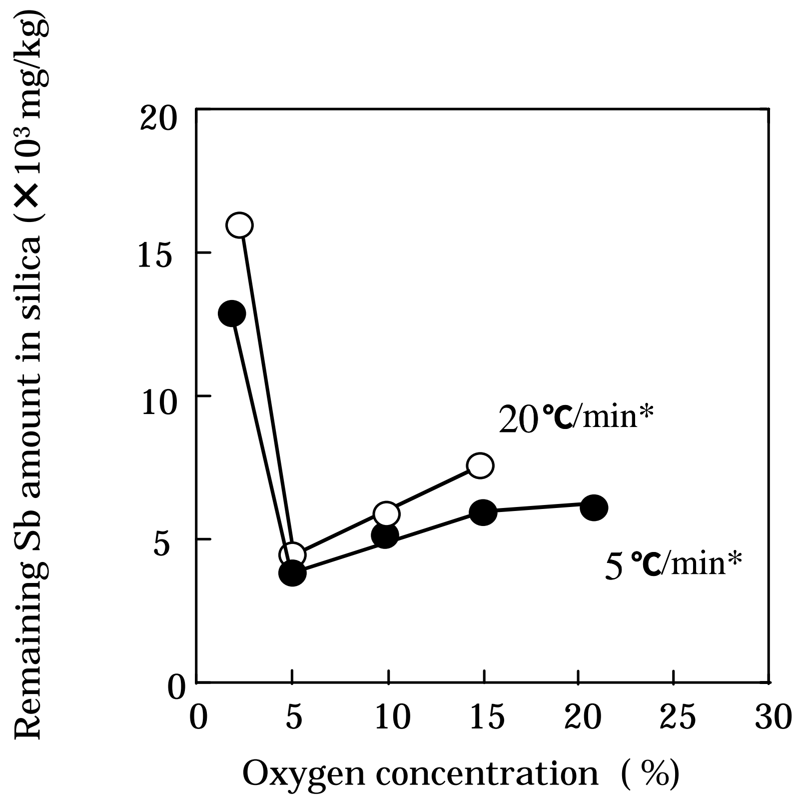


Fig 5-15 Relationship between oxygen concentration and remaining Sb in recovered silica (*Heating rate)

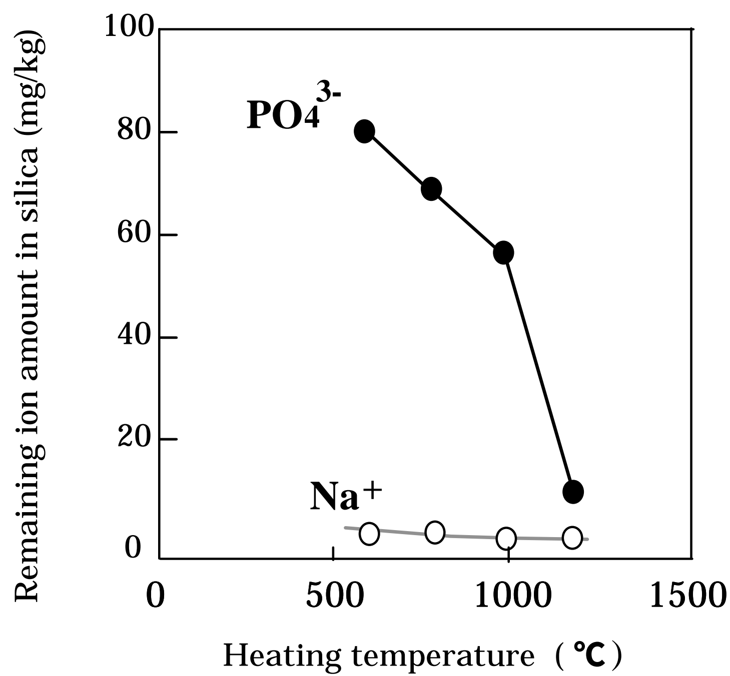


Fig. 5-16 Relationship between heating temperature and remaining ions in recovered silica

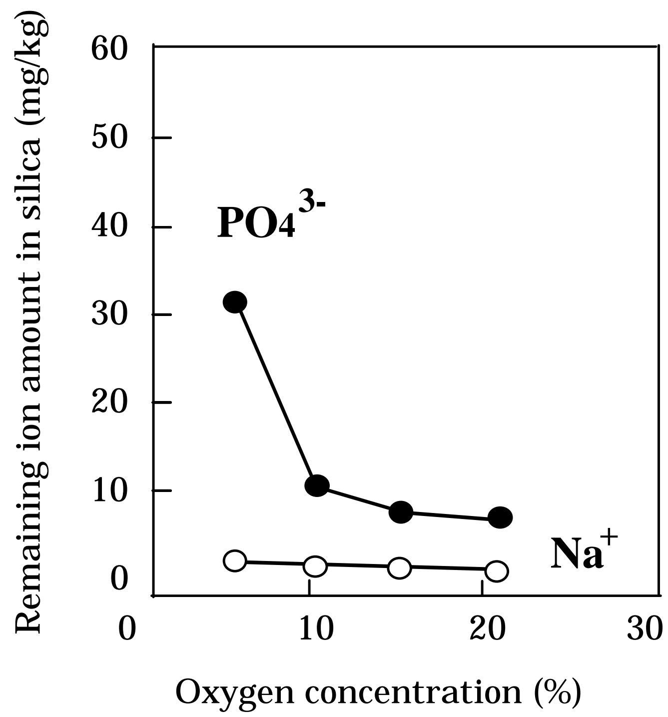


Fig. 5-17 Relationship between oxygen concentration and remaining ions in recovered silica

(3) Practical pyrolysis technology for recovering silica filler

A roller kiln-type furnace (Figures 5-6 and 5-7) was used as a prototype practical pyrolysis system for recovering high purity silica powder filler from the molding compound. Conventional kiln-type and stoker-type furnaces tend to contaminate the recovered silica because their walls directly touch both the molding compound and the recovered silica. The roller kiln-type furnace can avoid such contamination by conveying them on ceramics boards. This furnace offers separate control of the three zones (temp.-rise, temp.-hold, and cooling) through which the materials pass, and hence it is easy to adjust to the optimum pyrolysis condition based on the experimental results, as previously mentioned.

In the temperature-rise zone, the heating rate was initially kept low (to 5℃/min for the rise from 100 to 500℃) in order to promote sufficient formation of $SbBr_3$ and to enhance decomposition of the resin; above 500℃ the rate was increased to 15℃/min. to promote the overall productivity. In the temperature-hold zone, maximum heating temperature was kept to 1100-1250℃. While very high temperatures helped to reduce impurities, above about 1300℃, fused silica is partly transformed to crystallized silica (crystbarite) (21), whose high thermal expansion (higher than that of fused silica) is a disadvantage in thermal cracking resistance of molding compound containing it as a filler (22). A holding time of 30 minutes was determined to be most suitable in terms of pyrolysis efficiency and overall productivity. The control of oxygen concentration was also particularly important because the optimum concentration of oxygen for reducing Sb was different from those of C and the ionic substances. In the temperature-rise zone, the oxygen concentration was kept to a low value (7-10 vol.%) to prevent oxidation of the Sb_2O_3, but in the temperature-hold zone, they were increased to 10-13 vol.% to promote the removal of C and ionic substances.

As shown in Table 5-7, at heating temperatures between 1200-1250℃, a purity in the recovered silica of C <50 ppm, Sb <0.4wt%, and PO_4^{3-} <20 ppm

was achieved. Furthermore, the electronic conductivity of the eluting solution of the recovered silica, which mainly influences the insulating property of insulating materials that employ the recovered silica, was comparable to that of original silica.

(4) Reuse of recovered silica filler

The silica powder recovered from the molding compound by pyrolysis contained aggregated particles. They appeared mainly to be formed by the adhesion of silica particles with melting antimony oxides in the pyrolysis process. The presence of these aggregates necessitates a pulverizing process if the recovered silica is to be of practical use as a filler. While the conventional crushing method that uses shearing and compressing forces was effective in its pulverizing, the average size of the resulting silica particle was extremely small, reducing the moldability of molding compound containing it (see Table 5-8). By way of contrast, a jet-stream collision method that uses impact between particles in a jet-stream of nitrogen sufficiently pulverized the aggregates while maintaining the average particle size. This average size was sufficient for practical use as a filler. Additionally, the size distribution of the resulting silica powder as well as its surface area were as almost the same as those of the original silica powder.

The use of such jet-stream-treated silica as filler in an epoxy resin compound for cast-insulating electronic parts was studied. Table 5-9 contrasts the mechanical and electrical properties of the compounds containing this recovered silica with those of the original silica. The properties of the compound with the recovered silica were found to be comparable to those of the compound with the original silica, and its mechanical strength properties were, in fact, superior. The SEM photos of fractured surfaces of these cured epoxy resin (see Figure 5-18) indicate that the recovered silica adhered with the resin more strongly than did the

original silica. This appears to have produced the increase in strength. This better adhesion seemed mainly to be due to the increase in particle surface roughness produced by the jet-stream- treatment.

The same type of recovered silica also was experimentally used as a filler for the original molding compound. As shown in Table 5-10, a 50%/50% blend of recovered silica and original silica exhibited satisfactory molding compound properties.

Therefore recovered silica powder, after treating aggregates in it, was found to be feasible as an inorganic filler for cast-insulating materials and for molding compounds used in electronic parts.

.

Table 5-7 Recovered silica purity after pyrolysis with roller kiln-type furnace

Heating temperature (℃)	Remaining impurities in silica (mg/kg)						EC*
	C	Sb	Na^+	Fe^{2+}	Cl^-	PO_4^{3-}	(μs/cm)
1100	80	3600	3.9	4.6	2.1	18	20.5
1200	40	3800	3.3	2.2	1.9	14	9.9
1250	40	2300	5.3	2.3	1.2	18	7.2
Original silica	-	-	0.5	1.0	0.2	<1	6.8

* Electronic conductivity of eluting solution for recovered silica

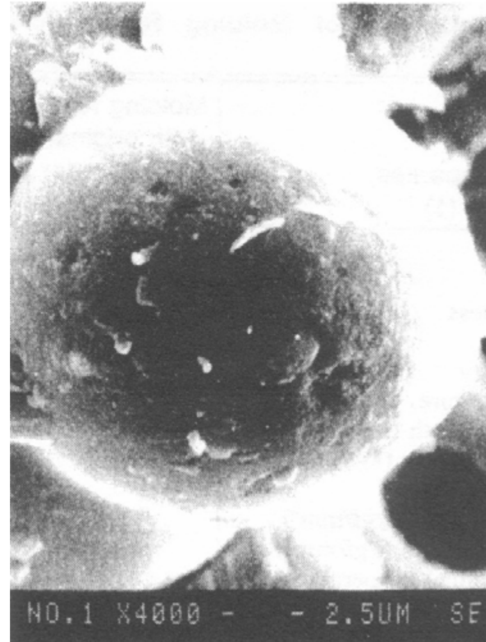
Table 5-8 Properties of recovered silica powder after being pulverized

	Average particle size (μm)	Surface area (m^2/cm^3)
Original silica powder	15.0	0.72
Recovered silica powder after being treated by crushing	< 9	
Recovered silica powder after being treated by jet-stream collision	12.0	0.79

Table 5-9 Properties of cast-insulating epoxy resin compounds containing silica powder

Properties	Epoxy resin with original silica	Epoxy resin with recovered silica
Flexural strength (kgf/mm^2)	8.6	10.0
Compressive strength (kgf/mm^2)	15.8	15.3
Charpy impact strength (kJ/mm^2)	3.0	4.2
Electronic breaking strength (kv /mm)	19.8	19.1
Insulating resistance ($\times 10^{14} \Omega$)	1.3	1.3

a) Epoxy resin compound containing original silica powder



b) Epoxy resin compound containing recovered silica powder after being treated by jet-stream collision

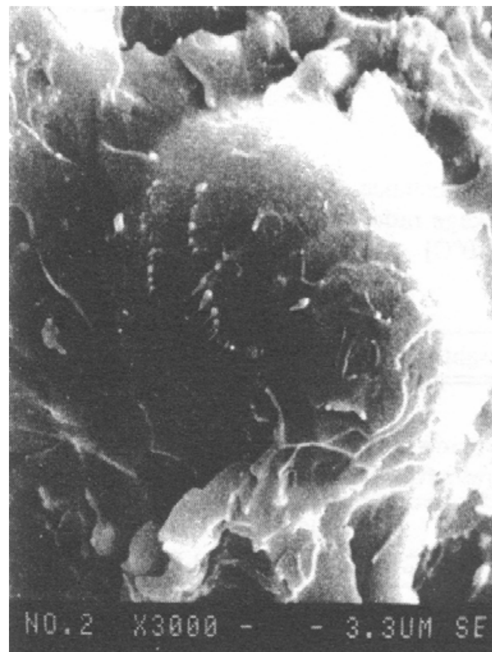


Fig. 5-18 Fractured surface of epoxy resin compounds containing silica filler

Table 5-10 Properties of molding compounds containing silica powder

Properties	Molding compound with original silica powder	Molding compound with recovered silica powder*
Moldability		
Flow (cm)	85	81
Barcol hardness	76	66
Burr (mm)	1.3	2.3
Strength property		
< Room temperature >		
Flexural strength (kgf/mm^2)	12.2	11.5
Flexural modulus (kgf/mm^2)	1361	1414
< 240℃ >		
Flexural strength (kgf/mm^2)	1.5	1.6
Flexural modulus (kgf/mm^2)	89	91
Thermal mechanical property		
Glass transition temperature (℃)	154	165
Thermal expansion coefficient α_1/α_2 ($\times 10^{-5}$/℃)	1.5 / 6.3	1.5 / 5.3
Water absorption (wt%) / 24hrs Boiling	0.219	0.218
Moisture resistance reliability		
(Defected package ratio) 120℃, 2.3 atm — 200 hours	0／10	0／10
(Defected package ratio) 120℃, 2.3 atm — 525 hours	0／10	0／10
Thermal impact resistance reliability		
(Defected package ratio) 150℃- -60℃ — 400 cycles	0／10	0／10
(Defected package ratio) 150℃- -60℃ — 800 cycles	0／10	0／10

* 50 wt% in total silica

(5) Combustion gas treatment

The combustion exhaust gas contained toxic organic bromine compounds and antimony bromide, generated from the flame-retarding additive in the molding compound during burning. A secondary combustion method was successfully applied to the decomposition of these toxic substances in the gas. Treatment by heating at 1100℃ decreased the toxic organic bromine compounds to a safe level (total amount of toxic equivalent factors as chlorinated dioxins and furans <0.045 ng/m^3), thus satisfying current international standards (18-21).

The secondary combustion treatment also resulted in the conversion of the antimony bromide in the exhaust gas to antimony oxide, which could be collected by a dry recovery process. Table 5-11 lists the concentrations of antimony compounds in the exhaust gas before and after the secondary combustion and the dry recovery processes. The antimony bromide (mainly $SbBr_3$) was efficiently converted into antimony oxide (mainly diantimony trioxide (Sb_2O_3) as shown by XRD analysis) at a high conversion rate (about 94 wt%) by the secondary combustion at 1100℃. The antimony oxide was collected at a high recovering rate (about >99 wt%) by the dry recovery process. The recovered antimony oxide was sufficient pure (91wt%) to be used as a raw material for the production of antimony. The antimony compounds and bromine compounds (HBr,Br_2) remaining in the gas after the dry recovery process were removed almost perfectly by the wet recovery process (>99.9 wt%). The solution used in the wet recovery process could be reused as the cooling water in the process for cooling the exhaust gas after secondary combustion, thus helping to create a nearly closed exhaust gas treatment system that generates no toxic waste.

Table 5-11 Concentration of antimony compounds in exhaust gas before and after treatments

Secondary combustion temperature (℃)	Concentration of antimony compounds in exhaust gas (mg/m^3)					
	Before treatment		After secondary combustion		After dry recovery	
	Sb_2O_3	$SbBr_3$	Sb_2O_3	$SbBr_3$	Sb_2O_3	$SbBr_3$
900	2.2	14.0	8.2	0.96	<0.10	0.32
1100	1.1	14.0	12.0	1.0	<0.10	0.60

5-3 Summary

Recycling technologies for epoxy resin compounds used as molding compounds for electronic parts such as IC packages were described for the purpose of reusing after grinding and recovering of valuable materials by pyrolysis.

The reuse of the ground molding compounds (mold residues) was studied. The ground residue (molding compound powder) showed good surface reactivity due to containing functional groups (silanol, hydroxy, and glycidyloxy) and reacted with polar resins such as epoxy resin and phenol resin in a similar manner to that silica powder did. Recycling a low-stress-type molding compound powder containing silicone elastomer into a standard molding compound yielded a new molding compound that had far better thermal impact resistance than that made with the original standard molding compound. Moreover, the molding compound powder was found to be suitable as a filler for epoxy resin products such as insulating materials, paints, and adhesives to supply them with sufficient insulating, strength and adhesive properties. Use of the powder as a decorating additive for an acrylic resin-type construction material also produced a marble-like appearance and improved the surface hardness of the material.

Further, a pyrolysis-based technology for the molding compounds (mold residue) was also developed for the purpose of recovering useful materials and reusing them. The molding compounds contain silica powder filler (70-90 wt%) and flame-retarding additives consisting of bromine compounds and antimony oxide. This study clarified those pyrolysis conditions best suited to reduction of the impurities (carbon, antimony, ionic substances) in the recovered silica filler. This contributed to the development of a practical pyrolysis technology in which a roller kiln-type furnace was used to recover high purity silica filler. The recovered silica filler was sufficiently pure to be employed as an inorganic filler in epoxy resin compounds used as cast-insulating materials and original molding compounds. The combustion

exhaust gas generated in the pyrolysis of the molding compounds was successfully treated by a treatment process consisting of secondary combustion, dry recovery, and wet recovery. The secondary combustion decomposed toxic organic bromine compounds in the gas to a safe level and converted antimony bromide to antimony oxide, which could then be collected by the dry recovery process at a useful purity (91%). The antimony compounds and bromine compounds (HBr,Br_2) remaining in the gas after the dry recovery process were removed almost perfectly by the wet recovery process (>99.9 wt%).

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Chapter 6

Recycling of Printed Wiring Boards with Mounted Electronic Parts

6-1 Introduction

Owing to the increased production of printed wiring boards (PWBs) to meet the recent growth in the electronic industry, the amount of PWB waste has also greatly increased. However, until now, the recycling of the waste has been difficult because PWBs are hard to pulverize because of containing glass fiber and various metals, and also they cannot be remelted by heating because of containing thermosetting plastics, mainly epoxy resin compounds, which are cured in the molding process. Furthermore, current PWBs contain toxic halogen-type flame-retarding additives as previously mentioned. Therefore, most of the PWB wastes have been disposed of in landfill dumps.

Actual recycling by refining PWB wastes to recover gold and copper is mainly performed for special PWBs that contain these metals in a high ratio (1), but it is not applied to general PWBs because of their lower cost effectiveness. Recycling general PWB wastes has been tried, in which they were pulverized as a whole and useful metals were separated by physical methods (2, 3). However, since these methods recovered mainly useful metals (copper, etc), other useful materials such as epoxy resin, glass fiber and solder were not sufficiently separated. Therefore, the actual recovery ratio of total useful materials from the PWBs was very low. In another study, recovering the raw epoxy resin and the glass fiber in PWB wastes was attempted (4). After pulverizing the PWBs and separating the metals by physical methods, the PWB powders were pyrolyzed, then the organic raw materials of the resin and halogen compounds originating from the halogen type-flame retarding additive in the resin were recovered from the exhaust gas, and the glass fiber was recovered from the residue. This method, however, needed strict treatment of the toxic exhaust gas and further control of the quality of the recovered glass fiber containing residues of carbon, halogen, and solder before actual reuse.

Each part of PWBs with mounted electronic parts has different useful materials. The glass-epoxy laminate boards contain copper, cured epoxy

resin, and glass fiber. The electronic parts mounted on the boards include gold, iron, nickel, silicon, cured epoxy resin, and silica powder. The solder exists at the interface between the boards and the electronic parts. Therefore, a recycling method consisting of separating the PWBs into each part and treating them independently seemed to be more effective.

In this chapter, a new PWB-recycling technology based on disassembling, pulverizing and separating was reported, which aims to recover a high ratio of useful materials and reuse them effectively. First, automatic removal techniques for electronic parts and solder were attempted. Separating copper and the mixture powder consisting of glass fiber and cured epoxy resin (glass fiber-resin powder) from the resin boards was then studied. Moreover, the reuse of the recovered materials was examined. (This recycling processes are shown in Figure 6-1)

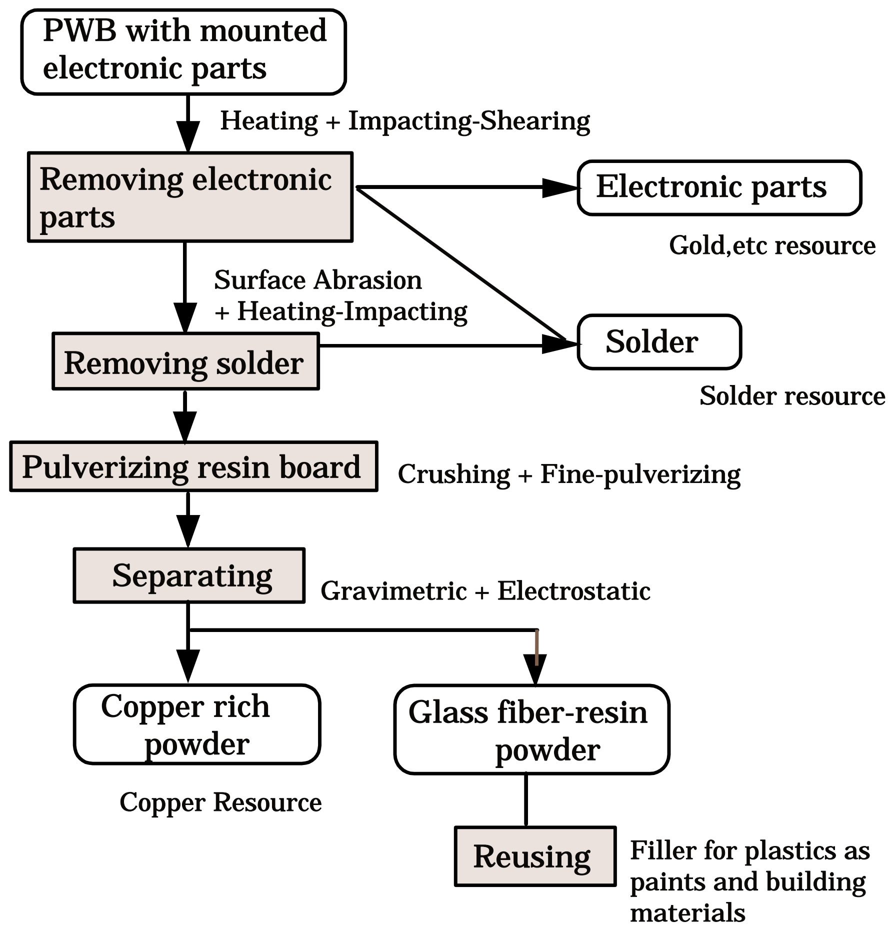


Fig. 6-1 Recycling process for PWBs

6-2 Experimental

6-2-1 Materials

The PWB sample (PC-9801-96, NEC Co., see Figure 1-1) was composed of a six-layer epoxy resin board, patterned with copper circuits, and mounted with electronic parts. The resin board consisted of bisphenol A-type epoxy resin, an amine hardener, a bromine-type flame-retarding additive and glass fiber (9 μm in diameter) made of E-glass. The resin in the board was cured at 150-160℃ for 2-3 hours. The mounted electronic parts were surface mounted devices (one 160-pin QFP, one 120-pin QFP, two 40-pin PLCCs, one 20-pin SOP, one 16-pin SOP, and two 14-pin SOPs), through-hole devices (three 10-pin DIPs, one 16-pin DIP, two 15-pin connectors) and chip components (115 pieces). The total weight ratio of the electronic parts for the PWB was 26.1wt%.

The main material content of the PWB was measured by chemical analysis. Each metal content in the pulverized PWB, after dissolving it in hydrochloric and nitric acids, was determined by measuring the content of the metal ion in the solution using an inductively coupled plasma (ICP) emission spectrometer (ICPS-1000, Shimazu Co.). The glass fiber content in the resin board was determined by measuring the total weight of SiO_2 content and the other material content in the E-glass. The SiO_2 content was measured according to JIS R 3101 after pyrolizing the pulverized resin board (500℃, two hours) and heating it in nitric acid (200℃, one hour). The other material content was determined based on its weight ratio to SiO_2 in E-glass (47 : 53) (5). The resin content in the resin board was calculated from the difference between the total board weight and the weights of the glass fiber and the metals (copper, solder) in the board. Table6-1 lists the analysis results.

6-2-2 Methods

(1) Measuring removal force for electronic parts from resin boards

The force required to detach electronic parts from the resin board was measured for through-hole devices (20-pin DIP, 168-pin CPU, 120-pin connector, and 234-pin connector), and a chip component (3 mm wide , 6 mm long, and 5 mm high) which was attached with an epoxy resin adhesive and solder. These electronic parts were pulled vertically from the board surface by using a force measurement apparatus (Tensilon UCT-5T, Orientec Co.) in a heating chamber. For the chip components, a horizontal pulling test also was performed.

(2) Recovery of electronic parts

The automatic removal apparatus developed for electronic parts (prototype, see Figure 6-2) consisted of a heating unit with an infrared lamp, an impacting unit, and a shearing unit. The PWB sample was clamped and carried on a rail into the heating unit where it was heated to 230℃ for two minutes. It was then carried to an impacting unit where the electronic parts and solder were removed by rotating the PWB and hitting it on the back side. After the PWB was again heated to 230℃ for two minutes in the heating unit, the PWB was carried to the shearing unit where the remaining parts and solder on the boards were removed by shearing with a rotating propeller made of a kind of stainless steel. The removed parts and solder were collected on a conveyer belt and separated into various-sized parts and solder particles by magnetic and sieving methods.

(3) Recovery of solder

The solder remaining on the board surface was removed by abrading with a belt sander (Multisander, Kensoh Co.) and a process consisting of heating (230℃, two minutes) and impacting using the above mentioned removal apparatus. The remaining solder on the resin board was measured

by the above-mentioned chemical analysis.

(4) Pulverizing and separating methods for resin boards

Figure 6-3 shows the pulverizing and separating processes for resin boards and the mechanisms of respective machine. The resin board, after removing its electronic parts and solder, was pulverized in a crushing machine using cutting and shearing forces (Orient Mill VM50, Orient Co.) and a fine-pulverizing machine using compressive and shearing forces (Roller Mill IS600, IHI Co.). The resulting powders were separated into a copper-rich powder and a glass fiber-resin powder using a gravimetric separating machine (Micron Classifier OMC100, Seisin Enterprise Co.) and an electrostatic separating machine (Eriz Model 1014HTS, Eriz Magnetic Japan Co.). The copper, glass fiber, and resin in the resin board powders were measured using the same chemical analysis mentioned previously.

(5) Reuse of recovered glass fiber-resin powder

The recovered glass fiber-resin powder was tested as a filler for epoxy resin compounds used for paints and construction materials, and ABS resin (acrylonitrile/ butadiene/ styrene copolymer) used for housings of products. In this test, a glass fiber-resin powder was used, which was recovered from the mold residue generated in the production process of a resin board (ELC 4756, Sumitomo Bakelite Co.), which had almost the same composition as the resin board. The average particle size of the powder was 13 μm and its glass content was 65 wt % .

The epoxy resin compound consisted of the glass fiber-resin powder (31.8 wt/%), bisphenol A-type epoxy resin (39.7 wt%, Epicoat 828, Yuka Shell Epoxy Co.), a diluting agent (7.9 wt%, propyrene-glycolether: Eponit 028, Asahidenka Co.), a leveling agent (0.2 wt%, acrylic co-polymer: Polyflow S, Kyoueisha Kagaku Co.), fine silica powder (0.2 wt%, Aerogiru 200, Nippon Aerogiru Co.), a silane coupling agent (0.2 wt%, γ - glycidoxypropyl-

trimethoxysilane, Shinetu Chemical Co.), and an amine-type hardener (20.0 wt%, X-4199, ACR Co.). These components were mixed in a mixer and then degassed in a vacuum at room temperature. The compounds were molded in a mold and cured at 23℃ for seven days. As conventional fillers, talc powder (average particle size: 11μm, Takehara Chemical Co.), calcium carbonate powder (average particle size: 9.2 μm and 2.6μm, Shiraishi Calcium Co.), and milled glass fiber (average particle sizes : 25μm and 16μm, Nittobo Co.) were used for comparison with the glass fiber- resin powder. Tensile strength, flexural strength, and charpy impact strength were measured for the molded resin samples according to JIS K 7111 and JIS K 7203. Their thermal expansion ratio was tested at a heating rate of 5 ℃/min. according to JIS K 7197. The viscosity of the resin samples before adding the hardener was measured at a rotating rate of 2 rpm on a BH-7 type viscometer (Tokyo Keiki Co.).

ABS resin (GA701, Sumitomo Daw Co.) was mixed with the glass fiber-resin powder using a twin screw extruder at 230 ℃ and the resulting resin was molded using an injection molding machine at 220 ℃. As conventional filler, the above-mentioned powders were used in the place of the glass fiber-resin powder. The properties of the molded resin samples were measured using the same method described above. The flow property of the resin during the molding process was determined by measuring the melt-flow rate (200 ℃) according to JIS K7210.

Table 6-1 Component contents of the PWB sample

Component	Content (wt%)
Copper	22
Glass fiber	30
Resin	16*
Lead	1.5
Tin	2.6
Gold	0.035
Iron	3.6
Nickel	0.32

* Resin in resin board = Glass fiber ratio × 0.54 (Calculated value)

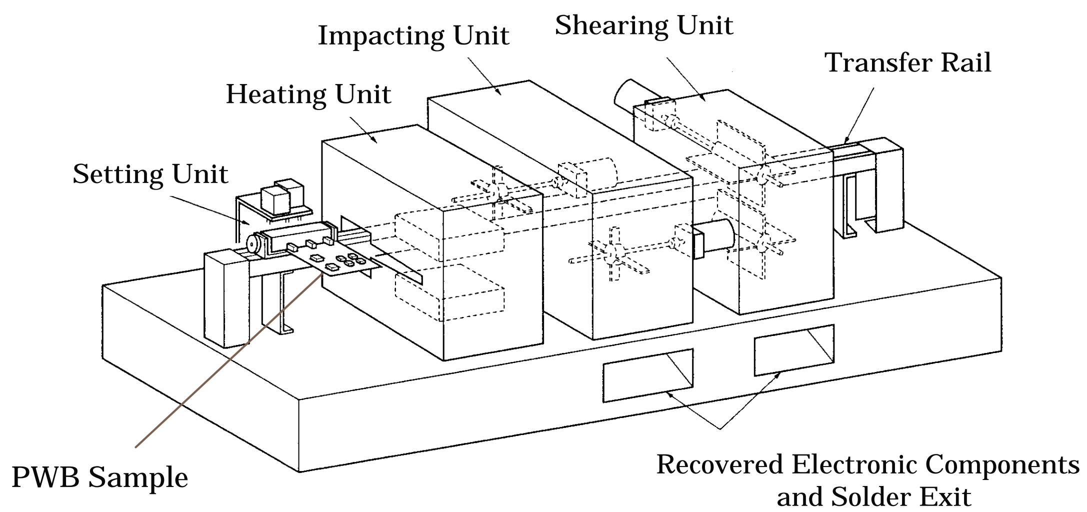


Fig. 6-2 Mechanism of automatic removal apparatus for electronic parts

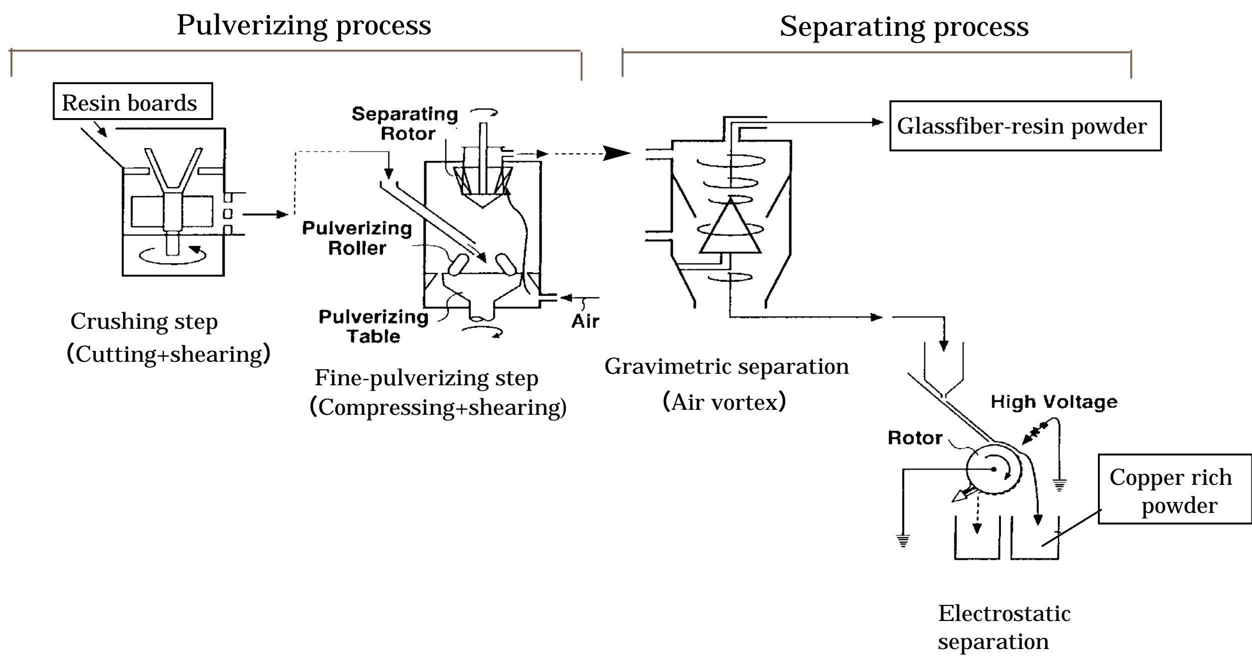


Fig. 6-3 Pulverizing and separating of resin boards

6-3 Results and Discussion

6-3-1 Recovery of electronic parts

Electronic parts mounted on PWBs are classified into surface mounted devices (SMDs), through-hole devices (THDs), chip components, and others. Since SMDs are only attached to the resin boards by soldering, they can be removed by heating them above the solder melting temperature. However, because THDs are attached with pins through the boards as well as solder, and chip components are attached with adhesive and solder, effective disassembly of these parts has been difficult.

The possibility of removing electronic parts by heating and applying forces was proposed (6). In this study, the force required to remove THDs and chip components from resin boards was actually measured when they were heated. Figure 6-4 shows the relation between heating temperature and vertical adhesion strength for THDs and chip components. The vertical adhesion strength for these parts was found to decrease dramatically at above the solder melting temperature. For the chip component, horizontal force was effective in removing them as well as vertical force. These results indicated that electronic parts such as SMDs, THDs and chip components can be effectively removed by a combination of heating to above the solder melting temperature and adequate removal forces such as impact applied to the board back and shear applied to the parts.

An automatic removal apparatus for electronic parts was developed on the basis of these mechanisms. As shown in Figure 6-2, this apparatus has a heating unit with an infrared lamp, an impacting unit, and a shearing unit. The SMDs, THDs, and chip components on the PWB sample were completely removed with this apparatus (Figure 6-5), and also the solder on the PWB was removed (54% of the total solder) as particles (Figure6-6). However, when PWBs have electronic parts mounted with screws and rivets, the parts must be removed before using this apparatus. In other words, changing these connecting methods to surface mounting-type or through

hole-type can greatly improve the recycling efficiency of this process, and this is expected to be one direction in designing recycling for PWBs.

The recovered electronic parts were found to contain more gold (average 560mg/kg) than usual gold resources (10-60 mg/kg) and could be used as a high-level gold resource for refining. The gold originated from wires in IC packages and connectors. In the present refining process for gold resources such as recovered electronic parts, most gold (about 95 wt %) and lead (about 90 wt %) in the solder adhering to the parts' pins can be recovered. The residue material in the electronic parts, such as silica, silicon, iron and remaining solder were melted to form a slag, which could be reused as a building material because the toxic heavy metals are molded with the melted silica and their eluting amounts are under regulated values.

Moreover, since the recovered electronic parts were almost without damage, there was a strong possibility of reuse for their original purpose after checking their reliability.

6-3-2 Recovery of solder

Table 6-2 shows the removal ratio of the solder for each process. In the removal process for electronic parts, the solder on the PWB was removed as solder particles and as forms adhering to the parts. The solder remaining on the surface and inside the through-holes of the resin board was 15wt% of the total solder. The solder on the board surface was recovered by using the surface abrasion method, and the solder inside the through-holes was recovered by using the heating-impacting method with the automatic removal apparatus above-mentioned. Through these steps, 96wt% of the solder in the PWB was removed. The solder recovered as particles and powders could be used as a valuable solder resource. Using the solder adhering to electronic parts, lead was recovered in the refining process of the electronic parts as above-mentioned.

The residue solder on the resin board after this process was treated

together with copper to form a slag as will be discussed later.

6-3-3 Pulverizing and separating of resin boards

A pulverizing and separating techniques for the mold residue which generates in the production process of glass-epoxy laminate boards was previously reported by the author and his co-worker (7). It has been found that this technique could successfully be applied to the resin board after removing the electronic parts and solder. Figure 6-3 shows the flow chart for these processes. The pulverizing process was highly effective and abrasion resistant for the resin board by the combination of the crushing step using cutting and shearing forces, and the fine-pulverizing step using compressive and shearing forces. The resulting powder was separated into a copper rich powder and a glass fiber-resin powder using a separating process involving the gravimetric and electrostatic separating methods.

The effective particle size (average particle size) was found to be between 100 and 300 μm in the recovery of copper by the gravimetric method (see Figure 6-7). In this particle size range, the copper recovery ratio was more than 90wt% (maximum 97wt% for 150μm-average particle size), and the copper content in the copper rich powder was more than 60wt% (maximum 61wt% for 150μm-average particle size). The copper recovery ratio means the ratio of copper content in the copper rich powder to total copper content in the resin board. Figure 6-8 shows the size distribution for each material (copper, glass fiber, and cured epoxy resin) in the resin-board powder with this average particle size (150μm). This demonstrates that the copper was pulverized more coarsely than the glass fiber and the cured epoxy resin because of their different brittleness. The effective recovery of copper from the board powder with this particle size was mainly due to the difference in the sizes of these materials in addition to the differences in specific gravity of the materials (copper: 8.9, glass: 2.5, resin: 1.2).

The copper-rich powder separated by the gravimetric separation method

was further purified by the electrostatic separation. The copper-rich powder having a copper content of 82 wt% was produced by this step and it can be used as a high-level copper resource for refining.

The glass fiber-resin powder (Figure 6-9) recovered by the gravimetric method consisted of glass fiber (64 wt%), cured epoxy resin (34 wt%), copper (2.1wt%), and solder (<0.1wt%).

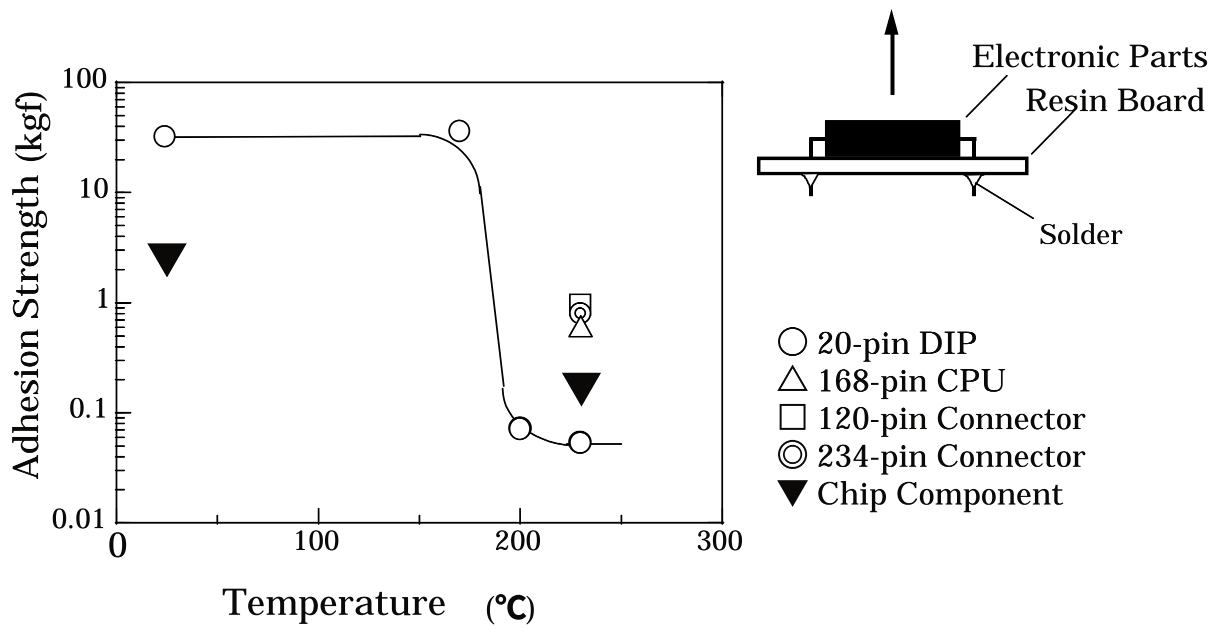


Fig. 6-4 Force for removing electronic parts from resin boards

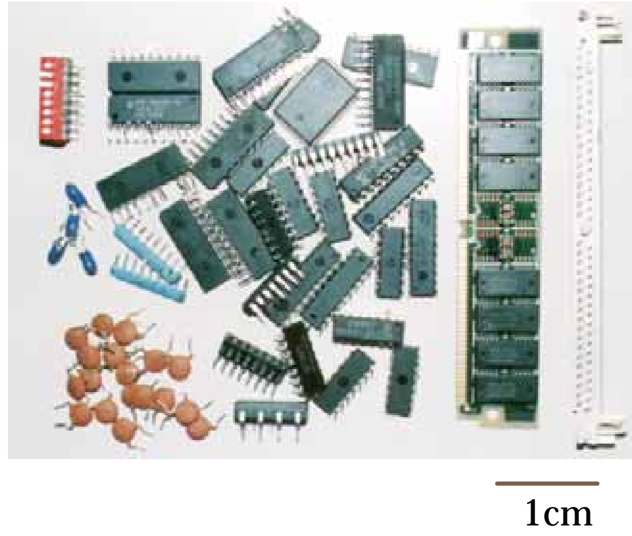


Fig. 6-5 Recovered electronic parts from PWB

Fig. 6-6 Recovered solder from PWB

Table 6-2 Removal ratio of solder from PWB in each process

Process	Removed solder form	Removal ratio by each process (%)
Removal together with electronic parts	Particles	54
	Adhesion to the electronic parts	31
Surface abrasion of resin board	Powder with resin	8.6
Impacting and heating	Particles	2.8
Total removal ratio (%)		96

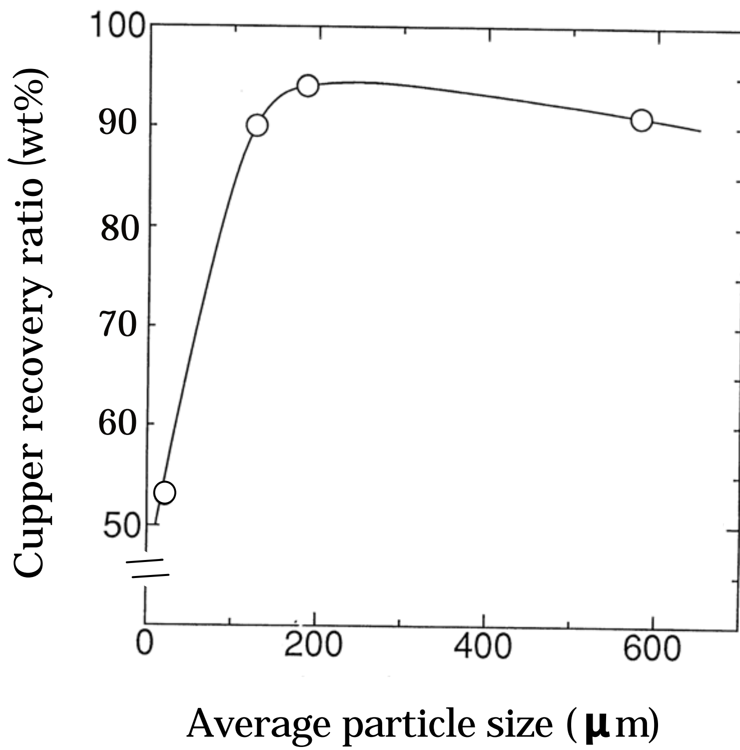


Fig. 6-7　Cupper recovery ratio from pulverized resin board

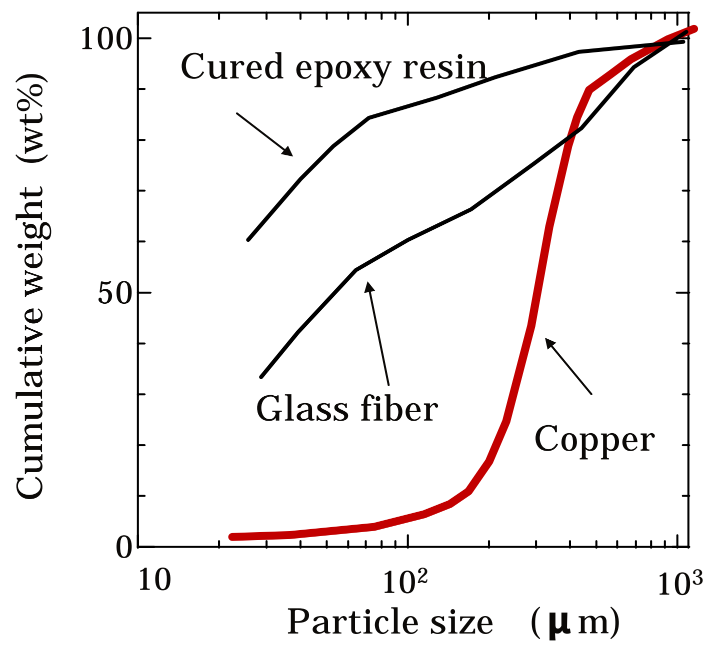


Fig. 6-8 Size distribution of each material of pulverized resin board

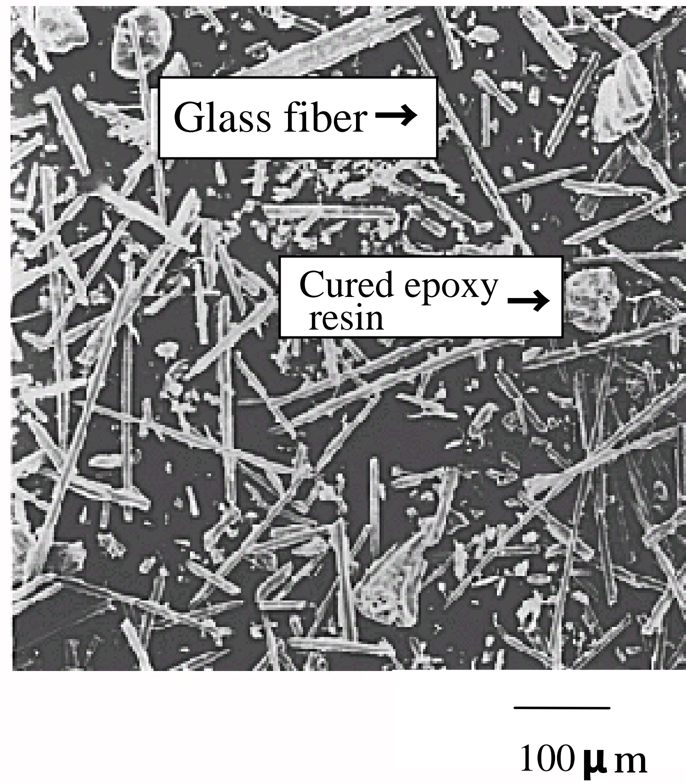


Fig. 6-9 Glass fiber-resin powder recovered from resin board

6-3-4 Reuse of recovered glass fiber-resin powder

The glass fiber-resin powder was tested as a filler for epoxy resin compounds used as paints and construction materials, which include a similar kind of epoxy resin (bisphenol A-type) as the cured epoxy resin in the glass fiber-resin powder. The powder was also tested as a filler for ABS resin representing other thermoplastics.

Table 6-3 lists the properties of the epoxy resin compounds including the glass fiber-resin powder and conventional fillers. The molded epoxy resin compound with the glass fiber-resin powder was found to be superior to those with conventional fillers such as talc powder, calcium carbonate powder, and milled glass fiber for the strength and thermal expansion properties. Figure 6-10 shows the fracture surface of the molded epoxy resin compounds with the glass fiber-resin powder and milled glass fiber. It indicates that the adhesion of the glass fiber in the powder with the matrix epoxy resin was excellent and better than that of milled glass fiber. Therefore, these good properties of the compound with the glass fiber-resin powder were mainly due to the good adhesion of the powder with the matrix epoxy resin in addition to the presence of long glass fibers in the powder. This better adhesion seemed to result from increase in the surface roughness of the glass fiber in pulverizing process of the resin board. The viscosity of the epoxy resin compound with the glass fiber-resin powder was higher than those with calcium carbonate powder and milled glass fiber, and near to that with talc powder. This indicated that glass fiber-resin powder was a suitable filler to improve paintability of epoxy resin-type paints by preventing dripping in the same manner in which talc powder does.

Table 6-4 listed the properties of ABS resin including the glass fiber-resin powder and the conventional fillers. The melt flow rate of the ABS resin with the glass fiber-resin powder was lower than those of resins with the conventional fillers, but was sufficient for molding. The thermal

expansion of the resin with the glass fiber-resin powder was lower than that of the resin with the calcium carbonate powder and higher than those of the resins with talc powder and milled glass fiber. Furthermore, the strength of the resin with the glass fiber-resin powder was better than those of the resins with the conventional filler except the impacting strength of the resin with milled glass fiber. The glass fiber-resin powder was therefore found to be a useful filler for ABS resin. However, the powder's effects on these properties of the ABS resin were not comparable to those of the above-mentioned epoxy resin compound. This seemed to be due to the lower solubility of the glass fiber-resin powder with ABS resin because the resin is less polar than epoxy resin.

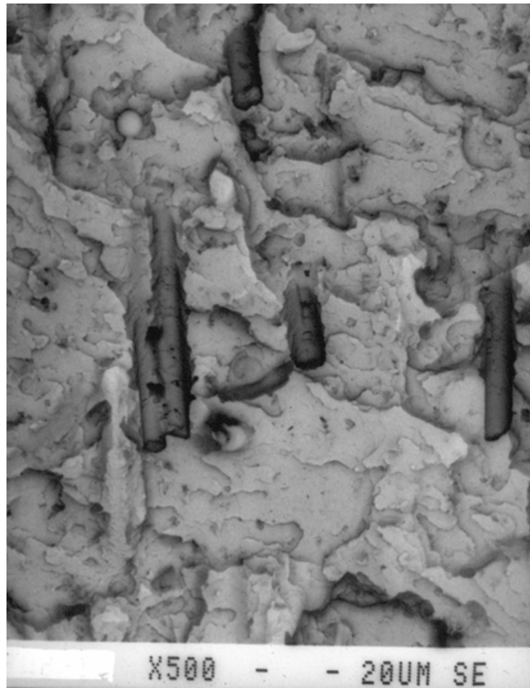
These results indicated that glass fiber-resin powder recovered from the resin boards was a valuable filler for epoxy resin products, particularly for paint, and ABS resin. There was also a strong possibility of using it in other thermosetting plastics and thermoplastics. However, when the resin part of the powder contains toxic halogen-type flame-retarding additive, the powder should be only used in the plastics products containing the same-type flame-retarding additives.

Table 6-3 Properties of epoxy resin compounds with glass fiber-resin powder and conventional fillers

Filler	Average Particle Size (μm)	Viscosity (Pa・s)	Tensile strength (kgf / mm²)	Flexural strength (kgf /mm²)	Charpy impact strength (kgf・cm/cm)	Coefficient of linear thermal expansion* (×10⁻⁵ / ℃)
None	—	2.4	4.4	8.2	2.3	13
Calcium carbonate powder	9.2	7.2	3.4	6.1	2.4	—
	2.6	25.8	4.8	6.6	2.5	14
Talc powder	11	69.2	2.8	5.8	2.5	9.5
Milled glass fiber	25	7.6	5.4	8.0	2.0	11
	16	6.4	4.0	8.0	1.6	10
Glass fiber-resin powder	13	63.2	5.9	9.7	3.6	5.0

* Heating conditions: Room temperature → 200℃

a) Epoxy resin compound with
glass fiber-resin powder



b) Epoxy resin compound with
milled glass fiber

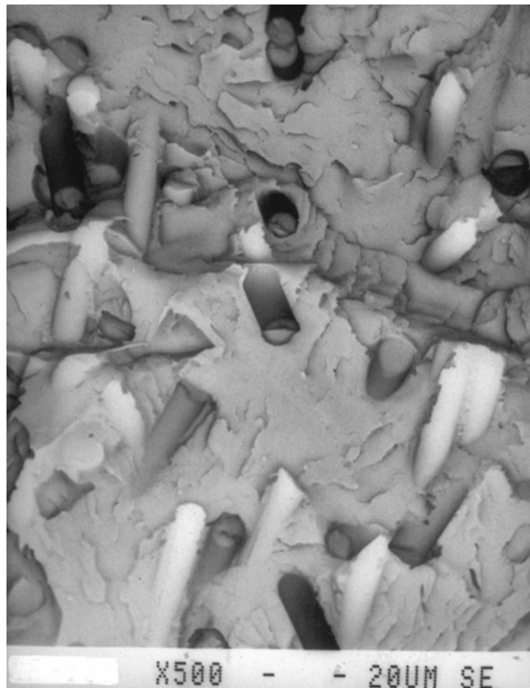


Fig. 6-10 Fracture surfaces of epoxy resin compounds with glass fiber-resin powder and milled glass fiber

Table 6-4 Properties of ABS resin with glass fiber-resin powder and conventional fillers

Filler	Average particle size (μm)	Melt flow rate (g / 10 min)	Tensile strength (kgf/mm^2)	Flexural strength (kgf/mm^2)	Charpy Impact strength (kgf·c m / cm)	Coefficient of linear thermal expansion* ($\times 10^{-5}$ / ℃)
None	—	6.3	2.6	6.3	23.6	9.6
Calcium carbonate powder	9.2	4.2	2.5	5.9	7.0	6.8
Talc powder	11	3.4	1.6	6.6	6.4	4.2
Milled glass fiber	16	3.6	2.1	6.1	10.1	3.5
Glass fiber-reisin powder	13	2.2	2.9	8.1	8.0	5.5

* Heating condition : room temperature → 90℃

6-3-5 Recovery ratio of valuable materials

The recovery ratio of valuable materials gained by using this new recycling technology was compared with that of previous technology which treats PWB waste as a whole by refining. The new technology can recover not only useful metals, such as copper and gold, but also glass fiber, resin and most solder. Consequently, as shown in Table 6-5, the recovery ratio for the test PWB increased from the 23% achieved by using the previous technology to 65% achieved by using the new technology.

The unrecovered components were mainly residue materials in the electronic parts after the recovery of gold and solder through refining process. These were silica, silicon, iron, nickel, resin and some solder. In the refining process, these materials are melted to a slag, which can be used as building material. Therefore, there was almost no waste generated in this recycling process.

Table 6-5 Recovery ratio of valuable materials from PWBs

Materials in PWB		Original content (wt%)	Recovered valuable material ratio (%)*	
			Previous technology (Refining as a whole)	This study
Gold		0.035	0.033	0.033
Copper		22	22	21
Solder	Lead	1.5	1.4	1.5
	Tin	2.6	0	1.8
Glass fiber + Resin		46 (30+16)	0	41
Others **		29	0	0
Total recovery ratio of valuable materials (%)			23	65

* Each recovered material weight / PWB weight ×100

** Iron, Nickel, Silicon, Silica, Molding compound, etc (Residues of electronic parts)

6-4 Summary

New recycling technology for glass-epoxy laminate-type printed wiring boards (PWBs) with mounted electronic parts was studied for the purpose of disassembling the boards, recovering useful materials, and reusing these materials. An automatic removal method for the electronic parts was developed on the basis of a combination of heating to above the solder melting temperature and applying impacting and shearing forces. Most of the electronic parts were recovered without damage and the solder was able to be recovered as particles. The solder remaining on the boards was recovered by abrading the board surfaces and by using the heating-impacting process. After these processes, the resin-boards (cured epoxy resin-glass fiber laminates) were pulverized and separated into a copper-rich powder (copper: max. 82 wt%) and a glass fiber and resin mixture powder (glass fiber-resin powder) by gravimetric and electrostatic methods. The recovered electronic parts, solder, and copper-rich powder were used as valuable metal resources for refining. Moreover, there was a strong possibility of reuse of the recovered electronic parts for their original purpose after checking their reliability. The recovered glass fiber-resin powder was found to be a useful filler for plastic products including epoxy resin compounds and ABS (acrylonitrile/ butadiene/ styrene copolymer) resin.

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Chapter 7

General Conclusion

In this thesis, the author presented environment technologies with respect to safe flame retardation and recycling of plastics used in electronic products. Highly safe flame-retarding technologies without using current toxic halogen-type flame-retarding additives and their application to flame-resistant plastics for main parts in electronic products were described. The technologies can produce highly safe treatment for plastic wastes and considerably progress toward their reuse for other purposes. Furthermore, recycling technologies for thermosetting plastics, especially epoxy resin compounds, used in electronic components were reported. By using these technologies, cured epoxy resin compounds, difficult to re-melt, can be reused and valuable materials are effectively recovered.

In chapter two, new silicone derivatives to be used as highly safe flame-retarding additive and their application to flame-resistant polycarbonate (PC) as a housing material were described. A silicone containing a branch chain structure, methyl and phenyl group in the chain, and methyl group in the chain terminals was mostly effective in flame-retarding for PC and its derivatives. The superior flame-retardant effect of the silicone was credited to its excellent dispersion in PC, its movement to the surface of PC during ignition, and its formation of a highly flame-resistant char barrier in combination with PC. The PC with the silicone, after being fabricated as a practical product, had sufficient flame resistance and other good characteristics as a housing plastic. Also, it maintained its initial properties at a good level after recycling.

Chapter three dealt with self-extinguishing epoxy resin compounds with no inclusion of flame-retarding additives and their application to molding compounds for electronic parts such as IC packages. Phenol aralkyl-type epoxy resin compounds containing novolac derivatives with specific aromatic moieties, especially biphenylene moiety extinguished themselves. The high flame resistance was achieved mainly by the formation of stable foam layers during ignition, which effectively retarded the transfer of heat to the insides.

An environmentally friendly molding compound was developed based on the self-extinguishing epoxy resin compounds. It had highly flame resistance without any toxic flame-retarding additives and other excellent characteristics, including moldability, water resistance, and package reliability. In fact, its resistance to soldering heat, humidity, and high-temperature storage was much better than that of current high-quality molding compounds containing halogen-type flame-retarding additives.

In chapter four, an environmentally friendly glass-epoxy laminate-type printed wiring board (PWB) free of halogen-type flame-retarding additives was described. The PWB containing the above-mentioned phenol aralkyl-type epoxy resin compound and a limited small amount of harmless metal hydroxide (aluminum hydroxide) had high flame resistance and other good characteristics, including resistance to solder heating and chemical agents in processing, electronic properties, and moldability, which made it a practical PWB. These characteristics were obtained by using the epoxy resin compound's superior properties, such as its pyrolysis resistance, hydrophobia, and non-polarity, and also by minimizing of the amount of metal hydroxide.

In chapter five, recycling technologies for epoxy resin compounds used as molding compounds for electronic parts such as IC packages were reported, which are for the purposes of reusing compounds after grinding and recovering valuable materials from the compounds by pyrolysis.

The ground mold residue of molding compounds (molding compound powder) showed good surface reactivity due to containing reactive functional groups (silanol, hydroxy, and glycidyloxy). Recycling a low-stress-type molding compound powder containing silicone elastomer into a standard molding compound yielded a new molding compound, which had far better thermal impact resistance than that made with the original standard molding compound. The molding compound powder was also found to be suitable as a filler for epoxy resin products, such as insulating materials,

paints, and adhesives. Use of the powder as a decorating agent was practical for an acrylic resin-type construction material.

Further, a pyrolysis-based technology for the molding compounds was studied for the purpose of recovering useful materials, especially silica filler, and reusing them. This study clarified those pyrolysis conditions best suited to reduce the impurities (carbon, etc) in the recovered silica filler. This contributed to the development of a practical pyrolysis technology in which a roller kiln-type furnace was used. The recovered silica was sufficiently pure to be employed as an inorganic filler in epoxy resin compounds used as cast-insulating materials and original molding compounds. When the molding compounds contain conventional flame-retarding additives consisting of bromine compounds and antimony oxide, the combustion exhaust gas generated in the pyrolysis was successfully treated by using a process consisting of secondary combustion, dry recovery and wet recovery.

Chapter six dealt with a new recycling technology for PWBs with mounted electronic parts. This involves removing the electronic parts and solder, pulverizing the resin board, separating the resulting powders into a copper-rich powder and a glass fiber-resin powder, and reusing them. The recovered electronic parts, solder, and copper-rich powder were useful as valuable metal resources for refining. The recovered glass fiber and resin mixture powder was used as a useful filler for plastics products such as epoxy resin compounds and ABS resin. In particular, since the recovered electronic parts were almost without damage, there was a possibility of reusing them for their original purpose after checking their reliability. Consequently, the recovery ratio of valuable materials for PWBs was greatly improved compared with that of previous technology treating the PWBs as a whole (23% → 65%).

These technologies described in this thesis can offer great advantages to overcome the environmental problems including safe treatment and recycling, which have been caused with the current electronic products containing plastics. In particular, the combination of these technologies concerning safety design and recycling will greatly advance recycling of the plastics. The safety design by replacing toxic flame-retarding additives with safer ones can considerably expand the reuse of recovered plastics for other purposes. It also improves the effectiveness of the recycling process including heating process by simplifying exhaust gas treatments. The author believes that these technologies can contribute to further progress of electronic industry while maintaining the environment.

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