Synthesis of New Flame-Retarding Epoxy Resin Based on 3',5',3'',5''-Tetrabromophenolphthalein

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Synopsis

New flame-retarding epoxy is synthesized by reacting 3',5',3'',5''-tetrabromophenolphthalein (TBPP) with epichlorohydrin and characterized in comparison with commercially available tetrabromobisphenol-A(TBBA) epoxy on their flame retardancy and thermostability. TBPP epoxy show better results in promoting flame resistance than TBBA epoxy. However, TBPP epoxy exhibits a greater effect on thermal decomposition temperature. The order of char yield at 800°C under nitrogen for the cured products is TBPP epoxy > phenolphthalein (PP) epoxy > TBBA epoxy. Meanwhile, there is a linear relationship between oxygen index and char yield for cured products of TBPP-PP epoxy and TBBA-BA epoxy systems.

INTRODUCTION

Epoxy resins have been used in many applications such as surface coating, electronic insulation, composites, adhesive, and etc.[1,2] Because of the recent requirement for flame-retarding materials, the study of flame-retardant epoxys has become of great importance now. Thermostability of epoxys can be achieved by introducing a high aromaticity structure to the chain backbone of the epoxy.[3] Kovosshak et al.[4] have discussed the effect of different structures on thermal stability. Fire-retardant epoxys can be obtained by incorporation of phosphorous compounds[5-7] or halide compounds[8-10] into the backbone structure of epoxys, or into the structure of the curing agent. Epoxys based on phenolphthalein or 4,5,6,7-tetrabromophenolphthalein[11,12] have been synthesized, and higher flame retardancy is found in these phthalide-containing resins. Van Krevelen[13] concludes that excellent flame resistance always existed with higher char yield which depends on the structure and substituents on the chain backbone of molecules.[13,14] There is linear relationship[3,15] between char yield and oxygen index (OI) for epoxys based on high aromaticity.

In this study, new flame-retarding epoxy based on 3',5',3'',5''-tetra-bromophenolphthalein is synthesized and characterized by infrared (IR) and nuclear magnetic resonance (NMR) spectra, and differential scanning calorimetry (DSC) is used to observe its curing behaviors. The relationship between OI and char yield for this epoxy is also studied by thermal gravimetric analysis (TGA) and OI analysis, and the effect of bromine content on polymer decomposition temperature was studied.

EXPERIMENTAL

Materials

Phenolphthalein (PP) and bromine were obtained from WAKO Chemical Co., and epichlorohydrin was from Hayashi Co. TBBA epoxy was supplied by Kokudo Co. and commercially used BA epoxy was adopted.

Polyoxypropylenediamine, amine equivalent = 217, was used as curing agent and was supplied by Pasico Chemical Co. without further purification.

Instrumentation

Jasco IRA-2 spectrometer was used to detect IR spectra, and NMR spectra were recorded by JEOL, JEN FX-90Q H^1NMR spectrometer. Thermograva-metric analysis (TGA) and differential scanning calorimetric analysis (DSC) were carried out by Du Pont 1090 thermal analyzer. Oxygen index (OI) was measured by Suga ON-1 meter.

Synthetic Method

Synthesis of 3′,5′,3″,5″-tetrabromophenolphthalein (TBPP). To 20 g (0.031 mol) of PP in a 1000 mL flask was added 500 mL of 60 wt% of aqueous acetic acid, and the solution was stirred and heated at 60°C until PP had been dissolved. Bromine 47.8 g (0.126 mol) was added drop by drop to the solution, which turned red at the end of addition of bromine. After the addition of bromine, the solution was stirred for another 2 h to assure the completeness of reaction, and then cooled and washed by distilled water until the solution became neutral. The mixture was filtered and the white solid powder obtained had a melting point (T_m) of 274–276°C (lit. 273–276°C).[16] The yield was over 90%.

Synthesis of epoxy based on 3′,5′,3″,5″-tetrabromophenolphthalein. To 30 g (0.047 mol) of TBPP in a 500 mL flask was added 43.5 g (0.47 mol) of epichlorohydrin and the solution was stirred and heated to reflux. Next, 9.4 g (0.094 mol of NaOH) of 40 wt% of aqueous sodium hydroxide was added in drops during reaction in 2 h. After the addition of aqueous sodium hydroxide, the color of solution turned from dark violet to pale yellow. The solution was again heated to reflux for another 2 h to complete the reaction, then cooled, and filtered. The unreacted epichlorohydrin and water formed after reaction was removed under reduced pressure, and the residue collected was dissolved in toluene and filtered to remove the salt. Toluene in the filtrate was driven out under reduced pressure at 120°C. The pale yellow solid resin obtained was TBPP epoxy and the yield was 91%. The weight per epoxide equivalent for the resin was 450 and the bromine content was 43.7%.

ANAL. Calcd for $C_{31.6}H_{21}Br_{4.8}O_{7.1}$: C, 41.9%; H, 2.3%; Br, 43.1%.
Found: C, 41.49%; H, 2.4%; Br, 43.7%.

Synthesis of epoxy based on phenolphthalein. The procedure for synthesis of PP epoxy was the same as that of TBPP epoxy illustrated above. The yield was 93% and the epoxied equivalent was 375.

Titration of Epoxide Equivalent

About 0.3 g of epoxy resin was placed in a 250 mL flask with 25 mL of $0.2N$ pyridinium chloride-pyridine solution (16 mL conc. HCI per liter of pyridine solution). The solution was stirred and heated for 25 min. After refluxing, the solution was cooled and 50 mL of methanol was added to the flask and was titrated with $0.5N$ standardized methanolic sodium hydroxide to a pink end point of 15 drops of phenolphthalein.

$$\text{weight per epoxide equivalent} = \frac{1000 \text{ (sample weight, g)}}{(A\text{-}B) \times (N)}$$

A: mL of NaOH for blank

B: mL of NaOH for samples

N: normality of NaOH

1000: calculational parameter

Curing Process

Equal equivalents of epoxy and curing agent were mixed and dissolved in acetone and put into the curing oven. The mixture was first heated at 50°C for 30 min to dry the solvent and then cured at 90°C for 2 h followed by 30 min postcuring at 110°C.

Thermal Analysis

TGA proceeded under 0.5 L/min of N_2 with 20°C/min heating rate and operating temperature from 50°C to 800°C. DSC study was also conducted under N_2 with 10°C/min heating rate.

Measurement of Oxygen Index

Oxygen index was measured according to ASTM-D2863-77. The sample was 14 cm in length, 5 cm in width, and 0.1 cm in thickness.

$$OI = \frac{O_2}{O_2 + N_2} \times 100\%$$

RESULTS AND DISCUSSION

Syntheses and Characterization of Epoxy Resins

Synthesis of 3′,5′,3″,5″-Tetrabromophenolphthalein. TBPP had been synthesized by direct bromination of PP.[16] In this study, PP was dissolved in aqueous acetic acid and bromine was added in drops to complete the reaction.

The use of acetic acid had the advantage of absorbing hydrogen bromide formed during reaction. The product obtained gave melting point, 274–276°C (lit. 273–276°C)[16] and the changes of integrals around (δ) 7 ppm on NMR spectrum confirmed the replacement of four hydrogen atoms by bromine atoms. Therefore, the reaction product was certified to be 3′,5′,3″,5″-tetra-bromophenolphthalein.

$$PP + 4\,Br_2 \xrightarrow[AcOH_{(aq)}]{} TBPP + 4\,HBr \qquad (1)$$
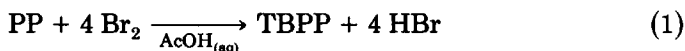
PP   = Phenolphthalein

TBPP = Tetrabromophenolphthalein

Synthesis and Characterization of TBPP or PP Epoxy. The synthesis of epoxy proceeded by reacting TBPP or PP with epichlorohydrin at molar ratio of 1/10 to obtain products of lower molecular weight.
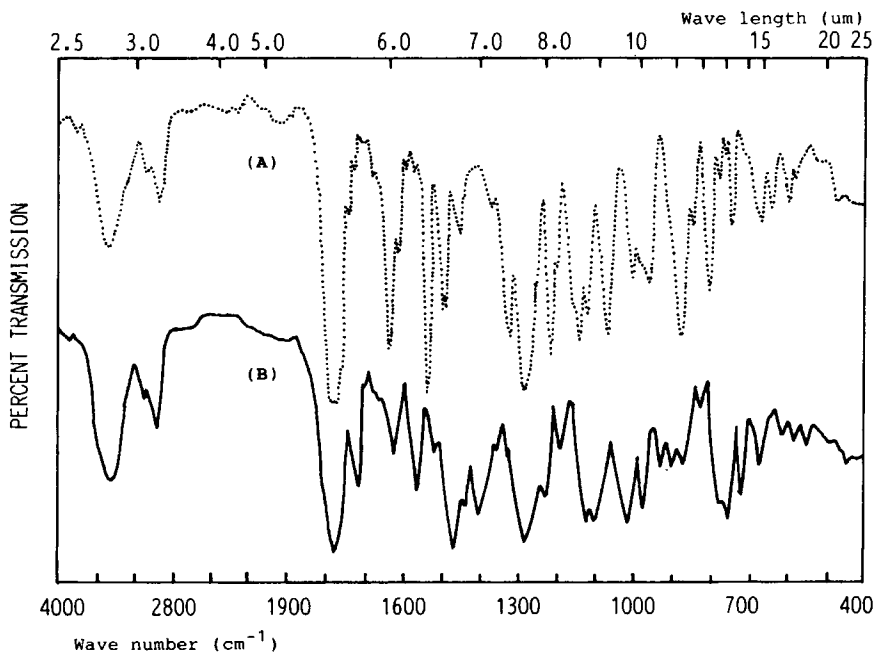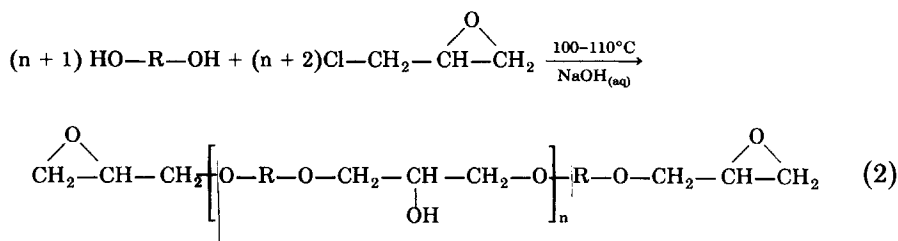
$$(n+1)\,HO-R-OH + (n+2)Cl-CH_2-\overset{\displaystyle O}{\overset{\displaystyle \diagup\!\diagdown}{CH}}-CH_2 \xrightarrow[NaOH_{(aq)}]{100-110°C}$$

$$\overset{O}{\overset{\diagup\!\diagdown}{CH_2}}-CH-CH_2\!\!\left[O-R-O-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-O\right]_n\!\!R-O-CH_2-\overset{O}{\overset{\diagup\!\diagdown}{CH}}-CH_2 \qquad (2)$$

Fig. 1. Infrared spectra for PP epoxy (A) and TBPP epoxy (B).

TABLE I
Infrared Transmittance Assignments for Epoxys

PP epoxy	TBPP epoxy	Functional group	Vibration mode
3450	3435	R—OH	(O—H)
3050	3030	Arylene	(C—H)
2930	2900	Methyl	(C—H)
1765	1700		
1702	1700	Carboxyl group	O ‖ (—C—)
1618	1600		
1588	1540	Phenylene	Quadrant stretching
–	1458	Ar-Br	(C—Br)
1100	1105	Ether	(—O—)
916	910	Epoxide Ring	Ring deformation

R=   (TBPP-Epoxy)

                                                       (PP-Epoxy)

                                                       (TBBA-Epoxy)

Scheme I.
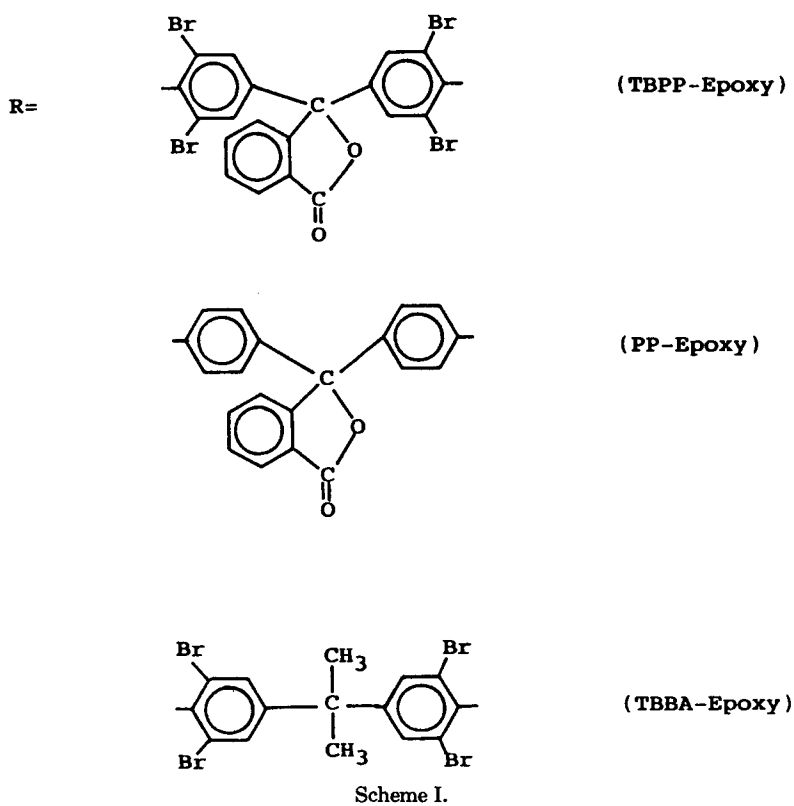
TABLE II
Characterization Data for Epoxy Resins

	TBPP epoxy	PP epoxy	TBBA epoxy
Epoxide Equiv.	450.0	190.0	450.0
n	0.22	0.45	0.43
Br, %	43.5	0	45.0
Color	pale yellow	orange	white

TBPP epoxy and PP epoxy obtained were characterized by IR spectra as shown in Figure 1. The band absorptions at 1700–1780 cm^{-1} were due to the structure of phthalic anhydride, the bands around 1100 cm^{-1} were the result of ether linkage, and the absorption peaks at 910 and 916 cm^{-1} were out of the existence of epoxide group. Table I showed the absorption data of epoxys upon IR spectra.

TBPP epoxy could also be certified on NMR spectra with the existence of the absorption of epoxide proton at (δ) 2.91–2.53 ppm. From the measurement of DSC on TBPP epoxy, and endothermal peak appeared around 170°C and this was its melting. PP epoxy existed as a liquid state at room temperature. The epoxide equivalent of TBPP epoxy was titrated to be 450.0 with n equal to 0.22 and bromine content, 43.5%. Table II showed the properties of neat epoxy resins.

DSC Study on Curing Reaction

Curing reaction of epoxy resins could be observed by DSC diagram (Fig. 2.). TBPP epoxy or PP epoxy were mixed with the equivalent of curing agent and underwent DSC test right away. It was observed on DSC diagrams that the reaction-onset temperature of TBPP epoxy appeared at 74°C and maximum polymerization temperature at 126°C; however, PP epoxy gave an onset temperature at 53°C and maximum polymerization temperature at 108°C. TBPP epoxy had greater polymerization temperature than PP epoxy, because the bromine atoms on the chain backbone of TBPP epoxy might give rise to a steric effect which hindered the crosslinking reaction between epoxide group and curing agent.

The reaction between epoxys and curing agent could also be observed on IR spectra (Fig. 3.). Since the peaks of epoxide group had disappeared, the epoxy group was proved to be fully reacted. The reaction between epoxide group and curing agent was shown as:
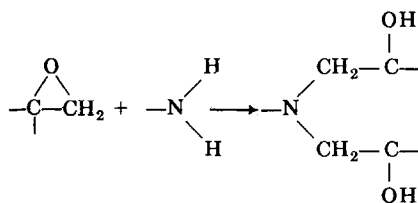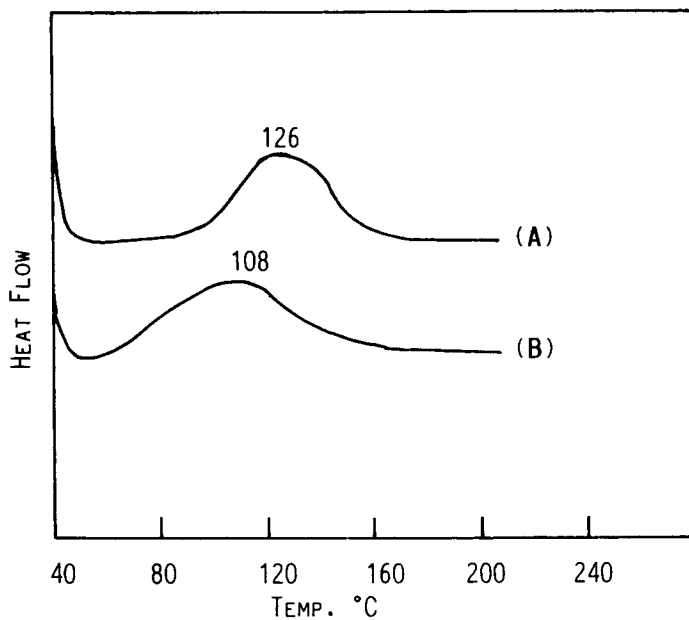
Fig. 2.   DSC diagrams for TBPP epoxy (A) and PP epoxy (B) after mixing with polyamine. Heating rate: 10°C/min; ATM: N_2.
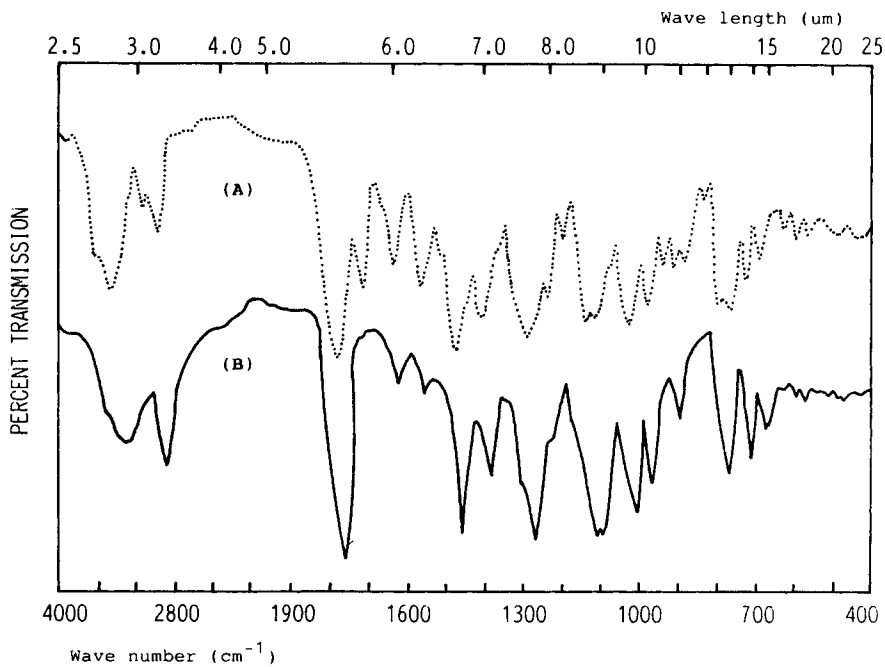

Fig. 3.   Infrared spectra for TBPP epoxy mixed with polyamine. (A) before curing, (B) after curing at 90°C for two hours.
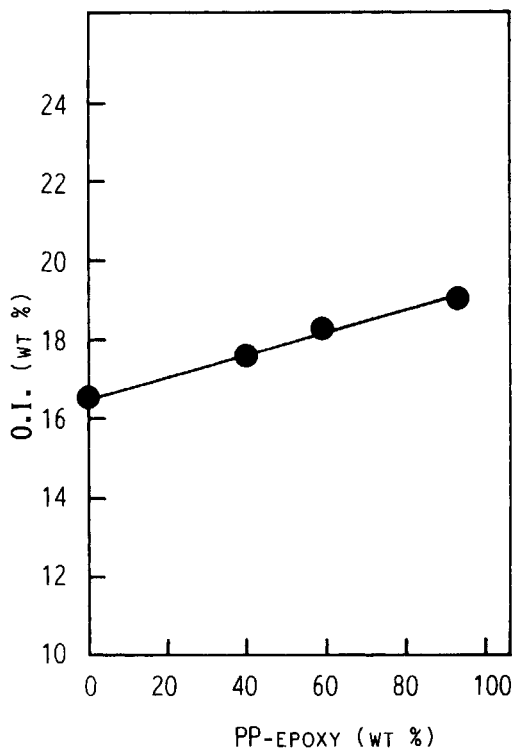
Fig. 4. Plot for oxygen index versus the content for PP epoxy in BA epoxy.

Relationships between OI and the Structure of Cured Epoxys

Pearce[3] had concluded that higher aromaticity in epoxy structure would exhibit greater char yield. This study was also concentrated on relationships between OI and the content of aromaticity in the structure of cured epoxys. Different amounts of PP epoxys were mixed with BA epoxy in various ratios and cured to measure the OI values. As shown in Figure 4, the higher the content of PP epoxy, the higher the OI of cured epoxy comixtures. Therefore, the addition of compound with high aromaticity structure would promote flame retardancy.

Besides the discussion of aromaticity effect on OI, the relationship between flame retardancy and cured epoxys containing bromine and aromaticity on their backbone structure was investigated in this study. TBPP epoxy which had bromine and high aromaticity on its chain backbone was mixed with PP epoxy and BA epoxy in comparison with TBBA epoxy which was added to BA epoxy. Figure 5 showed that when bromine-containing epoxy resins were added to their corresponding bromine-free resins, cured products of TBPP-PP epoxy systems had higher OI values than those of TBBA-BA epoxy systems. The increments of OI values for cured products of TBPP-BA epoxy systems were also greater than those of TBBA-BA epoxy systems. This meant that since TBPP epoxy contained both high aromaticity and bromine on its chain backbone, it exhibited an obvious effect on promoting flame retardancy. That is to say that the combination of both bromine and high aromaticity could
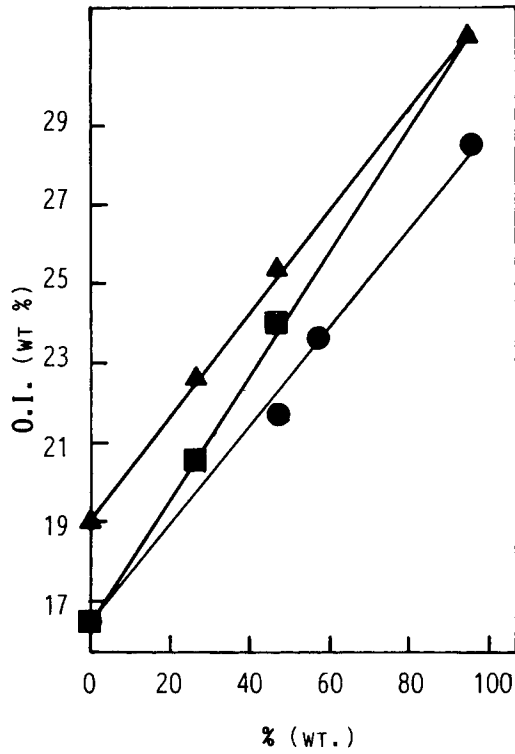
Fig. 5.   Plot for oxygen index versus the content of (▲) TBPP epoxy in PP epoxy; (■) TBPP epoxy in BA epoxy; and (●) TBBA epoxy in BA epoxy.
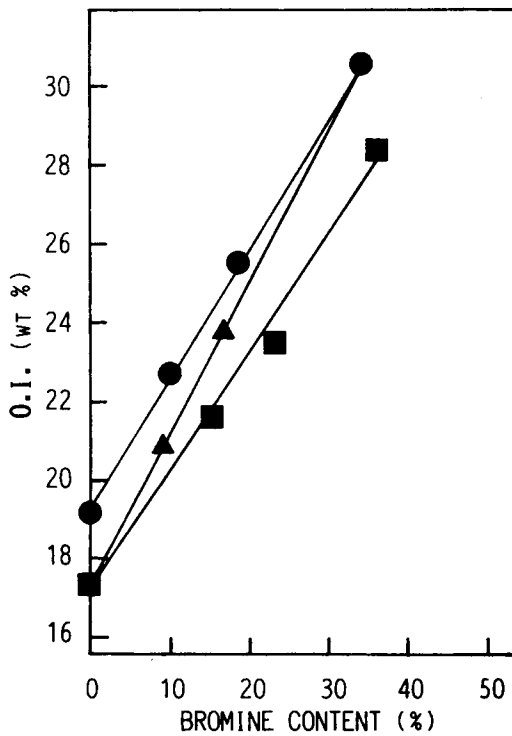

Fig. 6.   Plot for oxygen index versus the content of bromine in (●) TBPP-PP epoxy system; (▲) TBPP-BA epoxy; and (■) TBBA-BA epoxy system.

result in a better flame-retardancy. Figure 6 showed the relationship between oxygen index and the content of bromine.

Thermal Analysis for Cured Products

TGA was used to measure the thermostability for cured comixtures of TBPP-PP epoxy, TBPP-BA epoxy, and TBBA-BA epoxy systems (Table III). The effect of high aromaticity and bromine on thermal pyrolysis was shown on Figures 7 and 8. The thermal decomposition temperature (T_{dec}) decreased obviously with the increasing of the content of TBBA epoxy in TBBA-BA epoxy systems and the same result was found in TBPP-PP epoxy systems. It seemed that the addition of TBPP epoxy to bromine-free epoxys would cause

TABLE III
Data of TG Analysis for Cured Epoxy Resins

Resins	Br, %[a]	T_{dec}, °C	$T_{dec, max}$ °C	Char yield	OI
BA epoxy	0	357	430	5.53	16.5
BA-TBBA-22.5 epoxy	22.5	320	354	9.21	21.5
BA-TBBA-30 epoxy	30	292	316	11.42	23.5
TBBA epoxy	45	288	302	16.22	28.5
PP epoxy	0	346	391	22.16	19.0
PP-TBPP-14 epoxy	14	273	332	27.13	22.5
PP-TBPP-20 epoxy	20	265	320	29.52	25.5
TBPP epoxy	43.5	250	303	36.91	31.5

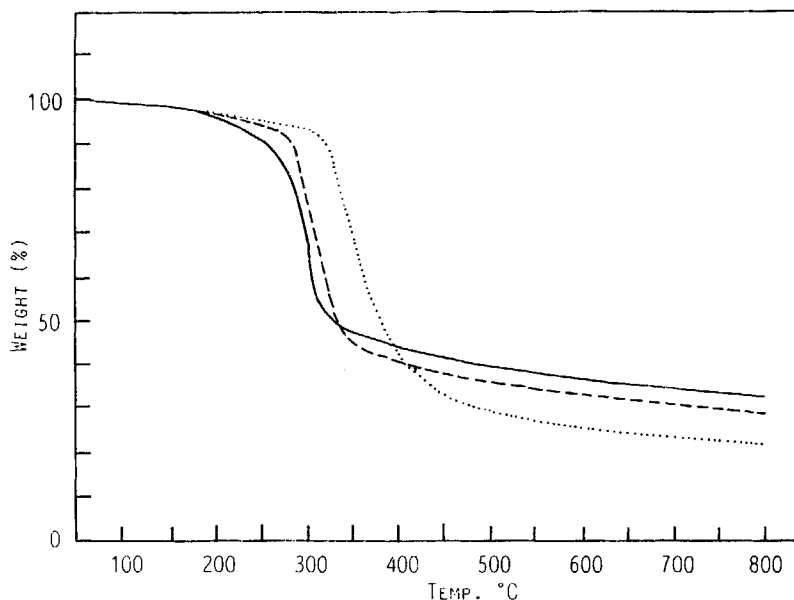[a]Weight percent of bromine content in epoxy mixtures.

Fig. 7. TGA diagrams for cured products of (——) TBPP epoxy; (- - -) TBPP-PP epoxy; and (·····) PP epoxy. Heating rate: 20°C/min; ATM: N_2. Curing agent: Polyamine, 1 equiv./epoxide equiv.
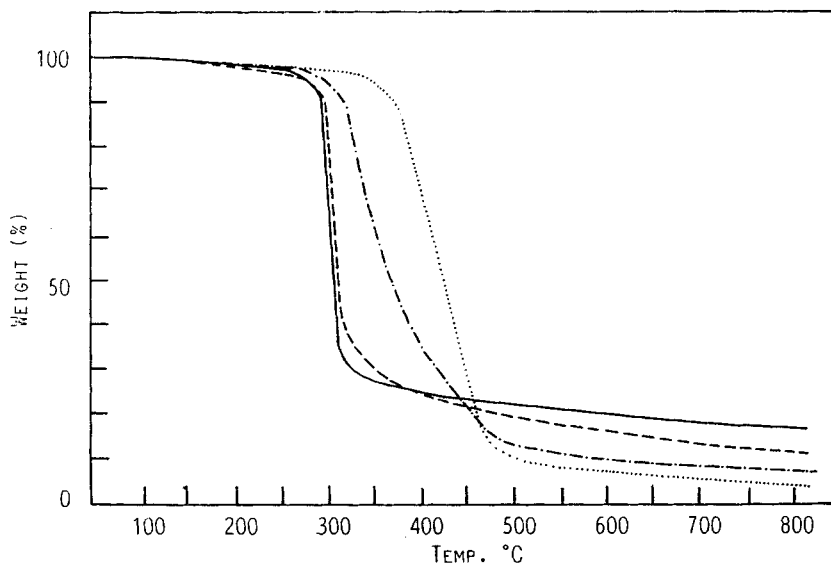
Fig. 8. TGA diagrams for cured products of (——) TBBA epoxy; (- - -) TBBA-BA-30 epoxy; (-·-·) TBBA-BA-20 epoxy; and (·····) BA epoxy. Heating rate: 20°C/min; ATM: N_2. Curing agent: Polyamine, 1 equiv./epoxide equiv.

a great effect on T_{dec} of their products. With the increasing of bromine, the T_{dec} would obviously decrease because the bromine atoms would reduce the extent of crosslinking. And the reduction of crosslinking extent was the main reason causing the decreasing of T_{dec}. It was also seen on TGA diagrams that cured products for the above epoxys showed a linear relationship on curves of
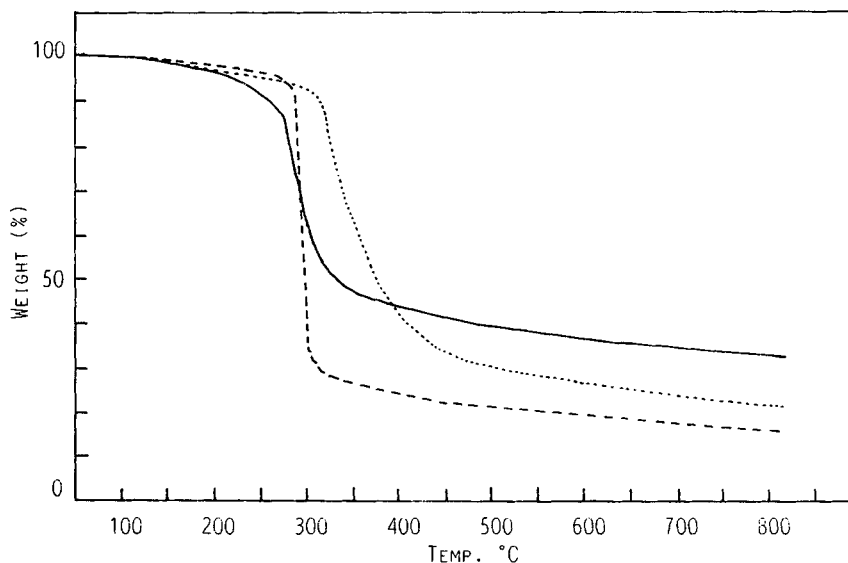

Fig. 9. TGA diagrams for cured products of (——) TBPP epoxy; (····) PP epoxy; and (- - -) TBBA epoxy. Heating rate: 20°C/min; ATM: N_2. Curing agent: Polyamine, 1 equiv./epoxide equiv.

char yield versus the content of epoxy containing bromine. Cured products of TBPP-PP epoxy had higher char yield than those of the other epoxy systems, because the combination of bromine and high aromaticity would make easy the char formation at high temperature. Meanwhile, since the char yield increased with the increasing of bromine content, bromine atoms might not be fully departed from the chain backbone and formed a steady structure to promote the char formation at high temperature. Figure 9 showed the TGA diagrams for cured TBPP epoxy, PP epoxy, and TBBA epoxy. Cured TBPP epoxy had the highest char yield.

Relationship Between OI and Char Yield

It had been shown[15] that there was a linear relationship between oxygen index and char yield for comixtures of high aromaticity-containing epoxy. Similarly, linear relationships between oxygen index and char yield for epoxy containing bromine atoms were found in this study as shown in Figure 10. This meant that since oxygen index increased with char yield, excellent flame retardancy always existed with high char yield. Beside, cured products of TBPP-PP epoxy had greater char yield than those of TBBA-BA epoxy system. This also indicated that TBPP epoxy had greater effects on promoting flame retardancy. Though the chard yield of TBBA epoxy was less than that of PP epoxy, TBBA epoxy gave higher value of oxygen index because the bromine atoms on its chain backbone would act as radical trap[17] to extinguish flame during burning procedure.
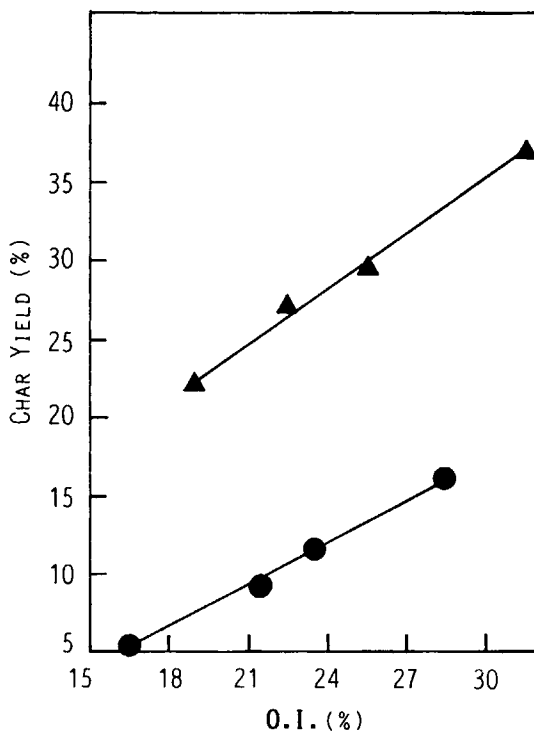

Fig. 10.   Plot for char yield versus oxygen index. (▲) TBPP-PP epoxy; (●) TBBA-BA epoxy.

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