

# Improving the Toughness and Flame Retardancy of Cured Epoxy Resin with Brominated Castor Oil

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**ABSTRACT:** Data from techniques such as limiting oxygen index, thermal analysis, scanning electron microscope, heat deformation curve, mechanical properties measurement, etc. show that cured epoxy resin modified by brominated castor oil possesses good flame retardation, toughness, moderate smoke suppression, and some degree of

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**Key words:** epoxy resin; brominated castor oil; compatibility; toughness; flame retardance

## INTRODUCTION

The use of the cured epoxy resin in high-performance structure materials is common practice because this resin possesses high strength, low creep, very low cure shrinkage, excellent resistance to corrosion, good adhesion to many substrates and appropriate electrical properties. Unfortunately, the unmodified cured epoxy resins are brittle and combustible, and these drawbacks extremely restrict their fields of use.<sup>1</sup> Cured epoxy resins are usually toughened with oligomers or liquid rubber; for examples, the copolymers of butadiene and acrylonitrile, polysulfide, polyacrylate, polysilicone, and polyurethane.<sup>2</sup> In general, the use of these materials to toughen the cured epoxy resins is effective. There are many methods to make epoxy resins flame retardant. Many flame-retardant compounds could be used effectively.<sup>3</sup> Frequently, the flame retardants are phosphates, such as tricresyl phosphate (TCP) and triphenyl phosphate (TPP); halides, such as hexabromobenzene (HBB), decabromodiphenyl oxide (DBDPO), tetrabromobiphenol A (TBA), and tetrachlorophthalic anhydride (TCPA); halogen phosphates, such as tri(2-bromo-3-chloropropyl) phosphate; and some inorganic substances, such as aluminum oxide trihydrate (ATH), zinc borate ( $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ ) and red phosphorus. Containing halogen and/or phosphorus epoxy resins, curing agents, and diluents is also useful for flame retardance. Our test results<sup>4</sup> indicate that diantimony trioxide can effectively flame retard epoxy resin cured by acid anhydride. In practice, flame retardation of poly-

mers generally causes deterioration of their inherent properties. There has been rapid development for years of techniques with the multifunction of imparting polymers with enduring flame retardation and maintaining their inherent properties. Castor oil, which is abundant in the Hubei Province of the People's Republic of China, can be converted by bromination to brominated castor oil (BCO). BCO is a good additive to bestow cured epoxy resin with good flame retardance, toughness, and other properties.

## EXPERIMENTAL

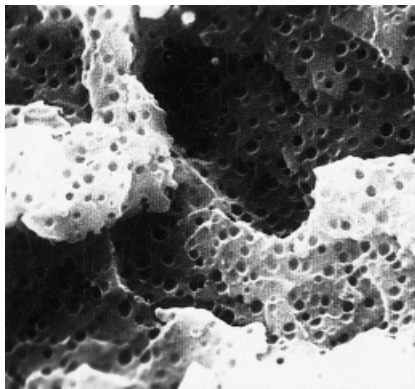
### Materials

The following chemicals were used: bromine (Lianyungang Haishui Chemical Factory, Jiangsu, China); castor oil (Hubei University Chemical Factory, Wuhan, China); E51 epoxy resin, a liquid diglycidylether of the bisphenol A type with a molecular weight of 370–416 (Baling General Petrochemical Factory, Hunan, China); HK-021 acid anhydride, a blend of tetrahydrophthalic anhydride and hexahydrophthalic anhydride (Qingming Chemical Factory, Zhejiang, China); and 2,4,6-tri(*N,N*-dimethyl amino)methyl phenol (DMP-30, CP reagent).

### Bromination of castor oil

In a 1000-mL round-bottomed flask with a reflux-water-cooled condenser, a thermometer that extended into the flask, a mechanical stirrer, and a constant pressure dropping funnel, 100 g of castor oil was dissolved in 250 mL of carbon tetrachloride, and the solution was chilled to 10°C. Then, with stirring, 54.4 g of bromine in the constant-pressure dropping funnel was introduced slowly, at a rate such that the temper-

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**Figure 1** SEM fracture image of the cured epoxy resin.

ature did not exceed 20°C. The reaction was over when the red color disappears. The excess bromine was removed by addition ~1 g of castor oil. Removal of carbon tetrachloride resulted in the product, brominated castor oil (BCO), which is a yellow and sticky liquid with a bromine content of ~35%.

#### Sample preparation

After epoxy resin, HK-021 acid anhydride, and DMP-30 were mixed in the proportion 100:80:1 (mass ratio), the flame retardants were added and cured for 2 h at 120°C. The samples were then cooled to ambient temperature for analysis.

#### Limiting oxygen index measurement

Limiting oxygen index (LOI) was measured according to the Chinese national standard GB 2406-93 (similar to ANSI/ASTM D2863-1977) at flow rate of 4.2 cm/s on a HC-2 oxygen index apparatus (Jiangning Analytical Instrument Factory, Nanjing, China).

#### Thermogravimetric analysis

Thermogravimetric analysis (TG) was performed in nitrogen with DT-30B (Shimadzu) at rates of 10°/min and 2.5 mm/min for programmed temperature controller and paper feeding, respectively.

#### Differential scanning calorimetry

A model CDR-1 differential scanning calorimetry (DSC) apparatus (Shanghai Weighing Instrument Factory, Shanghai, China) was used at rates 10°C/min and 5 mm/min for programmed temperature controller and paper feeding, respectively, in nitrogen.

#### Scanning electron microscope

The scanning electron microscopic (SEM) image was observed on a DSM-950 (West Germany) with the following parameters: HV, 20 kV; WD, 6 mm; MRG, 5000.

#### Heat deformation curve

With the results from a model J-1 polymer deformation temperature measure apparatus (Zhongshan University Scientific Instrument Factory, Guangzhou, China)  $\Delta L/L$  versus  $t$  curves were created. The heat deformation temperature (HDT) was determined and linear expansion coefficient ( $\alpha$ ) was calculated according to Chinese national standard GB 1036-70.

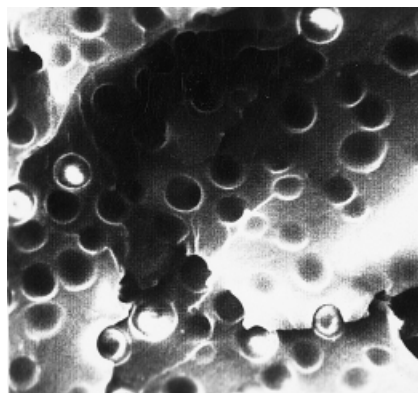
#### Mechanical properties measurement

The compression strength and impact resilience for cured resins were measured according to Chinese national standard GB 1041-70 and 1043-70.

## RESULT AND DISCUSSION

#### Compatibility between brominated castor oil and cured epoxy resin

Castor oil is not compatible with epoxy resin. It was noted that after bromination of castor oil, the compatibility between the oil and the resin is much improved because of the increase in polar groups within the castor oil molecules, which results in better dispersion without layer separation at a loading of 100 phr (phr is the added gram in 100 gram uncured epoxy resin) of BCO. Test samples with or without BCO all are transparent, but the samples with castor oil are not transparent and are oily on the surface. The SEM micrographs of the samples are shown in Figures 1–3. Comparison of these micrographs indicates that the section



**Figure 2** SEM fracture image of the cured epoxy resin treated with BCO (40 phr).



**Figure 3** SEM fracture image of the cured epoxy resin treated with castor oil (40 phr).

of the sample with castor oil is not distinct because of the noncompatible castor oil.

#### Flame retardation of cured epoxy resin treated with brominated castor oils

The experimental results are shown in Table I. The LOI grows steadily as long as the addition of BCO goes up and the sample can be extinguishable<sup>5</sup> at only 20 phr loading.

As an aliphatic bromine-containing flame retardant, BCO can play a vital role in both the gas phase<sup>6</sup> as a free radical scavenger and in the condensed phase<sup>7</sup> by promoting char formation, as evidenced by the residue increase in TG analysis results.

The results from experiments in which several flame retardants were used with BCO are shown in Table II, where X represents elements Sb, P, and B, corresponding to diantimony trioxide, triphenyl phosphate, and hydrated zinc borate ( $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ ), respectively, with LOIs denoted  $\text{LOI}_{\text{Sb}}$ ,  $\text{LOI}_{\text{P}}$ , and  $\text{LOI}_{\text{B}}$ , respectively. It is noted from the data in Table II that the maxima for the three additives are at the Br/X ratio of 3, 3–5, and 4, respectively. This result is in good agreement with the following stoichiometries:

**TABLE I**  
Effect of Brominated Castor Oil on LOI of Cured Epoxy Resin

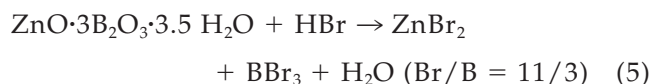
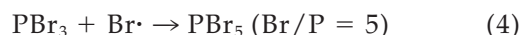
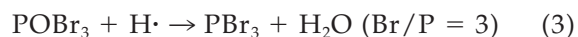
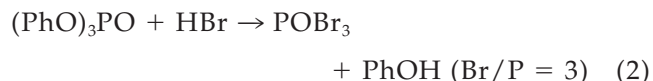
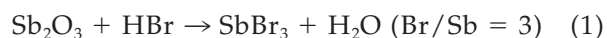
BCO (phr) <sup>a</sup>	LOI
0	19.4
10	21.5
20	22.6
30	22.9
40	23.1
50	23.5
60	24.0
70	24.6
80	25.1
90	24.7
100	24.8

<sup>a</sup> phr is the added gram in 100g of uncured epoxy resin.

**TABLE II**  
Flame Retardation Synergism between BCO and other Additives

LOI <sup>a</sup>	Br/X (mol/mol)							
	0	1	2	3	4	5	6	7
$\text{LOI}_{\text{Sb}}$	28.3	29.1	29.5	30.1	29.7	29.4	29.2	28.9
$\text{LOI}_{\text{P}}$	24.0	25.1	26.2	27.1	27.5	27.8	27.8	27.7
$\text{LOI}_{\text{B}}$	20.3	25.8	26.5	28.7	28.8	28.6	28.8	28.7

<sup>a</sup> Add-on of Sb, P, B all are 0.03 mol per 100 part uncured epoxy resin.



where HBr comes from the decomposition of BCO.

The bromides produced from flame retardants reacting with each other and phosphoric acid and phosphorous acid produced from the phosphorus bromides combining with water vapor can lead to effective flame retardation in the gas phase. In addition, the presence of  $\text{ZnBr}_2$  and  $\text{BBr}_3$  involves the formation of a glassy layer that protects the underlying surface of polymeric matrix from the attack by oxygen and heat released from burning. This results in more efficient synergistic effect, as already stated.<sup>8</sup>

#### Mechanical properties of the cured epoxy resin treated with brominated castor oil

The results in Table III demonstrate that addition of BCO to the cured epoxy resin can significantly en-

**TABLE III**  
Mechanical Properties of the Cured Epoxy Resin Treated with BCO

Parameter	Brominated castoe-oil (phr)				
	0	20	40	60	80
Compression strength (MPa)	116.0	113.1	111.3	107.0	106.5
Impact resilience strength ( $\text{kJ}/\text{M}^2$ )	11.0	13.0	14.2	16.0	18.0

TABLE IV  
Heat of Deformation of the Cured Epoxy Resins

Sample	HDT (°C)	$\alpha \cdot 10^{-5}$ (°C <sup>-1</sup> ) <sup>a</sup>
1	115	5.8
2	95	5.6
3	89	5.7
4	85	8.6
5	135	5.4

<sup>a</sup> From ambient temperature to 80°C.

hance the toughness of the cured epoxy resin, because of the existence of the longer carbon chain within the molecule of flame retardants, but results in very little reduction in stiffness.

From the microphotographic figures (Figures 1–3) it is seen that the section becomes flatter and more regular, and the micropores tend to be larger and uniform after adding BCO. This result implies the improvement of impact resilience.

#### Smoke suppression of the cured epoxy resin treated with brominated castor oil

When the sample with BCO at >40 phr was burned, the smoke became seldom and pale quickly and a lot of caked residues in an integral crust were formed. That is to say, the fused pyrolyzate from the condensed-phase flame retardation of BCO in the visco-flow state may absorb part of smoke dust and BCO possesses the ability to suppress smoke.

#### Thermal stability of the cured epoxy resin treated with brominated castor oil

Thermal deformation is shown in Table IV and Figure

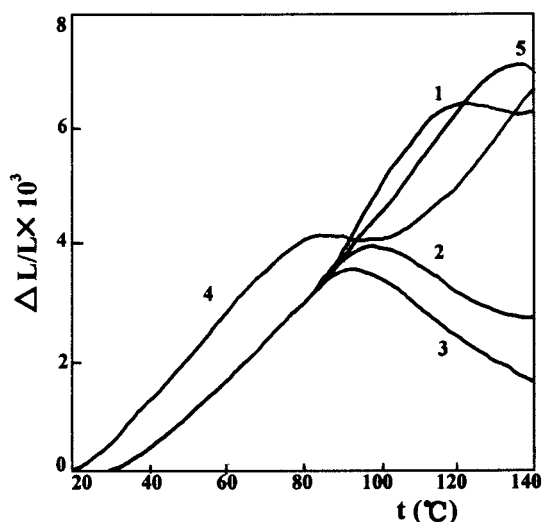


Figure 4  $\Delta L/L-t$  curves for the cured epoxy resins: nos. 1, 2, and 3 are the cured epoxy resin with BCO at 20, 40, and 60 phr, respectively, no. 4 is the cured epoxy resin with ortho-dibutyl dibenzoate at 40 phr, and no. 5 is the contrast sample cured epoxy resin.

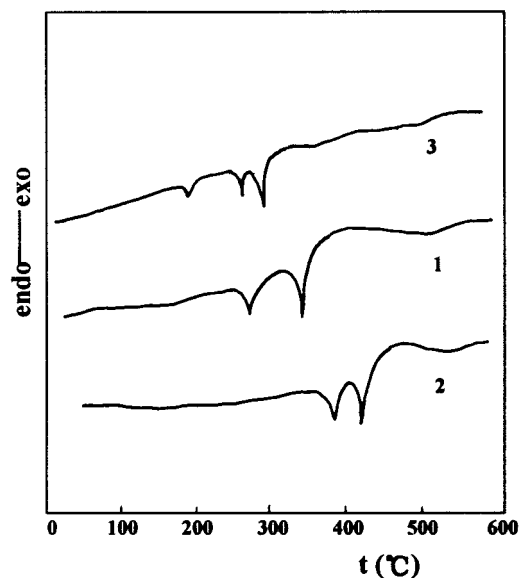
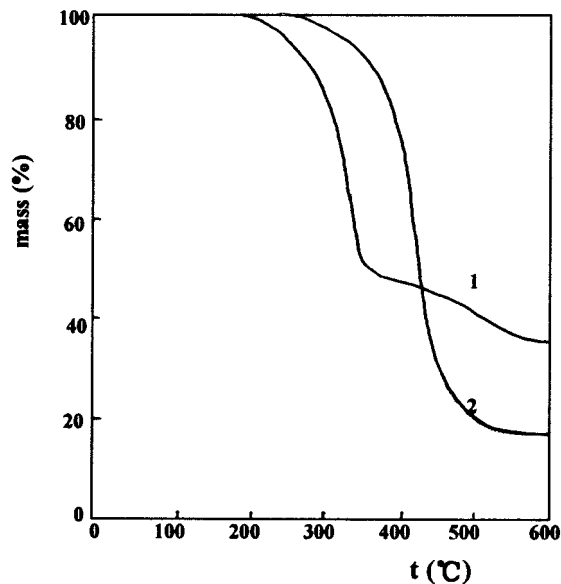


Figure 5 DSC curves for the cured epoxy resin: no. 1 is the cured epoxy resin with BCO at 40 phr; no. 2 is the contrast sample cured epoxy resin; and no. 3 is the BCO alone.

4, in which nos. 1, 2, and 3 are the cured epoxy resin with 20, 40, and 60 phr of the BCO, respectively, no. 4 is the cured epoxy resin with 40 phr ortho-dibutyl dibenzoate, and no. 5 is the contrast sample of cured epoxy resin for comparison. On one hand, like ortho-dibutyl dibenzoate, BCO causes a decrease in HDT. On the other hand, the effect of BCO on the line expansion coefficient of the cured resin is smaller than that of ortho-dibutyl dibenzoate; that is, the expansion coefficient remains nearly constant regardless of the levels of BCO. Especially at <80°C, the  $\Delta L/L-t$  curves are almost the same as that of the contrast sample. It is possible that the BCO may take part in the curing of the epoxy resin. This result is of great importance in industrial production and application of the epoxy resin.

The thermal decomposition behavior of the cured epoxy resin treated with BCO was studied by DSC and TG, as depicted in Figures 5 and 6, in which nos. 1, 2, and 3 are the cured epoxy resin with BCO at 40 phr, the contrast sample cured epoxy resin, and BCO alone, respectively.

The thermal decomposition temperature of the contrast sample was lowered and much influenced by the presence of BCO. Below 270°C, the elimination of HBr from BCO dominates the process.<sup>7</sup> At 300°C (270–350°C) scission of the ester bond of BCO and fused reaction of various kinds occur.<sup>9,10</sup> Above 350°C, the main process is the thermal decomposition of the cured epoxy resin. In general, for better flame retardation, the decomposition of the flame retardant should be ahead of that of the polymer. Therefore, it is not abnormal that flame retardation makes decomposition of polymeric system occur earlier. The residue at



**Figure 6** TG curves for the cured epoxy resin: no. 1 is the cured epoxy resin with BCO at 40 phr; and no. 2 is the contrast sample cured epoxy resin.

600°C (in Figure 6) of the sample with BCO is more than that of the contrast sample because of the intervening of BCO with the degradation products during burning. This result would be of great help to the flame retardation and resistance of heat of the product.

## CONCLUSIONS

BCO was synthesized and shown to be very compatible with epoxy resin. In comparison with the control sample, the use of BCO gives the cured epoxy resin many advantages, like good flame retardation, fair toughness and very little reduction of stiffness, suppression of smoke to a certain amount (although the thermal decomposition temperature and heat deformation temperature were decreased to a certain amount).

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