Studies on Characteristics and Mechanisms of X–MoO$_3$ Synergism in Fire-Retarded Epoxy Resin

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SYNOPSIS

Molybdenum trioxide was incorporated into epoxy resin, containing halogen additive, and the performance of the system was studied. The results from LOI measurements show that X–MoO$_3$ synergism in fire-retarded epoxy resin depends on the levels both of halogen and MoO$_3$, and that when Mo/X ratio is 1/3, the maximum fire retardancy is not found in the synergistic combination. The thermal analysis was carried out by thermogravimetry (TG), differential scanning calorimetry (DSC), X-ray diffraction, and laser Raman spectroscopy. The results indicate that MoO$_3$ acts as a synergist in condensed phase. The mode of X–MoO$_3$ synergism in fire-retarded epoxy resin is proposed.

INTRODUCTION

The conventional fire retardant synergism of X–Sb$_2$O$_3$ system has been extensively studied in the last decades. Incorporation of Sb$_2$O$_3$ into the polymers containing halogen or a halogen additive has been shown to possess a good synergistic effect on polymers, but also to produce a large amount of smoke on burning. The use of MoO$_3$ instead of Sb$_2$O$_3$ is effective in reducing the smoke on burning and in providing a synergistic effect, if halogen is present in the polymers or as a halogen-containing fire retardant additive.[1–5] However, the characteristics and mechanisms of the X–MoO$_3$ synergistic combination were not reported in detail.

The aim of this study is to investigate both the characteristics and mechanisms of the X–MoO$_3$ system applied to epoxy resin using techniques such as limiting oxygen index (LOI), TG, DSC, X-ray diffraction, and laser Raman spectroscopy.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol-A was used as epoxy resin, methyltetrahydrophthalic anhydride as curing

agent, and 2-ethyl-4-methylimida-zole as catalytic curing agent. All of the above materials, including fire retardant additives, are commercially available.

Preparation of Samples

The resin formulations for casting were mixed at elevated temperatures (50–60°C) by an agitator. The mixture was then cast into the molds.

The cure cycle was as follows: 90°C/2h, 120°C/1 h.

Evaluation of Samples

The LOI values of all samples were measured using an HC–Z LOI apparatus (Tian Jin Institute of Synthetic Materials). In the LOI test, the relative flammability of the samples was determined by measuring the minimum concentration of oxygen, in a flowing mixture of oxygen and nitrogen, that will just support flaming combustion.[6] The gas mixture is caused to flow upwards in a test column. The vertically positioned specimen, supported in a frame, is exposed to an ignition flame at its top. If ignition does not occur at the starting concentration, the oxygen percentage is increased until ignition takes place. The volume percent of oxygen used is reported as the limiting oxygen index.

The thermogravimetric analyses were performed in air with a Shimadzu thermogravimetric analyzer

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DT-30B, at a heating rate of 10°C/min from room temperature to 700°C. The DTG curves were obtained electronically.

A model CDR-1 differential scanning calorimeter (Scientific Instrument Factory, Shanghai) was used. The samples of about 5 mg were heated at heating rate of 10°C/min from room temperature to 700°C in air.

X-ray diffraction analyses were conducted on the Rugaku Cu Target X-ray diffraction spectrometer. Evaluation condition: 35 kv, 25 mA.

A Jobin-Yron U-1000 Laser Raman spectrometer was used. Laser: 150 MW, Lattice: 500 MIC, scan number: 4, time: 1s/PT.

RESULTS AND DISCUSSION

Synergistic Fire Retardation of the X–MoO₃ System

Since bispentabromobenzenyl ether contains only bromine and chlorinated tall oil contains only chlorine, combination of bispentabromobenzenyl ether with MoO_3 was studied essentially in the same way as used for the combination of chlorinated tall oil with MoO_3. The effects of MoO_3 on the LOI at various levels of bromine and chlorine can be seen from Figures 1 and 2, respectively.

Our experimental results indicate X–MoO₃ synergism in fire-retarded epoxy resin when the bromine or chlorine-containing flame retardant additive is
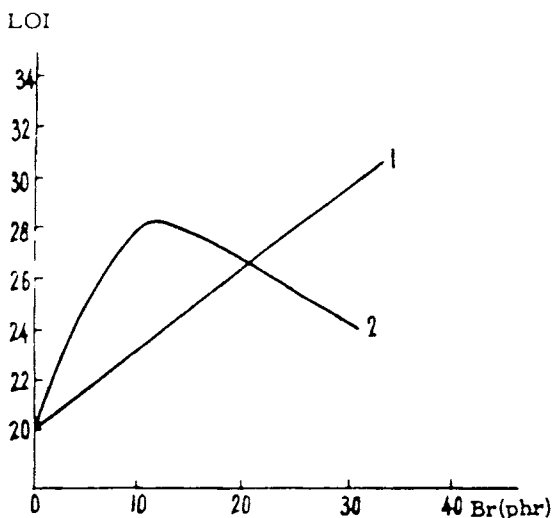
Figure 1   LOI response to samples treated with 10 phr MoO_3 as a function of bromine content. (1) Untreated samples, (2) Samples treated with MoO_3.
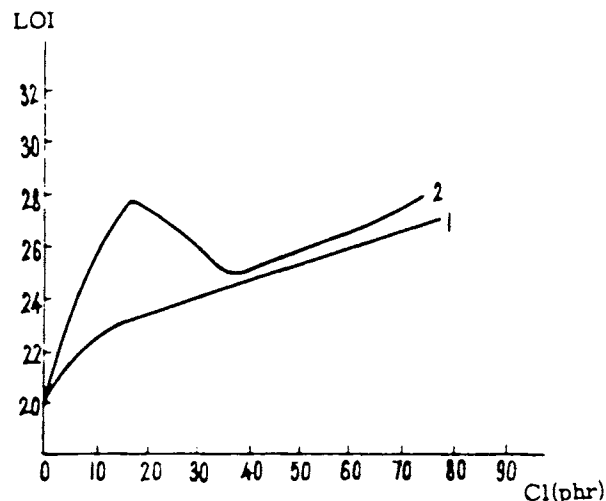
Figure 2   LOI response to samples treated with 15 phr MoO_3 as a function of bromine content. (1) Untreated samples, (2) Samples treated with MoO_3.

used in conjunction with MoO_3. On the other hand, the Cl–MoO₃ and Br–MoO₃ antagonism are found at higher loadings of halogen-containing flame retardants.

With bromine concentration remaining constant and MoO_3 concentration progressively increasing to the possible maximum value, the synergistic effects of MoO_3 on the flame retardancy of the epoxy resin containing bromine was measured, and the obtained data of Δ(LOI) are shown in Figure 3.

The response of synergism to the concentration of MoO_3 shows that Δ(LOI) increases remarkably with the slight increase in MoO_3 loading at first, but the improvement on Δ(LOI) becomes insignificant at higher MoO_3 loading.
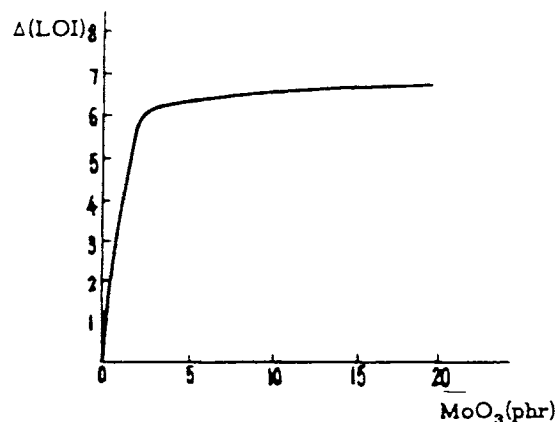
Figure 3   Δ(LOI) response to the concentration of MoO_3 at 20 phr level of bromine.
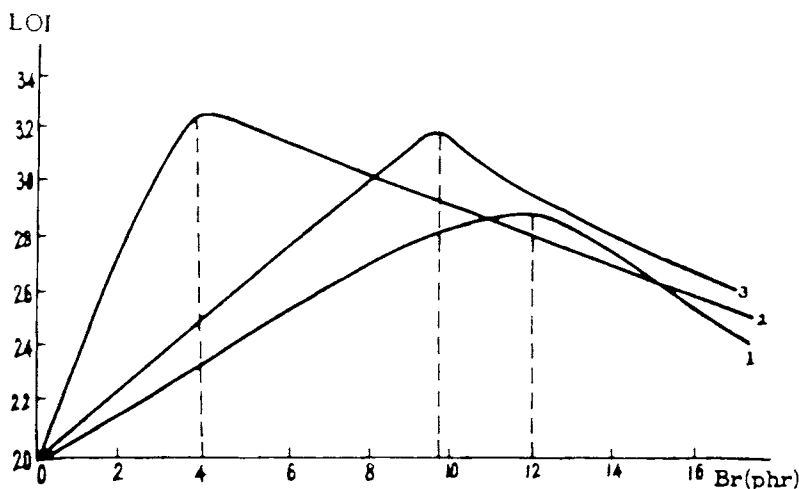
Figure 4 Dependence of LOI on bromine level (1) Samples with 5 phr MoO_3, (2) Samples with 10 phr MoO_3, (3) Samples with 15 phr MoO_3.

Optimization of MoO₃/Halogen Ratio

The plots in Figure 4 illustrates the dependence of LOI on bromine level for samples with different MoO_3 loadings. Figure 4 shows (a) For the samples with a higher concentration of MoO_3 (15 phr), the peak of the curve is located in the range of higher concentration of bromine (see curve 3), (b) For the samples with lower concentration of MoO_3 (10 phr), the location of the peak shifts toward lower level of bromine (see curve 2), (c) When MoO_3 loading is too low (5 phr), the location of the peak shifts toward the range of higher concentration of bromine adversely (see curve 1).

Based on the above measurements, the atomic ratios of Mo/Br for providing optimum fire retardancy for the experimental series shown in Figure 4 are listed in Table I.

It has been reported that the atomic ratio of Sb/X should be about 1/3 in order to achieve optimum fire retardancy for the polymers flame-retarded by the combination of Sb_2O_3 with halogenated additives.[7-9] It is widely accepted that the synergistic effect of the $X-Sb_2O_3$ system may attribute to the production of antimony trihalide, which is an effective fire retardant species. But the data shown in

Table I The Atomic Ratios of Mo/Br for Providing Optimum Fire Retardancy

Exp. Series	Br : MoO₃(wt)	Br : Mo(molar)
I	12 : 5	1 : 0.23
II	4 : 10	1 : 1.4
III	9.5 : 15	1 : 0.8

Table I suggest that the $X-MoO_3$ synergism might not be due to the formation of $MoCl_3$, as has been demonstrated for $X-Sb_2O_3$ synergism. An analysis of the flame retardance mechanism of $X-MoO_3$ system is described below.

Flame Retardance Mechanism of the X-MoO₃ System

Thermal behavior of the sample flame-retarded with both bromine-containing fire retardant and MoO_3 was studied by TG and DSC. The obtained TG and DSC curves are shown in Figures 5 and 6, respectively. For comparison, the same kinds of curves of the sample, treated with the bromine containing fire retardant singly, are also given.

Curves in Figure 5 show that there exist three decomposition stages for the two samples studied. The addition of MoO_3 leads to the following observations:

1. The first stage is moved to somewhat higher temperature with mass loss nearly unchanged.
2. The second stage is shifted to lower temperature with mass loss decreased.
3. In the third stage, MoO_3 lowers the temperature at which the peak of DTG curve appears besides altering the curve shape.

The results obtained from TG curves demonstrate that MoO_3 acts predominantly by catalyzing the decomposition of the resin in the condensed phase. DSC curves in Figure 6 indicate the effects of MoO_3
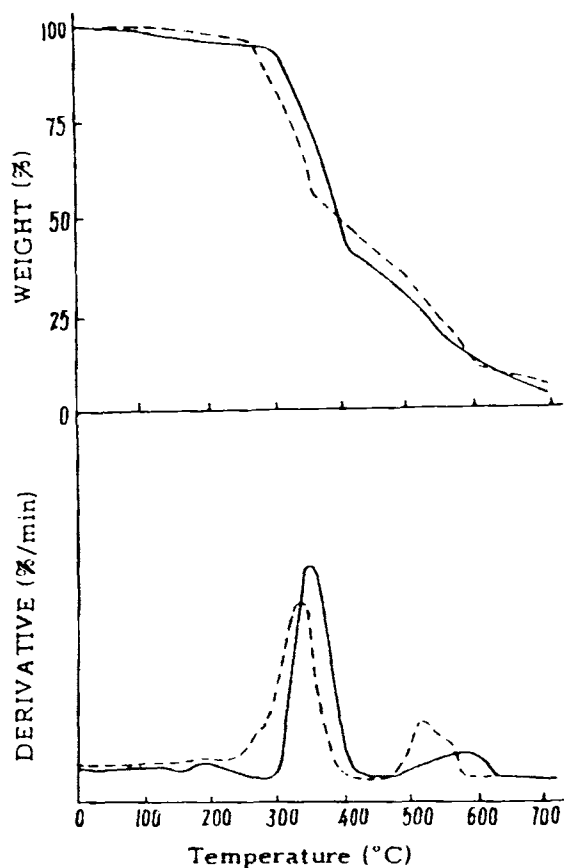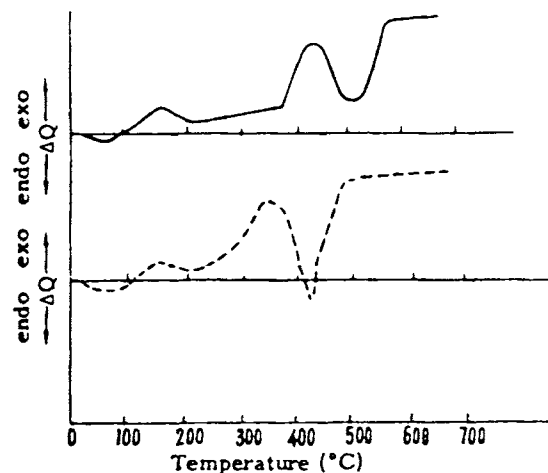
Figure 5 Comparison of TG curves for the two samples (in air, at a heating rate of 10°C/min). (——) With 10 phr bromine, (----) With 10 phr bromine and 10 phr MoO₃.

Figure 6 Comparison of DSC curves for the two samples (in air, at a heating rate of 10°C/min). (——) With 10 phr bromine, (----) With 10 phr bromine and 10 phr MoO₃.

on the thermicity of the above-mentioned 3 stages. In the first stage, the two samples exhibit similar behavior, corresponding with TG results. In the second stage, MoO_3 lowers the exothermic peak temperature to 310°C as compared with 350°C for the sample containing no MoO_3. As expected, the third exothermic peaks of two samples are located at above 410°C, but the strong endothermic peak appears at about 400°C for the sample with MoO_3, which is attributed to an action of MoO_3 by the condensed phase mechanism.[10]

The samples with both bromine-containing flame retardant and MoO_3 were heated in various temperatures, and then were examined by X-ray diffraction and laser Raman spectroscopy. These results are presented in Figures 7 and 8, respectively.
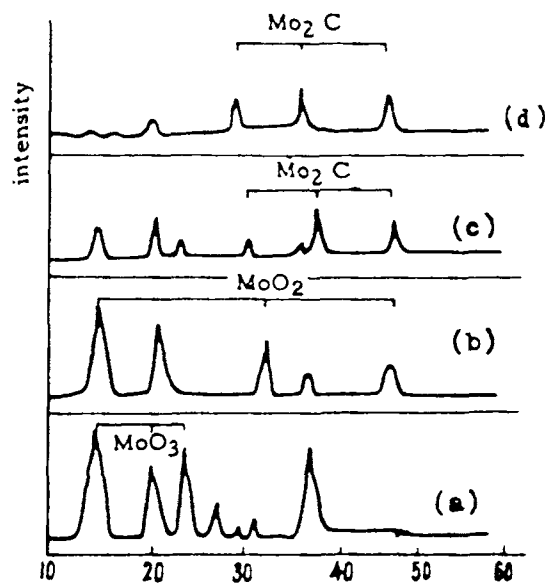
The spectra of X-ray diffraction shows that there exists mostly MoO_3 in the sample heated below 400°C, while MoO_2 above 400°C. The residues from the sample heated at 700°C, or from the burned sample, are shown to contain Mo_2C. The results

from X-ray diffraction reinforce the conclusion obtained from the TG and DSC analysis.

As seen in Figure 8, no evidence is found in the Raman spectra for Mo–Br stretching at 255 cm⁻¹, but only for the strong Mo–O stretching bands at 816 cm⁻¹ and 992 cm⁻¹.[11-12] This means that the MoO_3 acts in condensed phase in contrast to Sb_2O_3 in vapor phase. This can also be derived from the previous results of LOI measurements.

Figure 7 Spectra of X-ray diffraction of residues from the samples heated in air for ten minutes. (a) Unheated, (b) Heated at 400°C, (c) Heated at 700°C, (d) Burned sample. The ratio of MoO_3/Br is 10 phr/10 phr.

WAVE NUMBER (cm⁻¹)
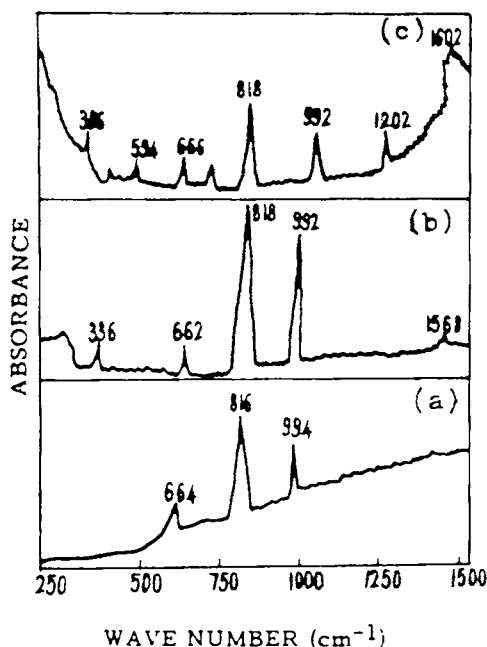
Figure 8 Raman spectra of the samples heated in air for ten min. (a) Unheated, (b) Heated at 400°C, (c) heated at 700°C.

CONCLUSIONS

X–MoO₃ synergism in fire-retarded epoxy resin depends both on the levels of applied halogen and of MoO₃. In our studies, MoO₃ is shown to act predominantly by catalyzing decomposition of the resin, by producing more char, and by changing the struc-ture of the char in condensed phase. It assumes that X–MoO₃ synergism in fire-retarded epoxy resin is due to the effects of halogen in vapor phase, and the effects of MoO₃, in condensed phase, synergistically.

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