International Journal of Biological, Life and Agricultural Sciences
ISSN: 2415-6612
Vol:4, No:5, 2010

The Smoke Suppression Effect of Copper Oxide on the Epoxy Resin/Intumescent Flame Retardant/Titanate Couple Agent System

Zhiping Wu, Meiqin Chen, Haikuan Yang, and Yunchu Hu

Abstract**—**Fire disaster is the major factor to endanger the public and environmental safety. People lost their life during fire disaster mainly be attributed to the dense smoke and toxic gas under combustion, which hinder the escape of people and the rescue of firefighters under fire disaster. The smoke suppression effect of several transitional metals oxide on the epoxy resin treated with intumescent flame retardant and titanate couple agent (EP/IFR/Titanate) system have been investigated. The results showed manganese dioxide has great effect on reducing the smoke density rate (SDR) of EP/IFR/Titanate system; however it has little effect to reduce the maximum smoke density (MSD) of EP/IFR/Titanate system. Copper oxide can decrease the maximum smoke density (MSD) and smoke density rate of EP/IFR/Titanate system substantially. The MSD and SDR of EP/IFR/Titanate system can reduce 20.3% and 39.1% respectively when 2% of copper oxide is introduced.

Keywords**—**copper oxide, epoxy resin, intumescent flame retardant, smoke suppression.

I. INTRODUCTION

Epoxy resin (EP) possess good mechanical properties, chemical stability, high binding strength and easy curing condition, and is widely used in many fields such as painting, adhesive, copper-clad laminate insulating materials etc[1]-[3]. However its easy combustion and produce dense smoke during combustion， which endanger the life safety and cause environmental pollution, so it is essential to improve the flame retardancy and smoke suppression of EP [4]. The traditional method to improve the flame retardancy of EP is to introduce halogen-contained flame retardant to polymer matrix [5]. However, EP treated with halogenated flame retardant will produce corrosive hydrogen halide and density smoke, which do great harm on the environmental and public safety[6], [7]. Halogen free flame retardant (HFFR) have become more popular to improve the flame redardance of polymer, intumescent flame retardant (IFR) is an effective HFFR [8]-[10]. The flame retarding behavior of IFR for polymer is the formation of an expanded charring layer at the burning surface, so that oxygen and heat transfer toward the undecomposed bulk is prevented. IFR formulation, first used in the painting industry, has been applied to the fire stabilization of polymeric materials. The typical formulation of IFR constitutes: Carbonic agent, carbonific catalyst, and blowing agent. In fire, carbonific catalyst can produce inorganic acid that can esterify with polyol in Carbonic agent, and then carbonizing with dehydration, viscous carbonized product can swell and form micro-porous char layer under the influence of volatile substance such as inert gas which blowing agent release. The porous char layer can extinguish fire owing to insulate heat and oxygen, which is responsible for the fire disaster. IFR can overcome the shortcoming of halogenated flame retardant that produce dense smoke and drip when combustion and can overcome the disadvantageous effect of mechanical property and processing technology of polymer to add inorganic flame retardant largely. Thus intumescent halogen-free flame retarding technology is glorified one of innovation of flame retarding technology and become one of active issue in flame retardant research field recently[11], [12].

In previous work [13], [14], the effect of IFR on the flame retardancy and smoke suppression of EP have been studied. The results showed that flame retardancy of EP improved substantially when intumescent flame retardant was incorporated into EP, however the mechanical properties decrease sharply and smoke density can not be reduced when EP treated with IFR. Many research demonstrated that the transitional metal compounds can depress smoke when polymer combustion [15]-[17]. Most of studies focus on the effect of transitional metal salts on the smoke of polyvinyl chloride (PVC) during combustion. In order to improve the mechanical properties, titanate couple agent was incorporated into EP/IFR system. This work is devoted to investigate the

Zhiping Wu is with the Central South University of Forestry and Technology, Changsha, CO 410004 China (corresponding author to provide phone: +86-731-85623305; fax: +86-731-85623305; e-mail: wuzhiping02@ 163.com).

Meiqin Chen is with the Central South University of Forestry and Technology, Changsha, CO 410004 China (e-mail: megin.chen@163.com).

Haikuan Yang is with the Central South University of Forestry and Technology, Changsha, CO 410004 China (e-mail: yanghaikuan2006 @yahoo.com.cn).

Yunchu Hu is with the Central South University of Forestry and Technology, Changsha, CO410004 China (e-mail:hucsfu@163.com)

This project was supported financially by the Creative Funds of Central South University of Forestry & Technology (07Y017) and the National Natural Scientific Funds of China (30871976).

effect of transitional metal oxide (TMO), especially copper oxide on the smoke suppression of epoxy resin/intumescent flame retardant/titanate couple agent (EP/IFR/Titanate) system.

Ⅱ. MATERIALS AND METHODS

A. Materials

Epoxy resin (EP, E-44, commercial grade) and polyamide resin (PA, curing agent)were supplied by zuoyue chem.of Jiangxi Yichun, China; intumescent flame retardant(IFR) was prepared in our laboratories; titanate couple agent (commercial agent) were purchased from market; copper oxide (CuO) and ferric oxide (Fe_2O_3) were supplied by kemiou chem. agent of Tianjin; Zinc oxide(ZnO), cobalt oxide(Co_2O_3), cadmium oxide (CdO) and manganese dioxide(MnO_2) were supplied guangfu fine chem. institute of Tianjin, China; titanium dioxide (TiO_2) was supplied xilong chem. of Guangdong, China.

B. Preparation

Intumescent flame retardant and different transitional metal oxides were mixed and grinded into ultrafine particles with agate mortar. The complex and couple agents were added to E-44 epoxy resin under stronger stir, polyamide curing agent was added to epoxy resin complex and stirred completely, deaerating and pouring to a specified size mould. The specification samples of testing were obtained through cutting after the curing of EP/IFR/Titanate system. The detailed procedures were illustrated as Fig. 1.

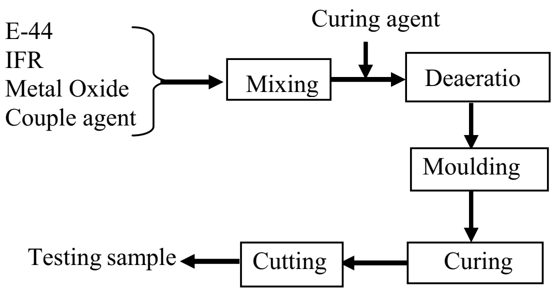

Fig. 1 The schematic procedure of sample preparation

C. Measures

Maximum smoke density and smoke density rate were performed according to ASTM E662-95 in smoke density tester (JCY-1, Nanjin jianglin analytical apparatus factory, China); the sample size was 40.0mm ×40.0mm×3.0mm.

III. RESULTS AND DISCUSSION

A. The Smoke Suppression Effect of Transitional Metal Oxides

The smoke density curves of different transitional metal oxides on EP/IFR/Titanate system were illustrated in Fig. 2. The maximum smoke density (MSD) and smoke density rate (SDR) of different transitional metal oxides were presented in Table I.

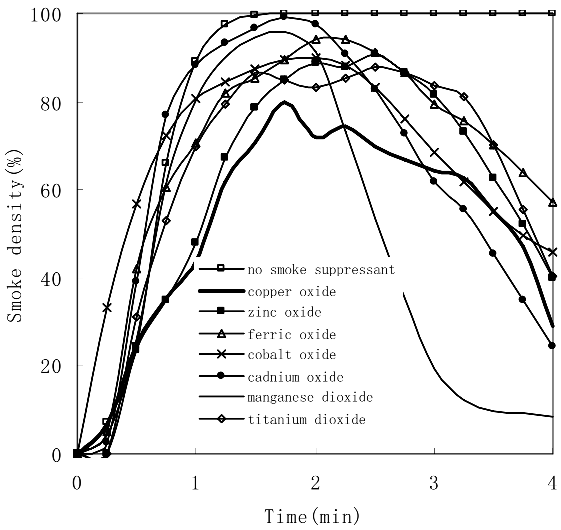

Fig. 2 The effect of transitional metal oxides on the smoke density of EP/IFR/Titanate system[a]

[a]The addition content of transitional metal oxides is 2% (based on epoxy resin mass)

TABLE Ⅰ

INFLUENCE OF TRANSITIONAL METAL OXIDES ON SMOKE DENSITY (SD) OF EP / IFR / TITANATE SYSTEM

Samples	Maximum SD (%)	SD rate (%)
No smoke suppressant	100.00	87.15
Copper oxide	79.68	53.09
Zinc oxide	90.56	61.59
Ferric oxide	94.30	72.46
Cobalt oxide	90.06	69.88
Cadmium oxide	99.10	68.15
Manganese dioxide	95.87	49.26
Titanium dioxide	87.79	66.58

It can be seen from Fig. 2 and Table Ⅰ that the smoke density of EP/IFR/Titanate system decreased when all transitional metal oxides were introduced. The smoke density rate(SDR)of EP/IFR/Titanate system reduced substantially (from 87.15% to 49.26%) although the maximum smoke density (MSD) only decrease a little (from 100% to 95.87%) when 2% manganese dioxide was introduced to EP/IFR/Titanate system. The maximum smoke density rate(MSD) and smoke density rate (SDR) of EP/IFR/Titanate system reduced from 100% and 87.15% to 87.79% and 66.58% respectively when 2% titanium dioxide was incorporated. Copper oxide can decrease the maximum smoke density (MSD) and smoke density rate (SDR) of EP/IFR/Titanate system substantially. The MSD and SDR decrease 20.3% and 39.1% compared to that of EP/IFR/Titanate system when 2% copper oxide was introduced to EP/IFR/Titanate system.

B. *The Smoke Suppression Effect of the Copper Oxide Content*

The smoke density curves of different content of copper oxide on EP/IFR/Titanate system were illustrated in Fig. 3. The maximum smoke density (MSD) and smoke density rate (SDR) of different content of copper oxide were presented in Table Ⅱ

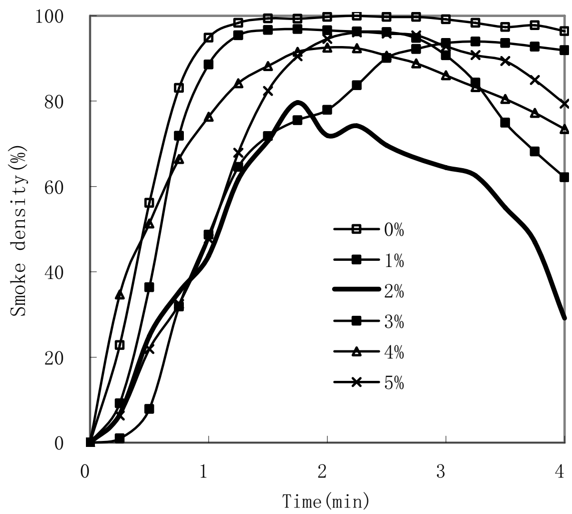

Fig. 3 The effect of copper oxide content on the smoke density of EP/IFR/Titanate system[b]

[b]The addition content of copper oxide is based on epoxy resin mass

TABLE Ⅱ
INFLUENCE OF CuO CONTENT ON SMOKE DENSITY OF EP / IFR / TITANATE SYSTEM

Samples	Maximum smoke density (MSD, %)	Smoke density rate (SDR, %)
0% CuO	100.00	87.15
1% CuO	96.87	76.76
2% CuO	79.68	53.05
3% CuO	93.93	66.58
4% CuO	92.57	76.33
5% CuO	94.94	70.55

It can be seen from Fig. 3 and Table Ⅱ that the smoke density of EP/IFR/Titanate system decreases when the content of copper oxide increase from 0% to 2%, however the smoke density of EP/IFR/Titanate system increases when the content of copper oxide increase from 2% to 4%. This can be explained that copper oxide can influence the pyrogenation process of EP/IFR/Titanate system, which result in reducing the combustible volatile gas and improve the residual charring, so it can reduce the smoke produced; however overdose of copper oxide will deteriorate the compatibility of EP and IFR, which reduce the smoke suppression effect of copper oxide. The detailed mechanism will describe elsewhere.

IV. CONCLUSIONS

Manganese dioxide is effective smoke suppressant to decrease the smoke density rate (SDR) of EP/IFR/Titanate system, however it has little effect to reduce the maximum smoke density (MSD) of EP/IFR/Titanate system. Copper oxide can decrease the maximum smoke density (MSD) and smoke density rate of EP/IFR/Titanate system substantially. The MSD and SDR of EP/IFR/Titanate system can reduce 20.3% and 39.1% respectively when 2% of copper oxide is introduced.

REFERENCES

[1] Y. Yin, Y. Xia, X. G. Jian, “Progress in research of halogen free flame retardant epoxy resin (in Chinese)” , Engineering Plastics Application, Vol. 35, no. 9, pp: 76-79, Sep. 2007.
[2] Y. B. Li, X. Y. Zhang, Z. G. Zhang, W. H. Zhong, “Development of flame retardant technology of epoxy resin (in Chinese)” , China Synthetic Resin and Plastics, Vol. 19, no. 2, pp:53-57, April 2002.
[3] D. T. Zhu, “Phosphorated epoxy resin for halogen-free and fire retardant copper clad laminate(in Chinese)”, Insulating materials, no. 5, pp: 61-64, Oct. 2004.
[4] W. Y. Chen, Y. Z. Wang, F. C. Chang, “Thermal and flame retardation properties of melamine phosphate-modified epoxy resins”, Journal of polymer Research, Vol. 11, no. 2, pp: 109-117, June 2004.
[5] D. Dollimore, J. M. Hoath, “The fire retardant behavior of various chlorides on cellulose”, Thermal Analysis and calorimetry, Vol. 49, no. 2, pp: 649-656, June 1997.
[6] X. W. Jia, Z. G. Liu, X. M. Fang, T. Ding, Y. Q. Xu, “Thermal characteristics and applications of flame retardants of borminated epoxy resins(in Chinese)”, China Plastics, Vol. 18, no. 12, pp:70-73, Dec. 2004.
[7] Z. P. Wu, W. Y. Shu, Y. C. Hu, “Synergist flame retarding effect of ultrafine zinc borate on LDPE/IFR system”, Journal of Applied Polymer Science, Vol. 103, no. 6, pp: 3667-3674, March 2007.
[8] J. G. Liu, D. S. Wang, L. Fan, S. Y. Yang, “Research and development progress in environment-friendly epoxy resin compounds without halogen, antimony and phosphorus (in Chinese)”, Thermosetting Resin, Vol. 19, no. 4, pp: 23-28, July 2004.
[9] M. Modesti, A. Lorenzetti, F. Simioni, “Expandable graphite as an intumescent flame retardant in polyisocyanurate-polyurethane foams”, Polymer Degradation and Stability, Vol. 77, no.2, pp: 195-202, March 2002.
[10] M. Gao, W. Wu, Y.Yan, “Thermal degradation and flame retardancy of epoxy resin containing intumescent flame retardant”, Journal of thermal analysis and calorimetry, Vol. 95, no. 2, pp: 605-608, Feb. 2009.
[11] Z. L. Zhang, Y. k. Zheng, L. B. GU, “Halogen free Intumescent Flame Retardanted System for LDPE (in Chinese)”, Plastics, Vol. 29,no. 3, pp: 15-21, March 2000.
[12] S. Y. Xiao, Z. R. Yang, H. Q. Chen, “Progress of studies on intumescent flame retardant (in Chinese)”, Chemical industry and engineering Vol. 17, no. 6, pp: 369-371, Dec.2000.
[13] Z. P. Wu, M. Q. Chen, Y. C. Hu, “Study of the epoxy resin treated with intumescent flame retardant contained microencapsulated red phosphorus(in Chinese)”, Journal of Central South University of Forestry & Technology, Vol. 29, no. 6, pp: 61-64, Dec. 2009.
[14] M. Q. Chen, Z. P. Wu, Y. C. Hu, H. K. Yang, “Preparation and application of intumescent flame retardant of microencapsulated red phosphorus(in Chinese)”, Plastics Science and Technology, Vol. 37, no. 5, pp: 82-85, May 2009.
[15] Sunil K. Sharma, N. K. Saxena, “Surface coating and metal-based organic additives-approaches for FRSS PVC cables”, Journal of Fire Sciences Vol. 25, no. 5, pp: 447-466, 2007.
[16] Z. H. Zhang, M. F. Zhu, B. Sun, Q. H. Zhang, C. M. Yan, S. M. Fang, “The effect of hydrotalcite and zinc oxide on smoke suppression of commercial rigid PVC”, Journal of Macromolecular Science. Pure and Applied Chemistry, Vol. 43, no. 11, pp: 1807-1814, 2006.
[17] S. M. Grimes, H. Lateef, A. J. Jafari, L. Mehta, “Studies of the effects of copper, copper(II) oxide and copper(II) chloride on the thermal degradation of poly(vinyl chloride)”, Polymer Degradation and Stability, Vol. 91, no. 12, pp: 3271-3280, Dec. 2006