Asian Journal of Chemistry; Vol. 27, No. 2 (2015), 621-624

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.17080

Thermal Degradation Mechanism of UV Curable Intumescent Flame Retardant Coating Based on Acryloyloxyethylneopentyl Phosphate

YANYU LIU, HONGBO LIANG*, LEI XIONG* and SHENGMEI HUANG

School of Material Science and Engineering, Nanchang Hangkong University, Nanchang 330063, P.R. China

*Corresponding authors: Tel: +86 791 83863025; E-mail: liahongbo@163.com; x_lei81@163.com

Received: 20 January 2014; *Accepted*: 10 April 2014; *Published online*: 10 January 2015; AJC-16632

In this work, series of UV curable intumescent flame retardants were prepared by blending acryloyloxyethylneopentyl phosphate with methacrylated phenolic melamine and pentaerythritol triacrylate. The thermal degradation mechanism of their cured films was studied by thermogravimetric analysis and *in situ* Fourier-transform infrared spectroscopy and a possible mechanism for the thermal degradation was proposed. The limiting oxygen index values of the cured films were measured. The expansion behaviors were also studied by unidirectional expansion degree. The results showed that the ANP/MAPM/PETA (35/25/40, wt/wt/wt) blend ($ANP_{35}MAPM_{25}PETA_{40}$) had the best comprehensive properties among all the samples.

Keywords: Intumescent flame retardant, UV curable, Thermal degradation mechanism, Limiting oxygen index.

INTRODUCTION

Intumescent flame retardant (IFR) has aroused widely concern due to its halogen free, low smoke, low toxicity and no melt dripping during combustion and it is applied to a wide variety of substrates, such as wood, plastic and metallic materials[1-5]. However, traditional additive intumescent flame retardant has some disadvantages, such as low compatibility with matrix resin and heavy loading, which deteriorate the UV stability and mechanical properties of coating greatly. Thus, the types and flame retardancy of intumescent flame retardant needs to be improved further[6-10].

In this study, a novel UV curable intumescent flame retardant system was prepared by blending acryloyloxyethylneopentyl phosphate (ANP), which was synthesized in previous work[11], with methacrylated phenolic melamine (MAPM) and pentaerythritol triacrylate (PETA) in different ratios. Their degradation process was monitored by thermogravimetric analysis and *in situ* fourier-transform infrared spectroscopy. The expansion behaviour was studied with unidirectional expansion degrees and char layer intensity values. The flame-retardant property of these resins was studied with limiting oxygen index (LOI) values.

EXPERIMENTAL

All reagents, purchased from the Shanghai First Reagent Co., China, were used without further purification. 2-Hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173) and phenylbis-(2,4,6-trimethylbenzoyl) phosphine oxide (Irgacure 819), kindly supplied by Ciba-Geigy Switzerland, were used as photoinitiators. Pentaerythritol triacrylate was purchased from Eternal Chemical Taiwan Co. Acryloyloxyethylneopentyl phosphate and methacrylated phenolic melamine were synthesized according to the reference[11,12].

Sample preparation: The mixtures of acryloyloxyethylneopentyl phosphate (ANP), methacrylated phenolic melamine (MAPM) and pentaerythritol triacrylate (PETA) in different ratios were stirred thoroughly to get various homogenous blends. Then the blends were exposed to a UV irradiation equipment in the presence of 3 wt % hybrid photoinitiators (2.25 wt % darocur 1173 and 0.75 wt % irgacure 819) and the cured films were obtained. The ultraviolet light source used for irradiation is a lamp (80 mW/cm^2, LantianTedeng Co., China), which emits light in the near UV (characterized wavelength, 100-150 nm). The distance between the samples and UV lamp was 10 cm and the exposure time was about 30 s. The formulations of blends are listed in Table-1.

The TG analysis was analyzed by Pyris 1 thermogravimetric analysis (TGA) analyzer (Perkin Elmer Co., USA), which was performed from 30 to 800 °C at heating rate of 20 °C/min under nitrogen. The limiting oxygen index values of the cured films were measured by using a HC-2 instrument on sheets of 120 × 6 × 3 mm^3 according to ASTM D2863-77. The thermal degradation of samples was analyzed by using Nicolet 5700 FTIR spectrometer with a muffle furnace and the temperature of the furnace was raised at a heating rate of

TABLE-1
COMPOSITIONS, TGA RESULTS AND THE LIMITING OXYGEN INDEX VALUES OF ANP/MAPM/PETA CURED FILMS

Sample	ANP (wt %)	MAPM (wt %)	PETA (wt %)	5 % Weight loss temperature (°C)	Char yield at 800 °C (%)	LOI
$ANP_{20}MAPM_{60}PETA_{20}$	20	60	20	254.89	24.24	25
$ANP_{30}MAPM_{50}PETA_{20}$	30	50	20	218.5	24.42	25.5
$ANP_{30}MAPM_{60}PETA_{10}$	30	60	10	216.53	25.29	26.5
$ANP_{35}MAPM_{25}PETA_{40}$	35	25	40	154.15	26.82	29.5
$ANP_{40}MAPM_{20}PETA_{40}$	40	20	40	156.21	25.27	28
$ANP_{45}MAPM_{25}PETA_{30}$	45	25	30	143.10	24.48	27

ANP: acryloyloxyethylneopentyl phosphate; MAPM: methacrylated phenolic melamine; PETA: pentaerythritol triacrylate; LOI: limiting oxygen index; TGA: thermogravimetric analysis

20 °C/min. The thermal degradation images of the mixture were recorded by a digital camera eyepiece (DCE-1, Ningbo-Xinzhi Co., China). The unidirectional expansion degree of ANP/MAPM/PETA cured films was obtained through measuring the thicknesses of the cured films before and after burning. The char layer intensity was characterized through measuring the ultimate collapse strength of carbon layer.

RESULTS AND DISCUSSION

Thermal degradation behaviour: The composition of cured resins and the limiting oxygen index values, as well the 5 % weight loss temperature and the char yield at 800 °C of cured films are given in Table-1. It can be seen that the limiting oxygen index and char residue of cured films first increase and then decrease after reaching a maximum value with increasing acryloyloxyethylneopentyl phosphate content. Generally, phosphorus and nitrogen component in a flame retardant system possess a synergistic effect during combustion and pentaerythritol triacrylate is a major contribution to the char yield as charring agent. Accordingly, $ANP_{35}MAPM_{25}PETA_{40}$ has the best retardant and char forming properties.

The TGA curves of six formulations in nitrogen are showed in Fig. 1. Fig. 1 showed that the weight loss before 300 °C increased from 6.7 to 18.2 % with the increase of the content of acryloyloxyethylneopentyl phosphate, which can be assumed to the lower decomposition temperature of acryloyloxyethylneopentyl phosphate. There is a weight loss of 52 to 64 % between 300 and 500 °C of all formulations, which may be ascribed to the emissions of nonflammable gas. It can be found that the thermal decomposition of ANP/MAPM/PETA cured films can be divided into three steps. The first step is from 160 to 270 °C, the second step occurs between 270 and 380 °C and the third step is in range of 380 to 520 °C.

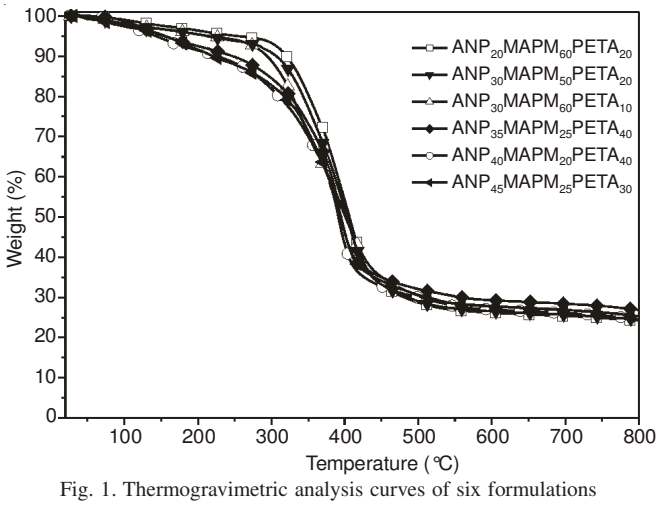

Fig. 1. Thermogravimetric analysis curves of six formulations

The specific degradation temperatures and the final char yields at 800 °C are listed in Table-1. The char yield of the $ANP_{35}MAPM_{25}PETA_{40}$ is 26.82 % at 800 °C, which is the highest among on all formulae. In order to further investigate the degradation mechanism, the *in situ* FTIR of the acryloyloxyethylneopentyl phosphate and $ANP_{35}MAPM_{25}PETA_{40}$ were implemented.

Degradation mechanism: The thermal degradation process of cured acryloyloxyethylneopentyl phosphate sample was characterized by *in situ* FTIR, which could provide the structure changes of the condensed phase. The FTIR spectra of acryloyloxyethylneopentyl phosphate under different temperature are shown in Fig. 2. The peaks at 1050, 1010, 984 and 852 cm^{-1} are completely disappeared at 300 °C, which clearly indicate the complete degradation of the P-O-C groups. The stretching vibration of C=O bond at 1730 cm^{-1} is disappeared before 400 °C. This indicates that the ester groups are decomposed between 300 and 400 °C after the degradation of phosphate groups. Meanwhile, the new peak at 1630 cm^{-1} can be assigned to C=C bond, as temperature raise to 700 °C. The peak at 1630 cm^{-1} disappeared and a new peak at 1580 cm^{-1} appeared, which indicates the generation of some complexes polycyclic. At 500 °C, the stretching of C-H_2 at 2920 cm^{-1} and the deformation vibration of C-H at 1470 and 1380 cm^{-1} are all disappeared, which indicates the complete degradation of alkyl chain. In summary, the decomposition of the cured acryloyloxyethylneopentyl phosphate film can be divided into

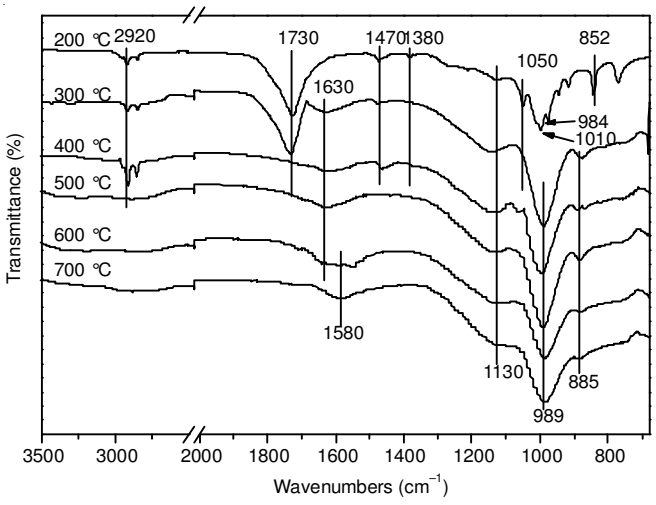

Fig. 2. *in situ* FTIR spectra for degradation process of acryloyloxyethylneopentyl phosphate under different temperature

three parts, including the degradation of phosphate groups, the degradation of ester groups and the degradation of alkyl chain, which is similar to the experimental results of Chen *et al.*[13].

The chemical structure changes during the thermal degradation of cured $ANP_{35}MAPM_{25}PETA_{40}$ film were monitored by *in situ* FTIR. The spectra are shown in Fig. 3. There is little change in the absorption peaks of the FTIR spectra before 300 °C, which is consistent with the TGA result. The peaks at 1733 and 1150 cm^{-1} can be assigned to the vibration of ester C=O bond, almost disappear at 300 °C. In addition, a new peak around 1700 cm^{-1} can be assigned to the stretching vibration of carboxylic acid occurs at 300 °C. This indicates that the ester bond degrades before 300 °C, resulting in the formation of acid. The peak around 1592 cm^{-1} can be assigned to the triazine-ring stretch of melamine, it becomes more clear above 300 °C and decreases slowly after 500 °C. This indicates that the side chain of melamine group in methacrylated phenolic melamine is less stable than triazine-ring and will be further thermally condensed with the eliminated nitrogen volatile[11]. The *in situ* FTIR result is not only a good analysis of the degradation process, but also a good description for the thermal gravimetric analysis results.

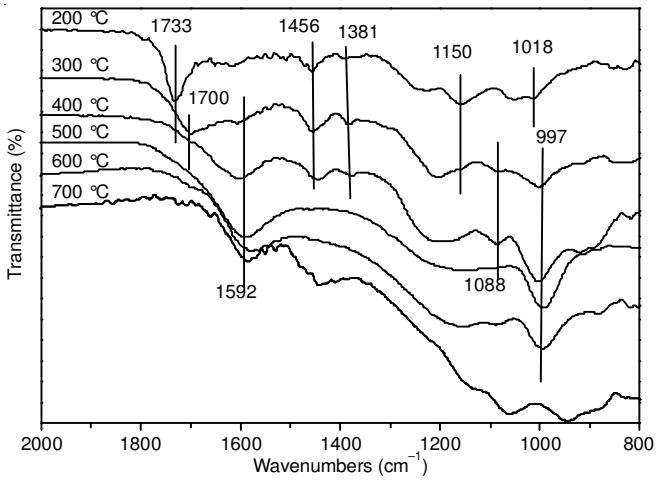

Fig. 3. FTIR spectra of cured $ANP_{35}MAPM_{25}PETA_{40}$ film during the thermal degradation in the range of 200 to 700 °C

Comprehensive analysis of the TGA and FTIR of $ANP_{35}MAPM_{25}PETA_{40}$, it can be drawn that the degradation mechanism of ANP/MAPM/PETA cured films shows a three steps of the thermal decomposition. The first step from 160 to 270 °C can be assigned to the decomposition of phosphate. The second step occurs between 270 and 380 °C. In this temperature range, polyphosphoric acid is formed and methacrylated phenolic melamine degrades to form melamine at 300 °C and melamine then further degraded into triazine-ring. Third step is the further decomposition of the triazine-ring and unstable structures may be degraded into non-flammable gas in the temperature range of 380 to 520 °C. The gas release during thermal degradation contributes to the weight loss.

Expansion behaviour: The digital photos of the specimens after heated under different temperatures from 200 to 700 °C are shown in Fig. 4. It can be found that there is no obvious swell before 300 °C, which is due to the degradable ingredients before 300 °C are main phosphate and there is not enough gas produced for expanding. Photoes of 400 and 500 °C have a greater degree of expansion because of the degradation of methacrylated phenolic melamine between 300 and 500 °C and a large number of non-combustible gases are released to make the specimens swell quickly, the maximum degree of expansion reached at 400 °C. As the temperature is above 500 °C, the carbon layer decreases gradually, this can be seen from the TGA curve. This indicates that the expansion process occurs mainly between 300 and 400 °C.

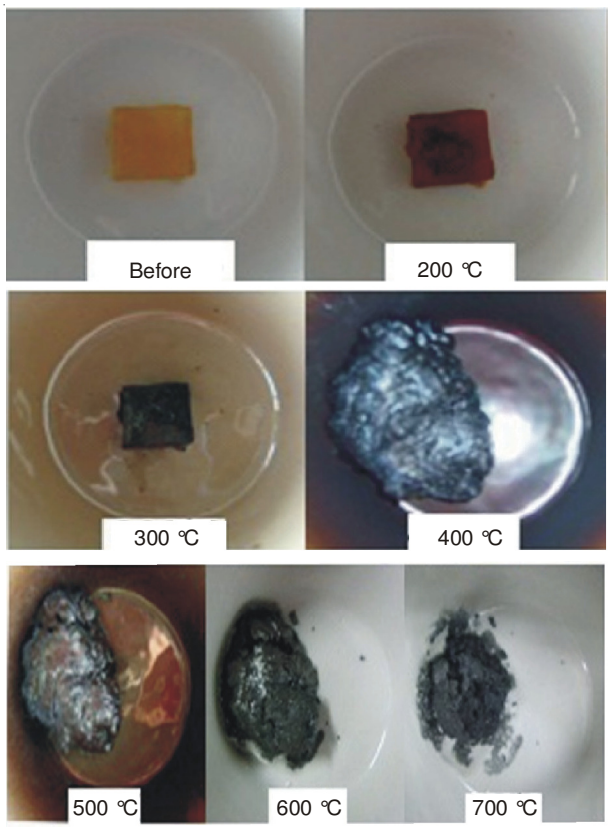

Fig. 4. Digital photoes of the $ANP_{35}MAPM_{25}PETA_{40}$ formula unheated and heated from 200 to 700 °C

The expansion degrees and char layer intensity values of the cured films are presented in Table-2. It can be seen that the unidirectional expansion degree increase with increasing methacrylated phenolic melamine content. With the addition of acryloyloxyethylneopentyl phosphate, char layer intensity values firstly increase and then decrease. The results indicate that methacrylated phenolic melamine plays more important role on expansion. However, excess methacrylated phenolic melamine addition degrades with excess gas emission, which causes the decrease of char layer intensity. Among all samples, $ANP_{35}MAPM_{25}PETA_{40}$ has the best expansion properties, which is similar with the flame retardant properties.

Conclusion

A series of UV curable intumescent flame retardant resins were obtained by blending acryloyloxyethylneopentyl phosphate (ANP, methacrylated phenolic melamine (MAPM) and pentaerythritol triacrylate (PETA) in different ratios and the resulted cured films displayed high flame resistance. The

TABLE-2
EXPANSION DEGREES AND CHAR LAYER INTENSITY VALUES OF FILMS

Sample	Film thickness (mm)		Unidirectional expansion degrees	Char layer intensity (KPa)
	Before burning	After burning		
$ANP_{20}MAPM_{60}PETA_{20}$	0.44	4.64	10.5	1.48
$ANP_{30}MAPM_{50}PETA_{20}$	0.56	4.44	7.7	1.73
$ANP_{30}MAPM_{60}PETA_{10}$	0.44	2.78	10.1	1.75
$ANP_{35}MAPM_{25}PETA_{40}$	0.58	4.26	7.76	2.20
$ANP_{40}MAPM_{20}PETA_{40}$	0.38	4.48	7.3	1.94
$ANP_{45}MAPM_{25}PETA_{30}$	0.70	4.5	6.4	1.81

ANP: acryloyloxyethylneopentyl phosphate; MAPM: methacrylated phenolic melamine; PETA: pentaerythritol triacrylate; LOI: limiting oxygen index

$ANP_{35}MAPM_{25}PETA_{40}$ blend shows the best flame retardance with limiting oxygen index value of 29.5. Thermal degradation behaviour shows that acryloyloxyethylneopentyl phosphate first degraded into phosphate to catalyze the degradation of the blend to form char. Simultaneously, methacrylated phenolic melamine degraded to form nitrogen volatiles, which were wrapped by the char and thus the cured films expanded mainly between 300 and 400 °C.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China (No. 51103069), Foundation of Jiangxi Educational Committe (No. GJJ12423), Natural Science Foundation of Jiangxi Province (No. 20122BAB216014) and Foundation of Aeronautics of China (No. 2011ZF56018).

REFERENCES

1. H.B. Liang, W.F. Shi and M. Gong, *Polym. Degrad. Stab*., **90**, 1 (2005).
2. Y. Chen, Y. Liu, Q. Wang, H. Yin, N. Aelmans and R. Kierkels, *Polym. Degrad. Stab*., **81**, 215 (2003).
3. Y. Cao, Y. Chen, L. Lu, Z. Xue and T. Mu, *Ind. Eng. Chem. Res*., **52**, 2073 (2013).
4. K. Cao, S.L. Wu, K.L. Wang and Z. Yao, *Ind. Eng. Chem. Res*., **50**, 8402 (2011).
5. Z.Z. Wang, K. Wu and Y. Hu, *Polym. Eng. Sci*., **48**, 2426 (2008).
6. Y.J. Chen, J. Zhan, P. Zhang, S.B. Nie, H.D. Lu, L. Song and Y. Hu, *Ind. Eng. Chem. Res*., **49**, 8200 (2010).
7. S. Bourbigot and S. Duquesne, *Mater. Chem*., **17**, 2283 (2007).
8. S. Bourbigot, M. Le Bras, S. Duquesne and M. Rochery, *Macromol. Mater. Eng*., **289**, 499 (2004).
9. L.J. Chen, L. Song, P. Lv, G.X. Jie, Q.L. Tai, W.Y. Xing and Y. Hu, *Prog. Org. Coat*., **70**, 59 (2011).
10. Y.X. Wang and H.W. Jiang, *Acta. Polym. Sin*, **9**, 325 (2009).
11. Y.M. Chen, H.B. Liang and L. Xiong, *Inform. Recording Mater*., **11**, 29 (2010).
12. H. Liang, A. Asif and W. Shi, *Polym. Degrad. Stab*., **87**, 495 (2005).
13. X.L. Chen, Y. Hu, C.M. Jiao and L. Song, *Prog. Org. Coat*., **59**, 318 (2007).