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XPS analysis of char residue from an intumescent flame retardant rigid PU composite foam

Ting Zheng[1,2], Linying Yang[1], Peibang Dai1*, Chang Qin[1], QichenTang[1]

1. School of Materials Science and Engineering, Guilin University of Electronic Technology, Guilin 541004, P.R.China,
2. Guilin institute of intelligence science and technology, Guilin 541004, P.R.China
*E-mail: daipeibang@163.com

Abstract: A flame retarded rigid PU foam was prepared using polyols and diisocyanates with a modified intumescent flame retardant (MIFR) via polyoxyethylene nonylphenol ether (surfactant TX-10). The MIFR included a new carbon source, calcium 3-hydroxy-2, 2-bis(hydroxymethyl) propyl phosphate. The carbon residue from the flame retardant rigid PU foams after UL-94 test was investigated with XPS. The data showed that the addition of MIFR into PU foams could promote formation of pure carbon char and P-C bond.

Keywords: Polyurethane; Intumescent flame retardant; Composite

1. Introduction

A traditional intumescent flame retardant (IFR) system contains generally three components that are the basic elements to form a char: acid donor (ammonium polyphosphate, APP), blowing agent (melamine, MA) and carbon donor (pentaerythritol). Material containing such flame retardant system will form a char layer at the surface during combustion to protect the material [1-4]. IFR is normally used as fire proof coating. In recent years, it has been added into polymer materials as flame retardant due to its superior flame retardant effect. A great amount of papers have reported flammability of intumescent flame retardant polymer composites, i.e. flame retarded polypropylene, polyethylene, poly[ethylene-co-(vinyl acetate) and ABS, etc., which were prepared by incorporating the components of intumescent flame retardant into the polymers directly.

However, high loading level of IFR is needed in flame retardant polymer composites for achieving superior flame retardancy. When high content of IFR is used, the mechanical and environmental durability of the materials can be severely degraded. It also causes an increase to the viscosity of the polymer melt which make processing more difficult. IFR systems are particularly sensitive to processing conditions and exhibit a limited processing window. Therefore, surface-modification is needed for intumescent flame retardant. The study in this paper aims to prepare flame retarded a rigid PU foam using polyols and diisocyanates with a modified intumescent flame retardant (MIFR) via surfactant TX-10 and investigate the carbon residue from the flame retardant rigid PU foams after UL-94 test. The MIFR included a new carbon source, calcium 3-hydroxy-2, 2-bis(hydroxymethyl) propyl phosphate.

2. Experimental

The MIFR included calcium 3-hydroxy-2, 2-bis(hydroxymethyl) propyl phosphate, APP and melamine and was modified with TX-10 via water solution method.

The MIFR were added into the compound of polyols and diisocyanates(the ratio is 1.0:1.0) and stirred for 1 minutes at high speed. After mixing, the mixture was molded under ambient temperature for 8 minutes to sheets of suitable thickness.

The UL-94 vertical burning tests were carried out using a CZF-1 type instrument (made in China) on the sheets of 127×12.7×3.0mm3 according to the standard UL-94 test ASTM D635.

The XPS characterization of the residue composition and chemistry was carried out on a XSAM800 System (Kratos Campany, UK) using Al Kα radiation.

3. Results and discussion

3.1 Flame retardancy

Table1 shows the effects of MIFR on the flame retardancy of the PU flame retardant composite foams. The formulation containing more than 22.5wt% MIFR was V-0 rating for UL-94 test while the formulation with 20.0wt% MIFRC could only pass V-2 rating of UL-94 test. The formulation containing less than 15.00wt% MIFR as well as the formulation no MIFR could not pass UL-94 test. When the formulations contained MIFR more than 20.0%, the flame retardancy of the flame retardant PU composite foams were improved effectively.

Table 1. Flame retardancy of flame retardant PU foams.

Sample	MIFR content(%)	UL-94 rating
PU	0	No Rating
PU/MIFR10	10.0	No rating
PU/MIFR20.0	20.0	V-2
PU/MIFR22.5	22.5	V-0

3.2 Char Residue Analysis

The chemical composition of residues from PU10.0 and PU/MIFR22.5 was quantitatively analyzed by XPS measurement. The composition of the residue is summarizes in Table2 and Figure1 illustrates single XPS spectra. For the two samples an additional broad phosphorus signal at between 137.0-131.0eV was detected and could be interpreted as an overlapping of peaks from phosphorus-oxygen species, such as metaphosphate(≈134.5eV), pyrophosphate(≈133eV) and phosphate(≈132.5eV). The carbon signal with a peak at 285eV identified the benzene hydrocarbon. The nitrogen peak at between 397eV and 403eV identified –CN and $-NH_2$ groups. Analysis of the phosphorus signal showed that different phosphorus species existed in PU/MIFR22.5 compared with in PU/MIFR10. The position of the peak between 131.5-137.5eV could be interpreted as an overlapping of peaks from phosphorus-oxygen species. The position of the shoulder between 129.0-132.0eV fits well with XPS features of phosphorus-carbon species (≈131eV). Analogous to PU/MIFR10, the carbon spectrum identified the benzene hydrocarbon and carbon

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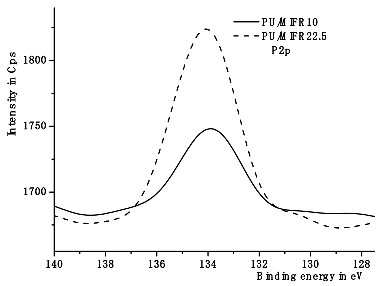
impurity. A shoulder peak between 283eV and 288eV indicated pure carbon char in good correspondence to the inhomogeneous black and grey color of the residue [4]. The nitrogen peak at between 397eV and 403eV identified –CN and $-NH_2$. Another nitrogen signal with a peak at 406eV indicated $-NO_2$.

Table 2. Chemical composition of the residue by XPS measurements.

Sample	Carbon (%)	Phosphorus (%)	Oxygen (%)	Nitrogen (%)	Calcium (%)
PU/MIFR10	59.72	14.24	23.85	2.19	
PU/MIFR22.5	58.31	19.66	15.69	4.05	2.29



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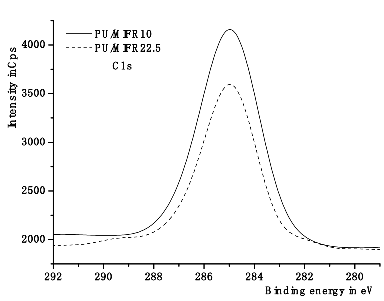

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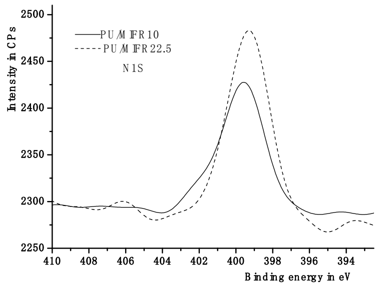

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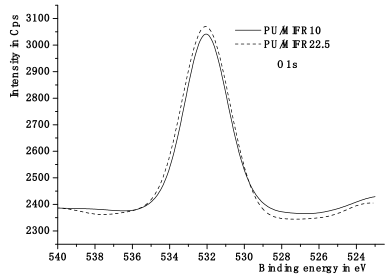

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Fig 1. XPS spectra of residue char obtained from PU/MIFR10 and PU/MIFR22.5.

4. Conclusion

A surface-modified intumescent flame retardant (MIFR) was prepared by compounding ammonium polyphosphate, melamine and Calsium 3-hydroxy-2, 2-bis(hydroxymethyl) propyl phosphate with TX-10 surfactant. The carbon residue from the flame retardant rigid PU foams after UL-94 test was investigated with XPS. The XPS characterization of the residue composition and chemistry revealed that a suitable amount of MIFR into PU foams could promote formation of pure carbon char and P-C bond.

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