

Study on Gas Phase Long-Lived Radicals in Modified Polyurethane Combustion and Decomposition

Y HU, W FAN and Q WANG

State Key Laboratory of Fire Science
University of Science and Technology of China
Hefei, Anhui 230026, China

Y AKUTSU and M TAMURA

Department of chemical System Engineering
The University of Tokyo
Hongo 7-3-1, Bunkyo-ku, Tokyo 113, Japan

ABSTRACT

Combustion and decomposition properties in polyurethane modified by flame retardant were investigated using the electron spin resonance(ESR) spin-trapping technique and thermogravimetry(TG). The long lived gas phase radicals in combustion and decomposition products of polyurethane were studied. It was shown that the concentration of radicals in combustion was reduced by adding hexachlorotriphosphazene containing chlorine, and also thermal decomposition in polyurethane was accelerated by phosphazene.

Keywords: polyurethane, flame retardant, radical

INTRODUCTION

Polyurethane(PU) Foams are widely used as construction components in upholstered furniture, bedding, transportation seating and building insulation systems. Polyurethane is easy to combustion, so there is concern about the products of combustion formed when these compounds are involved in either accidental or deliberate fires. People pay close attention to its fire-resistant property. The combustion products of most fires include heat, visible smoke, and a number of gaseous compounds. Usually polyurethane foams fire can produce CO, CO₂, NO_x, HCN and organic compounds. When Flame retardants are added into polyurethane, the products of PU combustion can be changed, so people hope that the toxic products can be reduced when flame retardants are added into PU for improving fire resistant property. Many researches have done work on these fields^[1-2].

However, Lowry et al.^[3-5] showed that, during the initial stage of combustion, fatal levels of toxic gas-phase radicals might be produced under certain combustion conditions. This suggests the presence of transient, highly toxic species that are produced by the interaction of gaseous components and that lead to incapacitation and or death in fire. Free radicals are produced in the combustion of many organic materials. Lowry have suggested that transient free radicals in smoke are responsible for these unexplained incapacitations and deaths. Gas phase radicals are reported to be a new kind of toxic material.

In this paper, we'll mainly study on its radical and mechanism of decomposition of PU modified by flame retardants. One kind of flame retardant was added directly into reaction system, and the other containing OH group was grafted to PU. All polyurethane was placed at different conditions for combustion and decomposition. Because oxygen concentration and burning temperature could be changed in fire, different temperature and oxygen concentration were chosen. Free radical in the smoke of PU had been detected by electron spin resonance (ESR) spin tripping technique by using a *p*-phenyl-*N*-tert-butylnitron(PBN)

as the spin trap. As a result, we found flame retardants changed radical concentration and decomposition procedure.

EXPERIMENTAL SECTION

Materials and Equipment

α -phenyl-N-tert-butyl nitron (PBN) from Aldrich was used for spin trapping without further purification. Special grade benzene obtained from Wako was purified by concentrated sulfuric acid and then distilled. 2,2,6,6-tetramethyl-4-oxopiperidinoxy was obtained from Aldrich and used as standard to determine the radical concentrations. ESR spectra were recorded on a JOEL FEIX spectrometer, the microwave power was 5mW, the modulation amplitude was 0.5G and the modulation frequency was 100kHz, a 0.1-s time constant was used with a 4-min scan time and a 50G scan range. Thermal analysis was done on TGD7000, rate 10°C/min, gas flow 120ml/min.

Preparation of $(\text{NPCl}_2)_3$ (CTPP)^[6-7]: Hexachlorocyclotriphosphazene (trimer) was synthesized from PCl_5 and NH_4Cl in $\text{Cl}_2\text{CH}_2\text{CH}_2\text{Cl}_2$ at catalyst ZnCl_2 , the purity trimer could be obtained by successive vacuum sublimation and recrystallization (n-heptane).

Preparation of $\text{N}_3\text{P}_3(\text{OPhCH}_2\text{OH})_6$ (HCTPP)^[8]: (a) $\text{N}_3\text{P}_3(\text{OPhCHO})_6$ was first prepared according to the literature; (b) hexa(4'-hydroxy-methylphenoxy)cyclotriphosphazene $\text{N}_3\text{P}_3(\text{OPhCH}_2\text{OH})_6$ was prepared by hydrogenation reaction of $\text{N}_3\text{P}_3(\text{OPhCHO})_6$ in tetrahydrofuran-methanol(1:1) by using sodium borohydride.

Preparation of modified Polyurethane:

PU compositions(wt%): Polyether 100, Diisocyanatoluene(TDI)(80/20) 36, H_2O 3, Triethylenediamine 0.16, Dibutyl tin dilaurin(DBTDL) 0.06, Silicone oil 0.8, Phosphazene compound 4.8.

Technological parameter: Raw material temperature 20-25°C, Mold temperature 45-70°C, TDI index 105, Stirring speed 3000R/min, Free foam method.

Combustion Experiment

Figure 1 showed an apparatus for gas-phase radicals from combustion and their trapping system. A 36mm × 700mm quartz tube was placed in a 40mm × 400mm electric furnace maintained at 200°C, 400°C, 600°C, 800°C. A 0.25g sample of PU in an alumina boat was quickly placed in the center of the quartz tube and then decomposed and ignited. A mixed gas of O_2 and N_2 was supplied through the quartz tube (500ml/min) to support burning and to carry away all combustion products. Part of the smoke produced was passed through the Cambridge filter to remove most of the tars and particles. The smoke was then passed through a vessel containing 4ml of benzene containing PBN for 30s (250ml/min) using a suction pump. It was then preserved in a cold medium(-78°C). About 0.5ml of the solution was transferred to a standard cylindrical ESR tube and degassed using a vacuum pump.

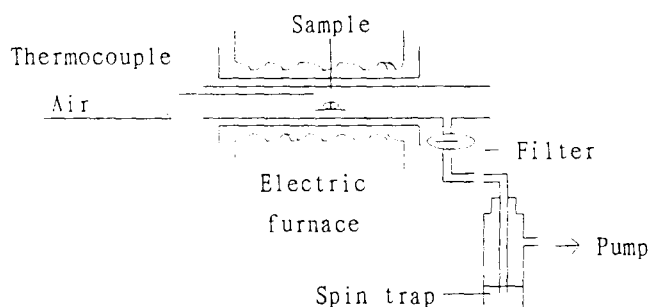


Figure 1. Apparatus for gas-phase radicals from combustion and their trapping system

RESULTS AND DISCUSSION

Sample Analysis

When Hexachlorocyclotriphosphazene(CTPP) and hexa(4'-hydroxy-methyl-phenoxy)cyclotriphosphazene(HCTPP) were added into PU monomer reaction, CTPP was mixed with PU only. When HCTPP was added into PU monomer TDI in catalyst DBTAL at mold temperature 60-70 °C for 30 minutes, there was 1547 cm^{-1} strong IR absorption peak(-NH curved vibration). It showed that HCTPP could react with PU monomer TDI, and be grafted into PU system.

ESR Analysis

Fig. 2 was typical ESR spectra observed from the combustion smoke of PU system in air at 600 °C. According to height and area of ESR peak, when CTPP was added into PU, it decreased the peak height and area, so it could inhibit production of the long live gas phase radicals. When HCTPP was added into PU, it increased the peak height and area, so it could increase production of the long lived gas phase radicals.

Table 1 showed concentration of gas-phase radicals, which was obtained by ESR spectra simulation^[9]. And there were more

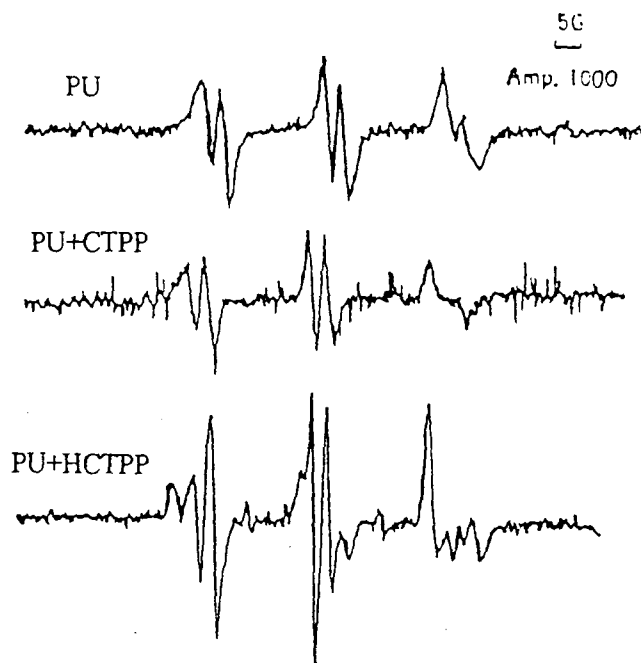


Figure 2 typical ESR spectra observed from the combustion smoke of PU system in air at 600 °C

than one kind of radical species in data underlined, its analytical results were arranged in table 2. There were little changed in gas phase radical concentration at 200 °C and 400 °C, because dissociation energy of C-C, C-H, C-O, and P-X bonds is about 376KJ/mol^[10], it needs 450 °C to 600 °C for dissociation, so radical concentration was changed little at low temperature.

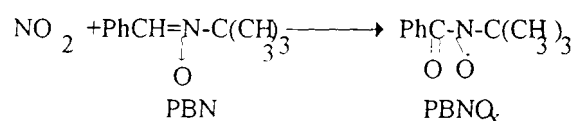
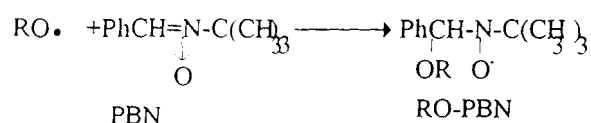
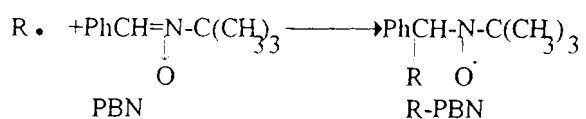
Table 1 Radical concentration in gas phase (ppm)

No.	Air				O ₂ (18.4%)+N ₂ (81.6%)			
	200°C	400°C	600°C	800°C	200°C	400°C	600°C	800°C
PU	0.026	0.037	0.110	0.381	0.028	0.047	0.110	0.182
PU+CTPP	0.026	0.036	0.070	0.048	0.028	0.047	0.082	0.059
PU+HCTPP	0.026	0.026	0.430	0.105	0.019	0.019	0.075	0.101

Table 2 Analysis of ESR spectra in PU series

T (°C)	No.	a _{N/G} a _{H/G} mol%				Radical species
		Air		O ₂ (18.4%)+N ₂		
600	PU	13.1	1.7	100	100	Alkoxy
600	PU+ HCTPP	13.1	1.7	40	73	Alkoxy
		14.9	4.4	58	27	unknown
		7.4		2	0	PBN-oxy
800	PU	13.1	1.7	78	77	Alkoxy
		14.9	4.4	22	23	unknown
800	PU+ HCTPP	13.1	1.7	71	70	Alkoxy
		14.9	4.4	29	30	unknown

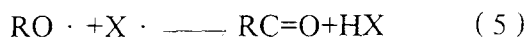
At 600 °C, there was one kind of radical species in PU and PU+CTPP combustion, but three kinds of radical species in PU+HCTPP. At 800 °C, it was shown that there was one kind of radical species in PU+CTPP and two kinds of radical species in PU and PU+HCTPP. Usually, PBN scavenger could react with radical as follows:



Gas-phase radicals could be produced from burning of PU series, which they first formed R ·, and then combined with oxygen to form ROO · and RO ·, and there was the following equation:



At 600 °C, Radical concentration from PU ESR spectrum was reduced by adding CTPP, because CTPP could give out HCL during heating and burning, there were some reaction equations between HCL and radicals:



so they caused radical concentration to decrease. But HCTPP, which didn't contain chlorine, could promote decomposition of PU and produce more RO· radical.

At 800 °C, because heat provided much energy to PU decomposition and burning, it produced more RO· and other radical species and increased radical concentration in pure PU. When phosphazene compounds were added into PU system, there were two reaction equations. One equation was that heat provided much energy to decompose and burn, it produced more radicals. The another equation was that flame retardant promoted PU to cross char, it decreased radical concentration. When there were flame retardants in PU at 800 °C, maybe the second equation occupied dominant position, so radical concentration began to decrease.

When materials were burned in limited space, oxygen concentration should decrease due to an increase in decomposition and burning products and temperature, so low oxygen concentration[O₂(18.4%)+N₂(81.6%)] was chosen in experiment. It was shown that there was a same tendency in radical concentration variation in Table1, but total radical concentration was decreased in low oxygen concentration. Because there were three main factors in material combustion, it was fuel, heat and oxygen. When oxygen concentration was decreased, it is difficult to burn and decompose in PU series, and also R· and RO· radicals were decreased. In the meantime, we found that PU series burned more quickly at 800 °C than 600 °C, and decomposition rate was speeded up and radical concentrations were increased.

There were many gases and peroxide radicals including NO₂ and ROO· et al. in PU combustion. They could oxidate PBN to PBNO_x compound while these compounds were drawn into PBN solution. Meanwhile, there was an unknown radical in Table 2, it was maybe Ph· radical from ESR standard spectrum and compound structure, and it also needed more experiment to confirm.

Thermal Analysis

Table 3 showed thermogravimetric analysis results. When phosphazene compounds were added into PU, they changed weight loss procedure and decreased start decomposition temperature and increased final decomposition temperature. There were more residue in PU series, it was easy to form a char film on the surface of PU series. These indicated that there were some fire retardant. At the same time, phosphazene compound increased Limited Oxygen Index (LOI) of PU, HCTPP containing -OH increase LOT more than CTPP. The

main mechanism for flame retardation was that there formed a char and inorganic compound film on the surface of PU and prevented PU from combustion.

Table 3 TG Analysis in PU series

No.	Air					
	Ts (°C)	Tf (°C)	Steps	lossWT (%)	Residue (%)	LOI (%)
PU	214	626	2	98.5	1.5	18.1
PU+ CTPP	82	812	4	92.6	7.4	20.5
PU+ HCTPP	162	635	3	93.7	6.3	20.1

*Ts and Tf indicate the start and final decomposition temperature;

*Steps mean decomposition steps; *Loss WT indicates total weight loss percent;

*LOI(%)=17.5+0.4CR; CR means char residue in Wt% at 850°C^[11].

CONCLUSION

1. Phosphazene trimer(CTPP) could decrease radical concentration during burning of PU;
2. Radical concentrations of PU series were decreased in low oxygen concentration. [O₂ (18.4%)+N₂ (81.6%)].
3. When phosphazene compound containing -OH group was grafted to PU, it could improve fire-resistant of PU more effectively;
4. When phosphazene compounds were added into PU, they could speed up PU decomposition at middle temperature, and increase final decomposition temperature.

REFERENCES

- 1.Herrington R.M.,The rate of heat, smoke and toxic gases release from polyurethane, J Fire &Flammability, 1979; 10, 308-325.
- 2.Prager F.H., Kimmerle G., et al., Toxicity of the combustion and decomposition products of polyurethanes, Fire and Materials, 1994, 18, 107-119.
- 3.Lowry W.T., et al., Free radical production from controlled low-Energy Fires: Toxicity Considerations,J. of Forensic Sci., 1985; 1, 73-85.
- 4.Lachocki T.M., Pryor W.A., Persistent free radicals in the smoke of common household materials:biological and clinical implications, Enviromemtal Research, 1988; 45, 127-139.
- 5.Lachocki T.M., Church D.F., Persistent free radicals in woodsmoke: An ESR spin trapping study, Free Radical Biology&Medicine, 1989, 7, 17-21.
- 6.Lund L G, Paddock N L, The preparation of cyclic and linear phosphonitrilic chlorides. J Chem. Soc., 1960, 2542-2548.
- 7.Hu Yuan, Shao Zonglong, Fan Weicheng et al., Synthesis and Application of Poly(diphenoxyphosphazene), First East-Asian Polymer Conference,1995(10),shanghai.
- 8.Allcock H.R.,et al.,Schiff Base Coupling of Cyclic and High-polymeric phosphazenes to Aldehydes and Amines:Chemotherapeutic models, Macromolecules, 1981, 14, 1616-1622.
- 9.Pryor W A, Davies J A, Free Radical Biology&Medicine, Pergamm Press 1987, 3(4), 273.

10 Robert C.W., Handbook of Chemistry and Physics, 56th, CRC Press, 1975, F215-F219.

11 Van Krevelin D.W., Some Basic aspects of flame resistance of polymeric materials, polymer, 1975, 16, 8, 615-620.

Acknowledgment

The authors thank the JSPS Cooperation Programmes with Southeast Asian Countries under the Core University System, and the State Key Lab of Fire Science of the University of Science and Technology of China, for support of this work.