

## PYROLYSIS REACTION OF POLYURETHANE FOAM AND EFFECT OF METALLIC COMPOUND FOR THERMAL DECOMPOSITION PRODUCT

T. Suzuki, H. Yanase, O. Terakado and M. Hirasawa

Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya University, Japan  
e-mail: suzuki.toshimi@c.mbox.nagoya-u.ac.jp

### Abstract

The effect of metal oxide ( $ZnO$ ,  $Fe_2O_3$ ,  $La_2O_3$ ,  $Nd_2O_3$ ) and metal chloride ( $ZnCl_2$ ,  $FeCl_2$ ,  $CuCl_2$ ,  $FeCl_3$ ) on polyurethane (PUR) foam pyrolysis was studied with thermogravimetric analysis (TGA), gas chromatography-mass spectrometry (GC/MS) analysis and ion meter. The addition of  $FeCl_2$ ,  $FeCl_3$  and  $CuCl_2$  decreased the weight loss temperature of PUR foam. On the other hand, the addition of  $ZnCl_2$  increased the temperature of the initial weight loss. The addition of metal chloride increased gaseous products and carbonaceous residue. As for the nitrogen-containing pyrolysis products, the addition of metallic oxide compounds increased ammonia production. This result indicates that the addition of metallic compounds is effective for a safe pyrolysis of PUR foam which avoids the emission of hazardous HCN and NOx.

**Keywords:** pyrolysis of polyurethane, metal oxides, metal chlorides, addition of metal compound

### 1. Introduction

One of the greatest advantages of the pyrolysis treatment is a significant volume reduction of polymeric wastes. Therefore, pyrolysis of PUR foam is very promising because of its low density. It is known that the production of PUR is about 1.5 weight percents in Japanese plastic industry, though the volumetric ratio reaches ca. 30% (Data in 1991). Thus, the volume reduction is a crucial issue in the management of waste PUR foam.

Moreover, in the view of the energy consumption in thermal treatment, it is important to develop an efficient pyrolysis method. The utilization of metallic compounds is an attractive option, because some of them are known to act as catalysts that change the degradation behavior of PUR and products distribution[1,2]. In this study, we report the thermal decomposition behavior of PUR under the presence of various metallic compounds.

### 2. Materials and Methods

The flexible and rigid types of PUR foam (Toyo rubber Ind. Co., Ltd.) were used in the present study. The weight of the flexible PUR foam was about 200mg for pyrolysis experiments and ca. 10 mg for TGA. The rigid PUR foam was pulverized by cutter mill and the particle diameter was less than 250 $\mu$ m. Density of flexible PUR foam was 4.5 $\times 10^{-2}$  g/cm<sup>3</sup> and that of rigid foam was 5.2 $\times 10^{-1}$  g/cm<sup>3</sup>.  $ZnO$ ,  $Fe_2O_3$ ,  $La_2O_3$  and  $Nd_2O_3$  were used as metal oxides.  $ZnCl_2$ ,  $FeCl_2$ ,  $CuCl_2$  and  $FeCl_3$  were used as metal chlorides. The sample of PUR-chloride was prepared by impregnation with acetone solution. The sample of PUR-oxide was prepared by mechanical mixing. The composition of [PUR foam]:[metallic compound]=1:1 in weight ratio was examined.

Thermal decomposition behavior was examined by TGA. A sample was heated up to 800°C with the heating rate of 5°C/min under helium atmosphere. Pyrolysis experiments were carried out in a horizontal reactor under helium atmosphere at 800°C. The experimental set-up was similar to that described elsewhere [3]. The collected gaseous and liquid products were examined by GC/MS, and one of the important nitrogen-containing products, i.e. ammonia, was captured in a water trap. The  $NH_4^+$  concentration was measured by an ion-meter with  $NH_4^+$ -selective electrode.

### 3. Results and Discussion

Fig.1 shows the TGA results of flexible PUR foam with metal chlorides. The addition of  $FeCl_2$ ,  $FeCl_3$  and  $CuCl_2$  decreased the temperature of the initial weight loss.

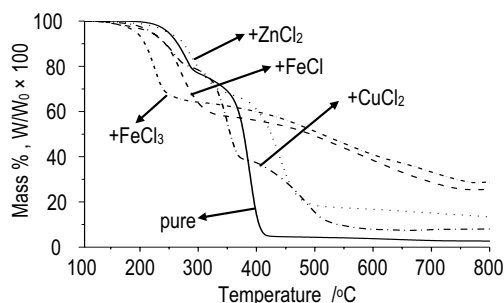


Fig.1. TGA results of PUR foam with metal chloride mixture under helium atmosphere. (heating rate = 5 °C/min)

The addition of  $ZnCl_2$  on the other hand, increased the weight loss temperature of PUR foam. It is known that the cleavage of urethane linkage is responsible for the initial decomposition of PUR [4]. The present results suggest that metal compound affects the cleavage of urethane linkage.

Fig.2 shows the GC/MS results of gaseous products of pyrolysis of rigid PUR foam metal chloride. The addition of metal chlorides increased the yield of gaseous products. Significant increase in the case of iron chloride is due to the carbothermic reduction of iron. Thus, the yield of gaseous products for the trivalent iron chloride is higher than that for the divalent  $FeCl_2$ . As for the tar and carbonaceous residue, the yield of them was increased by the addition of metal chloride. This can be ascribed to the Lewis-acidic nature of the salts, which enhances the bridging of the decomposition polyurethane moieties.

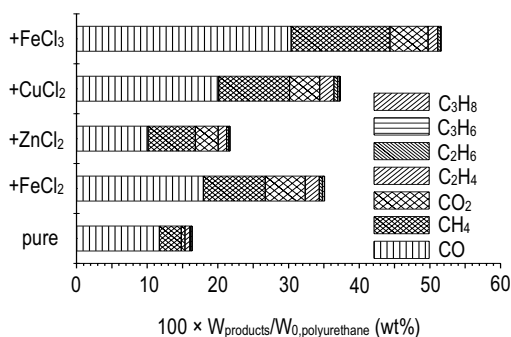


Fig.2. GC/MS results of gaseous products from rigid PUR foam pyrolysis with metal chloride.

It has been reported that nitrogen-containing compounds, such as hydrogen cyanide (HCN) and nitrogen oxide (NO<sub>x</sub>) are produced by pyrolysis of PUR [5]. The emission control of these hazardous products is, therefore, of special importance.

Fig.3 shows the results of quantitative analysis of ammonia. The yield of ammonia is increased by the addition of metallic compounds.

#### 4. Conclusions

In this study, we examined pyrolysis reaction of flexible and rigid PUR foam and effect of metallic compound for thermal decomposition product in inactive gas atmosphere.

The addition of metal chloride changes the behavior at the initial PUR degradation. These results suggest that metal compound affects the cleavage of urethane linkage. The addition of metal chloride increases the yield of gaseous products, tar and carbonaceous residue. Furthermore, the addition of metallic compounds increases the yield of ammonia products. Thus, the addition of metallic compound is effective for a safe pyrolysis of PUR foam which avoids the emission of hazardous HCN and NO<sub>x</sub>.

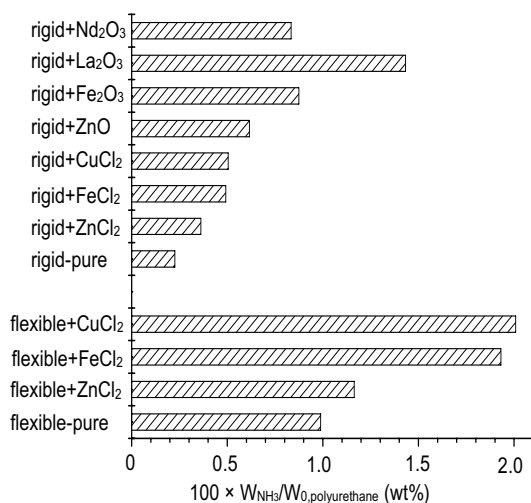


Fig.3. Yield of ammonia in pyrolysis of PUR foam-metallic compound.

#### References

- [1] G. Moroi, *J. Anal. Appl. Pyrolysis*, 71 (2004) 485-500
- [2] G. Moroi, C.Ciobanu, E.Costea, N.Blba, I.Palamaru, *Thermochimi. Acta*, 291 (1997) 95-99
- [3] Y. Masuda O.Terakado M.Hirasawa *Proceeding of The 13<sup>th</sup> APCCHE* (2010) 10370
- [4] P. Carty, E.Metcalf and S.White, *Polymer*, 33 (1992) 2704-2708
- [5] R. Font, A.Fullana, J.A.Caballero, L.Candela, A.Garcia, *J. Anal. Appl. Pyrolysis*, 58-59 (2001) 63-77