



# Pyrolysis treatment of waste polyurethane foam in the presence of metallic compounds



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## ABSTRACT

The influence of the presence of some metal salts and oxides on pyrolysis of polyurethane (PUR) foam has been studied with thermogravimetric analysis, TGA, and a lab-scale reactor. The pyrolysis products of the latter at 800 °C were analysed with gas chromatography–mass spectrometry, XRD and ion metre. The addition of metal chloride decreased the yield of liquid products, and increased the yield of carbonaceous residue, which could be ascribed to the Lewis acidic nature of the examined salts. Zinc chloride exhibited especially high ability to fix carbon in the polymer as char; the carbon yield reached more than 30% of the initial carbon in the sample. This is considerably high, as essentially no residue remained in the lab-scale pyrolysis of polyurethane foam at 800 °C. As for the nitrogen-containing pyrolysis products, the addition of metallic compounds enhanced the yield of ammonia. This result implies that the addition of metallic compounds is effective for the emission control of nitrogen-containing products from polyurethane foam.

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## 1. Introduction

Polyurethane, PUR, is synthesized by condensation reaction of diisocyanate with polyol. Variety of PURs can be synthesized by the combination of monomers, additives, and processing, so that wide range of application of PURs exists, e.g., paints, elastic fibres, or adhesives. Among them, PUR foam is a particularly important type of products. They are widely utilized as seat cushions or heat isolation materials.

As for the recycling of PUR foam wastes, one meets a serious difficulty arising from their considerably low density of 10–100 kg/m<sup>3</sup>. It is known that the production of PUR is about 1.5 wt.% in Japanese plastic industry, though the volumetric ratio reaches ca. 30%. (Data in 1991 [1]. More recent statistics in the volume scale is unfortunately not available in literature.) Thus, the volume reduction is a crucial issue in the management of waste PUR foam. With regard to this point, pyrolysis is a promising method, because it enables a significant volume reduction of polymeric wastes.

Pyrolysis of PUR foams has been discussed in many literature [2–7]. The main pathway of the thermal decomposition of PUR is, as will be discussed later, the depolymerization of the urethane linkage and the consequent decomposition to smaller molecules.

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 one of the attractive options. Moroi et al. studied the influence of metallic ion (Mn<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, Cu<sup>2+</sup>, Na<sup>+</sup>; all ions doped as chloride salts) on thermal decomposition of polyester-based PUR with thermogravimetric method, in which distinct role of the metal ions was observed. They reported that chromium and copper ions acted as catalysts enhancing the degradation of PUR at lower temperature but stabilize the intermediate pyrolysis products. On the other hand, other ions favoured the degradation of PUR without any stabilization of the intermediate products [8,9]. In the present study, we have examined the influence of iron, zinc and copper salts on thermal decomposition of PUR foam. Attention has been paid also for the influence of metal oxide on pyrolysis of rigid PUR foam in the view of our systematic studies on pyrolysis of the mixture of synthetic polymers and metal oxides [10,11]. For the rigid type of foam, powder samples are available so that the mechanical mixing of PUR and metal oxide is possible.

## 2. Experimental

### 2.1. Materials

The flexible and rigid types of PUR foams, supplied from Toyo Tire & Rubber Co., Ltd., were studied in the present work. The apparent densities were  $4.5 \times 10^{-2}$  and  $5.2 \times 10^{-1}$  g/cm<sup>3</sup>, respectively.

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**Table 1**  
Results of elemental analysis of PUR foams employed in the present study (in mass %).

	C	H	N	Others
Flexible	58	8.6	4.4	29
Rigid	57	6.8	8.0	29

The monomers of the former are toluene diisocyanate (TDI) and polyol with the molecular weight of  $\sim 3000$ , while those of the latter are methylene diphenyl diisocyanate (MDI) and polyol of molecular weight of  $\sim 300$ . The results of the elemental analysis of each foam are shown in Table 1. The relative abundance of nitrogen is higher in the rigid foam because of the smaller molecular weight of polyol monomer.

In order to study the influence of metallic compounds on the thermal decomposition of the PUR foams, we have examined variety of metal salts, including  $\text{ZnCl}_2$ ,  $\text{CuCl}_2$  and  $\text{FeCl}_3$  (Wako Pure Chem., Ltd.) and  $\text{FeCl}_2$  (Kojundo Chem. Lab., Co., Ltd.) as well as metal nitrate hydrates of iron, zinc (Kojundo Chem. Lab., Co., Ltd.), and copper (Wako Pure Chem., Ltd.). A severe difficulty arose with respect to the homogeneous mixing of the flexible PUR foam with metallic compounds. The mixture of the flexible foam and the chloride was prepared by the impregnation of the foam with acetone solution of the salt. A piece of the flexible foam was impregnated for 24 h, and then acetone was evaporated at  $105^\circ\text{C}$  under mechanical stirring. The doped sample specimen was homogeneously coloured by the salt after this procedure. Even this method may not realize the homogeneous distribution of the salt in PUR matrix because of the high salt content. Nevertheless, the satisfactory reproducibility of the pyrolysis results were observed.

As for the rigid foam, powder form of the sample was prepared by a cutter mill followed by sieving under  $250\ \mu\text{m}$ . The powders were mixed mechanically with salts, and pelletized into a disc of the diameter of 8 mm. In some experiments, metal oxides ( $\text{ZnO}$  and  $\text{Fe}_2\text{O}_3$ , supplied from Kanto Chem., Co., Inc. and  $\text{La}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$  from Kishida Chem., Co., Ltd.) have been also examined, as mentioned in Section 1.

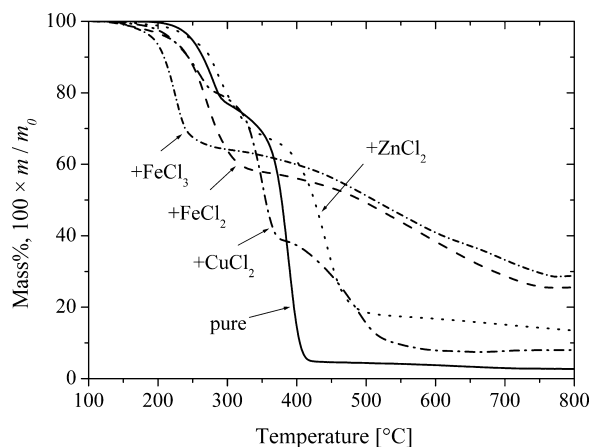
The composition of [PUR foam]:[metallic compound]=1:1 in mass ratio was examined in the present work. Relatively high composition of the metallic compound was chosen for the purpose of the intensification of the influence of the metallic compounds and the possible application of the process for a simultaneous treatment of waste polymers and metallic wastes, e.g., slag and dusts, discharged from metallurgical industries.

## 2.2. TGA

Thermal decomposition was studied by thermogravimetric analysis, TGA, with TGA2050 equipment (TA Instruments). Sample specimen of ca. 10 mg was first dried at  $105^\circ\text{C}$  for 60 min, and heated up to  $800^\circ\text{C}$  at the heating rate of  $5^\circ\text{C}/\text{min}$  under helium atmosphere. Because of the possible inhomogeneity of the salt in flexible PUR foam, the maximum experimental error of the analysis was 20%. Thus, we have not carried out detailed analysis of TG curves, such as the comparison of the decomposition onset temperature and maximum mass loss temperature.

## 2.3. Pyrolysis test with a lab-scale reactor

Lab-scale pyrolysis experiments were carried out in a horizontal quartz reactor under helium atmosphere at  $800^\circ\text{C}$  for 10 min. Typical mass of the flexible PUR foam was 200 mg for a pyrolysis run. The experimental set-up was similar to that described elsewhere [10]. Evolved products were collected in a glass trap, cooled with liquid nitrogen, denoted hereafter as cold trap. After the experimental



**Fig. 1.** Results of TGA of the flexible PUR foam in the presence of metal chloride under helium atmosphere (heating rate =  $5^\circ\text{C}/\text{min}$ ).

run, the trap was exposed at ambient temperature. The gaseous products were then introduced in an aluminium gasbag, while the liquid products captured in the cold trap were collected with acetone. Both the gaseous and liquid products were analysed by GC/MS (GC/MS 6890/5973, Hewlett Packard) with HP-PLOQ column (30 m,  $\phi$  0.32 mm, Hewlett Packard). For major products, quantitative analysis was carried out by a conventional calibration curve method of the standard solutions utilizing selected ion chromatogram, SIC, mode. Detailed analysis conditions will be described in Section 3.2. Pyrolysis runs were carried out in duplicate or triplicate. The representative experimental error of the GC–MS analysis was 15%.

In separate experiments, we studied the evolution of ammonia, one of the important nitrogen-containing products, which was captured in a water trap instead of the cold trap. The  $\text{NH}_4^+$  concentration was measured by an ion-metre (IM-40, TOA-DKK) with a  $\text{NH}_4^+$ -selective electrode (AE-235, TOA-DKK). The pyrolysis residue was characterized by X-ray diffractometer (XRD-6100, Shimadzu). The residues were further washed with acetone and 10% HCl aqueous solution to remove volatile organic matters and metallic compounds. The obtained carbonaceous materials were characterized by nitrogen-adsorption at  $-196^\circ\text{C}$  with Tristar 3000 equipment (Micrometrics).

## 3. Results and discussion

### 3.1. TGA

Figs. 1 and 2 show the TGA results of flexible and rigid PUR foams in the presence of metal chlorides, respectively. The degradation of pure flexible PUR is characterized by two mass reduction stages, one around  $250^\circ\text{C}$ , and the other around  $400^\circ\text{C}$ . It is known that the cleavage of urethane linkage and the consequent evaporation of the products as well as the dissociation to amine, olefin and carbon dioxide are responsible in the initial decomposition stage [2,3,7,8]. The latter stage results from further decomposition of the products formed at the first stage. On the other hand, thermal degradation of rigid PUR takes place at  $300\text{--}370^\circ\text{C}$  apparently with a single mass reduction stage. The difference in TG curves between the flexible and rigid foams may be due to the molecular size of polyol monomers. It is expected that the flexible type has larger polyol moieties after the first degradation stage, i.e. cleavage of urethane linkage, which are supposed to require longer degradation time than the case of the rigid foam.

The addition of metal chloride gives rise to different thermogravimetric curves. As for the flexible foam (Fig. 1), the presence of iron chloride decreases the temperature of the initial weight loss. The

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