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Reheating decomposition process as chemical recycling for rigid polyurethane foam

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Abstract

We have found that a reheating process for the products in the chemical recycling of rigid polyurethane foam by an extruder with diethanolamine as a decomposing agent is effective for improving the product stability. The product with stable viscosity was obtained by the reheating process at 175–200 °C for 2 h, regardless of the extruding condition. An amine adduct, which is an intermediate, was found to be the cause of instability of the discharged product from the extruder. At the initial stage of reheating, the intermediate decomposed, releasing toluenediamine, which promoted further decomposition of the discharged products. We have succeeded in controlling the quality of the recycled products.

Keywords: Rigid polyurethane; Chemical recycling; Reheating; Decomposition process; Extruder

1. Introduction

Rigid polyurethane foam has been widely used as a heat insulating material in refrigerators and in building materials. However, most polyurethane foam after use is disposed off by landfill or incineration, because a sufficiently efficient recycling process has not been established yet. Chemical decomposition, thermal decomposition and the like are the known methods for the decomposition of a urethane resin. However, in the view point of its recycling, thermal decomposition is unsuitable, because heating decomposition of polyurethane will generate too many kinds of compounds [1]. Therefore, polyurethane-recycling process should be preformed by chemical decomposition. Several chemical recycling techniques such as hydrolysis [2], glycolysis [3] or aminolysis [4] including the decomposition process with alkanolamine, have been reported. In these studies, however, it takes considerable time to complete the decomposition reaction, because of the low density and low thermal conductivity of foam structure, even though an excess amount of decomposing agent is used. In our previous study, we found that continuous urethane decomposition process using extruder enables remarkable reduction of reaction time, which had been improved to 1/15–1/30 [5], and that the decomposed polyurethane, polyol, can be used as the raw material for recycling urethane resin [5] or epoxy resin [6] without eliminating the surplus decomposing agent, diethanolamine.

We sometimes observed further decomposition reaction detected by decreasing viscosity, when cooling was insufficient after discharging from the extruder. Since high viscosity makes handling difficult, it is useful to lower the viscosity to a usable value by reheating. In this study, therefore, we have optimized the reheating decomposition condition of polyurethane with extruder and diethanolamine. Partially decomposed polyurethane with diethanolamine as the decomposing agent was obtained by operating the extruder with high extrusion rate, and then, the samples with varied decomposition state were prepared by reheating the product to various

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Table 1
Conditions and results of decomposition process

	Sample D1	Sample D2
DEA/polyurethane weight ratio	1/3	1/3
Reactor temperature (°C)	250	250
Reaction time (min)	2	4
Viscosity at 60 °C (mPa s) Discharged sample	7110	2880
Viscosity at 60 °C (mPa s) Reheated at 200 °C for 2 h	889	896

temperatures. The influence of reheating condition on the properties of decomposed polyurethane and the analytical results of the generated compounds are discussed in this report.

2. Experimental

2.1. Rigid polyurethane foam and decomposing agent

In this experiment, rigid polyurethane foam for heat insulator exhausted from its manufacturing process was used as the decomposing sample, whose raw materials were polyol, catalyst, surfactant, foaming agent and toluenediisocyanate (TDI). The polyurethane was smashed to pieces by a pulverizer until passing through a 5 mm mesh. Diethanolamine (DEA, Mitsui Chemical, Inc.), the decomposing agent, was mixed with the smashed polyurethane before feeding into the extruder.

2.2. Decomposition process

The samples with various decomposing conditions were prepared by the following process. In the first step, the polyurethane was partially decomposed with DEA in the extruder, and the discharged product, which was homogeneous and viscous clear brown liquid, was soon cooled to room temperature. Then, the discharged product was reheated to proceed with decomposition under varied condition in dry ovens (reheating process).

Smashed pieces of rigid polyurethane foam, on which DEA was sprayed, were fed into the extruder [6] (Toshiba Machine Co., Ltd., $\varphi = 65$ mm, $L/D = 30$). The mixture was mashed and kneaded in conditions shown in Tables 1 and 2. In the case of the sample with low DEA/polyurethane weight ratio, it was necessary to raise the temperature from 250 °C to 280 °C in order to obtain homogeneous product within several minutes.

In the reheating process, ca. 10 g of each of the discharged products listed in Tables 1 and 2 was encased in 50 ml glass vessel and reheated in a dry oven.

Table 2
Conditions of decomposition process

	Sample D3	Sample D4	Sample D5
DEA/polyurethane weight ratio	1/4	1/5.7	1/9
Reactor temperature (°C)	250	250	280
Residence time (min)	4	4	6

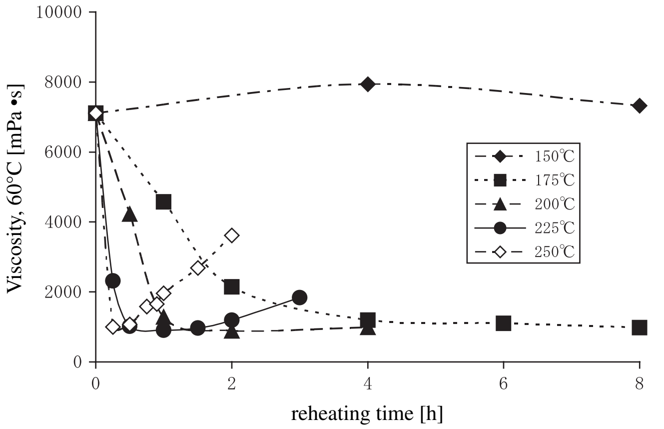

Fig. 1. Influence of reheating temperature and time on viscosity of decomposed samples (reheated in oven, reheating temperature 150 °C (◆), 175 °C (■), 200 °C (▲), 225 °C (●), 250 °C (◇), amount of sample is ca. 10 g).

2.3. Measurements

Viscosity (Haake RheoStress 600), molecular weight distribution (GPC; Hewlett Packard Series 1100, solvent: THF, calibration: polystyrene standard), and GC/MS spectrum (HP6890plus, Agilent Co. Ltd.) were measured. Viscosity was used as the indicator of degree of decomposition. In preparing for GC/MS analysis, samples were reacted with BSTFA (*N*,*O*-bis(trimethylsilyl)-Trifluoroacetamide, Tokyo Kasei Co. Ltd.) for the analysis of involatile compounds.

3. Results and discussion

3.1. Influence of decomposing condition in extruder

Table 1 shows the viscosity of decomposed products with the extruding decomposition conditions. These samples were both discharged products from extruder without further reheating. Decreasing viscosity suggests that further decomposition of sample D2 progressed in 2 min from the degree of sample D1.

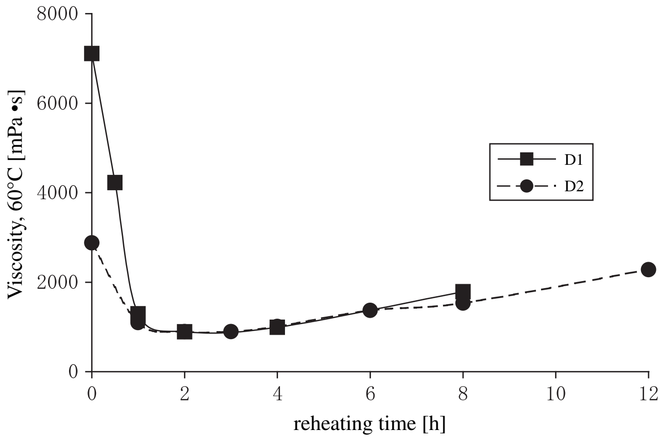

Fig. 2. Influence of residence time in extruder on viscosity of decomposed samples at 200 °C reheating (D1 (■): reaction time in extruder is 2 min, reaction temperature is 250 °C, D2 (●): reaction time in extruder is 4 min, reaction temperature is 250 °C).