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Improving chemical recycling rate by reclaiming polyurethane elastomer from polyurethane foam

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Abstract

Flexible polyurethane foam was decomposed into a polyol mixture by an extruder with diethanolamine (DEA) as a decomposing agent. The resulting decomposed product could be used as an alternative virgin polyol in reclaiming polyurethane. In the case of reclaiming elastomer by using the decomposed product without any purification, virgin polyol could be alternated by the decomposed product up to 80%. It is a great improvement compared with the reclamation to foam, whose percentage was maximum 5%. Furthermore, the percentage could be improved up to 100% by purifying the decomposed product. We have found that physical properties of reclaimed polyurethane elastomer, such as tensile strength, hardness, and elongation, can be regulated by the ratio of unrefined/refined polyol. Whereas the tensile strength and the hardness increased as the content increased, the elongation decreased.

Keywords: Polyurethane; Chemical recycling; Foam; Elastomer; Reclamation

1. Introduction

Flexible polyurethane foam is one of the most widely used cushion materials in automobiles, furniture, and so on. However, a considerable amount of scrapped polyurethane foam is disposed off by landfill or by incineration, because a recycle process capable of treating all scrapped polyurethane with sufficient efficiency has not been established yet. In the mechanical recycling process, flexible polyurethane foam is smashed into fine powder and used as recycled urethane filler [1–3]. However, the amount of polyurethane foam treated by this process has not increased significantly up to date.

On the other hand, several chemical recycling techniques, such as hydrolysis [4], glycolysis [3,5–7] and aminolysis [8,9], including the decomposition process with alkanolamines 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 the foam structure, even though an excessive amount of the decomposing agent is used.

Our previous study revealed that a continuous urethane decomposition process using an extruder enables a remarkable reduction in the amount of decomposing agent required and the reaction time. In the present study, we examined, firstly, the applicability of this method for flexible polyurethane and secondly, the process of reclaiming polyurethane elastomer from the decomposed product. Our reclamation process from foam to elastomer without purification is expected to save cost and processing energy, because the former reclamation process from foam to foam generally requires intensive purification [10]. In this study, the characteristics of reclaimed elastomer with various decomposed polyurethane content are evaluated and the issue of whether purification of the decomposed product is required is discussed.

2. Experimental

2.1. Preparation of flexible polyurethane foam

Three kinds of flexible polyurethane foam were evaluated. Two of them (samples 1 and 2) were urethane scraps supplied by Toyo Tire and Rubber Co., Ltd. The other one (sample 3)

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was a reference polyurethane foam prepared in order to have a polyurethane foam, whose composition was known, for chemical analysis of the decomposed products. Samples 1 and 2 were used for reclamation to elastomer and sample 3 was used for chemical analysis.

In preparing sample 3, the contents of which are shown in Table 1, three catalysts, water as a blowing agent and a chain extender were added to virgin polyol and premixed with a stirrer (T.K. homodisper f-model, Tokushu Kika Kogyo Co., Ltd.). And then, isocyanate was added to the mixture and stirred to react. The foam was cured at 25 °C for more than 24 h before use in order to react and be stiffened securely.

2.2. Decomposition of flexible polyurethane foam

Polyurethanes (samples 1–3) were decomposed by the following process. Smashed flexible polyurethane (3–20 mm) was premixed with equivalent mol of diethanolamine (DEA, Mitsui Chemicals, Inc.). The mixing ratio (w/w) is shown in Table 2.

Then the mixture was fed into an extruder (one screw, diameter of screw: 65 mm, length of screw: 1830 mm, reaction volume: 4×10^{-3} m^3, Toshiba Machine Co., Ltd.) (Fig. 1). The working conditions of the extruder are also shown in Table 2. In this process, all foam samples were fully decomposed in a few minutes. The reaction scheme is shown in Fig. 2.

The decomposed polyurethane discharged from the extruder separated into two layers spontaneously. The upper layer was composed mainly of polyol and the lower layer was composed mainly of amines and other low molecular weight compounds. (Composition of the layers is discussed in detail in the next section.) However, the upper layer included a few amines and other low molecular weight compounds except for polyol. Hereafter, the upper layer is called "unrefined polyol" in this paper.

2.3. Purification of unrefined polyol

The amines and the other low molecular weight compounds in unrefined polyol were distilled out under reduced pressure. The pressure was kept at 1.0 kPa or less and the temperature was raised from room temperature to 300 °C, and these conditions were kept until the condensed drop was not observed. In this paper, the residue of the process is called "refined polyol".

Table 1
The components and the composition of the foam

Item	Chemicals	Manufacturer	Content
Virgin polyol	Polyethertriol (Mn3050)	Mitsui Takeda Chemicals	100
Isocyanate	Toluene diisocyanate (T-80[a])	Mitsui Takeda Chemicals	NCO/OH (mol/mol) = 1.0[b]
Blowing agent	Water		8.0
Catalyst	Tetramethylene-diamine	Wako Pure Chemical Industries	2.0
Catalyst	Dibutyltin dilaurate	Wako Pure Chemical Industries	0.2
Catalyst	Surfactant (SZ-1923)	Dow Corning Toray	2.0
Chain extender	Glycerol	Kanto Chemical	2.0

[a] T-80: 2,4-/2,6-toluene diisocyanate = 8/2.

[b] NCO index: actual amount of isocyanate per calculated amount of isocyanate.

Table 2
The decomposition conditions

Polyurethane	PU/DEA (w/w)	Reaction time (s)	Temperature of a cylinder in the extruder (°C)	Feed amount (kg/h)
Sample 1	8/1	240	250	13.0
Sample 2	10/1	190	270	6.2
Sample 3	10/1	220	270	5.5

2.4. Reclamation to polyurethane elastomer

The surfactant (TSA720; GE Toshiba Silicones) and unrefined or refined polyol obtained by the decomposition were added to the virgin polyol (Mn3050; Mitsui Takeda Chemicals, Inc.) and premixed with a stirrer. Then, the isocyanate pre-polymer (Mn3050 with toluene diisocyanate at both ends) was added and the mixture was stirred for 3 min. The mixture was molded to No. 3 dumbbell shape and plates whose thickness is more than 12 mm, according to Japanese Industrial Standard (JISK-7312: physical testing methods for molded products of thermosetting polyurethane elastomers). The composition of the reclaimed elastomer and the reaction scheme are shown in Table 3 and Figs. 2 and 3, respectively.

The content of unrefined or refined polyol was defined as follows:

$$\text{The content of unrefined/refined polyol} = \text{unrefined/refined polyol (g)}/(\text{unrefined/refined polyol} + \text{virgin polyol})\ (\text{g}) \times 100.$$

In this process, bubbles generated in the mixture were eliminated by setting the mold in vacuum for about 5 min.

After curing at room temperature for more than 24 h, test samples for measurement of characteristics were formed according to the Japanese Industrial Standard (JISK-

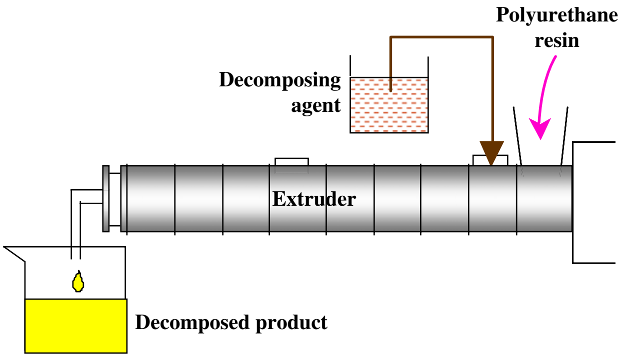

Fig. 1. A model of the extruder used for the decomposition of polyurethane foam.