

Recycling of Polyurethane using High-pressure Steam Treatment

Ai Noritake¹, Mikiji Shigematsu^{1,2}, Tetsuya Tsujii³ and Mitsuhiko Tanahashi^{1,2}

¹Graduate school of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan
Fax: 81-58-293-2922

²Faculty of Applied Biological Sciences, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan
Fax: 81-58-293-2917, e-mail: tanah@cc.gifu-u.ac.jp

³CCI Corporation, 12 Shinhazama, Seki, Gifu 501-3923, Japan
Fax: 81-575-24-6175, e-mail: tetsuya-tsujii@ccijp.co.jp

In this experiment, polyurethane was liquefied by high-pressure steam treatment without using acidic or alkaline catalysts and solvent. The results of the viscosity and GPC (Gel Permeation Chromatography) showed that part of the molecular weight of the liquefied urethane attained either diamine level or prepolymer level. Furthermore, variation in the hydroxyl number, the amine value and FT-IR spectroscopy with high-pressure steam treatment time showed that urea and urethane bonds in the polyurethane were specifically broken. In addition, the decomposed liquid could readily react with cross-linking agents, and mechanical properties of recycled polyurethane such as shore hardness, tensile strength, 300% modulus, tearing strength and compression set were almost equal to the original polyurethane. This investigation therefore shows that urethane recycling method we can be established easily. More importantly this recycling method does not adversely affect the environment.

Key words: polyurethane, recycle, high-pressure steam

1. INTRODUCTION

Polyurethane is conveniently and widely used in various fields, such as in construction materials, automobiles and electric appliances. It is a thermosetting resin with reticulated structure of a three-dimensional network like epoxy resin. It is very difficult to reclaim polyurethane, as it does not decompose by heating nor melt in the solvent. As urethane wastes are difficult to recycle, in many cases it has been disposed of by incineration or burial. Recently people are increasingly concerned about environmental issues which have led to flourishing studies on recycling of waste plastic. Nowadays different methods exist for recycling urethane wastes such as thermal recycling^[1] that uses the same combustion energy degree as coal, and material recycling^[2] by heat press and injection molding etc, have been adopted. Moreover, chemical treatment are also well known, e.g., by hydrolysis,^[3,4] amine decomposition,^[5,6] ammonia decomposition^[7] and or glycol decomposition. However, such chemical treatments require the use of expensive catalysts or solvent. For industrial utilization, they additionally require secondary treatment of decomposed products, which involve an additional cost factor. Occasionally it is required to remove urethane portions from composite metal articles such as urethane wheels before treating urethane wastes.

We propose a unique urethane recycling method by high-pressure steam treatment. Liquefied urethane can be easily obtained using this method without acidic or alkaline catalysts and solvent. Moreover, it can save time and money necessary for urethane recycling.

We have therefore, suggested the possibility of recycling urethane that polymerize the liquefied urethane again by using a cross-linking agent.

2. MATERIALS AND METHODS

2.1 Test sample

Polyurethane was prepared by combining diamine (CUAMINE: Ihara Chemical industry co., LTD) and prepolymer (PANDEX 4030: Dainippon ink and chemicals, incorporated) at 110 °C. The prepolymer is derived from polyoxy tetramethylene glycol and toluene diisocyanate (TDI). The urethane block obtained was crushed into smaller particles of about 5mm size by a crushing machine.

2.2 Liquefaction of urethane by the high-pressure steam treatment

The sample particles were treated in high-pressure steam apparatus HTP 40/60 which was manufactured by Hisaka Works, LTD as indicated in Fig. 1. The device was set to 1.6 MPa at 200°C by introducing steam. The 5 samples "a", "b", "c", "d" and "e" taken were subjected to high-pressure steam treatment for 30, 60, 120, 240 and 360 minutes respectively (see Table I). All samples turned into the liquefied urethane.

Table I Test samples condition

Samples	High-pressure steam treatment time (min)	Temp (°C)	Pressure (MPa)
a	30	200	1.6
b	60		
c	120		
d	240		
e	360		

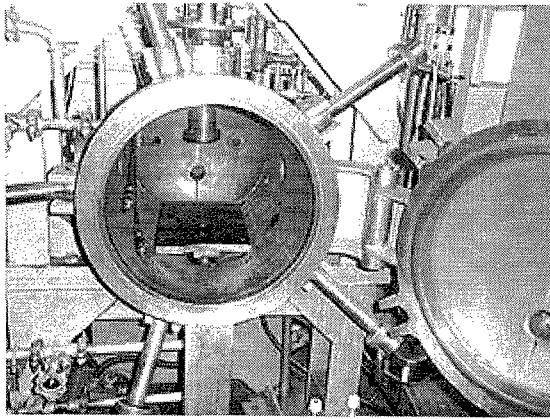


Fig. 1 High-Pressure Steam Treatment Apparatus

2.3 Analysis of the liquefied urethane

To analyze the molecular weight of the liquefied urethane, the viscosity and the GPC (Gel Permeation Chromatography) were measured. The viscosity was determined according to JIS K 1557 (Japan Industrial Standard). The GPC used was a HCL-8220 model (Tosoh Corp.) equipped with UV and RI (refractive index) detectors. The eluent tetrahydrofuran (THF) which was passed through 3 series of column namely: TSK gel G1000H_{XL}, TSK gel G2000H_{XL}, TSK gel G2000H_{XL} at a flow rate of 1 ml/min. The column temperature was 40 °C. In order to analyze the liquefied urethane, hydroxyl value, amine value, and FT-IR spectra (Fourier Transform Infrared Spectroscopy) were measured. The hydroxyl number and the amine value were measured according to JIS K 0070 and JIS K 7237. The FT-IR spectra of the liquefied urethane mixed with KBr was recorded using FT/IR-660 Plus VST spectrometer (JASCO Corp.).

2.4 The synthesis of polyurethane from liquefied urethane and its mechanical properties

In the urethane recycling process, the polyurethane was put under high-pressure steam for two hours, and subsequently dewatered. PANDEX P-910C which contains 4.42% isocyanate group (Dainippon ink and chemicals, incorporated), F650 which contains 7.65% isocyanate group (Uniroyal Chemical Company Inc.) and CPP1500 which contains 8.59% isocyanate group (Urethane & Research & Chemicals, Ltd.) were used as cross-linking agents. An amount of 33.3% of the liquefied urethane was blended with 66.7% of PANDEX P-910C, 32.5% of the liquefied urethane was blended with 67.5% of F650 and 39.4% of the liquefied urethane was blended with 60.4% of CPP1500, to obtain urethane sheets. The mechanical properties of each urethane sheet were determined. The values for shore hardness, tensile strength, 300% modulus, tearing strength, impact resilience and compression set were determined according to JIS K 6253, JIS K 6251, JIS K 6251, JIS K 6252, JIS K 6255 and JIS K 6262, respectively.

3. RESULTS AND DISCUSSIONS

3.1 Test results of the liquefied urethane

All tested urethane particles changed into viscous

transparent liquids. The uncrushed urethane blocks were also tested under the high-pressure steam treatment. Then viscous transparent liquid from the deformed surface began to drip out. For example the composite metal product such as a urethane-covered wheel is very difficult to recycle because it required removing urethane portions from the composite metal products. However this technology could easily separate polyurethane from its metallic part as shown in Fig. 2.

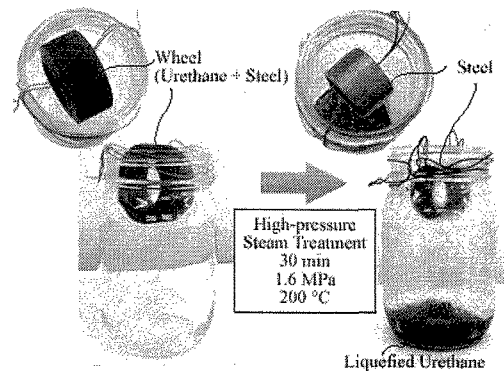


Fig. 2 Separation of urethane composite metal products (e.g. wheel)

The viscosities of the liquefied urethane at various temperatures were determined as shown in Fig. 3. For comparison purpose, the viscosity of urethane prepolymer is also shown in Fig. 3. As can be seen from the figure, the viscosities of the liquid samples decreased as the treatment time lengthened, eventually decreasing to as low as that of the urethane prepolymer. This decrease in viscosity may be attributed to the presumed progressive decrease in the molecular weights of polymer materials under high-pressure steam treatment.

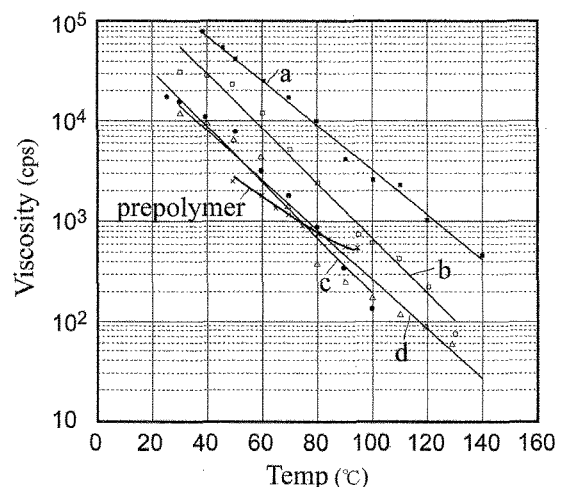


Fig. 3 The viscosities of the liquefied urethane at various temperature (see Table I for symbols)

The molecular weights valuation of the liquefied urethane measured by GPC is shown in Fig. 4. The figure shows that as the treatment time lengthened, molecular weights progressively decreased. Variations of the first

peak in GPC analysis is shown in Table II. It can be seen that percentage area cover and PDI (poly-dispersity index from GPC) value of the first peak decreased with increasing treatment time. On the other hand, the molecular weight continued to decrease to the lowest peak at a retention time of about 38 minutes and the value obtained was similar to diamine which is raw material of polyurethane (Table III). Consequently, the percentage area cover increased with increasing treatment time.

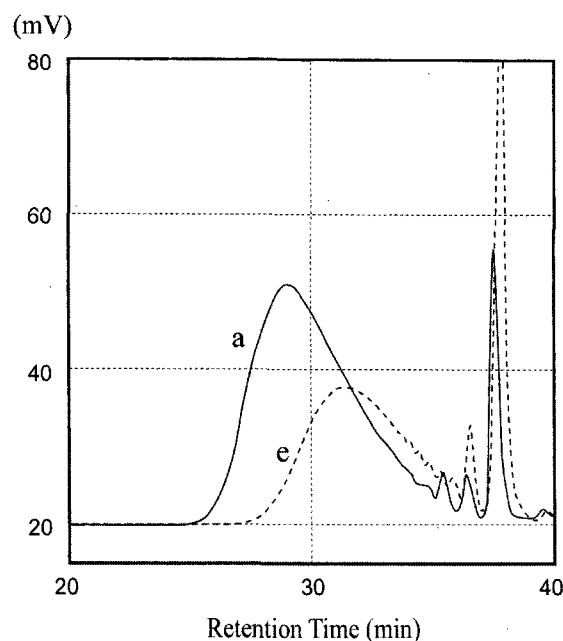


Fig. 4 Molecular weights distribution of the liquefied urethane with time under high-pressure steam treatment (see Table I for symbols)

Table II Variations of the first peak in GPC analysis (see Table I for symbols)

high-pressure treatment time (min)	Mw	percentage area cover (%)	PDI (Mw/Mn)
30	4,729	77.7	1.65
60	4,079	75.3	1.58
120	3,609	70.2	1.52
240	3,350	65.3	1.47
360	3,282	60.9	1.39

Table III Variations of the lowest molecular weight peak in GPC analysis (see Table I for symbols)

high-pressure treatment time (min)	Mw	percentage area cover (%)	PDI (Mw/Mn)
30	232	9.0	1.02
60	233	17.5	1.02
120	229	18.4	1.02
240	225	21.0	1.03
360	225	25.8	1.03

The structural analysis of hydroxyl number and the amine value of the liquefied urethane were measured over the high-pressure steam treatment time. The result in Fig.5 suggests that increasing the hydroxyl number and amine value promotes decomposition of polyurethane by partially shearing the chains and 3-D networks of the polyurethane.

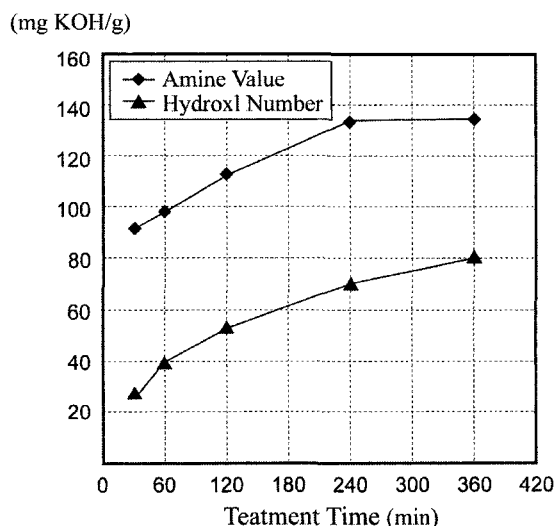


Fig.5. Variation in hydroxyl number and amine value of urethane with time under high-pressure steam treatment

The FT-IR analysis shown in Fig.6 supports the above-mentioned hypothesis, which indicates the progressively decreasing peak of the stretching vibration of "C=O" (1), and the progressively increasing peak of the scissoring vibration of "NH₂" (2) as the treatment time reaches 30, 60, 120, and 240 minutes respectively.

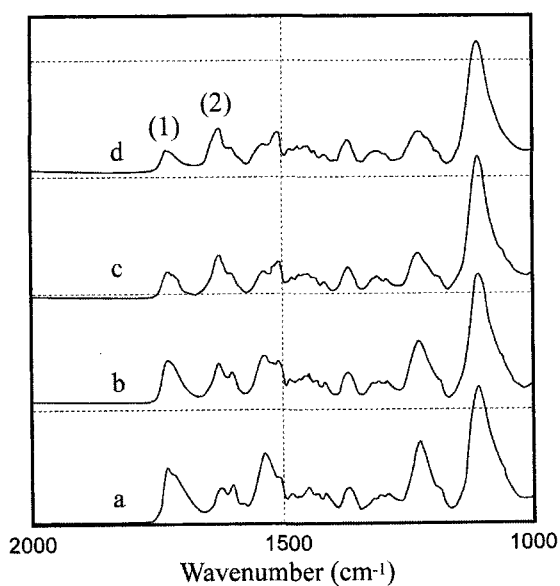


Fig. 6 Variation of FT-IR spectra of urethane with time under high-pressure steam treatment (see Table I for symbols)

Table III Mechanical Properties of Recycled Urethane

item (amount of isocyanate group)	original polyurethane	recycled polyurethane		
		CPP 1500 (8.59 %)	F 650 (7.65 %)	P-910C (4.42 %)
shore hardness (Hs)	90	92	80	62
tensile strength (kgf/cm ²)	470	464	441	61
300% modulus (kgf/cm ²)	229	243	182	25
tearing strength (kgf/cm)	88	85	52	23
impact resilience (%)	55	24	23	20
compression set (%)	21	18	14	31

The results of the above analysis show that urea bonds and urethane bonds in the polyurethane might have broken during the high-pressure steam treatment period.

3.2 Recycling Test

It was confirmed in the foregoing test that the decomposed urethane liquids involve hydroxyl groups and amino groups. They readily react with cross-linking agents such as isocyanate and the obtained material can be recycled. The recycled material obtained was heated with cross-linking agents and the mechanical properties of the recycled urethane were measured and the results are shown in Table III.

The mechanical properties of the recycling urethane changed depending on the content of isocyanate group. When the CPP1500 which has the highest amount of isocyanate group was used as the cross-linking agent, all the mechanical properties except impact resilience were almost equal to the original polyurethane by this recycling method. However, it is also possible to obtain urethane foam if the liquefied urethane doesn't dehydrate.

We suggested that liquefaction urethane can be customized for its usage depending on the amount of moisture and the type of cross-linking agent used.

4. CONCLUSION

It has been confirmed that urethane wastes can be effectively recycled by high-pressure steam treatment when they are decomposed into a liquid with substantially decreased molecular weight. This recycling method does not require the use of acidic or alkaline catalysts, solvent and post-treatment refining. More importantly, this recycling treatment does not adversely affect the environment.

The decomposed liquid is a compound consisting of hydroxyl groups or amino groups, and is highly reactive with cross-linking agents such as isocyanate, which can be freshly remade into polyurethane or epoxy resin products. In addition, it will be possible to control the mechanical properties of recycled products by carefully selecting the cross-linking agents to be added.

Furthermore, composite metal products such as urethane-covered wheels may be directly subjected to this method without removing the urethane covers. Both

the metal parts and the urethane covers can be efficiently recycled at a low cost.

We hope that this recycling technology will assist in environmental protection through the elimination of hazardous treatment or disposal of urethane wastes.

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