

PAPER • OPEN ACCESS

Recovery of Polyols from Polyurethane Foam Wastes by Solvent Decomposition

To cite this article: Qi Li *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **310** 042014

View the [article online](#) for updates and enhancements.

Recovery of Polyols from Polyurethane Foam Wastes by Solvent Decomposition

Qi Li^{1,2,3}, Weitao Xu⁴, Enhua Xi^{1,3}, Yanfang Pang^{1,3}, Xiaosheng Liu^{1,3}, and An Mao^{1,2,3*}

¹Key Laboratory of State Forestry Administration for Silviculture of the lower Yellow River, Shandong Agricultural University, Taian, Shandong, 271018, China

²Beijing Key Laboratory of Wood Science and Engineering, Beijing Forestry University, Beijing 100083, China

³College of Forestry, Shandong Agricultural University, Taian, Shandong, 271018, China

⁴Planning & Design Institute of Forest Products Industry, State Forestry and Grassland Administration, Beijing, 100010, China

*Corresponding author's e-mail: dannymaoan@126.com

Abstract. The objective of this study was to investigate the feasibility of recovering the polyols from the polyurethane (PU) foam wastes obtained from automobile shredder residue (ASR) by chemical decomposition using the diethylene glycol (DEG) as the decomposing solvent and sodium hydroxide (NaOH) as the catalyst, respectively. The effects of temperature (180 °C and 210 °C), time (0.5, 1, 1.5, 2, 2.5, and 3 hours), and DEG/FPU weight ratio (2:1, 3:1, and 4:1) on the decomposition reaction and the properties of the recovered polyols were investigated. Higher temperature and DEG/FPU weight ratio promoted the FPU decomposition reaction and resulted in lower viscosity, higher hydroxyl number, and higher amine number of the recovered polyols. The hydroxyl number and amine number increased as the reaction progressed, while the viscosity decreased. Once the reaction was completed, little change was observed for the hydroxyl number and viscosity of the recovered polyols. The recovered polyol obtained at 210 °C and DEG/FPU weight ratio of 3:1 showed about the same length of time for the reaction, as well as the physical properties to that obtained at 180 °C and DEG/FPU weight ratio of 4:1.

1. Introduction

The increasing use of the polyurethane (PU) foam materials in the automobile makes their recycling a great challenge. Currently, only a small fraction of the PU foams is recycled, most of them go to the landfill creating an environment impact. PU foams can be recycled through thermal, mechanical and chemical processes. Chemical recycling decomposes the PU materials into feedstock chemicals in the presence of solvent under a high temperature with or without catalyst. The polyols from the waste PU materials can be recovered for new PU products. The solvents used in the decomposition reaction include water, alcohols, inorganic or organic acids, amines, and alkalines [1]. It was known that the PU foams could be decomposed by low molecule weight glycols with high boiling point, such as



ethylene glycol (EG), diethylene glycol (DEG), propylene glycol (PPG), and dipropylene glycol (DPG) at high temperatures (200-270 °C) into liquid products which are mixtures of compounds containing hydroxyl groups [2]. The choice of solvent, reaction temperature, reaction time, solvent/PU weight ratio, as well as the catalyst type and its concentration can be important factors affecting the decomposition reaction. When the glycols are used as the decomposing solvent, they break the urethane linkages resulting in short chain hydroxyl functional urethane oligomers and the starting polyols used in the reaction of the original PU foams are thus released [1].

The objective of this study was to investigate the feasibility of recovering polyols from the PU foam wastes obtained from the automobile shredder residue (ASR) by chemical decomposition using the DEG as the decomposing solvent and sodium hydroxide (NaOH) as the catalyst. The effects of the reaction temperature, reaction time, and DEG/FPU weight ratio on the decomposition reaction and properties of the recovered polyols were investigated.

2. Materials and Methods

2.1. Preparation of FPU powders

Flexible PU (FPU) foams were obtained from Metal Management Inc., Greenville, MS. The foams were washed by water and acetone. Then, the foams were air-dried and grounded into powders with a size of 1 mm. The FPU powders were then dried at 100 °C until the water in the materials is removed.

2.2. Reaction variables

DEG and NaOH were used as decomposing solvent and catalyst, respectively. DEG has a water content of up to 0.5% and a hydroxyl number of about 1057 mg KOH/g. Two reaction temperatures, 210 °C and 180 °C, six reaction times, 0.5, 1, 1.5, 2, 2.5, and 3 hours, and three DEG/FPU weight ratios, 2:1, 3:1, and 4:1 were used in the experiments.

2.3. Decomposition of FPU foams to obtain recovered polyols

The decomposition reaction was carried out in a three-neck round-bottom jacketed flask equipped with stirrer and refluxing condenser. The DEG was placed in the flask and heated to 180-210 °C. Then the catalyst and FPU powders were charged into the flask. After the charging was completed, the reaction mixture was maintained at 180-210 °C for 0.5, 1, 1.5, 2, 2.5, and 3 hours. The mixtures obtained from the different reaction conditions were then subjected to the vacuum distillation to remove the excess DEG. The obtained liquids were filtrated through a No. 4 filter paper to obtain the recovered polyols.

2.4. Material Characterization

The hydroxyl number was measured in accordance with the American Oil Chemists' Society (AOCS) Official Method Cd 13-60. The amine number was measured in accordance with the procedures described in American Society for Testing and Materials (ASTM) D 2073-92 (reapproved 1998). The viscosity was measured at 25 °C by a Rotational Brookfield Viscometer (Brookfield Engineering Laboratories, Inc., MA). PH value was determined by an Accumet basic AB15 pH meter (Fisher Scientific Co., PA) at 25 °C. The yield of the recovered polyols was calculated as follows:

$$\text{Yield \%} = (P/F) \times 100\%$$

Where:

P- Weight of the recovered polyols, g

F- Weight of the FPU foam powder, g

3. Results and Discussion

3.1. Decomposition reaction of the FPU foams by DEG

Because of their hydrophobic nature, the FPU powders did not wet very easily to the decomposing solvent. Since the FPU was in low density, it had a tendency to float on the surface of the hot DEG

solvent. The addition of the FPU powders to the DEG was slow, which took about 20 minutes. Almost all the FPU powders dissolved in the DEG solution within the first 0.5 hour under all reaction conditions. The regular temperatures used in the decomposition reaction of PUs by glycols were 200-270 °C [1]. Two reaction temperatures were used in the experiments. One was 210 °C, which is among the regular temperature range (200-270 °C). Higher temperature may increase the side reaction rates and produce more by-products [3]. The other temperature was 180 °C. It was observed that the dissolution of the FPU powders in the DEG was slower at 180 °C than that at 210 °C. The color of the reaction mixtures at 210 °C was a slightly darker than that at 180 °C.

3.2. Effects of the reaction conditions on the properties of the recovered polyols

It was reported that the hydroxyl number of the decomposed PU foams could be largely influenced by the presence of the excess solvent if the solvent was not separated after reaction [4]. In that case, higher hydroxyl number of the reaction mixtures could be obtained due to the high hydroxyl number of the DEG (1057 mg KOH/g). In this study, the reaction mixtures obtained from the different reaction conditions were subjected to the vacuum distillation to remove excess DEG. The obtained liquids were filtrated to obtain the recovered polyols with uniform phase. The influence of the DEG on the hydroxyl number of the recovered polyols was thus minimized. The recovered polyols were subjected to the further measurements. Table 1 showed the hydroxyl numbers of the recovered polyols under different reaction times, temperatures, and DEG/FPU weight ratios. These numbers were in the range of 147-292 mg KOH/g for the samples after 3 hours of reaction. It was noted that within the first one-hour reaction, the hydroxyl number increased as a function of reaction time due to the substitution of the polyols by the DEG and releasing of polyols. As the reaction continued, the hydroxyl number reached nearly constant values for all the samples with the DEG/FPU weight ratios of 3:1 and 4:1. For example, for the DEG/FPU weight ratio of 3:1 and reaction temperature of 210 °C, the hydroxyl number became relatively stable after 2 hours of reaction. The results suggested that the adequate reaction time to decompose FPU foams under this condition was about 2 hours. It was also observed that lower reaction temperature (180 °C) required more reaction time (2.5 hours) to obtain the constant hydroxyl number because the lower temperature reduced the activity of the catalyst. Moreover, higher DEG/FPU weight ratio resulted in higher hydroxyl number and required less time to obtain the constant hydroxyl number. This is because DEG served both as reactant and solvent in the decomposition reaction of the FPU foams. Higher DEG/FPU weight ratio enhanced the decomposition reaction and thus shortened the reaction complete time. Therefore, the reactions with a DEG/FPU weight ratio of 2:1 may need more than 3 hours to complete the total reaction.

Table 1. Hydroxyl numbers of the recovered polyols at different reaction conditions

Reaction temperature (°C)	DEG/FPU weight ratio	Hydroxyl number (mg KOH/g)					
		0.5 h	1 h	1.5 h	2 h	2.5 h	3 h
180	2:1	65	78	102	115	128	147
180	3:1	77	107	146	195	227	241
180	4:1	108	158	207	239	247	250
210	2:1	77	107	141	160	193	201
210	3:1	92	159	219	260	251	246
210	4:1	116	178	258	247	261	292

The extent of the decomposition of the FPU foams was estimated from the variation of the viscosities with reaction time as shown in Table 2. It was obvious that the viscosity decreased rapidly within the first one-hour reaction due to the fast reaction rate. Then the change of the viscosity slowed down gradually and reached constant values. The viscosity of the recovered polyols decreased from 601-1026 mPa.s at a reaction time of 0.5 hour to 239-432 mPa.s at a reaction time of 3 hours. As the reaction progressed, the polyurethane chains were attacked by the DEG, and got broken, and the

molecular weight of the polymer thus decreased resulting in a lower viscosity value. A lower DEG/FPU weight ratio needed a longer time to obtain a stabled viscosity. The viscosity of the recovered polyols is strongly depended on the reaction temperature. Higher reaction temperature resulted in a lower viscosity. Other than the reaction conditions, the viscosity of the recovered polyols could also be influenced by the residual DEG and other by-products derived from the aromatic segments of the isocyanate [5].

Table 2. Viscosities of the recovered polyols at different reaction conditions

Reaction temperature (°C)	DEG/FPU weight ratio	Viscosity (mPa.s)					
		0.5 h	1 h	1.5 h	2 h	2.5 h	3 h
180	2:1	1026	793	677	547	451	432
180	3:1	768	612	431	357	312	321
180	4:1	659	453	334	281	270	288
210	2:1	855	663	530	421	406	369
210	3:1	622	456	345	279	262	271
210	4:1	601	423	341	246	231	239

Table 3. Amine numbers of the recovered polyols at different reaction conditions

Reaction temperature (°C)	DEG/FPU weight ratio	Amine number (mg KOH/g)					
		0.5 h	1 h	1.5 h	2 h	2.5 h	3 h
180	2:1	2.01	2.27	2.81	3.57	3.69	4.23
180	3:1	3.02	3.33	4.21	4.69	4.97	5.46
180	4:1	3.01	3.45	4.29	4.73	5.28	5.91
210	2:1	3.11	4.48	4.87	4.91	5.88	5.98
210	3:1	4.21	4.54	4.97	4.81	5.86	6.01
210	4:1	4.87	4.13	5.98	5.93	6.78	6.91

The amine number which indicates the concentration of the amine compounds is also an important index for the application the recovered polyols in the PU products [4]. The effects of the reaction conditions on the amine number of the recovered polyols are shown in Table 3. Generally, the higher the reaction temperature and DEG/FPU weight ratio, and the longer the reaction time, the higher the amine number was obtained. The amine compounds could come from the hydrolysis of the urethane groups as a side reaction [6]. The hydrolysis is not desirable in the decomposition reaction, however it is unavoidable. At a temperature around 200 °C, the hydrolysis of the urethane groups by water occurred with the main reaction producing unstable carbamate acids, which was readily decarboxylated and formed aromatic amines [5]. Although most water in the FPU foams was removed during the oven drying, the DEG which has a water content of up to 0.5% could bring in water. Higher DEG/FPU weight ratio would result in a higher amine number because more water was brought in through the DEG. Higher temperature increased the rate of the side reactions and favored the formation of the amine compounds. Another source of the amine compounds could be the decomposition of the urea groups contained in the FPU foam backbones. The urea groups were formed by the reaction between water and isocyanate. The water was usually involved in the preparation of the PU foams as surfactant. Although the amount of the urea groups was in a small quantity, they could affect the properties of the PU foams and thus also the properties of the recovered polyols. If the recovered polyols were reused in the preparation of new PU foams, the amine compounds might negatively affect the PU foaming reaction. They could accelerate the foaming reaction and form excessive rigid urea groups. In this study, because the amine compounds might serve as catalysts for certain polyurethane reactions in the preparation of PU products, the recovered polyols were not further purified. The understanding of the function of the amine compounds for certain PU reactions in the preparation of PU products, such as PU adhesives will be in the future study.

The yields of the recovered polyols under different reaction conditions are shown in Table 4. As reaction time increased, the yield increased. Same yield was obtained for the samples with DEG/FPU

weight ratios of 3:1 and 4:1. There was no significant difference in yield between the samples obtained at DEG/FPU weight ratio of 3:1 and 4:1 under the same temperature once the reaction was considered complete. The difference between pH values of the recovered polyols was negligible and most of the values were obtained in the range of 7.5-8.0. It was noted that the recovered polyol obtained at the DEG/FPU weight ratio of 3:1 and reaction temperature of 210 °C showed similar reaction completion time. And the properties of those obtained at the DEG/FPU weight ratio of 4:1 and reaction temperature of 180 °C are similar.

Table 4. Yields of recovered polyols at different reaction conditions

Reaction temperature (°C)	DEG/FPU weight ratio	Yield (%)					
		0.5 h	1 h	1.5 h	2 h	2.5 h	3 h
180	2:1	19	32	49	60	63	82
180	3:1	34	59	73	87	118	125
180	4:1	41	86	114	121	125	127
210	2:1	26	56	69	93	99	107
210	3:1	39	77	86	100	133	129
210	4:1	44	73	99	137	127	136

Table 5. Properties of typical commercial polyols

Commercial polyether polyols	OH number (mg KOH/g)	Viscosity (mPa.s)	PH value	Use
BASF Pluracol GP730	222-237	270	6.6	Elastomers, adhesives, and sealants
BASF Pluracol P1010	102-112	150	6.5	Foams, coatings, adhesives, and sealants

The application of the recovered polyols was introduced in a number of studies, most of which focused on the preparation of the PU foams [7]. However, either the recovered polyols could only partially (5-50%) replace the commercial polyols or the prepared PU foams had deteriorated properties compared with the commercial PU foams. In this study, after compared with the properties of two typical commercial polyols (Table 5), the properties of some obtained recovered polyols were similar to those of the GP730 which have been used in the preparation of PU coatings, adhesives, and sealants. Therefore, it is proposed that the recovered polyols obtained in this study may be more suitable for the preparation of PU products in addition to the PU foams.

4. Conclusions

FPU foam wastes from ASR were decomposed by the DEG as solvent and NaOH as catalyst under different reaction conditions. The reaction mixtures were vacuum distilled and filtrated to obtain the recovered polyols. The effects of the reaction temperature, time, and DEG/FPU weight ratio on the properties of the recovered polyols. It was found that: (1) higher temperature promoted the FPU decomposition reaction and resulted in a lower viscosity, higher hydroxyl number, and higher amine number; (2) higher DEG/FPU weight ratio shortened the reaction time and resulted in a higher amine number and lower viscosity; (3) the complete reaction time greatly depended on the reaction conditions. The recovered polyol obtained at the DEG/FPU weight ratio of 3:1 and reaction temperature of 210 °C showed similar reaction completion time and properties to those obtained at the DEG/FPU weight ratio of 4:1 and reaction temperature of 180 °C. Some recovered polyols showed similar properties to those of a commercial polyol. The future study will be focused on the utilization of the recovered polyols in the preparation of suitable PU products.

Acknowledgments

The authors are grateful for the supports of the Fundamental Research Funds for the Central Universities (Project No. BJFUKF201912), Youth Foundation of Shandong Natural Science

Foundation (Project No. ZR2017QC006), Scientific Research Project of Colleges and Universities in Shandong Province (Project No. J17KA147) and National Student Innovation and Entrepreneurship Training Program (Project No. 201810434013).

References

- [1] Behrendt, G., Naber, B. W. (2009) The chemical recycling of polyurethanes (review). *J. Univ. Chem. Technol. Metallurgy.*, 44: 3-23.
- [2] Nikje, M. M. A., Nikrah, M. (2007) Glycerin as a new glycolysing agent for chemical recycling of cold cure polyurethane foam wastes in “split-phase” condition *Polymer Bulletin* 58: 411-423.
- [3] Modesti, M., Lorenzetti, M., Simioni, F., Checchin, M. (2001) Influence of different flame retardants on fire behavior of modified PIR/PUR polymers. *Polym Degrad Stabil* 74: 475-479.
- [4] Wu, C. H., Chang, C. Y., Cheng, C. M., Huang, H. C. (2003) Glycolysis of waste flexible polyurethane foam. *Polym Degrad Stabil* 80: 103-111.
- [5] Mitova, V., Grancharov, G., Molero, C. Borreguero A. M. (2013) Chemical degradation of polymers (polyurethanes, polycarbonate and polyamide) by esters of h-phosphonic and phosphoric acids. *J Macromol Sci A* 50: 774-795.
- [6] Modesti, M., Simioni, F. (1996) Chemical recycling of reinforced polyurethane from the automotive industry. *Polym Eng Sci* 36: 2173-2178.
- [7] Simon, D., Lucas, A. D., Rodriguez, J. F., Borreguero A. M. (2017) Flexible polyurethane foams synthesized employing recovered polyols from glycolysis: physical and structure properties. *J Appl Polym Sci* 134: 617-625.