

Chemical Recycling of Rigid Polyurethane Foam Scrap via Base Catalyzed Aminolysis

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Abstract

Rigid polyurethane foam scrap was depolymerized by aminolysis using diethylenetriamine (DETA) as a degrading agent and sodium hydroxide (NaOH) as both a reactant and catalyst. The reaction was done at 180°C for 70 minutes and yielded 4,4'-methylenedianiline (MDA). It was found that higher completion of depolymerization increased as the amount of NaOH increased. In contrast, the amount of MDA decreased due to the aminolysis of PU foam by MDA catalyzed with NaOH.

Keywords: polyurethane, chemical recycling, aminolysis, 4,4'-methylenedianiline

Introduction

Polyurethane or PU is one of the synthetic polymers widely used for many applications. It is synthesized from the reaction between polyol such as polyester polyol, diol such as ethylene glycol or diamine such as diethyltoluenediamine, and diisocyanate such as diphenylmethane diisocyanate (MDI). In the synthesis of rigid PU foams, a blowing agent such as fluorotrichloromethane is added. Rigid PU foam exhibits excellent insulating properties; consequently, it is used as insulation for water heaters, tanks, pipes, refrigerators and freezers (O dian, 1991). However, its wastes from manufacturing processes or from human use are not physically recycled or reused by manufacturers due to the possibility of contamination by impurities. They are left as 'plastic waste', causing environmental problems since it cannot be degraded by natural processes. An alternative solution that has been done to solve this problem is to chemically recycle these PU wastes. Several chemical reactions have been applied such as aminolysis (Xue, *et al.* 1995) and glycolysis (Xue, *et al.* 1994). The reaction usually yields PU monomers, such as polyol and 4,4'-methylenedianiline (MDA). MDA is currently of interest since it is a monomer used for poly(*p*-diphenylmethylterephthalamide) synthesis (Higashi, *et al.* 1981). This polymer is an aromatic polyamide generally used to improve several properties of some polymers, such as

Nylon 6 and Kevlar. Furthermore, MDA can be used as a hardener for epoxy resin (Xue, *et al.* 1995).

It was reported by Xue and coworkers (Xue, *et al.* 1995) that the depolymerization rate of PU foam was related to the basicity of the degrading agent. They found that diethylene triamine (DETA) made the depolymerization rate of PU foam faster, more complete and led to a lower viscosity of aminolyzed product than triethylene tetramine (TETA) and tetraethylene pentamine (TETP) did. However, no catalyst was used in this aminolysis. On the other hand, it was observed by Van der Wal (Van Der Wal, 1994) that potassium hydroxide can catalyze the depolymerization of PU foam when alkanolamine was used as a degrading agent.

Therefore, the main objective of this research is to study the possibility of using a catalyst for the aminolysis of rigid PU foam scrap using DETA as a degrading agent. Sodium hydroxide (NaOH) was selected to be used as a catalyst for this reaction.

Experimental

Materials

Rigid polyurethane foam scrap was donated from the DOW Chemical company. DETA, NaOH and cyclohexane were purchased from Fluka. Practical grade MDA used as a

reference for characterization was also purchased from Fluka. All chemicals were used as received without further purification.

Methods

Depolymerization of Rigid PU Foam

DETA (50 g) was put in a 500 ml 4-necked round bottom flask equipped with a stirrer, a thermometer, a condenser and a N₂ gas inlet. It was heated and maintained at a temperature of 180°C. Ground PU foam (100 g) was then continuously added into the flask. After that, the desired amount of NaOH* was added. The reaction time was begun as soon as the foam was added into the flask and it was maintained for 70 minutes. Then the aminolyzed product was cooled down to room temperature and MDA was extracted from the product using cyclohexane and distilled water. The cyclohexane layer was left at room temperature for 7 days for MDA crystallization. MDA was collected and put in a desiccator.

*The amounts of NaOH used were 0, 15, 30, 45 and 60 g.

Characterization

The amounts of MDA were determined using HPLC (Lichrospher-100 RP18 column with size of 125 x 4 ml, mobile phase = 35/65 acetonitrile/water with ammonium acetate).

Structural analysis was carried out using ¹³C-NMR spectroscopy (NMR Spectrometer 500 MHz using *d*-chloroform as solvent) and the obtained ¹³C-NMR spectrum was compared with that of practical grade MDA.

Results and Discussion

As shown in **Table 1**, the viscosity of the aminolyzed products after cooling down to room temperature increases as the amount of NaOH decreases. Since higher viscosity indicates higher molecular weight, this suggests that the aminolyzed products with a higher viscosity are composed of molecules with higher molecular weights. These results are in good agreement with that reported by Xue and coworkers (Xue, *et al.* 1995). Furthermore, it was also observed that there were small amounts of PU foams present in the aminolyzed products prepared with NaOH (15 g) and without NaOH. These small amounts of PU foams were removed before extraction.

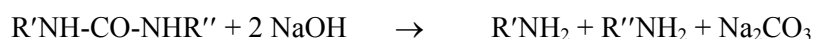
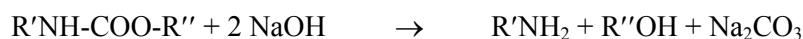
Table 1 The Physical Characteristics of The Aminolyzed Products

Aminolyzed Product No.	Amount of NaOH (g)	Characteristics
1	0	Very high viscous liquid with small amount of PU foam scrap
2	15	High viscous liquid with small amount of PU foam scrap
3	30	Medium viscous liquid
4	45	Low viscous liquid
5	60	Low viscous liquid

The above results suggest that the aminolysis was more complete by increasing the amount of NaOH. This may be because not only NaOH acts as a catalyst for aminolysis but it also reacts with urethane linkage and urea linkage of

PU foam to form related amines and polyols as shown below. These reactions were proposed by Van Der Wal (1994) when he depolymerized PU using KOH as a catalyst.

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After extracting the aminolyzed products with cyclohexane and analyzing the cyclohexane solution by HPLC, it was found that as the amounts of NaOH increase, the amounts of MDA obtained decrease, as shown in **Table 2**. This is because MDA obtained from depolymerization either by DETA which was catalyzed by NaOH

or decomposition by NaOH itself can further degrade PU as shown below (Van Der Wal, 1994). This reaction can be also catalyzed by NaOH. Therefore, as the amount of NaOH was increased, the rate of this reaction increased and the consumption of MDA was increased.

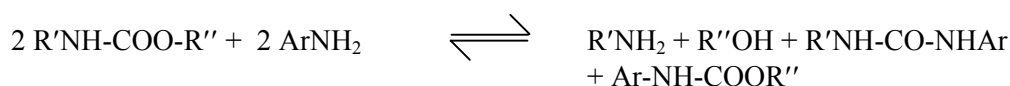


Table 2 Amounts of MDA Obtained from Base Catalyzed Aminolysis of PU Foam Determined by HPLC

Amount of NaOH (g)	Amount of MDA (g)
0	48.71
15	25.32
30	21.48
45	15.85
60	15.67

After maintaining the cyclohexane solutions at room temperature for 7 days, it was observed that in all solutions, there were caramel-like layers separated from the cyclohexane solutions. After separating these layers from the solutions and maintaining the solutions for seven days, it was found that there was the crystallization of white solid in the sample prepared without NaOH. Therefore, these caramel-like layers and the white solid were characterized by ^{13}C -NMR spectroscopy. From ^{13}C -NMR spectra shown in **Figure 1**, it can be seen that white solid obtained from chemical recycling of PU was MDA since it exhibits the characteristic peaks of MDA which are the same as the one obtained from practical grade MDA. On the other hand, the caramel-like layer also exhibits the aromatic characteristic peaks of

MDA (chemical shifts: 115, 129, 132 and 144 ppm) contaminated with the aromatic characteristic peaks of molecules containing urethane/urea bonds (chemical shifts: 116, 126, 127, 128, 131, 143 and 145) (Kanaya and Takahashi, 1994). All other caramel-like layers prepared with NaOH also showed similar spectra. These results indicate that the caramel-like layer was a mixture of MDA and low molecular weight urethane/urea oligomers. This suggests that most of MDA crystallized and precipitated with low molecular weight urethane/urea oligomers that were not completely depolymerized. Since the sample prepared without NaOH had a higher amount of the MDA as previously mentioned in **Table 2**, some of MDA did not crystallize during the first 7 days period but they crystallized after removing the caramel-like layer.

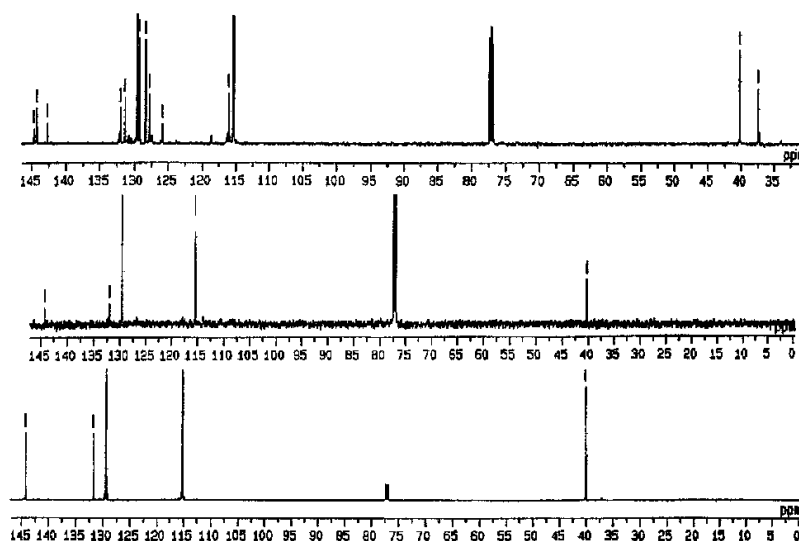


Figure 1 The ^{13}C -NMR spectra of a caramel-like layer (top), white solid (middle) of the extracted sample prepared without NaOH and practical grade MDA (bottom).

Conclusions

Aminolysis of rigid PU foam can be catalyzed by using a catalyst, such as NaOH. The reaction yielded MDA, low molecular weight urethane oligomers and other chemicals. These products can be separated by extraction with cyclohexane and distilled water. The amount of NaOH used has significant effects on the rate of aminolysis and the amount of MDA obtained.

Acknowledgements

We gratefully acknowledge Chulalongkorn University for financial, material and instrument support. We also thank the Dow Chemical Company for donating rigid PU foam scrap.

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