

Deamination of MDA in the Recycled Polyol Obtained from the Glycolysis of Waste MDI Based Polyurethane Foam

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Abstract : Recycled polyol was obtained by glycolysis of MDI-based Polyurethane(PU) rigid foam. The chemical structure of the recycled polyol was confirmed by GC(gas chromatography) and ¹H-NMR. The recycled polyol throughout the glycolysis contained liquid polyol and methylenedianiline(MDA). MDA which could cause liver cancer is carcinogenic material. TWA(Time Weighted Average.) amount for MDA in MSDS(Material Safety Data Sheets) was confined less than 0.1ppm. The melting temperature of MDA is 92°C, and boiling temperature is 398°C. During the glycolysis most of MDA was dissolved in liquid polyol. The probability that MDA diffuses into the atmosphere is low but there could be an absorption of MDA into skin. Furthermore because MDA is amine compound, recycled polyol which contained MDA had a difficulty in reaction control of polyurethane. Therefore reduction of MDA amount was needed strongly. In this study the elimination of MDA were performed through deamination of the recycled polyol by glycidyl ether compounds. As glycolysis was proceeded, the amount of MDA was 9.8 wt % at early stage and increased up to 14.0 wt % after 8 hours reaction. It was found that 2-Ethylhexyl glycidyl ether which contains aliphatic moiety was very effective compound for eliminating the primary aromatic amine compound and the optimal mole ratio of 2-ethylhexyl glycidyl ether to MDA was 3. The final polyol after deamination by 2-ethylhexyl glycidyl ether has an appropriate viscosity(less than 500 centi poise) for polyurethane reaction.

Key words : Deamination, Glycolysis, 2-ethylhexyl glycidyl ether, methylenedianiline

1. Introduction

Polyurethane(PU) has been the subject of intensive research due to a wide range applications such as foam, elastomer, adhesive, plastics, and etc. [1]. However, a lot of waste PU has been also produced in industry because of its difficulty in physical and energy recycle process and in chemical recycle reaction. Many attempts have been recently focused on the recycling of PU via physical and chemical methods [2-6]. Among them, it has been well known that the glycolysis reaction of PU has several advantages in a view point of economic and industrial applications because of high recycling efficiency [7-21]. Glycolysis reaction of PU depends on many factors such as mixing ratio of PU to glycol, type of glycol, catalyst, reaction temperature, the amount of polyol, and etc.. It was also known that in case of using

glycolysis reaction for PU, the recyclates including polyols contain primary aromatic amine derivatives which are carcinogens and barriers to reuse. Methylenedianiline(MDA) which could cause liver cancer is carcinogenic material. TWA(Time Weighted Average.) amount for MDA in MSDS(Material Safety Data Sheets) was confined less than 0.1ppm. The melting temperature of MDA is 92°C, and boiling temperature is 398°C. During the glycolysis most of MDA was dissolved in liquid polyol. The probability that MDA diffuses into the atmosphere is low but there could be an absorption of MDA into skin. Furthermore because MDA is amine compound, recycled polyol which contained MDA had a difficulty in reaction control of polyurethane. Therefore reduction of MDA amount was needed strongly. In this study the elimination of MDA were performed through deamination of the recycled polyol by glycidyl ether compounds. Aromatic amine derivatives in recycled polyols of rigid PU foam by using gas chromatog-

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raphy and $^1\text{H-NMR}$.

2. Experimentals

Glycolysis reaction of rigid PU foam, which was crushed was carried out in ethylene glycol(EG) in a four neck flask equipped with reflux condenser and agitator. The reaction temperature was 200°C after adding catalysis under N_2 atmosphere with stirring. The reaction has proceeded until the crushed PU foam became an homogenous liquid phase by a naked eye. To check the content of aromatic amine in recycle, sampling has been done as a function of reaction time of 2, 4, 6, 8, and 10 hrs, respectively.

Quantitative analysis was carried out by GC-MSD(HP 5890 series) with a column with HP-5 capillary column ($25\text{m} \times 0.2\text{ mm} \times 0.33\text{ }\mu\text{m}$ film thickness) and HP-5971A mass spectrometer(70eV) as a detector. GC-MSD experiment was done at 150°C for 3min. The temperature of column increased from 100°C to 250°C at a rate $20^\circ\text{C}/\text{min}$ after the temperature of column was kept at 100°C for 3 min, keeping the temperature of detector 270°C . $^1\text{H-NMR}$ spectra were recorded with Bruker AM-200 spectrometer in CDCl_3 containing 3% (v/v) tetramethylsilane(TMS) as a solvent and chemical shifts were recorded in ppm units .

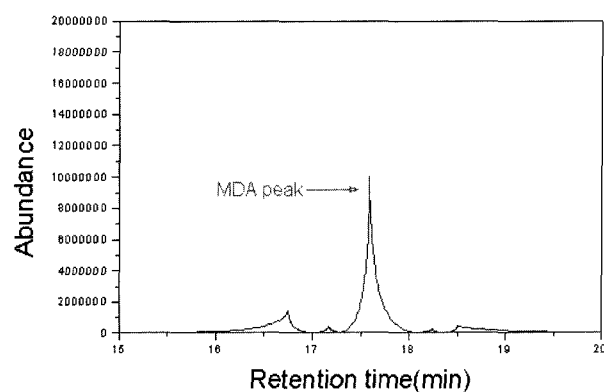
Deamination reaction proceeded with glycolysis reaction together at one time as follows. EG, base catalyst, and 2-ethylhexyl glycidyl ether or C13-15 alkyl chained glycidyl ether were added into four neck flask equipped with reflux condenser and agitator. To this mixture, with stirring, the crushed PU powder was added and kept at 200°C in N_2 atmosphere. Deamination reaction proceeded until PU became an homogenous liquid phase of polyol.

3. Results and Discussion

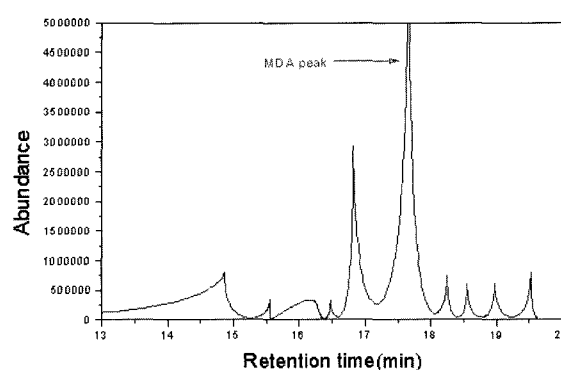
In order to verify aromatic diamine in recycle, MDI based rigid PU foam was used as waste. GC-MSD spectra were obtained from pure methylenediamine (MDA) which is corresponding with MDI and the recycle which has been reacted with PU and ethylene glycol, respectively. As shown in Fig. 1.

MDA with molecular weight of 198 showed its peak position at 17.6 min, the recycle also showed characteristic peak position at 17.6 min indicating MDA.

After separation of MDA from the recycle by column chromatography, the structure was also identified by $^1\text{H-NMR}$. As the glycolysis reaction proceeded, primary amine proton peak appeared around 3.4-3.5 ppm



(a) pure MDA



(b) after glycolysis reaction of PU.

Fig. 1. GC-MSD spectra of pure MDA and recycle

in NMR and the integral area ratio of amine proton peak was consist with the integral area of aromatic proton(6.57, 6.94ppm) and methylene proton(3.77ppm).

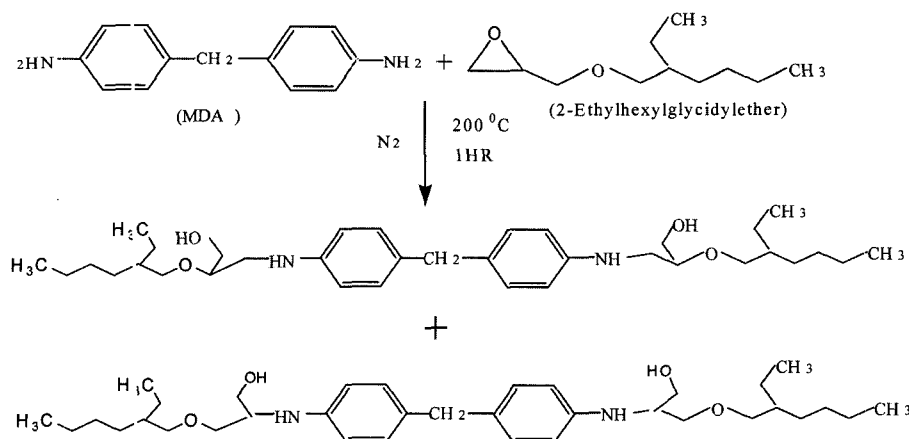
Table 1 shows the change of MDA contents as a function of glycolysis reaction time. MDA content was increased from 10 wt % at 2 hours reaction time to 14 wt% after 8 hours reaction.

As we mentioned, MDA component is a barrier for recycle application [11].

It has been well known that deamination reaction was carried out using epoxide compound with low molecular weight. But there are same disadvantages in low molecular weight oxide compound such as hazard of explosion due to its low ignition temperature and difficulty in controlling reaction conditions at atmosphere. Also it might be not easy to get polyol product with good sol-

Table 1. Change of MDA contents as a function of glycolysis reaction time.

Reaction Time(hours)	MDA Content (wt %)
2	9.78
4	9.82
6	11.63
8	14.10



Scheme I. Deamination reaction of MDA and 2-ethylhexyl glycidyl ether.

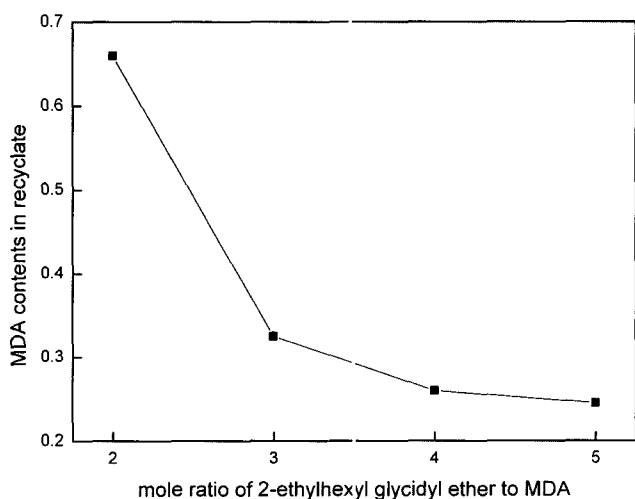


Fig. 2. MDA contents in recyclate vs mole ratio of 2-ethylhexyl glycidyl ether to MDA during deamination.

ubility as well as relatively low viscosity from recyclate by using aromatic glycidylether for deamination.

Therefore several aliphatic glycidyl ether derivatives were introduced in deamination reaction for removing primary aromatic amine functional group of MDA. Our motivation for the deamination reaction for removing aromatic amine is based on fact that primary aromatic amine reacts well with epoxy ring of glycidyl ether. (Scheme I) And in another aspect, long alkyl chained (C13-15) and short alkyl chained (2-ethylhexyl) glycidylether were used for deamination reaction for controlling proper viscosity. The reactivity of 2-ethylhexyl glycidyl ether in deamination reaction was better than long alkyl chained glycidyl ether's.

Fig. 2. shows the dependence of MDA content in recyclate on 2-ethylhexyl glycidyl ether ratio to MDA during deamination reaction. MDA content was rapidly decreased as 2-ethylhexyl glycidyl ether ratio increased.

The optimal mole ratio of 2-ethylhexyl glycidyl ether to MDA for deamination reaction was 3. Also, recycled PU product obtained from deamination reaction of 2-ethylhexyl glycidyl ether reagent showed good solubility and proper viscosity (less than 500cps) for reuse.

4. Conclusion

We have demonstrated that the recyclate obtained from glycolysis reaction of waste MDI based polyurethane foam contained aromatic amine components which are carcinogenes. 2-Ethylhexyl glycidyl ether in recycle reaction effectively removed primary aromatic amine and improved the physical property of recycled PU foam, which has good solubility and relatively low viscosity.

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