

Desaminated Glycolysis of Water-Blown Rigid Polyurethane Foams

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ABSTRACT: Glycolysis reaction kinetics of methylene diphenyl diisocyanate-based water-blown polyurethane foams was examined by gel permeation chromatography. Glycolysates were reacted with butyl glycidyl ether to convert toxic aromatic amines to polyols, and their products were identified by $^1\text{H-NMR}$ spectroscopy. To examine the quality of recycled polyol, polyurethane foams were reprepared using the virgin and recycled polyol mixtures with varying compositions. Cell structures and sizes of reprepared foams were similar to those of original ones when the recycled polyols were mixed up to 30 wt %. Density, thermal conductivity, and flexural strength of the reprepared foams were compared with those of the original ones, and no difference was observed below the recycled polyol concentration of 30 wt %. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2646–2656, 2000

Key words: rigid polyurethane foam; polyol; desamination; glycolysis

INTRODUCTION

Polyurethane (PU) foams have been used in a variety of fields as insulating materials, associated with their low thermal conductivity, good mechanical and chemical properties, and good processability.^{1,2} A number of natural or synthetic materials have been effectively replaced by PU foams, so that the current consumption of PU foams reaches 7 million tons per year.³ The recycling of PU foams is thus now one of the most important issues in view of worldwide environmental protection. A few techniques for the recycling of flexible PU waste foams, whether those are chemical or physical, have been reported and even successfully applied to the commercial plant.^{4–13} The recycling techniques of rigid PU waste foams are, however, not acknowledged as widely as those of flexible ones, due to the economical and technical limitations associated with

their inherently dense properties. About 93% of rigid foams are reported to be land-filled nowadays.

The chemical recycling processes, solvolysis processes, involve the degradation of C—X bonds by appropriate solvents. The hydrolysis, glycolysis, and hydroglycolysis processes induced by water, glycol, and both water and glycol, respectively, are reported as the most effective techniques for the chemical recycling of rigid foams so far.¹⁴ All these techniques involve the production of polyols, major reactants for PU synthesis. The hydrolysis process has some strength compared with other processes in the production of polyols with similar chemical structure to the virgin ones, but also has some drawbacks associated with the complication of process. The glycolysis process, otherwise, has its strength in its simplicity, but drawbacks associated with the production of polyols with somewhat different chemical structure from the virgin ones.

As toxic amines are usually produced from the side reaction of glycolysis, those very undesirable chemicals must be eliminated by appropriate sep-

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Table I Formulation for the Preparation of Rigid PU Foams

| Reagent | PPG-490 | PPG-420 | Glycerine | Dimethylcyclohexylamine | Silicone | H ₂ O | Poly-MDI |
|------------------------|-----------------|-----------------|--------------------|-------------------------|----------------|------------------|---------------------|
| Use | Reactive Polyol | Reactive Polyol | Crosslinking Agent | Catalyst | Cell Regulator | Foaming Agent | Reactive Isocyanate |
| Formulation (wt ratio) | 70 | 30 | 5 | 1 | 1 | 1.5 | 158.96 |

aration techniques. Considering a variety of separation techniques, one of the most efficient and economic methods for the elimination of toxic amines is throughout the chemical reaction, the desamination reaction,¹⁰ where amines are converted to polyols by reaction with glycidether.

In this study, glycolysis reactions of rigid PU foams were conducted with different types of glycolic solvents, and the solvent effect on the reaction kinetics was investigated. Comparison of the morphology and physical properties between the original and the reprepared PU foams led to the determination of the optimal composition of recycled and virgin polyol mixtures. The desamination reaction was conducted with butyl glycidyl ether and its efficiency was analyzed.

EXPERIMENTAL

Materials

Ether-type polyols and polymeric methylene diphenyl diisocyanate (polymeric MDI) were used for the synthesis of rigid PU foams. Two kinds of poly(propylene glycol) (PPG) with OH values of 490 and 420, respectively, were blended and used as the reactive polyols. Polymeric MDI with average functionality of 2.7 was used as the reactive isocyanate. Glycerine and silicone were added as the crosslinking agent and surfactant, respectively. Methyl cyclohexyl amine was used as a catalyst. All the chemicals for the preparation of rigid urethane foams were provided by Miwon Chemical Co. (Ansan, Korea).

The glycolysis reaction was performed using three different types of glycols—ethylene glycol (EG; Kanto Chemical, Tokyo, Japan), propylene glycol (PG; Kanto Chemical), and diethylene glycol (DEG; Duksan Chemical, Yongin, South Korea). Sodium acetate was used as the catalyst for this reaction.

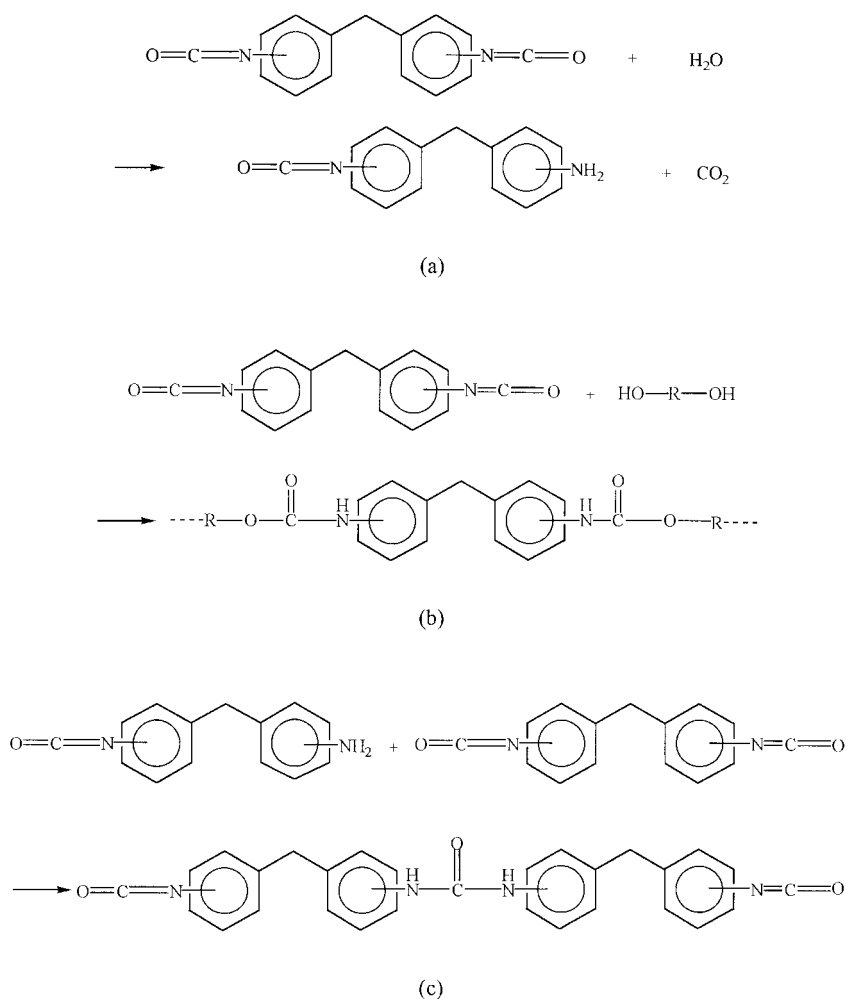
Pyridine (Duksan Chemical) was purified by distillation. Phthalic anhydride was dissolved in pyridine and used for the measurement of OH values of polyols. Sodium hydroxide, 0.1*N*, was prepared and used for the titration. Butyl glycidyl ether (Aldrich Chemical, Milwaukee, WI) was used for the desamination reaction with the catalyst of dimethylcyclohexylamine. Methylene dianiline (MDA; Aldrich Chemical) was used as a standard reagent for the gel permeation chromatography (GPC) measurement.

Preparation of PU Foams

PU foams were prepared by the reaction of polyols with polymeric MDI in the presence of a cell regulator (surfactant), crosslinking agent, and catalyst in a polyethylene (PE) container. A small amount of water was added as a foaming agent. PU foams were produced by agitating the mixture with a motor-driven impeller at 3000 rpm for 10 s. The formulation for the synthesis of PU foams is represented in Table I. After the prepared forms were crushed to a particle diameter of about 1 mm, they were stored in a vacuum oven at 80°C for at least for 2 h for dehumidification. The reparation method of PU foams with recycled polyols was the same as the one mentioned above except the compositions of the reactant polyols, 10, 20, 30, and 40 wt % of the recycled polyols, were mixed with the virgin ones.

Glycolysis Reaction

Glycols and other additives were placed in a 500-mL three-neck flask. The ground foams were put in the glycol-containing flask when the temperature of the glycols reached and then stabilized at 190°C. The glycolysis reaction was conducted for about 5 h under a nitrogen atmosphere. During the reaction, the reactants were well agitated by a motor-driven impeller. A part of the glycols that evaporated during the reaction was recycled by a refluxing condenser.



Scheme 1 Reaction mechanisms in the preparation of PU foams: (a) production of CO_2 gas; (b) synthesis of urethane group; (c) synthesis of urea group.

Desamination Reaction

The desamination reaction was conducted after the glycolysis reaction. Butyl glycidether, 10 wt %, and 1 wt % of dimethylcyclohexylamine were added to the glycolysates. This reaction was conducted at 150°C for 5 h in a 500-mL flask.

Glycolysis Kinetics Measurement

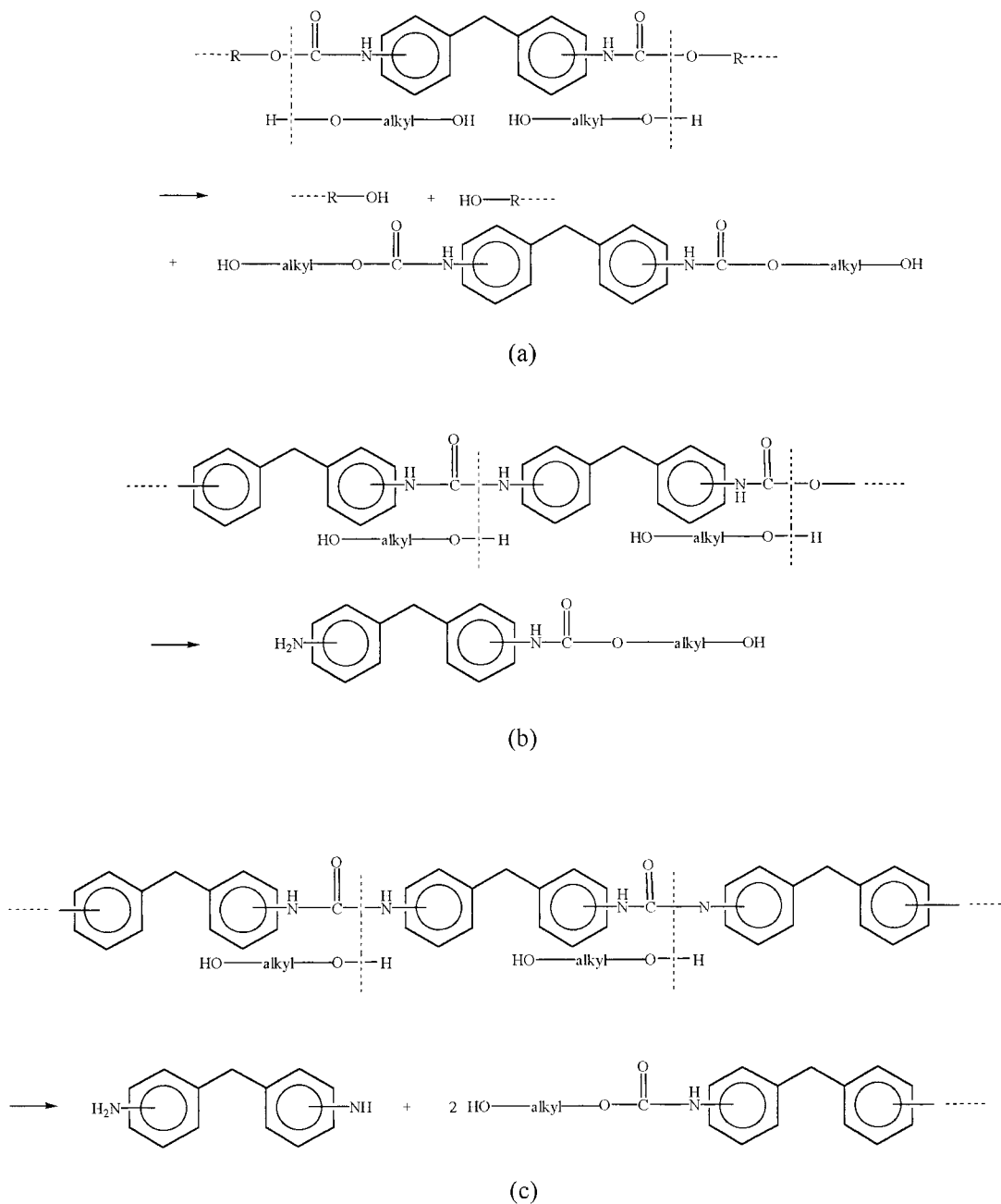
The composition change during the glycolysis reaction was investigated using gel permeation chromatography (GPC, Model 410, Waters). Tetrahydrofuran was used for the mobile phase with the flow rate of 1 mL/min. The reactants were periodically sampled every 20 min and the chromatographic intensity was measured until the completion of the reaction.

Characterization

The OH values of the recycled polyols were measured according to ASTM D4272. Phthalic an-

hydride, 116 g, was dissolved in 700 mL of dehumidified pyridine. A certain amount of the polyol samples, in 0.1 mg accuracy, was reacted with 25 mL of a phthalic anhydride solution at 115.2°C for 1 h in a refluxing condenser-installed flask. After the reaction, the condenser was washed with 50 mL of pyridine, and the products were titrated with a 0.1N NaOH solution. The same experiments were conducted without the polyol samples.

The density, thermal conductivity, and flexural strength of both the original and repaired PU foams were measured and compared to investigate the quality of the recycled polyols. The thermal conductivity was measured according to KS L9016. The sample dimension for this measurement was $30 \times 30 \times 3$ cm. The flexural strength was measured according to KS M3830 for the samples in the dimension of $2 \times 2.5 \times 12$ cm. The



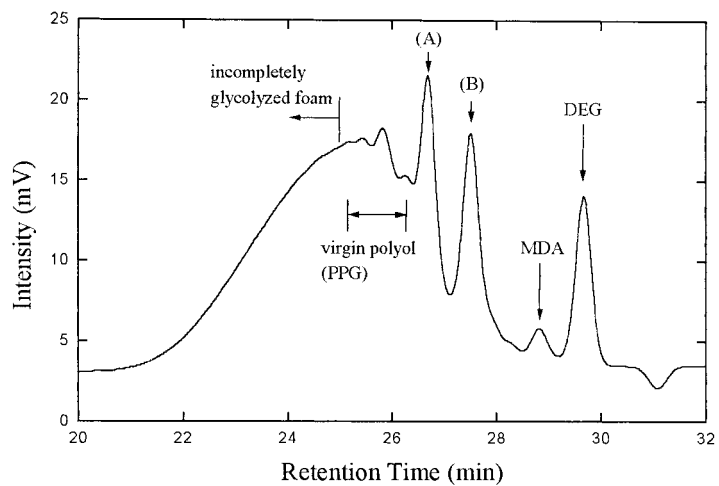
Scheme 2 Major production schemes from the glycolysis reaction: (a) dicarbamates; (b) monocarbamates; (c) diamines.

measurements were performed using a universal tensile machine (Instron, Model 4302) with the crosshead speed of 10 mm/min. The loads were read when the samples were fractured and saved to calculate their flexural strength.

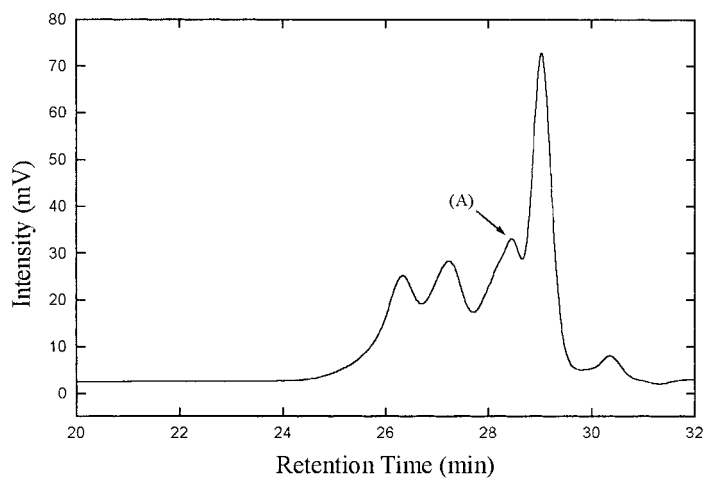
The microphotographs of both the original and reprepared PU foams were taken by a scanning electron microscope (SEM, Model S-2400, Hitachi) to observe the cell structure and size. The

samples were fractured after being quenched in the liquid nitrogen. The fractured surface was observed using SEM.

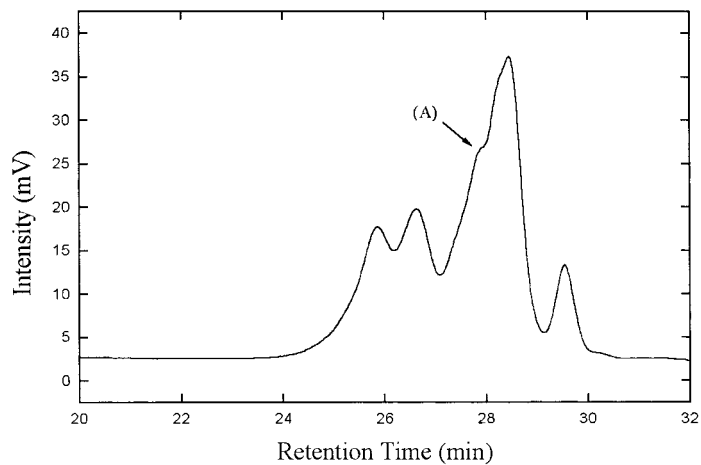
The chemical structures of the glycolysates before and after the desamination reaction were analyzed and compared using ^1H -nuclear magnetic resonance spectroscopy (^1H -NMR, 500 MHz, Varian Unity). Chloroform was used as the solvent for this measurement.



(a)



(b)



(c)

Figure 1 GPC results of glycolysates after reaction for 2 h with different solvents of (a) DEG, (b) PG, and (c) EG. (A) indicates dicarbamate, and (B), monocarbamate peaks.

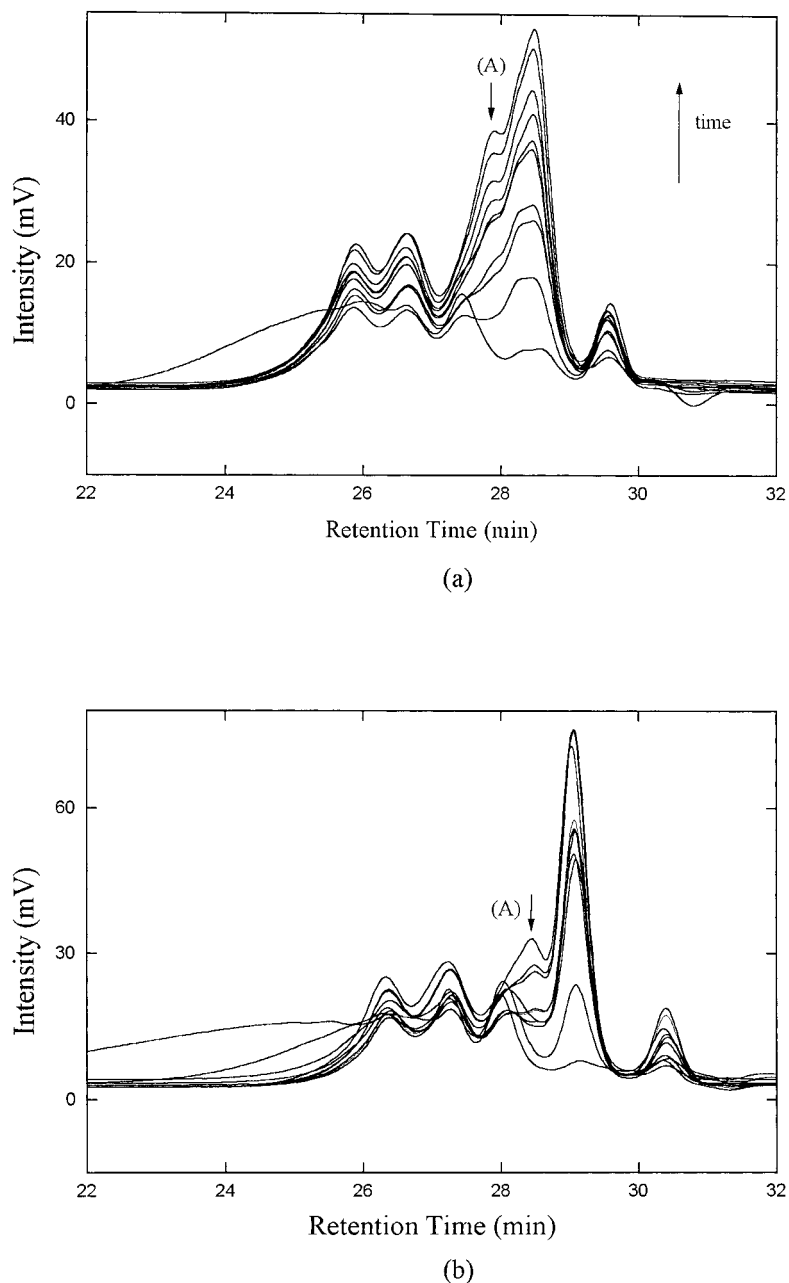


Figure 2 GPC results of glycolysates sampled every 20 min during the glycolysis reaction with (a) PG and (b) EG.

RESULTS AND DISCUSSION

Synthetic Scheme of Rigid PU Foams

The reaction mechanism for the preparation of PU foams was well reported. A small amount of water was reacted with excess diisocyanates to produce amines and CO_2 gas following the mechanism represented in (a) of Reaction Scheme 1. The CO_2 gas being produced acted as the foaming agent during

the PU synthesis reaction in the presence of polyols and diisocyanates following the mechanism represented in (b). During the synthesis of PU foams, the amines also reacted with diisocyanates to produce ureas through mechanism (c).

Glycolysates

The PU forms were degraded into a gray-colored viscous liquid, after being reacted with 30–40 wt

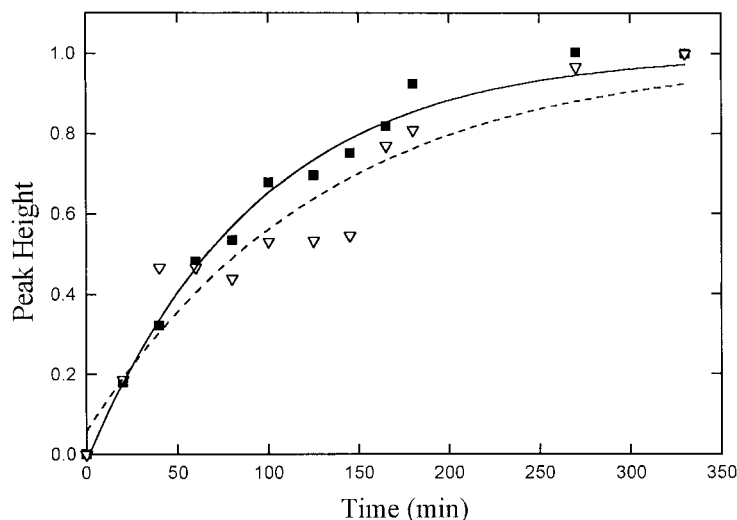


Figure 3 Comparison of monocarbamate production kinetics during the glycolysis reaction of PU foams with (■) PG and (▽) EG.

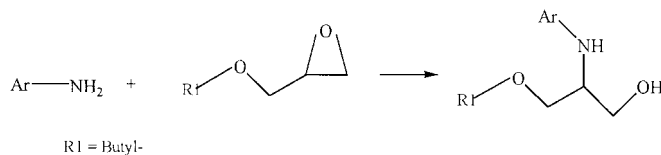
% of the glycols. The products from this reaction were expected as follows: The dicarbamate-type polyols would be the major products through the reaction mechanism shown in Scheme 2(a). The monocarbamate-type polyols and diamines would also be produced from the side reactions through the mechanisms illustrated in Scheme 2(b, c), respectively. Other chemicals possibly included in the glycolysate products were unreacted glycols, once completion of the glycolysis reaction of the PU foams was assured. Figure 1 shows the GPC results of the glycolysates after PU foams were reacted with three different types of glycols—DEG, EG, and PG. As the polyols produced from the reaction with DEG were more viscous than those from PG or EG due to the higher molecular weight of DEG and a slower reaction process, the polyols produced from DEG were noted as not effective for the regeneration of PU foams. Comparison of the GPC peak positions of the glycolysates with those of the standard chemicals led one to confirm the presence of five different chemical structures. The five peaks observed from the retention time of 20–32 min were correspondent to the two types of virgin polyols, dicarbamate-type polyols (A), monocarbamate-type polyols (B), and unreacted glycols, respectively. Another small peak between the two peaks corresponding to monocarbamate and DEG in Figure 1(a) was attributed to the presence of MDA. This MDA peak was not observed in Figure 1(b, c), because it was in a minute presence and was absorbed in its surrounding peaks, especially corresponding to dicarbamates.

Solvent Effect on Glycolysis Kinetics

Figure 2(a, b) shows the GPC results of the glycolysates sampled every 20 min during the degradation reaction by PG and EG, respectively. The intensities of the first four peaks, originated from two types of virgin polyols, dicarbamate-type polyols, monocarbamate-type polyols, respectively, increased, but the fifth peak, originated from the reactant glycols, decreased with the progress of the reaction. The reason that the GPC peaks of the glycolysates from the reaction with PG were observed at a lower evolution time than those with EG was that the molecular weight of PG was slightly higher than that of EG. Figure 3 shows the comparison between the production kinetics of monocarbamates from the reaction with PG and that from EG. The rate of the glycolysis reaction with PG was not very different from that with PE. The glycolysis reactions were completed in about 5 h.

Desaminated Products

The desamination reaction produced OH-terminated functional groups by the mechanism represented in Reaction Scheme 3 and these products were used for the reparation of PU foams. Figure 4 shows the $^1\text{H-NMR}$ spectra of the glycolysates before and after the desamination reaction. The $^1\text{H-NMR}$ peaks observed from 6 to 8 ppm were originated from the protons in aromatic rings, and those from 1 to 2 ppm, from those of alkyl groups. The major difference between these two NMR spectra was observed in the chemical shift ranging from 3 to 4 ppm. (A) and (B) peaks



Scheme 3 Desamination reaction.

observed from 3 to 4 ppm before desamination reaction were originated from the protons included in the epoxide groups of butyl glycidyl ether. These two peaks disappeared after the desamination reaction, as the epoxide groups in butyl glycidyl ether were reacted with the amines.

Characterization

The OH values of recycled polyols were determined from eq. (1):

$$\text{OH value (mgKOH/g)} = [(B - A)N \times 56.1]/W \quad (1)$$

Here, A and B are the amounts (mL) of the NaOH solution used to neutralize the sample solution and standard solution, respectively. N is the normal concentration of the NaOH solution, and W , the sample weight.

The OH values of recycled polyols before and after the desamination reaction were about 580 and 605 mg KOH/g, respectively, and were somewhat higher than those of the virgin ones, 490 and 420 mg KOH/g. Even higher OH values of the recycled polyols were reported by other investiga-

tors,¹⁵ when the ester-type polyols were used instead of the ether type because of the possibility of a transesterification reaction of the polyols. PU foams were reprepared using the equivalent amount of recycled polyols, based on the OH values determined.

Figure 5 shows the microphotographs of PU foams reprepared. The polyols, 10–40 wt %, for the reparation of PU foams were the recycled ones produced from the glycolysis reaction. The photocells of the reprepared foams were smaller and more uniform than were those of the original foams when the recycled polyol concentration was 10 wt %. The cell structures were kept uniform, and their sizes were similar to those of the virgin foams up to the recycled polyol concentration of 30 wt %. The cells were ruptured when the recycled polyol concentration was above 30 wt %.

Figures 6–8 show the density, thermal conductivity, and flexural strength of PU foams, respectively, reprepared from the reaction of polymeric MDI with the recycled and virgin polyol mixtures. The density behavior of reprepared PU foams was well explained by the cell structure and size. Den-

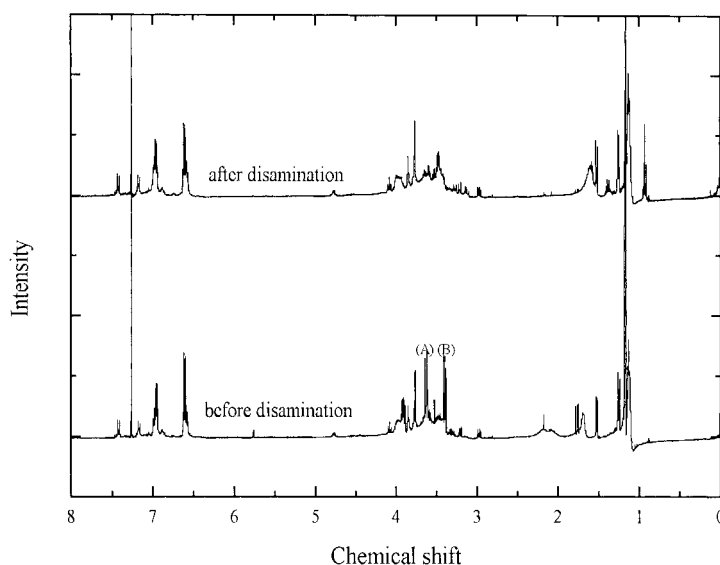


Figure 4 $^1\text{H-NMR}$ spectra of glycolysates before and after desamination reaction.

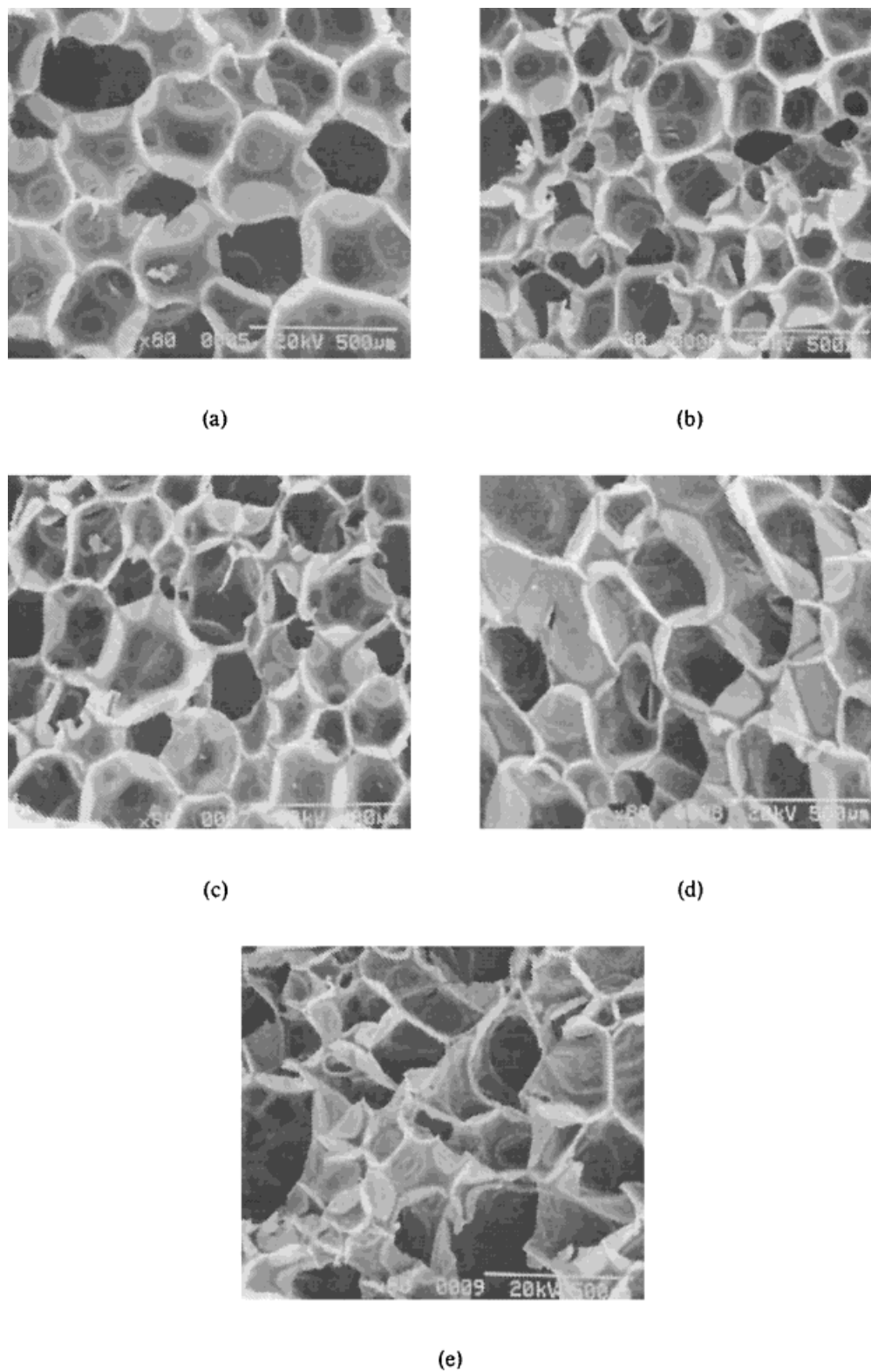


Figure 5 Microphotographs of cell structure of reprepared PU foams: (a) 0% recycled polyol; (b) 10% recycled polyol; (c) 20% recycled polyol; (d) 30% recycled polyol; (e) 40% recycled polyol.

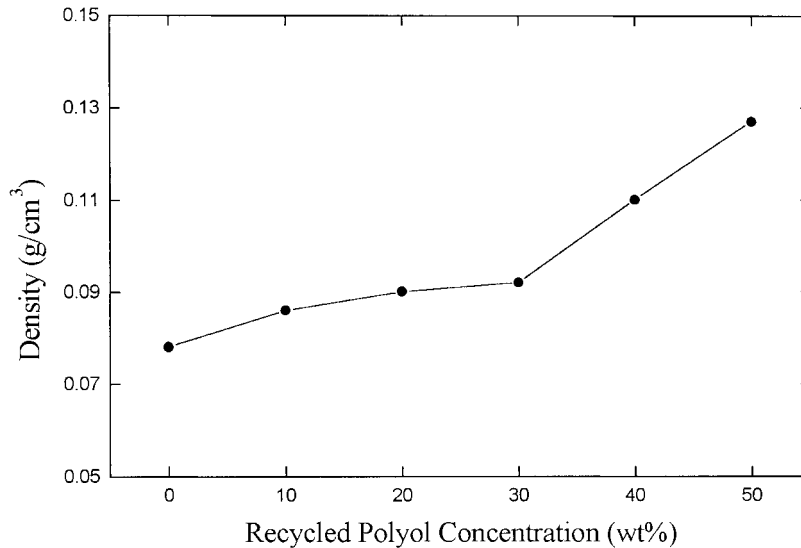


Figure 6 Density of PU foams as a function of polyol composition.

sity did not change significantly with increasing recycled polyol concentrations up to 30 wt %, but was abruptly increased above 30 wt %. The thermal conductivity and flexural strength of reprepared PU foams did not deviate much from those of the original ones when the recycled polyol concentration was less than 30 wt %, but they also increased significantly above that concentration.

CONCLUSION

Production of five types of polyols from the glycolysis reaction of PU foams—two virgin-type poly-

ols, mono- and dicarbamate-type polyols, and unreacted glycols—were identified using GPC. The rate of the glycolysis reaction with PG was similar to that with EG. The glycolysates from the reaction with DEG were more viscous because of the higher molecules of DEG and its slow reaction process. The recycled polyols resulted in higher OH values due to the presence of unreacted glycols. Toxic amines in the glycolysates were reacted with butyl glycidyl ether to produce the polyols, and it was confirmed by ¹H-NMR spectroscopy. It was concluded from the observation of the cell structure, density, thermal conductivity, and flexural strength behaviors that the concen-

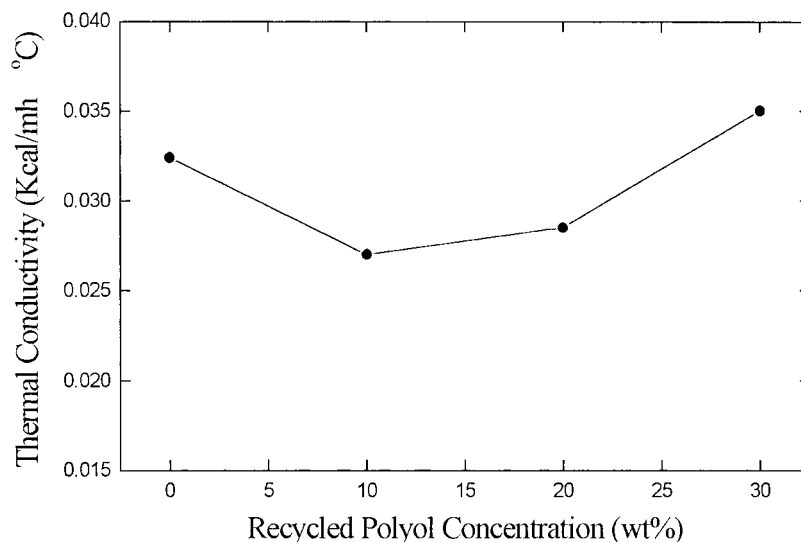


Figure 7 Thermal conductivity of PU foams as a function of polyol composition.

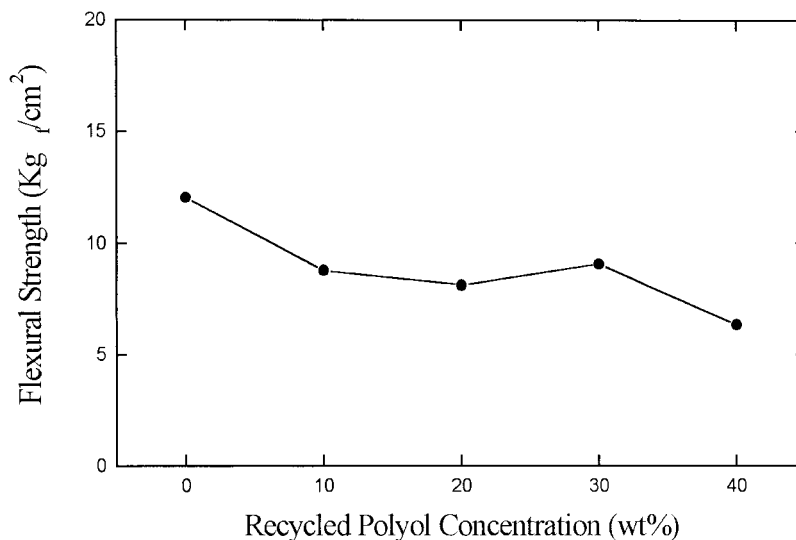


Figure 8 Flexural strength PU foams as a function of polyol composition.

tration of recycled polyols for the reproduction of PU foams without any deterioration of physical properties was less than 30 wt %.

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