Recycling of Polyurethane Foam as a Hardener for Epoxy Resin

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Polyurethane foam was recycled by glycolysis through the transesterification reaction. The glycolyzed products were characterized using infrared spectroscopy, nuclear magnetic resonance spectroscopy, and gel permeation chromatography. It was found that the decomposed products were mainly mixtures of low molecular weight amines and polyols. Such mixtures were used to harden epoxy resin without further purification. The curing reaction between glycolyzed products and epoxy was studied using differential scanning calorimetry. The cured epoxy samples showed good thermal and mechanical properties characterized by dynamic mechanical analysis and hardness measurements.

Key words: Polyurethane foam, recycling, epoxy resin, glycolysis.

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การเชื่อมขวางอีพอกซีเรซีน โดยการใช้ผลิตภัณฑ์จากการรีไซเคิลของโพมพอลิยูรีเทน

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โฟมพอลิยูรีเทนชนิดแข็งสามารถย่อยสลายได้โดยกระบวนการไกลโคลิซิสโดยผ่านปฏิกิริยาทรานเอสเทอริฟิเคชัน เทคนิคที่ใช้ศึกษาสมบัติของผลิตภัณฑ์จากการสลายตัวของโฟมพอลิยูรีเทนคืออินฟราเรดสเปกโทรสโกปี (IR) นิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโทรสโกปี (NMR) และเจลเพอร์มิเอชันโครมาโทกราฟี (GPC) ผลิตภัณฑ์หลักที่ได้จากปฏิกิริยาคือของผสมของแอมีน และพอลิออลที่มีน้ำหนักโมเลกุลต่ำ ผลิตภัณฑ์เหล่านี้ถูกใช้เป็นสารเชื่อมขวางสำหรับอีพอกซีเรซินได้โดยไม่ต้องผ่านขั้นตอนการแยก การศึกษาปฏิกิริยาเชื่อมขวางทำโดยเทคนิคดิฟเฟอเรนเชียล สแกนนิง คาลอริเมทรี (DSC) นอกจากนั้นในงานวิจัยนี้ยังศึกษาถึงสมบัติของอีพอกซีเรซินที่ถูกเชื่อมขวางแล้วด้วยเทคนิคการวิเคราะห์สมบัติเชิงกลพลวัต และการวัดความแข็ง พบว่าอีพอกซีเรซินที่ถูกเชื่อมขวางแล้วมีสมบัติทางความร้อน และทางกลที่ดี

คำสำคัญ โฟมพอลิยูรีเทน รีไซเคิล อีพอกซีเรซิน ไกลโคลิซิส

INTRODUCTION

There has been a significant increase in plastic wastes leading to a great impact on our living environment. Therefore, the development of novel recycling techniques for wastes from both thermoplastics and thermosets has become an important subject. Thermosets are especially difficult for recycling since they are not melt processable. Polyurethane (PU) foams, being thermosetting materials, have been recycled chemically by various ways including glycolysis,(1-3) hydrolysis,(4-8) and others.(9,10) Among these techniques, glycolysis is the most widely studied method for the decomposition of rigid polyurethane foams. Decomposers used in this method are mainly low molecular weight compounds containing hydroxyl groups. Such decomposers can chemically break down the urethane linkages through transesterification reactions. Types of glycolyzed products obtained depend upon the types of decomposers used. Glycolysis of these foams mainly results in polyols while secondary reactions involve the decomposition of urea linkages and the formation of amines. The liquid reaction products were usually processed further in order to retrieve polyol, one of the starting materials for making PU foam. Most of the investigations in the literature emphasized the regeneration of the polyol from PU foam wastes for re-use in foam preparation.(1,2)

To date, there have only been a few works on the use of chemically recycled PU products to make materials other than foams.(3,9) There is also a lack of detailed characterizations on the liquid products derived from recycled PU. Kanaya and Takahashi(11) have reported that the decomposition process of polyurethane foam by pure alkanolamines is not aminolysis but rather alcoholysis. There was no report on the application of their reaction product. In addition, their conclusions may not be the same provided a catalyst, such as a metal hydroxide, is present. Xue et al.(3) reported the preparation of adhesives using epoxy resin and glycolyzed products from PU foam. In their work, it was necessary to add amines, which are typical commercial hardeners for epoxy resins, in order to achieve better material performance. Thus, it is interesting to develop a technique to use the glycolyzed products as a hardener for epoxy resin directly without the addition of hardeners and without using complicated separation processes for the polyols and amines.

In this paper, a novel approach for the recycling of PU foam is reported. Diethanolamine (DEA) was used as a decomposer for the glycolysis of PU foam. Sodium hydroxide was introduced to facilitate the glycolysis reaction.(2) Since the reaction between the epoxide ring and hydroxyl group can be catalyzed by metal hydroxides,(12,13) sodium hydroxide in the glycolyzed product can also promote the crosslinking reaction in our polymer system. The synthesis and characterization of the glycolyzed product as well as the properties of the cured epoxy samples are reported.

EXPERIMENTAL

Materials

PU foam used in this experiment is rigid PU foam for construction provided by Pacific Plastics (Thailand) Co., Ltd. (DOW). The preparation of the PU foam was mainly based on methylene diphenyl diisocyanate (MDI) and multifunctional hydroxyl compounds. Diglycidyl ether of bisphenol-A (DGEBA) epoxy resin (Epiclon 850) was provided by Siam Chemical Industry Co., Ltd. DEA and sodium hydroxide obtained from M&B and J.T. Baker, respectively, were used as received.

Instruments

The infrared (IR) spectra were recorded on a Nicolet FTIR spectrophotometer. The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Fourier Transform NMR spectrometer. The curing reaction of the glycolyzed product and epoxy resin was studied using differential scanning calorimetry (Perkin-Elmer DSC 7). Thermograms obtained from dynamic mechanical analysis (DMA) were recorded on a Netzsch DMA 242 device. The hardness of the cured resin was measured by a Shore Durometer Type D (ASTM D 2240-86).

Glycolysis of Foam

Glycolysis was carried out under a nitrogen atmosphere in a four-neck round-bottom flask equipped with a reflux condenser, a thermometer, and a mechanical stirrer. Polyurethane foam (450 g) in a cubic shape of about 1 cm^3 was added portion-wise into this flask containing 150 g DEA and 1.8 g (0.3 wt %) pulverized NaOH. The decomposition reaction proceeded at 130-150°C until the foam was completely dissolved.

Preparation of Crosslinked Epoxy Resin

DGEBA epoxy resin was mixed with the glycolyzed product at different weight ratios. These mixtures were heated in an oven at 150°C for 100 minutes. The cured resin was then cooled down rapidly in a freezer.

RESULTS AND DISCUSSION

Glycolysis of Rigid Polyurethane Foam

Polyurethane foam was broken down into a clear brown viscous liquid by DEA with NaOH as a catalyst at 130-150°C. It was reported that the decomposition reaction[2] may proceed as shown in Figure 1. Kanaya and Takahashi(11) also reported that both glycolysis and aminolysis can occur during the decomposition process. The glycolysis of the urethane group preserves the same urethane linkages and the aminolysis of urethane leads to the formation of urea linkages. As both reactions continued, PU foam was converted into low molecular weight compounds. In addition, NaOH reacted further with both urethane and urea linkages forming aromatic amines and polyols(2) as shown in Figure 1.

$$R_1\text{-NH-COO-}R_2 + 2HN(ROH)_2 \longrightarrow R_1\text{-NH-COO-R-NH-R-OH} + HO\text{-}R_2$$

$$+ R_1\text{-NH-CO-N}(ROH)_2$$

$$R_1\text{-NH-CO-NH-}R_2 + HN(ROH)_2 \longrightarrow R_1\text{-NH-COO-R-NH-R-OH} + R_2NH_2$$

$$+ HO\text{-R-NH-R-OCO-NH-}R_2 + R_1NH_2$$

$$+ R_2\text{-NH-CO-N}(ROH)_2$$

$$R'\text{-NH-CO-NH-}R'' + 2\,NaOH \longrightarrow R'NH_2 + R''NH_2 + Na_2CO_3$$

$$R'\text{-NH-COO-}R'' + 2\,NaOH \longrightarrow R'NH_2 + R''OH + Na_2CO_3$$

Figure 1. Decomposition of polyurethane foam.

The decomposition product was characterized by NMR spectroscopy. The ^1H and ^{13}C NMR spectra are shown in Figure 2 and Figure 3, respectively. Figure 4(a) shows a segment of molecules with urethane linkages composed in the foam prepared based on MDI. After the decomposition, the generation of methylene diphenyl amine (MDA) or its analog is expected. The chemical structure of MDA is also shown in Figure 4(b).

Figure 2. **^{1}H NMR spectrum of the glycolyzed product.**

Figure 3. **^{13}C NMR spectrum of the glycolyzed product.**

**Figure 4. (a) A segment of molecules composed in the polyurethane foam.
(b) Chemical structure of methylene diphenyl amine.**

From ^{13}C NMR results (Figure 3), two small peaks at around 128 and 118 ppm(11) are attributed to carbon atoms at positions 1 and 2 shown in Figure 4(a). Two prominent peaks at around 129 and 115 ppm correspond to carbon atoms of the aromatic amine(11) at positions 3 and 4 in Figure 4(b). The results suggested the decomposition of urethane linkages and the formation of aromatic amines during the reaction. In the case of ^{1}H NMR results shown in Figure 2, two large peaks at around 6.95 and 6.60 ppm resulted from protons at positions 3 and 4 showing the formation of aromatic amines. The broad shape of these peaks also suggested that the sample contains a mixture of aromatic compounds. Protons at positions 1 and 2 lead to peaks at around 7.20 and 7.05 ppm. Both peaks are small, indicating that there is a significant decrease in urethane linkages after reaction.

From both ^{1}H and ^{13}C NMR spectra, it was found that a large amount of aromatic amines was generated from the decomposition process of polyurethane. A small amount of urethane, however, still remained in the decomposition product. In addition, a trace of DEA, used as a decomposer, still existed in the reaction product. This is indicated by peaks at 50.5 and 60 ppm in the ^{13}C NMR spectrum as well as a peak at 2.7 ppm in the ^{1}H NMR spectrum.

IR spectra of the glycolyzed product, foam and DEA are shown in Figure 5. The IR spectrum of the decomposition product was compared with that of the polyurethane foam. The decreasing of a peak at around 1730 cm^{-1} indicates that urethane groups were consumed. The IR spectrum of the decomposition product was also compared with that of DEA. It can be seen that a peak at around 1654 cm^{-1} increases significantly. This peak indicates the occurrence of N-H bending from the newly generated primary aromatic amines. In addition, a large peak at around 3300-3400 cm^{-1} in the spectrum of the decomposition product shows the presence of a large amount of hydroxyl groups which may come from DEA or the glycolyzed products.

According to these spectroscopic analyses, it can be concluded that DEA can be used as a decomposer for the glycolysis of PU foam, since a significant decrease of DEA in the reaction product was observed. In addition, urethane groups were broken down during the decomposition process and a large amount of aromatic amines was generated. Therefore, the recycled product is mainly composed of hydroxyl compounds, aromatic primary amines and aliphatic secondary amines. The molecular weight of the recycled product was measured by gel permeation chromatography. The results showed that molecular weights were mostly in the range from 280 to 1,100 g/mole.

Figure 5. IR spectra of diethanolamine (DEA), decomposition product (GP), and polyurethan foam (PU foam).

Crosslinking of Epoxy Resin

Crosslinking of epoxy resin by the recycled product containing NaOH was studied by DSC. Ethylenediamine was used as a model compound in order to examine the reaction between amine and epoxy resin. It was found that the reaction started at an onset temperature at around 65^{o}C and was completed at around 130^{o}C. Figure 6 shows a DSC scan of amixture of GP and DGEBA at a weight ratio of 1 to 1. An onset temperature of the reaction between epoxy resin and the glycolyzed product at around 80^{o}C and an exothermic peak at around 120^{o}C were observed. The initial reaction is the reaction of aliphatic amines with epoxy resin because it requires a lower reaction temperature than that of aromatic amines. The onset temperature, however, is higher than that of the model compound. This is because the concentration of aliphatic amine in the glycolyzed product is lower compared with that of the pure aliphatic amine. Typically, aromatic amines react with epoxy resin at a temperature higher than that for aliphatic amines. Therefore, the crosslinking process was extended by the reaction of aromatic amines and epoxy resin together with the reaction between hydroxyl groups and epoxy resin. The two reactions are not distinguishable in our DSC measurements. The curing conditions of the polymer system were also determined to be 150^{o}C for 100 minutes from a DSC isothermal experiment. Diethylene glycol was used as a model ompound to confirm the reaction of epoxy resin and polyols composed in the glycolyzed product. The viscosity of a mixture of diethylene glycol and DGEBA increased significantly after heating at 150^{o}C for 100 minutes. This observation is evidence of the reaction between the hydroxyl group and epoxide ring at these conditions.

Figure 6. DSC reaction scan of a mixture of GP and DGEBA at a weight ratio of 1 to 1.

Characterization of Cured Epoxy Resin

DGEBA epoxy resin was cured by the recycled product at various weight ratios. Names of cured samples prepared in this work indicate the weight ratio of recycled product to epoxy resin. For example, P12 is the cured epoxy resin prepared from the recycled product and epoxy resin at a weight ratio of 1 to 2.

The glass transition temperatures (T_g) of the cured samples were determined by the tan δ peak temperatures from DMA measurements.

The DMA results are shown in the Table 1. P13 possessed the highest T_g among the samples investigated. It might be because the ratio 1 to 3 is close to the stoichiometric ratio of reactants. When the ratio was outside the range presented in the Table, the materials became soft and had much lower T_g.

Samples	T_g (°C)	Shore D Hardness (std. dev.)
P11	61.5	70.2 (2.9)
P12	97.7	70.8 (1.8)
P13	103.8	75.0 (0.0)
P14	92.4	72.0 (2.7)

Table 1. T_g and hardness of the cured epoxy resin samples.

The DMA thermogram of sample P14 is shown in Figure 7. The sample possesses a high storage modulus, E', at room temperature similar to those of common unfilled rigid thermosetting materials.(14) The fact that the E' value remains high even at temperatures higher than T_g (rubbery plateau region) is due to the crosslinked structure in the sample. It is also suggested that the service temperature of these samples is higher than for typical uncrosslinked amorphous polymers with a similar T_g whose mechanical properties drop several orders of magnitude during the T_g transition.

Figure 7. DMA thermogram of sample P14.

Hardness of the cured samples was measured at ambient temperature. The results showed that there was no significant difference in hardness for the samples in Table 1. Each hardness value was obtained by averaging five measurements. All hardness values are in the range of 65 to 75 Shore D, which is close to those of polypropylenes.(15)

Figure 8 shows a sample prepared by P14. In order to prepare this sample, pigment was dispersed in the polymer resin and the resin was then precured at ambient temperature. When the resin became rubbery, it was shaped into a desired configuration. The sample can then be further cured at ambient temperature for a few days or at an elevated temperature for a shorter time. The preparation of this sample demonstrated that the polymer resins developed in this study possess good processibility and can potentially be used in various applications.

CONCLUSIONS

Rigid polyurethane foam was glycolyzed by DEA with the presence of sodium hydroxide. The brown viscous liquid obtained is composed of amines and polyols as suggested by IR, ^{1}H NMR, and ^{13}C NMR results. This glycolyzed product was used directly as a curing agent for DGEBA epoxy resin. The cured epoxy resin exhibited good processibility and mechanical properties. Optimized samples exhibited a T_g much higher than room temperature with hardness values of approximately 70 Shore D. This study has demonstrated an alternative method for the

Figure 8. A pigmented sample (P14) made by epoxy resin using a hardener prepared from the glycolysis of PU foam.

recycling of rigid PU foam wastes. It is anticipated that the same scheme can be applied for the recycling of various types of PU products.

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