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Chemical Recycling and Liquefaction of Rigid Polyurethane Foam Wastes through Microwave Assisted Glycolysis Process

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Glycolysis of polyurethane rigid foams (PUFs) was performed utilizing microwave irradiation at atmospheric pressure. The effects of various metal hydroxide and acetate catalysts as well as different microwave powers were investigated. All reactions were monitored by FTIR spectroscopy. The recovered liquid product containing OH functional groups was applied as a portion of the polyol in formulation of a new polyurethane rigid foam product. The reactivity factors and densities were compared with the foam produced from totally virgin polyol.

Keywords: polyurethane rigid foam; microwave; glycolysis; polyol recovery

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1 Introduction

The polyurethane (PU) foam market has shown continuous and fast growth in recent years. This development is relative to the physical and mechanical properties of polyurethane foams, their chemical composition and density, which render them particularly suitable for many applications, such as upholstering, insulation, and packing (1, 2).

Rigid PU foam constitutes an important group of PU foams and its demand is increasing rapidly because of wide applications as a heat insulator in refrigerators, buildings and construction materials (3, 4), floatation and packaging/padding materials, encapsulates to isolate and support thermally sensitive components within weapon systems, a shock absorber in industry, etc. (5–7). Due to such a broad range of applications, a large volume of waste is produced, causing considerable disposal problems. Among different recycling methods and procedures, chemical recycling has been the subject of research studies since the 1980's, because of waste conversion into starting materials and reuse in the new foam production process (8). Glycolysis (9, 10) is the most researched method and involves heating the PU scraps in the presence of glycols and catalysts, performing transesterification reactions, to obtain low molecular weight products (11). Walter and David have glycolyzed the rigid PU foam using diethylene glycol (DEG) in combination with an appropriate catalyst and amine capping agent to produce a polyol which is useable in later foam formulations (12). Murai and his colleagues investigated the dissolution time of rigid PU foam under various reaction conditions. They found that reaction temperature, catalyst concentration, PU foam particle size, glycol type and its molecular weight affected the process (13). Frulla and his coworkers studied the reaction conditions for conversion of scrap rigid PU foam to the corresponding polyol. In their research, a binary mixture of DEG (95%) and diethanolamine (DEA) (5%) was found to be useful to recover PU scraps (14). Kondo provided a process for obtaining a homogeneous liquid polyol. In his study, the glycolysis reaction was performed at 150–220°C in the presence of a binary mixture containing an aliphatic diol and a monoalkanolamine. The recovered polyol was useful in the preparation of new rigid PU foam (15). The optimum glycolysis conditions (time, destroying solvent, and catalyst) were also investigated for the recycling of waste rigid PU derived from refrigerators using DEG and potassium acetate (KAc) as the solvent and catalyst, respectively (16).

Today, reports have indicated that microwave (MW) could evidently accelerate chemical reactions and increase the rate factor over one thousand (17–21). Microwave heating arises from the ability of some liquids and solids to transform the absorbed electromagnetic energy into heat (22, 23). In microwave heating, the energy can be applied directly to the sample rather than conductively, via the vessel. Heating can be started or stopped instantly, or the power level can be adjusted to match if that is required. If the sample is mixed efficiently during irradiation, bulk heating occurs (24).

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The effect of microwaves on chemical reactions is generally evaluated by comparing the time needed to obtain a given yield of the final products with results made of conventional heating methods (22). For instance, microwaves were shown to be effective in poly(ethylene terephthalate) solvolysis, with complete depolymerization achieved in 5–10 min (25, 26). Also a novel method has been introduced for rapid microwave induced depolymerization of polyamide-6 employing concentrated phosphoric acid (27).

The laboratory use of domestic microwave ovens has been reported for the first time in 1975 for metal trace analysis of biological samples (28). Later, many researchers have utilized domestic ovens for chemical reactions performance. In the continuation of our previous works concerning glycolysis of cold cure flexible PU foam wastes by microwave irradiation (29), investigating a microwave assisted glycolysis process of rigid PU foam wastes was tried

2 Experimental

2.1 Materials and Instruments

Rigid PU foam samples were formulated by using virgin (not recycled) polyol (Daltofoam® TA 14066), 100 *pbw* and diphenylmethane diisocyanate (MDI) based prepolymer (Suprasec® 5005), 133 *pbw* purchased from the Huntsman® Company. The specifications of virgin polyol and isocyanate have been detailed in Tables 1 and 2, respectively. The FT-IR spectra obtained by using a Bruker Tensor 27 spectrometer (droplet samples were impregnated on KBr pellets). Microwave irradiations were performed by using a Samsung domestic microwave oven.

The prefix "VIRGIN" is used in order to differentiate the first time used polyol from a recycled one. The virgin polyol was provided as a system containing all additives needed for foaming process.

2.2 Dissolution of Rigid PU Foam Wastes

Rigid polyurethane foam wastes were glycolyzed using DEG as the solvent and various catalysts containing sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium acetate (NaAc) and zinc acetate ($Zn(Ac)_2$). The solvent/foam ratio was 2:1. In a typical procedure, rigid polyurethane foam wastes (3 g) were added to a mixture of DEG (6 g) and catalyst (0.03 g). The reaction mixture was placed in a 100 mL pyrex beaker and treated for a specified time in the microwave oven at atmospheric pressure. In all experiments, the foams were completely smeared in the destroying solvent, before reaction beginning. The reaction was done at different 180, 300, 450, 600, and 900 watt microwave powers in order to investigation the effect of various powers on the foam dissolution rate. In all reactions, the complete disappearance of the foam particles in the reaction mixture was set as reaction completion time. Therefore, all reactions were allowed to proceed until complete foam dissolution. Then, the reaction container was removed from the microwave oven, solid contaminants and unreacted particles were filtered and the obtained liquid product was characterized. FT-IR spectroscopy studies and the reactivity factors were compared with a rigid PUF produced by virgin polyol.

Table 1. Virgin polyol (DALTOFOAM® TA 14066) specifications used for foam manufacturing

Color	Viscous yellow liquid
Viscosity (Pa · s at 25°C)	5.263
Specific gravity (g · cm^{-3} at 25°C)	1.06
Water content (%)	2.3
pH	9.45
Practical OH number (mg KOH · g^{-1})	430 ± 20

Table 2. MDI (SUPRASEC® 5005) specifications

Color	Dark brown liquid
Viscosity (Pa · s at 25°C)	0.22
Specific gravity (g · cm^{-3} at 25°C)	1.23
Practical NCO value (% by wt NCO groups[a])	30.9
Average functionality	2.7
Flash point (°C)	233
Fire point (°C)	245

[a]Group weight: 42 g · mol^{-1}.

3 Results and Discussion

The glycolysis of PU rigid foam leads to a OH containing product which is liquid at room temperature. The chemistry of the reaction involves the trans-urethanization of the urethane bonds by a low molecular weight glycol (Scheme 1). As shown in the scheme, there are two pathways for the urethane bonds incision. The first mechanism produces an OH containing urethane oligomer and followed until liberation of the original polyol. The second mechanism is C-N bond cleavage which results in an unstable carbonate and aromatic amine (30).

According to the results, the kinetics of catalytic reaction is different with a non-catalytic one. The transesterification reaction is difficult to carry out without a catalyst, even under high MW powers. On the other hand, the comparison of foam dissolution times in the presence of various catalysts reveals the weak catalytic effect of zinc acetate in comparison with other catalysts. Sodium and potassium hydroxides are convenient catalysts in transesterification reactions, which can accelerate the glycolysis reaction and reduce the dissolution time (Figure 1).

FT-IR spectra indicate that PU chain incision is not completed even with utilizing a convenient catalyst, sufficient

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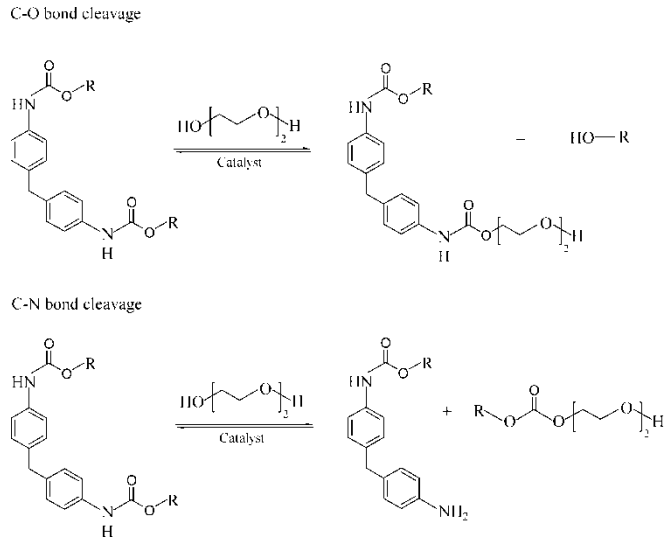

Sch. 1. The trans-urethanization mechanism of the urethane bonds by low molecular weight glycols.

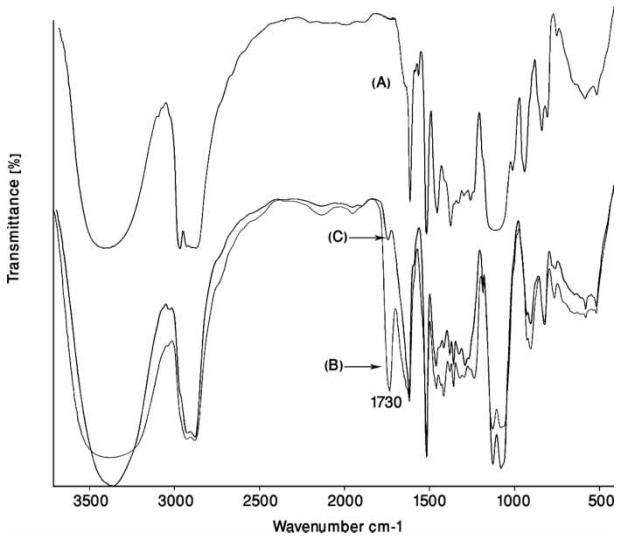

Fig. 2. FT-IR spectra of (A) DALTOFOAM® TA 14066, (B) recovered polyol sampled immediately after perfect foam dissolution, and (C) 60 s after perfect foam dissolution using NaOH as the catalyst at 900 watt MW power.

MW power and long time reaction. In other words, there are certain amounts of polyurethane oligomers in the reaction mixture due to the presence of urethane and biuret bonds (1760–1749 cm^{-1}) in recovered products (31, 32). It is noteworthy that the absorbance intensity of the remained functional groups in recycled products decreases if the irradiation is continued after complete foam dissolution (Figure 2).

Another important observation in these reactions is the compatibility of the recycled polyol with virgin one which causes it to be usable in a similar formulation for producing new rigid PU foam. Accordingly, the recovered polyol was directly mixed in different ratios in combination with virgin polyol consisting of activated polyether polyols, aliphatic

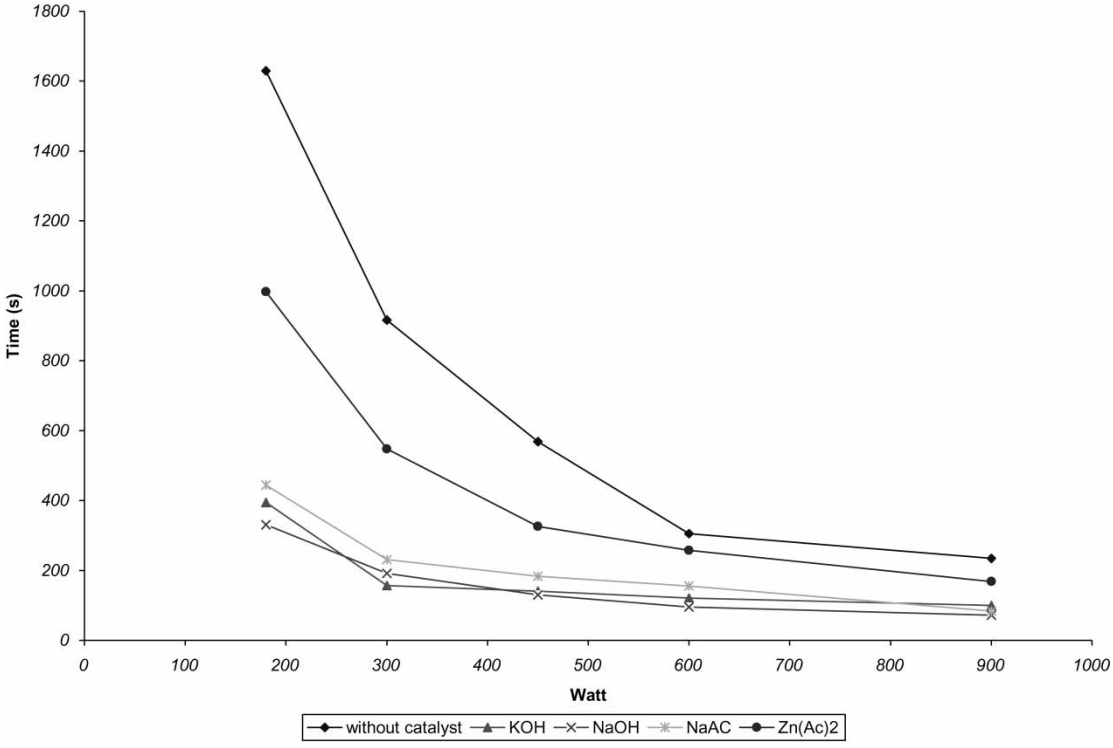

Fig. 1. The comparison of the various catalysts and MW powers on the foam dissolution time.

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Table 3. Rigid polyurethane foam formulation

Sample	Virgin polyol[a]	Recycled polyol	MDI[b]
PUF1	100	0	100
PUF2	90	10	100
PUF3	80	20	100
PUF4	70	30	100
PUF5	60	40	100
PUF6	50	50	100
PUF7	40	60	100

[a]DALTOFOAM® TA 14066.
[b]SUPRASEC® 5005.

Table 4. Reactivity parameters of PU foam samples during formation

	Reactivity factors			
Sample	Cream time (s)	String time (s)	End of rise time (s)	Tack-free time (s)
PUF1	4	45	82	83
PUF2	4	34	54	55
PUF3	6	31	51	51
PUF4	4	25	30	31
PUF5	4	20	36	36
PUF6	4	—	25	25
PUF7	5	—	20	20

amines catalysts, surfactant and water. The virgin-recycled polyol blend was then mixed with isocyanate in a free rise condition (cup test) for production of rigid foam (Table 3). The reactivity parameters (cream, string, end of rise and tack-free times) and densities of the produced foams were measured. All data obtained from these tests are detailed in Tables 4 and 5, respectively.

As shown in Table 4, the reactivity factors are reduced by increasing the recycled polyol content in polyol blend. On the other hand, the foaming process of blends containing high recycle contents is more exothermic and the heat release during foaming process is higher with increasing the recycle content in the polyol blend. The density of produced foam also increases with increasing the recycle content in the recycled-virgin polyol blend.

Table 5. Density of free rise PU foam samples

Sample	Density ($g \cdot cm^{-3}$)
PUF1	0.0386
PUF2	0.0448
PUF3	0.0466
PUF4	0.0614
PUF5	0.0712
PUF6	0.1012
PUF7	0.1154

4 Conclusions

The glycolysis process of rigid PU foam wastes is performed by DEG as the solvent and different catalysts such as sodium hydroxide, potassium hydroxide, sodium acetate and zinc acetate under various microwave powers at atmospheric pressure. The experiments are performed in a 2:1 ratio of solvent to foam. According to the obtained results, sodium and potassium hydroxides are convenient catalysts for fast polyol recovering. FT-IR spectra analysis reveals the incomplete incision of PU linkages. The obtained liquid product can mix directly with virgin polyol at different ratios (up to 40%) for use in the new rigid PU foam formulation.

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