Using Different Catalysts in the Chemical Recycling of Waste From Flexible Polyurethane Foams

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Abstract: Due to their versatility, polyurethane (PU) foams have many different applications, such as sponges, filling materials in furniture, automotive seats and clothes, among others. It is also one of the main refrigerator components serving as a heat insulating material. As PUs find different application niches, they must be largely produced and, consequently, lots of waste are generated. In this work we intend to contribute to the recycle of this waste. The recovery of polyol from flexible polyurethane foams was carried out using the glycolysis process and testing different catalysts. Grounded polyurethane and a solvent, diethyleneglycol (DEG), were kept at 200 °C and under nitrogen atmosphere during three hours in the presence of a catalyst. All catalysts tested promoted the polyol mixture formation, with Zinc acetate producing the best depolymerization rate. The catalysts efficiency for the depolymerization reaction follows the order: DBTDL< BTO< HBTO< DEA ≈ Ba(Ac)$_2$< MEA ≈ KAc< Zn(Ac)$_2$.

Keywords: *Recycling, polyurethane, glycolysis.*

Introduction

Polyurethane (PU) is one of the most versatile polymers, and has been developed in the world for use in a wide range of applications[1,2]. There are many examples of flexible polyurethane foams use in the households like pillows, sponges, and as filling materials in furniture, automotive seats, and clothes, among others[2]. Rigid polyurethane foam is used to encapsulate electronic components aiming to mitigate rigorous thermal and mechanical shock and to provide electrical isolation. It also is one of the main refrigerator components serving as a heat insulating material[3,4]. In this scenario, is clear that the quantity of polyurethane waste is increasing and recycling has become an urgent and important issue[5]. The majority of this waste has no specific use and is dumped on landfill sites[6]. For instance, only in the US, approximately 1.3 million tons, by weight, of waste polyurethanes are generated each year. This amount represents five percent of all current plastic waste[7]. In the case of polyurethane foams, due their crosslinked structure, adequate processes to treating this residue with sufficient efficiency are under investigation[8,9]. For example, the mechanical recycling process where flexible polyurethane foam is smashed into fine powder has not developed significantly due to its use in specific applications[8]. Thermal decomposition of polyurethane also presents same problems; this process generates too many kinds of compounds[10]. The use of chemical decomposition of polyurethane in the recycling process appears as an interesting option, where a mixture of polyols and amines can be obtained and reused in the production of new foams[5-10]. Several chemicals recycling process such as, hydrolysis, aminolysis and glycolysis have been described as viable recovery process for polyurethane foams[8,11,12]. Some studies have revealed that a proper glycolysis process may be used to resolve the disposal problems of waste PU and to obtain high quality polyols[12]. Other important variable in the efficiency of the process is the catalysts choice. Studies show that metals catalysts have been employed instead of traditional amine catalysts[1]. The use of metallic catalysts appears as an economic alternative and an option to reach the reaction total conversion in shorter times. The main objectives of this work are the recovery of the polyol from flexible polyurethane foams and the use of different catalysts in the glycolysis process (depolymerization reaction).

Experimental

In the study of recycling of PU foams were used flexible polyurethane foams. The commercial PU foam is, typically, obtained by the polymerization reaction between a polyol and an isocyanate accompanied by the expansion provided by a physical blowing agent. It was utilized foam residues or waste trade, whose nucleus density is between 32-35.4 kg/m^3 (NBR 8537) and compressive strength between 100.3 and 109.1kPa (DIN 53421).

Depolymerization Reaction

The reactions were carried out in a glass reactor with internal capacity of 500 mL equipped with thermocouple and reflux. In a typical reaction, grounded polyurethane (15 g) and a solvent, diethyleneglycol- DEG (Merck) were kept at 200 °C and under nitrogen atmosphere during the desired time in the presence of a catalyst (1% w/w). The tested catalysts were monoethanolamine, MEA (Merck),

diethylamine, DEA (Merck), barium, zinc and potassium acetate, Ba(Ac)$_2$, Zn(Ac)$_2$, KAc respectively (Nuclear), dibutyl tin dilaurate DBTDL (Miracema Nuodex), butyl tin oxide, BTO (Miracema Nuodex) and hydroxy butyl tin oxide, HBTO (Merck).

Characterization

The depolymerization reactions were accompanied by infrared spectroscopy (Perkin Elmer Instruments Spectrum One FT-IR, 4000 to 650 cm^{-1}, ATR acessory) by the decrease in the area of the urethane band group (1729 cm^{-1}) in absorbance. Brookfield viscosity was measured by Brookfield Viscometer (RVDV-I Prime, 20 °C, spindle SC4-21, 50 rpm), and the molecular weight of the depolymerized products were obtained by gel permeation chromatography (Waters Instruments, columns set of Styragel – temp. 40 °C, refraction index detector 2412- temp. 35 °C, eluent THF – 1 mL/min).

Results and Discussion

Aiming to find the best depolymerization reaction conditions, it was initially carried out a reaction without catalyst (Table 1, entry 1) and then reactions using well-known catalysts, such as MEA[1,13] (Table 1, entry 2,3 and 4) and DEA[1,13] (Table 1, entry 5) were performed. Also the effect of the amount of solvent (DEG) (Table 1, entry 2 and 3) on the final viscosity of the products was evaluated and the results showed similar values (around 40 mPa.s). Table 1 shows the reactions conditions for depolymerization reactions and the final viscosity for the products of these reactions.

Figure 1 presents the depolymerization products in function of the time. It was seen that, the reaction performed without catalyst (Table 1, entry 1) showed the highest final viscosity (170 mPa.s) when compared to catalyzed reactions. The use of different quantities of MEA, as catalyst, changes the final viscosity, showing that higher catalyst content results in lower viscosities values in the same reaction time (Table 1, entry 4-29mPa.s). Nevertheless, with 1% (w/w) of MEA the value obtained for the viscosity (39 mPa.s) was adequate for this kind of reaction, so this catalyst amount was assumed for all reactions carried out in this work. In all cases depicted in

Figure 1 the viscosity values are lower than the original polyol (71 mPa.s) and lower than the values found in the literature for glycolysis reaction using different DEG/PU and catalyst/PU ratio (90-3252 mPa.s[3].

To evaluate the depolymerization reaction using different catalysts, the process was monitored by infrared spectroscopy analysis observing the decrease of urethane bond band around 1729 cm^{-1}. The reaction was carried out at different times using MEA as catalyst (Table 1, entry 3). The FTIR spectra are presented in Figure 2.

It was seen at Figure 2, the urethane bond band (1729 cm^{-1}) decrease was more accentuated up to two hours of reaction time. These results are in agreement with the viscosity data depicted in Figure 1, suggesting that the depolymerization reaction is completed between two and three hours, being in agreement with the literature[3]. In a study of the influence of the reaction time in the PU depolymerization, Wu et al.[3] found that two hours is an appropriate time. The Figure 3 presents the behavior of different catalyst in depolymerization reactions (Table 1, entry 3, 5, 7), it was seen that decrease of the band of the urethane bond occurred in the catalysts sequence: DEA < MEA < Zn(Ac)$_2$, for the same reaction time (3h).

Using the FTIR spectra depicted in Figure 3, the band area decrease, (percentage area), of the urethane bond for the different catalysts were calculated (Table 2).
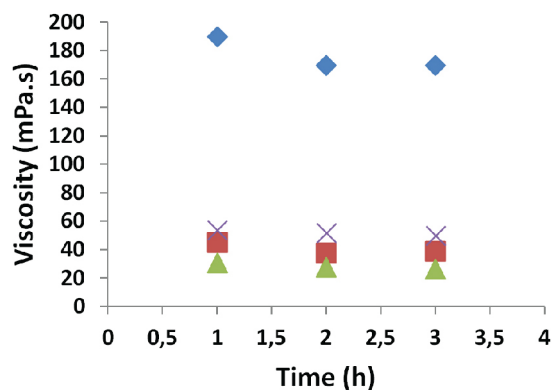

Figure 1. Viscosity versus time of depolymerization reactions with no catalyst (♦), MEA (1% w/w) (■), MEA (2.5%w/w) (■), diethylamine (1% w/w) (▲).

Table 1. Depolymerization reactions conditions (at 200 °C, 1% w/w of catalyst, 3h of reaction) and the final viscosity for the reaction products.

Entry	DEG	Catalyst (1% w/w)	Viscosity (mPa.s)
1	0.2	-----	170
2	0.2	MEA	40
3	0.2	MEA	39
4	0.2	MEA[a]	29
5	0.2	DEA	50
6	0.2	Ba(Ac)$_2$	46
7	0.2	Zn(Ac)$_2$	38
8	0.2	KAc	36
9	0.2	DBTDL	43
10	0.2	HBTO	42
11	0.2	BTO	46

[a]2.5% w/w.

These values are explicitly shown in Table 2, which also presents the values for the other catalysts after 1h and 3h of reaction and also for the reaction without catalyst.

With $Zn(Ac)_2$ a decrease of 48% was reached while with MEA and DEA 25% and 17% was reached. This shows that zinc acetate is more effective when compared to amine catalysts in this kind of depolymerization reaction.

Molero et al.[1,14] demonstrated that octoates could be an alternative to conventional catalysts. To study the influence of acetate compounds in the depolymerization reaction, it was performed the PU depolymerization reaction with different acetate catalysts. Figure 4 presents the FTIR spectra of the reactions conducted with barium, zinc and potassium acetates (Table 1, entry 6, 7 and 8).

The depolymerization rate, confirmed by FTIR through the calculated value of the decrease of band area of the urethane bond for the different catalysts showed that for $Zn(Ac)_2$ a decrease of 48% was reached while with KAc the decrease was 25% and with $Ba(Ac)_2$ the

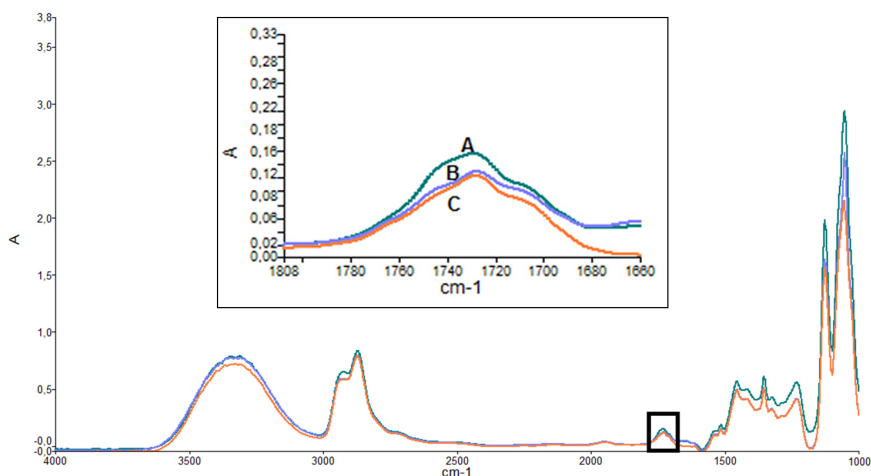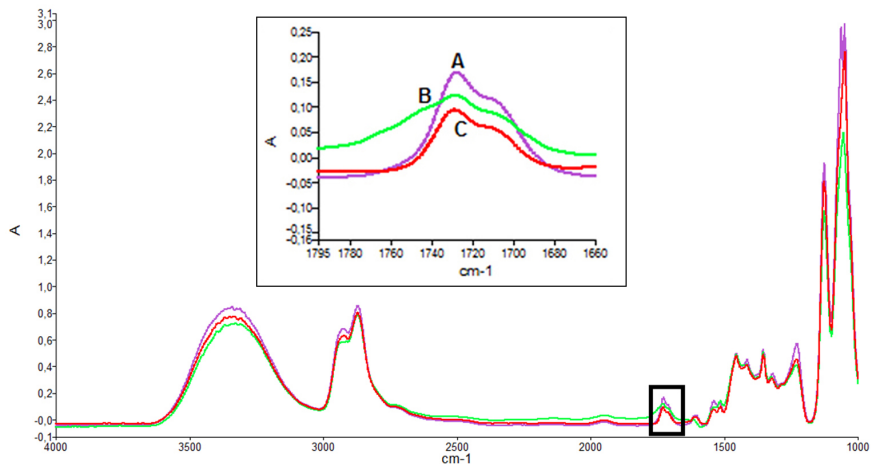**Figure 2.** Infrared spectra of reaction with MEA catalyst: 1h **(A)**, 2h **(B)** and 3h **(C)**.

Figure 3. Infrared spectra of reaction with different catalysts: DEA **(A)**, MEA **(B)**, $Zn(Ac)_2$ **(C)**. Reaction time: 3h.

Table 2. Area of urethane bond band calculated at 1 hour and 3hour of reaction and the percentage of decrease calculated by FTIR spectra.

Catalyst	Area $_{NHCOO}$ (A.cm^{-1}) 1h	Area $_{NHCOO}$ (A.cm^{-1}) 3h	Decrease in area (%)
MEA	5.8492	4.3776	25
DEA	12.6361	10.4319	17
$Ba(Ac)_2$	7.6209	6.2503	18
$Zn(Ac)_2$	5.3255	2.7747	48
KAc	8.0745	6.0749	25
DBTDL	8.0912	7.8033	4
HBTO	6.2018	5.3066	14
BTO	9.9896	9.0500	9
Without Catalyst	16.2286	15.9010	2

decrease was 18%, proving that zinc acetate is much more effective when compared to other catalysts in this kind of depolymerization reaction, Table 2. The depolymerization rate increased in this order: barium acetate < potassium acetate < zinc acetate. The activity order of the transesterification reaction obtained for polyurethane degradation is in agreement with the results reported in the literature for different metallic complexes in the transesterification reaction[15]. In this way, it is possible to assume that a similar catalytic mechanism is taking place for PU depolymerization by $Zn(Ac)_2$, as presented in Figure 5.

The polyurethane degradation in the glycolysis process occurs via successive transesterification reaction of the urethane bond with low molecular weight glycols[14]. Divalente metallic complexes used as catalyst in the transesterification reaction can act as a Lewis acid, activating the carbonyl group of the urethane (coordinated to the cation), to nucleophilic attack by the oxygen of the alcohol[15].

It was also studied the behavior of well known Tin catalysts- DBTDL, HBTO and BTO (Table 1, entry 9, 10 and 11) in the PU depolymerization . The infrared spectra of the products of these reactions, Figure 6,

confirmed by the calculated value of the decrease (percentage) of band area of the urethane bond for the different catalysts showed that the depolymerization rate increases: DBTDL (4 %)< BTO (9 %)< HBTO (14 %), Table 2.

These complexes are less active when compared to $Zn(Ac)_2$ probably due to the reaction mechanism, in this case, occurring by alcohol addition in the tin complexes resulting in a tin alcoxyde intermediate **(A)**, as described in the literature, for DBTDL[16].

In this Figure 7 intermediate alkoxide **(A)**, the coordination of a urethane group probably occurs (intermediate **B**) with subsequent nucleophilic attack of a hydroxyl group of an alcohol molecule .

Figures 8 presents the kinetic parameters for depolymerization reactions of polyurethane using BTO and $Zn(Ac)_2$ as catalysts. They were obtained using a Lambert-Beer Law as described in reference[17]. It is worth to note that the kinetic constant of $Zn(Ac)_2$ (3×10^{-2}mol-1.min-1) is ten times higher than BTO (~8×10^{-3}mol-1.min-1). This results indicate that the formation of the active specie of the $Zn(Ac)_2$ is faster when compared to tin complexes.
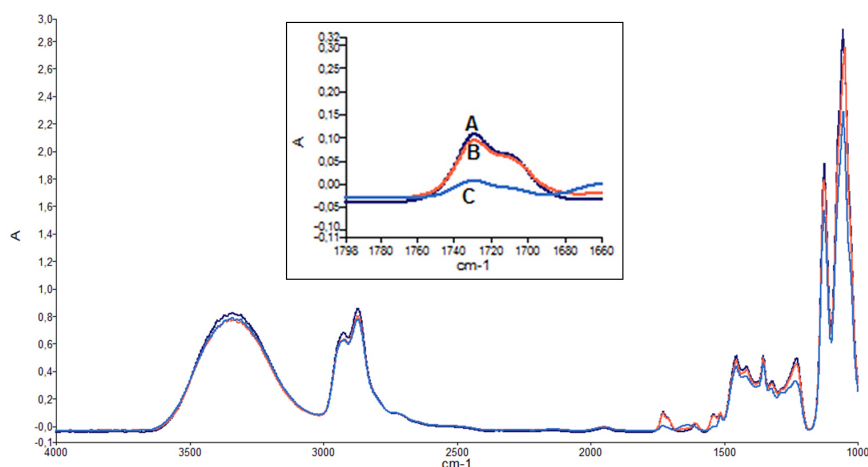

Figure 4. Infrared spectra of reaction with catalysts barium acetate **(A)**, potassium acetate **(B)** and zinc acetate **(C)**. Reaction time: 3 h.
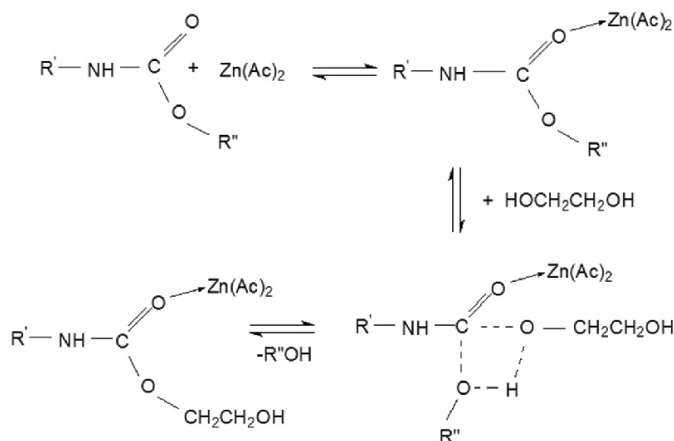

Figure 5. Proposed mechanism for PU transesterification, catalyzed by $Zn(Ac)_2$.
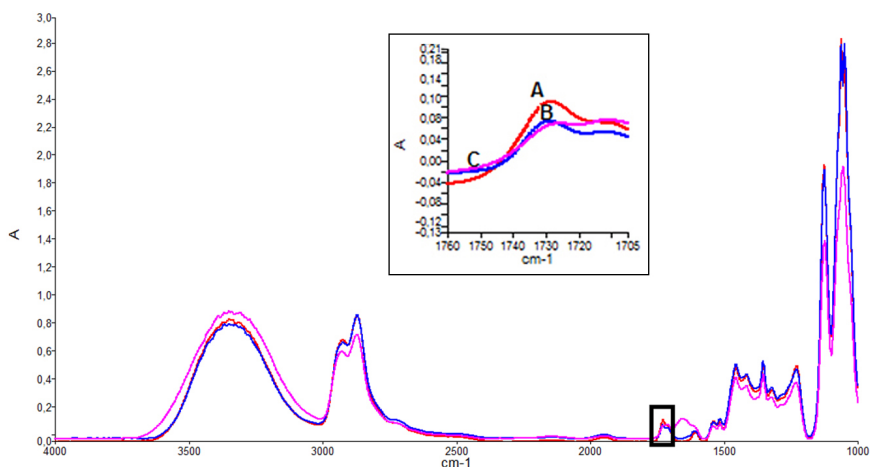
Figure 6. Infrared spectra of reaction with catalysts dibuthyl tin dilaurate(DBDTL) **(A)**, and butyl tin oxide **(B),** butyl hydroxide tin oxide **(C)**. Reaction time: 3h.
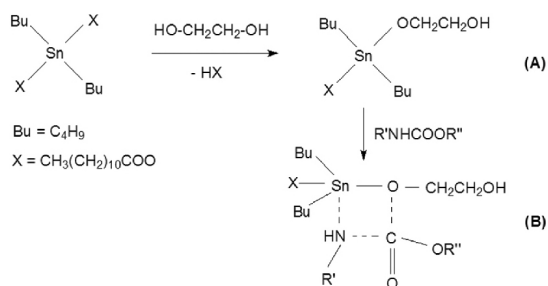

Figure 7. Proposed mechanism for PU depolymerization catalyzed by DBTDL
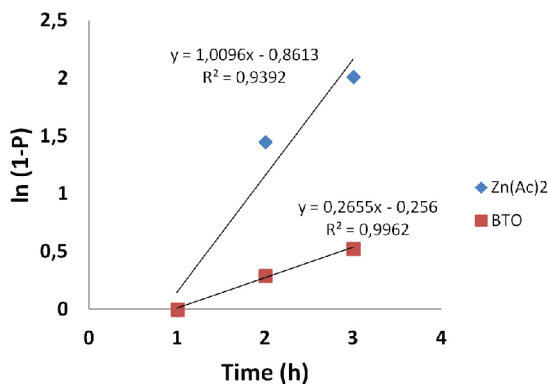

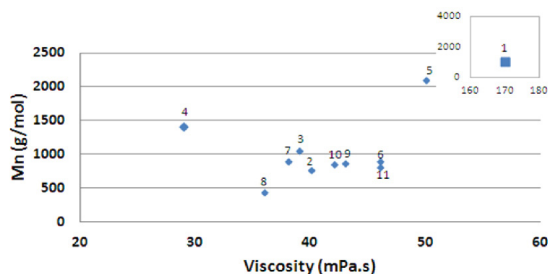
Figure 8. Curve ln(1-p) versus time(minutes).

Figure 9. Curve average numerical molecular weight versus viscosity (the numbers in the Figure corresponds to entry 1-11 in Table 1).

The depolymerizated products, obtained from reactions catalyzed by metallic complexes, presented an average numerical molecular weight between 440-902 g/mol, similar to the values found to the reference polyol (Mn less than 1000 g/mol), showing the efficiency of these catalysts on depolymerization reactions to obtain a polyol mixture with adequate molecular weight. In the same way, the viscosity interval found for these products (39-50 mPa.s) is comparable to the values found for the reference polyol (71 mPa.s). However, the products obtained from non catalyzed reaction presented the highest values of Mn (higher than 1000 g/mol) and, consequently, the highest viscosity values (170 mPa.s), indicating that the viscosity of the products is affected by their average molecular weight, as shown in Figure 9.

Conclusions

In this work we have found that glycolysis is an efficient method for polyol recovery from flexible polyurethane foams. Three hours of reaction, 200 °C of temperature and diethyleneglycol as solvent are adequate parameters for the process. All the catalysts tested promoted the polyol mixture formation, but the best result was found with Zinc acetate. The catalysts efficiency for the depolimerization reaction follows the order: DBTDL< BTO< HBTO< DEA ≈ Ba(Ac)$_2$ < MEA ≈ KAc < Zn(Ac)$_2$. This work showed that metallic catalysts showed higher efficiency than conventional amine catalysts.

Acknowledgements

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