

Chemical recycling of semi-rigid polyurethane foams by using an eco-friendly and green method

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ABSTRACT

Degradation of integral skin polyurethane foams (ISPUFs) was performed using diethylene glycol (DEG)/-sorbitol/water ternary green solvent system as an effective polyurethane bond destroying agent in combination with basic catalysts, namely sodium and potassium hydroxides, sodium acetate and sodium carbonate. The effects of studied catalysts were investigated and data showed the high performances of sodium hydroxide in recycling process. After completion of the reactions, appeared split phases contained recycled polyols in the upper phase. Reactions were studied using various DEG/-sorbitol/water ratios and the recovered polyols were characterized and data compared with an authentic sample.

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1. Introduction

Since the last 40 years, polyurethanes have been used in an ever increasing range of applications e.g. flexible and rigid foams over thermoplastic elastomers to adhesives, paints and varnishes. This wide variety of applications would result in a huge amount of consumption and wastes, causing some environmental problems¹. In recent years, public awareness of environmental issues has increased enormously, especially awareness of the facts that the world has limited natural resources and a limited capacity to manage the volume of wastes which human activities generate. As polyurethane production volumes increase, the amount of PU waste is also on the rise. By weight, approximately 1.3 Million tons of waste polyurethanes are generated each year only in the US as part of the municipal solid wastes (MSW) representing five percent of all current plastic wastes². Recycling of

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polymeric products has been investigated to enhance the environmental protection and avoid land filling. Traditional and uncontrolled waste destroying methods are not particularly acceptable due to combination of the recycling by pollution of the air and water environments. Because of aforementioned environmental problems, chemical recycling methods proposed in the past three decades. In the recent years and among chemical recycling methods the glycolysis one has been mentioned due to simple process operations as well as economical point of views. This process means using destroying diols and/ or diamines compounds as a solvent system in order to breaking down of polyurethane functional groups and liberation of the polyol as well as other valued chemicals. So the glycolysis of waste PUFs into raw materials is one of the principle methods for its recycling³. Some studies have revealed that a proper glycolysis process may be used to resolve the disposal problems of PU wastes, along with obtaining a high quality polyol⁴⁻⁷. Simioni and his coworkers investigated the effect of different glycols and found ethylene glycol as a suitable solvent allowing the process to be performed in higher polymer / glycol ratios and the product was used as a part of raw materials for RIM of rigid PUF⁸. Gassan has examined polyols recycling from glycolysis of PU and or polyurethane urea⁹. Datta and his co-workers investigated the recycling of PUR foams by using monomeric and polymeric diols and polyols¹⁰⁻¹³. Kanaya and Takahashi reported the decomposition of flexible PUR foam in the presence of alkanol amines without a catalyst at 150 °C¹⁴. Our research team has reported some studies on glycol-treated PU foams in the last few years. Integral skin PUF recycling, split-phase development, glycerin-assisted recycling and application of microwave power source for chemical recycling of PUF constitute the main research activities performed in our laboratory¹⁵⁻²¹. In the current work and in the continuing of glycolysis of PUFs waste, an attempt was made to use sorbitol/DEG/water ternary system as a new and eco-friendly solvent-reactant mixture to investigate efficiency in polyol recovering for the first time.

2. Experimental

2.1. Materials and methods

Polyol (Daltorim[®] EK 20350) and MDI (Suprasec[®] 2082) used for polyurethane integral skin foam formulation in 100 and 41 portions and purchased from Huntsman Company. The technical data of Daltorim[®] EK 20350 and Suprasec[®] 2082 are listed in Tables 1 and 2, respectively. Sorbitol solution (70%) purchased from Roquette (France). Other chemicals purchased from Merck and used as received without any purification.

FT-IR spectra were recorded by a Bruker Tensor 27 spectrometer (droplet samples were impregnated on KBr pellets). ¹HNMR and ¹³CNMR spectra were recorded by a Bruker CRX 300 instrument and data were compared with an authentic sample data.

Table 1. Specification of Virgin Polyol (Daltorim[®] EK 20350)

Appearance	Viscosity, 25 °C	Specific gravity, 25°C	Print point, °C	Burning point, °C
Brown liquid	340 mPas	1.23 g/cm ³	204	204

Table 2. Specification of MDI (Suprasec[®] 2082)

Appearance	Viscosity	Specific gravity	Flash point	Fire point
White viscous liquid	1740 cps	1.025 g/cm ³	265°C	290°C

2.2. Hydroglycolysis of the integral skin foam – General procedure

The scraps of Integral skin foams (15 g) segmented into small sizes, base catalyst (1 % w/w) and solvent were poured in a three necked flask equipped with a mechanical stirrer and a removable reflux condenser as represented in the table 3. Heating performed using an oil bath by setting the oil at 195±5 °C and the mixture was stirred at 1000 rpm. Transesterification reaction carried out at atmospheric pressure and the reaction extends to complete dissolution of the foams. After completion of the reaction, mixture transferred to a

decanted funnel and was left to be cooled in room temperature. After cooling it was separated into clear brown upper and dark brown lower split phases. The upper layer was recycled polyol and identified by spectroscopy techniques.

Table 3. Effects of the solvent system composition on the split phase ratios

Sample	DEG (% w/w)	Sorbitol (% w/w)	Water (% w/w)	Time (min)	Upper phase (%)	Lower phase (%)
GSF1	95	3.5	1.5	8	42	58
GSF2	90	7.0	3.0	9	50	50
GSF3	85	10.5	4.5	9	50	50
GSF4	80	14.0	6.0	10	54	46
GSF5	75	17.5	7.5	10	58	42

3. Results and Discussion

3.1. Recovered polyol characterization

One of the main goals in this study was using sorbitol as a portion of destroying solvent system in the recycling process. For this propose and in order to studying the effects of sorbitol in the glycolysis reaction, we examined the dependence of reaction times to the sorbitol content by using different basic catalysts. We found out that with the increasing sorbitol content, reaction time increased probably due to increasing viscosity of the reaction media and strong intra and intermolecular H-bonds formations between sorbitol molecules and/ or other hydroxyl content compounds. When the viscosity is increased, the chain motion for nucleophiles attaching of nucleophiles restricted and reaction rate is dropping significantly. In the meantime, in order to examine the role of the base catalyst in the foam dissolution, the first reaction performed on uncatalyzed condition and data showed incompleteness of the reaction even at the longer reaction times. This observation reveals the role of the basic catalysts in glycolysis process. In the other words, for complete and adequate foam dissolution, reaction should be catalyzed using appropriate bases. Therefore, different catalysts were examined in combination with solvent system in order to decreasing the dissolution time. To overcoming of the viscosity increasing of the media, solvent system was held as DEG (95%wt), sorbitol (3.5% wt) and water (1.5% wt) in combination with various catalysts in 1 *pbw* ratios. Results showed the perfect dissolution of the foam at adequate reaction times in the presence of studied bases, but NaOH had significant effect in decreasing of the dissolution times. All data collected in the Table 4.

Table 4. Dissolution time of ISPUFs by different catalysts

Catalyst	NaOH	KOH	NaOAc	K ₂ CO ₃
Dissolution time (min)	8	9	11	9

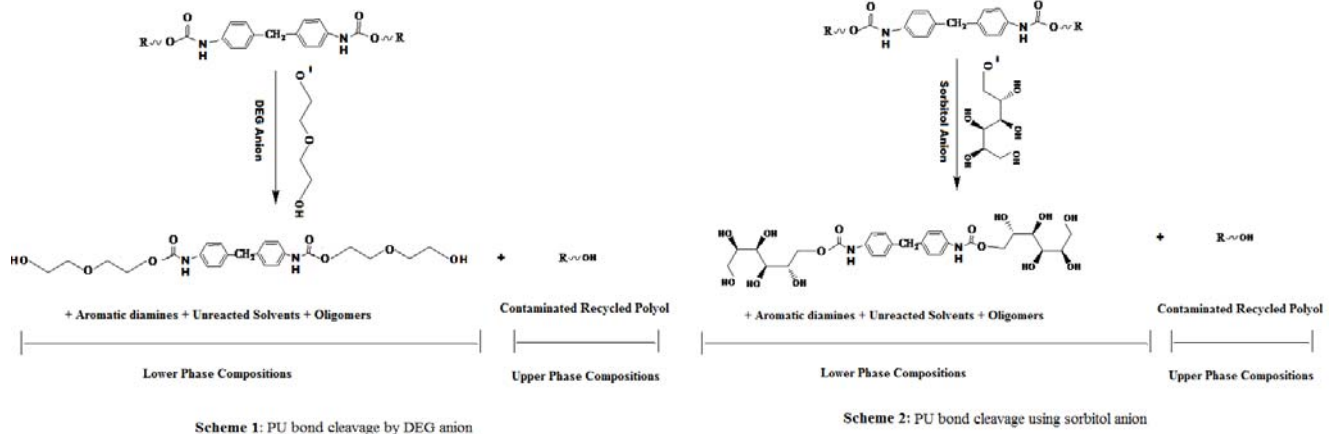
Another goal in this study was the reduction of consumed energy by avoiding of mass losses and several tests were performed to finding the best reaction temperature using NaOH as a catalyst. The best reaction temperature was found in the range of 200–205 °C. Results for adjusting of the reaction parameters are shown in the Table 5.

Table 5. Dissolution studies of ISPUF in different temperatures

Solution no.	PUF(g)	Solvent (g)	Temperature(°C)	Time (min)	Result
1	15	15	150±5	20	<i>Foam not dissolved</i>
2	15	15	180±5	20	<i>Foam dissolved within 14 min</i>
3	15	15	190±5	20	<i>Foam dissolved within 8 min.</i>
4	15	15	205±5	20	<i>Excellent dissolution with solvent evaporation</i>

3.2. Reaction scheme

Schemes 1 and 2 show the reaction mechanism of the polyurethane bond break down by DEG and sorbitol anions as the effective nucleophiles, respectively.



As shown in the schemes, the first step is the conversion of the DEG and sorbitol molecules to the corresponding anions and further attaching of the anions to the PU functional groups. The results of the PU bond breaking is liberation of the polyol as a value material in combination with other functionalized chemicals.

3.3. Structural elucidation of recycled polyol using spectroscopy methods

^1H NMR spectra of virgin and recycled polyols are shown in the figure 1. The peak in the region 1.1 ppm is corresponding to methyl equivalent hydrogen's and the peaks in the 3.0-4.0 ppm regions are relative to hydrogen's located in the β position to the oxygen atoms. The comparison of ^1H NMR spectra of virgin polyol and recycled product in the upper phase represents that chemical structures of the compared compounds are too similar, except the peaks in the region about 6.6-7.1 ppm and 6.9-7.2 ppm which is showed in figure 2 (b) which are related to the aromatic ring hydrogens which remained as aromatic diamines and contaminate the upper phase.

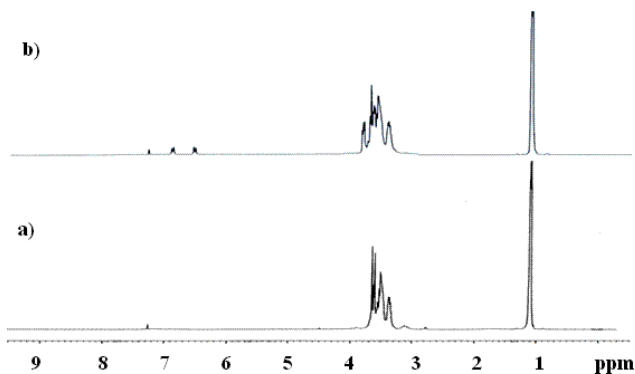


Fig. 1. ^1H NMR spectra of virgin (a) and recycled (b) polyols

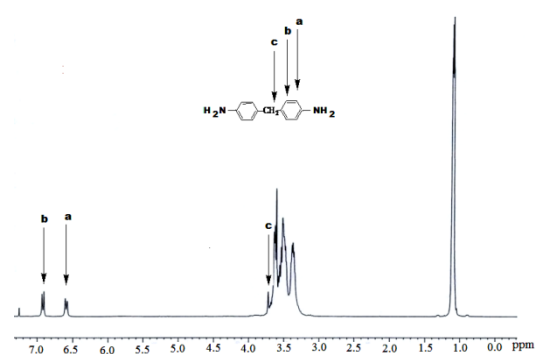


Fig. 2. ^1H NMR spectrum of contaminated polyols by aromatic diamine

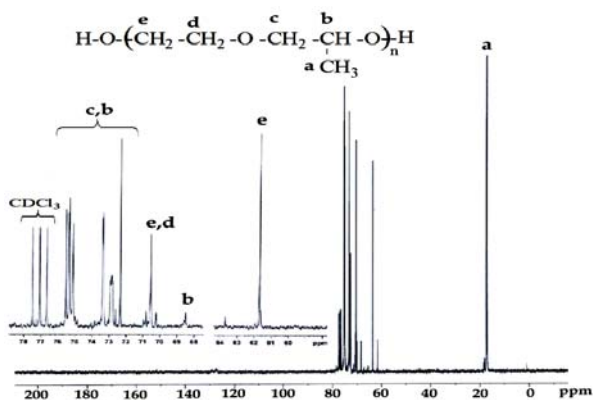


Fig. 3. ^{13}C NMR spectrum of integral skin virgin polyol

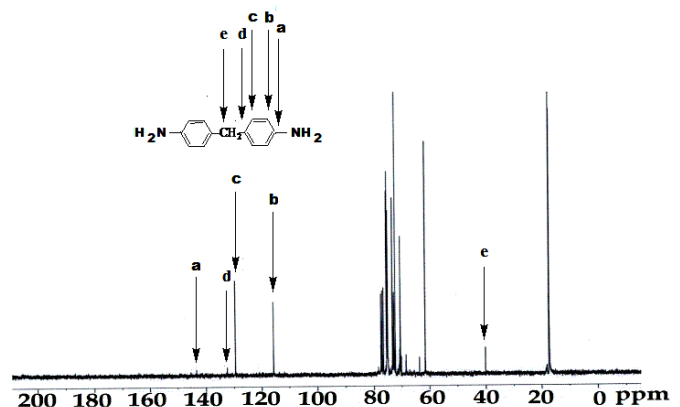


Fig. 4. ^{13}C NMR spectrum of contaminated integral skin recycled polyols

The ^{13}C NMR spectra of recycled polyols at different conditions were quite similar to virgin polyol except 5 new peaks at 40, 114.5, 130.5, 129 and 146 ppm are caused by aromatic diamines compounds that slightly had been dissolved in the upper phase. (Fig. 3, Fig. 4 and Fig. 5).

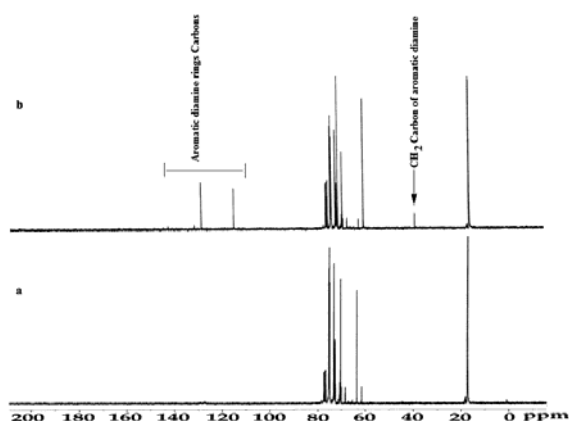


Fig. 5. ^{13}C NMR spectra of virgin (a) and contaminated recycled (b) polyols

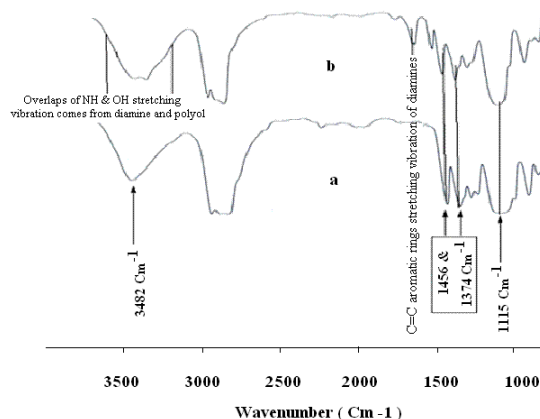
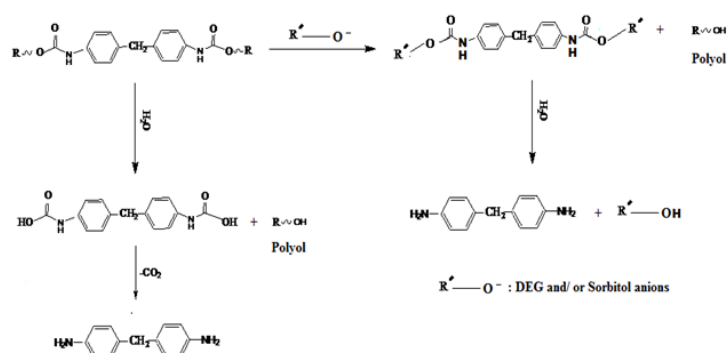


Fig. 6. FTIR spectra of virgin (a) and amine contaminated recycled (b) polyols

FTIR spectroscopy was another method in order to confirmation of successful recycling process and contamination of the recyclate by aromatic diamines. Figure 6 shows the FTIR spectrum of contaminated recyclate. In the FTIR spectrum, the absorption band at 1115 cm^{-1} related to aliphatic ether group of polyether polyol. Bending vibrations of methylene groups appear in the polyol chain at 1374 and 1456 cm^{-1} , stretching vibrations of CH bonds in aliphatic carbons are found at $2970\text{--}2868\text{ cm}^{-1}$ and stretching vibrations of OH groups are found at 3482 cm^{-1} . The expected results from FTIR spectra are similar to NMR spectra results and some additional signals are appeared due to presence of aromatic diamines contaminants in combination with respected signals to virgin polyol.

3.4. Proposed mechanisms of PU bonds degradations

There are two mechanistic alternatives for formation of aromatic diamines. The first mechanism is the reaction of the water with NCO groups and formation of unstable intermediate carbamic acid, which results in elimination of CO_2 and formation of aromatic diamines. The second mechanism is C-N bond cleavage mechanism which results in an unstable carbonate and aromatic amine. The proposed mechanisms are shown in the Scheme 3.



Scheme 3: Reaction scheme for aromatic diamine formation

4. Conclusions

Hydroglycolysis of ISPUFs has been carried out at atmospheric pressure using DEG /sorbitol/ water mixtures as destroying solvent system and NaOH as the catalyst, respectively. By increasing the sorbitol concentration in the solvent system, the prolonged reaction times were absorbed. This phenomenon is related to increasing in the viscosity of the media and preventing the nucleophilic

attaching of the DEG and/ or sorbitol anions to the urethane functional groups. The reported process is eco-friendly one and can be added in the PUFs wastes recycling as a versatile and convenient process.

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