Polymer Bulletin 56, 257–265 (2006)
DOI 10.1007/s00289-005-0470-6

Polymer Bulletin

Preparation and application of glycolysed polyurethane integral skin foams recyclate from automotive wastes

Mir Mohammad Alavi Nikje[1] (✉), **Moslem Haghshenas**[2],
Amir Bagheri Garmarudi[1,2]

[1]Department of Chemistry, Faculty of Science, Imam Khomeini International University, Qazvin, Iran (P.O. Box 288)

[2]Polymer and Chemistry Laboratory, ERI, 16 Km Old Karaj Road, Tehran, Iran

Fax: +98 281 3780040; Email: alavi-m@ikiu.ac.ir

Received: 11 June 2005 / Revised version: 30 October 2005 / Accepted: 4 November 2005

Summary

Glycolysis of isocyanate derived foams with glycol and amine mixture is a simple and economically attractive chemical recycling process. A mixture of diethylene glycol (DEG) and diethanol amine (DEA) is used as solvent system and sodium hydroxide as the catalyst. The obtained polyols can be completely reused in the formulation of integral skin foams in blend with virgin polyol.

Keywords:

Glycolysis; Polyurethane waste; Recycling; Integral skin foam

Introduction

Flexible integral skin foams have found wide application in the automotive industry today as wide-ranging physical characteristics after polymerization. New styling trends, surface design, safety functions and comfort are made possible by these materials. The interior of cars, trucks and public transportation (bus, rail, and airplane) must satisfy functional and passive safety requirement; e.g. crash energy should possibly be absorbed reversibly by the protection padding. Steering wheels manufactured with integral skin foam have found wide application in automotive industry.

Over the last 40 years, polyurethane materials have been used in an ever increasing range of applications. Today, polyurethane products are an important part of everyday life. 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. Traditional methods of destroying this waste are not particularly acceptable. Burning polyurethane waste sends oxide of nitrogen, hydrocyanic acid, carbon dioxide and other toxins into the atmosphere [1, 2] , and when it is buried it is broken down by the action of water to give urea. These processes combine to pollute the air and water environments. At the same time the non-renewable nature of natural resources and their high cost are creating an urgent need to make use of secondary raw materials.

The most effective method of polyurethane waste processing is glycolysing, based on thermochemical interaction between polyurethanes and hydroxyl containing compounds [3,4].

Literature survey indicated glycolysis process may be used to resolve the disposal problems of waste PU and obtain high quality polyols [3-7]. Most of these researches indicate the method to design a comfort path for PU recycling.

It has been investigated by many scientists to find the reaction condition and make a real proportion between reactants. It has been reported to glycolysis the PUF by various glycols using tertiary amines as catalyst and collecting a double phased product [8]. It is known as a fact that the polyol derived from recycling process of flexible PUF is better to be used in preparation of rigid foams [9]. It is also reported that recycling is performed by using of alkylene oxides at 120-140 ºC, permitting efficient recovery and re-use of PU materials. Krescher has investigated the glycolysis of PUF from automobile interiors and high quality product was obtained from RIM and RRIM-PU recycling [10]. Borda [11] has recycled flexible polyurethane foams applying the product as an industrial adhesive. In most of these papers and literatures it is seen that the product of glycolysis is usable without any other treatments. While ethylene glycol (EG) is used as solvent and an organometallic catalyst is employed, under an inert environment and at the boiling point of EG, the process is performable with a high polymer/solvent ratio (4:1). All of conditions are so optimized in order to achieve an adequate result. For example, at a temperature greater than 220 ºC, unwanted reaction rates becoming competitive with main reaction, leading to a product with considerable amine content [7, 12]. It has been offered to add, glycidyl ethers in to the system in order to obtain a low-amine and homogenous recycled polyol. There is another method proposing a two-step reaction. In the first step, the polymer is broken down with an alkanol amine and a catalyst into a highly concentrated emulsion –dispersion of carbamates, ureas, amines and polyol. In the second step, this emulsion-dispersion is alkoxylated to remove any aromatic amine and obtaining a relatively high-performance, low color and high-functional polyol. This method is so useful for RRIM and TDI based flexible foams [13]. By collecting the results and observations made in all researches, it is known that the choice of degradation solvent and catalyst, as well as the reaction time and temperature are important factors, affecting the glycolysis product for further foam formulations. It was thus the aim of the present study to apply the optimum glycolysis condition for treatment of polyurethane integral skin foams from steering wheel in order to define an economical – industrial process that would be applicable in every situation and would not need any special pre – post curing for the product. Also the aim of this study was to look at the glycolysis of integral skin foam and the application of glycolized product in the new foam formulations. In spite of many studies, to the best of our knowledge, there are no reports which glycolized integral skin foam in addition use of the glycolized in new foam formulation.

Experimental

Materials

Polyether polyol (Daltorim® EK 20350), MDI (Suprasec® 2082) and additives were purchased from HUNTSMAN Company and used for polyurethane integral skin foam formulation. Technical data of virgin polyol (Daltorim® EK 20350) and MDI (Suprasec® 2082) are listed in tables 1 and 2, respectively. The prefix “virgin” is used in order to differentiate the polyol (Daltorim® EK 20350) from recycled polyol. Diethylene glycol, diethanol amine and all catalysts were purchased from Iranian Petrochemical Company.

Spectroscopy grade tetrahydrofuran (Merck, Germany) and polystyrene standards (Merck, Germany) for GPC analysis were used as received.

Table 1 - Specification of Virgin Polyol (Daltorim® EK 20350)

Daltorim® EK 20350	
Appearance	White viscous liquid
Viscosity, 25 ºC	1740 mPas
Specific gravity, 25 ºC	1.025 g/cm^3
Flash point, ºC	265
Fire point, ºC	290

Table 2 - Specification of MDI (Suprasec® 2082)

Suprasec® 2082	
Appearance	Brown liquid
Viscosity, 25 ºC	340 mPas
Specific gravity, 25 ºC	1.23 g/cm^3
Print point, ºC	204
Burning point, ºC	220

Measurements

Molecular weight distributions were determined by using 6A SHIMIDZU gel permeation chromatography (GPC) instrument.

Conditions in GPC determination:

Mobile phase: tetrahyrofuran (THF), temperature: 40 ºC, flow rate: 1 cm^3.min^{-1}, injection volume: 100 *uL*, calibration: polystyrene standards (950, 2200, 5100, 11600 Mw’s), detection: RI (Refractive Index).

Water contents were measured by using Karl Fischer titrator. The viscosity of samples was obtained using HAAKE viscometer and pH was measured by SCHOTTE GERATE pH meter. All performed in standard condition (25 ºC , 1 atm)

Integral skin foam formulation

The material used for the glycolysis was integral skin foam prepared using Reaction Injection Molding (RIM) with the formulation given in table 3.

Table 3 - Integral skin foam formulation at 20±2 °C

Component	*pbw (parts by weight)*
Virgin Polyol (Daltorim® EK 20350)	100
Tertiary Amine Catalyst (Dabco® 33 LV/Teda)	0.93
Pigment (Black Paste)	10
Blowing Agent (CFC 11)	4
MDI Curing Agent (Suprasec® 2082)	40

Molding density 300-500 kg.m^{-3}, mould temperature 40±5 °C

Typical reactivity

Foam produced in a small scale laboratory cup test, using the mixing ratio represented on the table 3 will have the reactivity listed in table 4.

Table 4 - Typical reactivity of integral skin foam prepared according to table 3

Time Records	
Cream time	50 sec.
String time	88 sec.
End of rise	107 sec.
Free rise density	188 kg.m^{-3}

Solubility of PUF

To examine the dissolution time for PUF in various glycolysis conditions, we adapted a simple experimental procedure. After the solution was heated to a temperature of 200-205 °C, a 3 cm^3 of integral skin PUF was completely immersed in a glycol solution of catalyst. The time from immersing the PUF to its complete disappearance was recorded as the PUF dissolution time and is listed in table 5.

Glycolysis of the integral skin foam – General procedure

A three necked round bottom flask was used for all reactions. The flask was equipped with a condenser, a thermometer and an agitator. The reactor was heated by heating mantel at atmospheric pressure. Known mass of solvent system (a mixture of diethylene glycol (95% *pbw*) and diethanol amine (5% *pbw*) and NaOH (1% *pbw*) was poured in the reactor. The speed of the stirrer was set at 700 rpm and the temperature of the heating mantel was set at 175 °C first in order to dissolve the catalyst in solvent and then increased to 200-205 °C below the boiling point of DEG(244-5 °C). When the temperature of the mixture (DEG/DEA/NaOH) reached the specified value, the crushed integral skin PUF was poured with feeding rate of 4-5 g/min. The glycolysis process was continued up to the reaction time of 5 h and the properties of the product were determined using instrumental and classical methods respectively.

Typical reactivity of formulated foams derived from virgin polyol and blends of virgin and recycled polyol was measured at 20± 2 °C using digital timer (table 9).

Results and discussions

Degradation and solubility of PUF in solvent system

The degradation of polyurethane integral skin foams was carried out with diethylene glycol/diethylene amine as solvent system and sodium hydroxide as the catalyst. It was observed that digestion of PUF in solvent system without catalyst is extremely difficult. There for different catalysts were used with the solvent system in order to decrease the digestion time.

In each sample, 50 g of PU foam was dissolved in 50 g solvent and 0.5 g catalyst. In our experiments it was found that NaOH has the most decreasing effect on the dissolution times. Reduction in dissolution time made by different catalysts is shown in table 5.

Table 5 - Dissolution time of PU made by different catalysts

Catalyst[a]	Dissolution time (min)
NaOH	10
KOH	14.5
KAc	57
NaAc	39
No Catalyst	162

[a] NaOH: sodium hydroxide, KOH: potassium hydroxide, KAc: potassium acetate, NaAc: sodium acetate

Table 5 shows integral skin foam dissolution times in diethylene glycol (95 parts by weight) and diethanol amine (5 parts by weight) solutions of various catalysts in equal concentrations. The solutions of alkaline metal hydroxide such as sodium hydroxide and potassium hydroxide dissolve foam more effectively than the solutions of potassium and sodium acetates.

To examine the dissolution time for PU integral skin foam in various glycolysis temperature, we adapted a simple experimental procedure. After the solution (containing 9.5 g DEG, 0.5 g DEA and 0.1 g NaOH) was heated to a defined temperature, a 3 cm^3 of integral skin foam was completely immersed in solvent system containing NaOH catalyst. The time from immersing the PU to it's completely disappearance was recorded as the PUF dissolution times. Table 6 shows the dependence of the PUF dissolution time to the reaction temperature.

Table 6 - Dissolution manner in different temperatures

*Sample No.	Reaction temperature (ºC)	Result
1	150	The foam not dissolved in solvent system after 20 minutes
2	160	The foam not dissolved in solvent system after 20 minutes
3	170	Only 10% of foam dissolved in solvent system after 20 minutes
4	180	The foam dissolved in 17 min.
5	190	The foam dissolved in 13 min.
6	200	The foam dissolved in 10 min.
7	210	Dissolution together with solvent evaporation
8	220	Dissolution together with rapid solvent evaporation

*PUF prepared according to Table 3, solvent system (95 *pbw* diethylene glycol + 5 *pbw* diethanol amine) and NaOH (1 *pbw*) as the catalyst

As shown in the table the best reaction condition was performed from sample No. 6 which dissolution occurred without any solvent evaporation. In the other hand the foam in reaction temperatures in the range of 150 – 190 ºC would not be dissolved at all (samples No. 1 and 2) or only approximately 10% dissolution (sample No. 3) occurs. By the way both 17 and 13 minutes are enough for complete dissolution (samples No. 4 and 5). When the reaction temperature raised to 210 and 220 ºC, dissolution completes at short time together with solvent evaporation (samples No. 7 and 8). As one of the main goals in this study was to reduce the energy and material losses, several tests were performed to find the best reaction temperature using NaOH as catalyst. The best reaction temperature was selected in the range of 200-205 ºC. Results observed from different temperature conditions are shown in table 6.

Gel permeation chromatography (GPC) of virgin polyol and glycolysis product

The reaction was monitored by GPC and comparison of Mw distribution of virgin polyol with recyclate at various reaction times. Operating with a polymer/solvent ratio of 2:1 at the temperature at 200 ºC and 5 hours, a product was obtained that by cooling at room temperature, separates into two liquid upper and lower phases in 60:40 ratios. Simple heating at 60 ºC restores a single phase. Secondary hydrogen bonds between the components seem to be responsible of the separation of a dense phase with very high viscosity at room temperature. In the other words, the upper phase was a light brown liquid with low viscosity. Molecular weight distributions and the GPC of virgin polyol and upper phase are given in table 7 and figure 1 respectively.

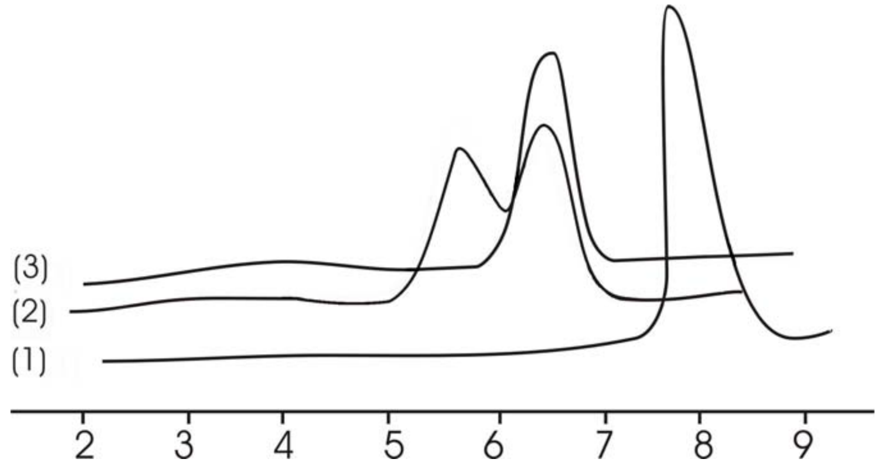

Figure 1 - Gel permeation chromatogram of (1) DEG, (2) virgin polyol and (3) recycled polyol

To identify the upper liquid phase industrial polyol standard (Daltorim® EK 20350) was used, and it was found that this upper liquid phase was similar to the starting polyol in the case of integral skin polyol. Since the upper phase is essentially the polyol. The GPC of recycled polyol shows only one peak for molecular weight distributions which is identical to the highest peak in GPC of virgin polyol. In the other words, the high molecular weights recycled polyols, separated from low molecular weights and migrate to the lower phase probably due to their higher specific gravities.

Table 7 - Molecular weight distribution of virgin polyol (Daltorim® EK 20350) and upper phase derived from glycolysis reaction

Time range (min)		Mw range		Abundance %	
From	To	From	To	Virgin	Recycled
0	5.59	*	24000	17.08	0.09
5.59	5.65	24000	22000	4.18	0.15
5.65	5.716	22000	20000	3.39	0.34
5.716	5.79	20000	18000	2.57	0.73
5.79	5.872	18000	16000	2.58	1.85
5.872	5.965	16000	14000	4.15	4.43
5.965	6.072	14000	12000	7.03	9.01
6.072	6.199	12000	10000	9.53	18.46
6.199	6.354	10000	8000	15.79	30.36
6.354	6.554	8000	6000	25.7	32.25
6.554	6.836	6000	4000	15.85	10.45
6.836	*	4000	0	1.2	0.34

The most advantage of this process is that both phases of glycolysis product are useable in future foam formulating. It is before noted that main components of lower phase are glycols and amines therefore upper phase was selected to be analyzed and processed in further integral skin PUF formulating. The lower phase showed acceptable result while using in rigid PUF formulating.

Viscosity, specific gravity, water content and pH of virgin polyol and recycling product

After investigation on product's Mw and making assurance of process result, it was important to compare the recycled polyol with virgin sample. Comparative results of some necessary quality control tests are shown in table 8.

Table 8 - Result of quality control tests on virgin and recycled polyol

Parameter	Virgin polyol (Daltorim® EK 20350)	Recycled product
Viscosity at 25 ºC (cPs)	1740	1870
Specific gravity at 25 ºC (g.cm^{-3})	1.025	1.069
Water content (%)	1.16	0.76
pH	10.10	10.15

Polyol's viscosity is the most physical parameter, influencing the PU foam injection. If the viscosity extends from its limit, the polyol currency will make a pressure destroying the injection molding machine. From table 8, the viscosity of virgin polyol is 1740 cPs, while recycled polyol has a viscosity of 1870 cPs. Accordingly, there is no considerable difference between them in viscosity.

Furthermore, the specific gravity of the product and virgin polyol was measured using Picnometer in order to observe if any difference has been made while recycling. Specific gravity is 1.025 g.cm^{-3} for virgin sample and 1.069 g.cm^{-3}for recycled one.

The presence of water as a blowing agent is another important factor in foam formulation. The water content of recycled polyol was determined by Karl-Fischer titrator comparing with virgin polyol's water content in order to recognize any value changes. The product of experiment done to recycle the PUF, have water content less than virgin polyol. So it was needed to add water as reach the virgin polyol's water content. (Recycled polyol: 0.76% and virgin polyol: 1.16%)

Finally, from table 8, it is appeared the relationship between the pH of virgin polyol and recycling product. pH measured by pH meter is 10.10 for virgin polyol and 10.15 for recycling product respectively.

Reuse of recycled polyol in integral skin foam applications

The formulation of typical integral skin polyurethane foam used in our study is shown in table 9. The polyol obtained from the degradation of integral skin foam of RIM, was blended with the virgin polyol in amounts of 30, 40, 50, and 60% of total polyol. The results of derived foams are listed in table 9.

It is evident that levels of higher than 30% of recycled polyol can be tolerated by increasing the MDI usage. In fact, the narrow molecular weight distributions of recycled polyol enhance the functionality that parallel to OH-value of the polyol. In the other words, it was observed that as increasing the percentage of recycled polyol, it is necessary to add more MDI.

Another important observation in this study was the effects of CFC-11 on the cell structure of formulated foams. In fact, cell size increased with increasing the amount of CFC-11, thus one of the sample foams collapsed (S_3).

Table 9 - Integral skin foam formulation, properties and reactivity

Foam Components (*pbw*)	S_1	S_2	S_3	S_4	S_5	S_6	S_7
Virgin Polyol (Daltorim® EK 20350)	100	70	70	70	60	50	40
Tertiary Amine Catalyst (Dabco® 33 LV/Teda)	0.93	0.93	0.93	0.93	0.93	0.93	0.93
Pigment (Black Paste)	10	10	10	10	10	10	10
Blowing Agent (CFC 11)	4	4	7	5	5	5	5
Recycled Polyol (Glycolysis Product)	0	30	30	30	40	50	60
MDI Curing Agent (Suprasec® 2082)	40	40	60	65	80	100	120
Free rise density ($kg.m^{-3}$)	188	169.3	-	142.6	124.4	120.1	119.6
Molded density ($kg.m^{-3}$)	209	199.4	-	203.3	208.3	200.7	206.1
Hardness (Shore A)	85±1	87±1	-	93±1	95±1	95±1	94±1
Cream time (sec.)	50	46	-	44	47	42	43
String time (sec.)	88	79	-	72	79	74	77
End of rise (sec.)	107	100	-	93	96	89	93

One of the other ways to compare recycled and virgin polyol was to compare the reactivity of them by clocking some time data during the foaming procedure (Table 9).

Conclusions

Glycolysis of integral skin polyurethane foam products with diethylene glycol/diethanol amine and NaOH afford two liquid upper and lower phases, which the upper phase was homogeneous polyol that can be reused in the manufacture of integral skin polyurethane foams.

Results calculated from GPC analysis show that upper phase of product has a structure the same as virgin polyol. Results collected from quality control of recycled polyol maintained that it is applicable in a polyol blend for foam formulation. It was noticeable to add enough water to the recycling product in order to terminate the same water content of virgin polyol. As shown in table 9, comparing the main physical properties of foams formulated by virgin and recycled polyol confirms the glycolysis method and its product has an approximately similarity with foam formulated by virgin polyol.

This simple recycling process could take care of scrap generated in the RIM of integral skin polyurethane foams.

References

[1] Markovic V, Hicks DA (1997) Design for Chemical Recycling. Phil. Trans. R. Soc. Lond. A.

[2] Hicks DA (1994) Krommenhoek M. Polyurethane Recycling and Waste Management. ICI Polyurethanes presentation UTECH 94 Conf., The Hague.

[3] Liubartovich SA , Morozov YuL , Tretiakov OB (1990) Polyurethane formation by reaction. Kimiia, Moscow.

[4] Hopper JFG, Parrinello G, Parfondry A, Kroesen KW (1992) Recent Developments in the Chemical Recycling of Flexible Polyurethanes. Utech 92 Conference, 31st March to 2nd April, The Hague, The Netherlands.

[5] Hartel JJ (1993) New Developments in Thermoset Recycling and Environmentally Friendly Processing Systems. In: Proceedings of Polyurethanes World Congress, 10-13 October.

[6] Weigand E, Rasshofer W, Herrmann M, Baumann GF, Nakamura M (1993) Recycling og Polyurethane Put into Practice. In: Proceedings of Polyurethane World Congress, 10-13 October.

[7] Scheirs J (1998) Polymer Recycling. UK: John Wiley and Sons.

[8] Kinoshita O (1972) Process for decomposition of a polyurethane resin. US Patent 3632530.

[9] Tucker B, Ulrich H (1976) Novel process of reclaiming polyurethane foam. US Patent 3983087.

[10] Krescher J, Schwager H, RaBhofer W, Pfefferkorn R (1996) Chemical Recycling of an All-Polyurethane Instrument Panel – Industrial Realisa, Utech.

[11] Borda J, Pasztor G, Zsuga M (2000) Glycolysis of polyurethane foams and elastomers. Polymer Degradation and Stability. 68:419-22.

[12] Simioni F, Modesti M, Rienzi SA (1987) Polyol Recovery from Elastomer Polyurethane Waste. Cellular Polymers. 6(6):27.

[13] Van der Wal HR (1994) New chemical recycling process for polyurethane. J Reinforced Plastics and Composites 13:87.

Definition of acronyms:

1- Integral Skin Foam: Skin surfaced foam which would be resistant against contact to other surfaces.
2- PU: Polyurethane
3- PUF: Polyurethane Foam
4- RIM: Reaction Injection Molding
5- RRIM: Reinforced Reaction Injection Molding
6- TDI: Toluene-2,4-Di Isocyanate
7- MDI: Methylene Diphenyl Di Isocyanate
8- Cream Time: The time from mix start to when there appears to be reaction with foam beginning to rise
9- String Time: The time when there is obvious gel strength developed in the rising foam
10- Rise Time: The time when the foam reaches its maximum height of rise