Conversion of polyurethane technological foam waste and post-consumer polyurethane mattresses into polyols – industrial applications

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Abstract: Researches were carried out to determine the possibility of reusing polyols produced in the chemical recycling process of polyurethane (PUR) foam technological waste and post-consumer mattresses for the production of mattresses and thermal insulation panels. It was found that such PUR waste can be converted into repolyol by similar processes that are currently used at Dendro Poland LTD Sp. z o.o. The mixture containing repolyols was used to produce rigid and flexible polyurethane-polyisocyanurate (PUR-PIR) foams. It was found that a mixture of polyols containing up to 50 wt % of repolyols can be used in the production of flexible PUR-PIR foams. The most suitable application for recycled polyol from post-consumer foam waste was identified as rigid PUR-PIR foam for thermal insulation. The produced rigid foams showed good performance in the foaming process, foam structure and dimensional stability. The practical application of chemical recycling of post-consumer mattresses is of great environmental importance and, additionally, the obtained repolyol is cheaper than the standard polyol.

Keywords: polyurethane, chemical recycling, polyol, post-consumer mattress.

Przetwarzanie technologicznych odpadów pianek poliuretanowych i poużytkowych materacy poliuretanowych na poliole – zastosowania przemysłowe

Streszczenie: Przeprowadzono badania zmierzające do określenia możliwości ponownego wykorzystania polioli wytworzonych w procesie recyklingu chemicznego technologicznych odpadów pianek poliuretanowych (PUR) i materacy poużytkowych do produkcji materacy i paneli termoizolacyjnych. Stwierdzono, że odpady pianek PUR oraz poużytkowe materace można przetworzyć na repoliole w prostym procesie stosowanym obecnie w zakładach Dendro Poland LTD Sp. z o.o. Mieszaninę repolioli otrzymanych w pilotowej instalacji przemysłowej stosowano do produkcji elastycznych i sztywnych pianek poliuretanowo-poliizocyjanurowych (PUR-PIR). Stwierdzono, że do wytwarzania elastycznej pianki o wymaganych właściwościach można zastosować mieszaninę poliolu zawierającą do 50 % mas. repoliolu. Repoliol można też używać do produkcji pianek sztywnych, całkowicie zastępując surowce pierwotne. Otrzymane w ten sposób panele charakteryzują się dobrymi właściwościami termoizolacyjnymi i stabilnością wymiarową. Praktyczne zastosowanie chemicznego recyklingu poużytkowych materacy ma duże znaczenie proekologiczne, a także korzystny aspekt ekonomiczny – repoliol jest tańszy od standardowego poliolu.

Słowa kluczowe: poliuretan, recykling chemiczny, poliol, materac poużytkowy.

In 2017, it was 80 years since the first patent application for polyurethane (PUR) manufacture. Isocyanate reactions make it possible to obtain many types of solid and porous PUR differing in structure, properties and applications [1–5]. The possibility of modifications according to the requirements of users using the same production installation is also important. Some 20.5 Mt of PUR goods were produced worldwide in 2015. This was up by *ca.* 4 %

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from 2014. The forecasts for 2018 indicate a slight increase to 12 % [6]. The situation in Europe is identical. The European PUR industry is undergoing strong growth because of the new economic incentives presented in Table 1.

T a b l e 1. PUR production in Europe for 2015 and 2016 [10]

Sector	PUR production, kt	
	2015	2016
Flexible slabstock foam	1450	1490
Rigid foam	1570	1625
Elastomers	400	410
Glue	360	367

The main driver for the growth of PUR foams is residential and commercial demand for better and more durable mattresses and greater demand for better insulation materials. There is also a growing application of PUR foams as antivibration mats to suppress the vibration of railway and tram tracks, also in industrial and residential buildings [7–10].

The number of used mattresses in landfills increases every year. About 25 million units of mattresses are produced annually in Europe [11]. The amount of PUR mattresses grows extremely fast. In 2005, PUR mattresses were 28 % and 37 % in 2010 of the total number of produced mattresses. The exact information about the ratio is unavailable today, but it is assumed that 10 million PUR mattresses are sold in Europe every year. In Germany about 800 million euros worth of mattresses are produced per year. There is a lack of precision in details on waste mattresses, but in 1999, the Union b.v.s.e.-Bundesverband Sekundärrohstoffe und Entsorgung e.V. reported that over 1.6 million mattresses per year end up in landfills [12]. The quantity can be estimated at 22–200 kt per year.

Because of environmental, economic and hygienic reasons, mattresses cannot easily be reused. Flexible PUR foam residues can be mechanically recycled by powdering or reused for foam production. Both have a very limited application and are not profitable. At this time, most mattresses are burned in order to generate energy. The disadvantages of this method are emerging poisonous gases and unevenly generated energy (a major problem for industrial furnaces such as cement plants). Another significant drawback is the additional, irreversible withdrawal of raw materials from the cycle of valuable substances.

In recent years, Dendro Poland has undertaken work to create the technology for the effective reuse of PUR foam waste and used mattresses by chemical recycling.

Chemical PUR recycling is represented by several technologies. It is common knowledge that flexible PUR-PIR foam can be chemically converted into polyols by means of amines, alcohols, acids and their combination.

The literature describes various glycolysis procedures, for example [2, 4, 13, 14].

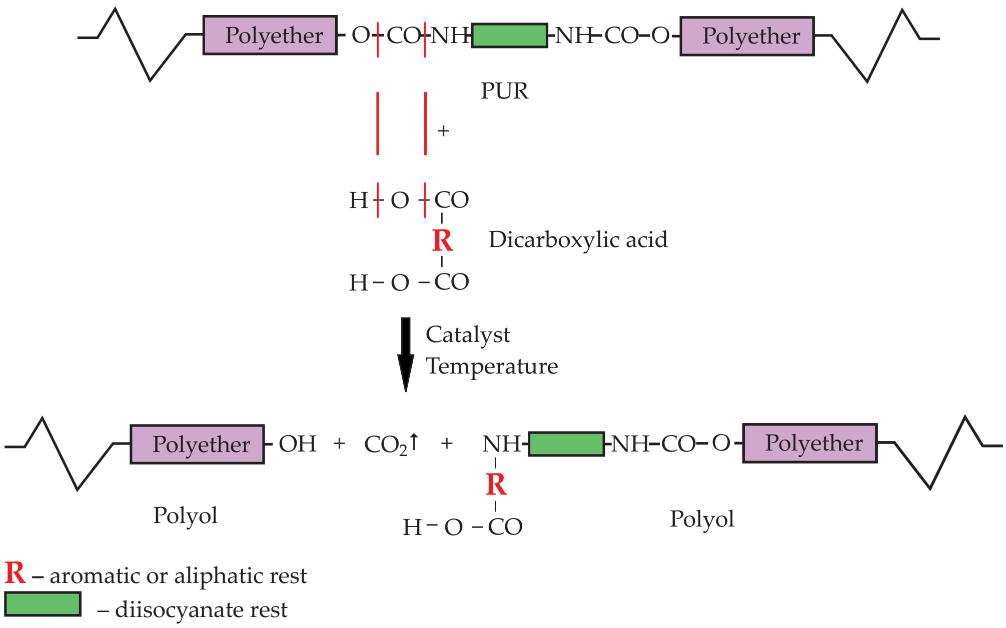
After the hydrolysis, glycolysis, acidolysis, and aminolysis reactions with PUR foam, various chemical substances are available for further use [15–17]. These reactions are relatively simple to implement on a small scale but the application of them on an industrial scale encounters great difficulties.

The process is based on a balanced reaction in which urethane groups are split by means of hyperstoichiometric amounts of hydroxyl groups in the form of diols [2, 4, 13–18]. The glycolysis reaction runs relatively slowly and at a high temperature. The resulting polyols have high hydroxyl numbers and can be implemented in rigid PUR-PIR foam production. Glycols cut PUR chains too short to make flexible polyols. The hydroxyl number of polyols regenerated in this way is about L_{OH} = 400 mg KOH/g. The reclaimed products, in reaction with polyisocyanate, form solid segments and the resulting PUR foam is semirigid or rigid. Moreover, all known glycolysis methods are disadvantageous due to the build-up of aromatic amines as by-products in a high percentage, which is not acceptable for bedding and upholstery PUR foam. The reagents used for aminolysis are different di- and tertiary amines. The advantages of aminolysis include a high percentage of PUR residues that can be used in the formulation up to 80 wt % and that the reaction runs rapidly at relatively low temperatures. The results of the conversion are two phases in the reaction mixture: a low viscosity polyol phase and a solid oligourea phase. The polyol phase mixed with isocyanate can be used for generating flexible PUR and can replace up to 10 wt % of the genuine polyol. The disadvantage of this process is that the lower phase, which makes 40 wt % from the total amount, is unusable and must be disposed of as a chemical waste. Also, the resulting polyol has a very intensive odor and contains primary aromatic amines in higher percentages, which is not acceptable.

The advantages of the acidolysis technology are appropriate molecular chain structures for any generated PUR and the absence of aromatic amines. The process is distinguished by a rapid reaction in the presence of dicarboxylic acids and their derivatives at a high temperature. Acidolysis of PUR by dicarboxylic acids is shown in Scheme A. In contrast to other methods, the use of dicarboxylic acids does not lead to the formation of any primary aromatic amines, such as toluene diamine (TDA) and methylene diamine (MDA), that are classified as carcinogenic.

Following a successful laboratory study conducted in cooperation with the Faculty of Chemical Technology and Engineering of the University of Science and Technology in Bydgoszcz, Dendro proceeded to conduct industrial tests. For this purpose, a pilot installation with a 700 dm^3 stainless steel reactor, shown in Fig. 1, was installed at the beginning of 2017. Pilot tests were carried out to investigate the production of recycled polyol from chemical recycling of flexible PUR foams.

Thus far, Dendro has succeeded in creating a method for the production of recycled polyols from a mixture of post-consumer PUR mattresses. In the course of the research, the product (recycled polyol) has been modified to be suitable for the production of high-quality PUR rigid insulating foam and structural elements. In this way,



Scheme A

by using an environmentally-friendly product, high-quality insulating material was created at an extremely competitive price.

The aim of this work was to determine the possibility of reusing polyols produced in the chemical recycling process of PUR foam waste for the production of mattresses and thermal insulation panels.

EXPERIMENTAL PART

Materials

Our own PUR technology waste from foaming processes and mattress production, as well as post-consumer foam waste supplied by customer's stores was used during this study. The delivered post-consumer sample was a mixture of standard foams and the impact of different foam types (Standard, HR and Visco) could not be investigated thoroughly. The impact of flame retarding chemicals and filler was also not investigated.

As a polyol component, conventional polyether polyols with a functionality from 2 to 6 and molecular weight from 200 to 6000 Da were used.

Repolyol was produced using the pilot installation for PUR foam chemical recycling in Dendro Poland according to Scheme A. Details of the acidolysis and production of PUR-PIR foams are described in the literature [2, 4, 13–18]. The industrial high-pressure QFM foaming machine by Hennecke, storage tanks by H&S and Metalko, as well as the cutting and storage system for long blocks by Baeumer for PUR foaming and mattress production were used for flexible PUR foam production.

Fig. 1. General view of pilot installation for chemical recycling of PUR

Methods of testing

The basic properties of the obtained repolyols were characterized by standard laboratory equipment. Hydroxylic number, amine number, and acid number were determined with a titrator Mettler Toledo T5. Viscosity was measured with a Brookfield viscometer DV-II+Pro and density with a helium pycnometer Pyctomatic ATC. The samples of sandwich panels prepared with a mixture of 60 wt % standard polyol and 40 wt % of repolyol were made under laboratory conditions. The thermal conductivity (λ) at different temperatures was established according to EN 12667, and parallel compression resistance according to EN 826. The thermal stability and fire resistance were characterized according to PN-EN ISO 11925-2. To determine the amount of closed cells according to PN-EN ISO 4590:2005, a gas pycnometer ULTRAPYC 1200e was used.

The mechanical properties of the obtained foams were examined with Zwick 3107, Zwick Z005, and Zwick Roell machines. All investigated properties of foams were determined according to the proper Standards (listed in Table 3).

Table 2. Comparative properties of panels made with the standard polyol and its mixture with repolyol at 40 wt %

Temperature	Panel with standard polyol	Panel with mixture of standard polyol and repolyol
Thermal conductivity at specified temperature W/(m · K)		
0 °C	0.020 ± 0.001	0.020 ± 0.001
5 °C	0.020 ± 0.001	0.020 ± 0.001
10 °C	0.020 ± 0.001	0.020 ± 0.001
15 °C	0.021 ± 0.001	0.021 ± 0.001
20 °C	0.022 ± 0.001	0.021 ± 0.001
23 °C	0.022 ± 0.001	0.022 ± 0.001
Closed cells, %	94 ± 2	94 ± 2
Density, kg/m^3	2.78 ± 0.1	2.81 ± 0.1
Parallel compression, %	2.40 ± 0.2	2.58 ± 0.2
Stability at 20 °C % of shrinkage	0.45 ± 0.02	0.40 ± 0.02
Stability at 80 °C % of shrinkage	1.22 ± 0.02	0.89 ± 0.02
Fire resistance, cm	12.0 ± 0.3	11.8 ± 0.3

RESULTS AND DISCUSSION

Properties of repolyol and prepared foams

The resulting repolyol product has the following properties: L_{OH} = 160–220 mg KOH/g, amine number maximally 10 mg KOH/g, viscosity 4000 ± 500 mPa · s, acid number maximally 2 mg KOH/g. The value of L_{OH} is at the same level as for typical polyols used for rigid isocyanurate foam production and any unusual change from the isocyanate index is not necessary. This makes it very easy to implement recycled polyol in already existing PUR systems. During the production of rigid foams, the polyols and catalysts are mixed in batches. This makes it possible to adjust the process' critical parameters, such as viscosity and hydroxyl number, which can vary for an inhomogeneous starting material. Post-consumer foam waste will contain small amounts of latex adhesives. This can cause a slight, rubber-like smell of the recycled polyols. The smell is not relevant for rigid PUR foam due to the closed cell structure. Such good properties of the polyol enable the use of a high percentage of polyol replacement, which reached 40 wt % for panels and sandwich elements. The properties of these products are compared with the properties of panels made with original materials, without repolyol, and are collected in Table 2.

As a polyol component in the process, a polyether polyol was chosen. The use of this kind of polyol leads to a lower cost of the polyol mixture and a lower viscosity, which is better for producing new rigid foams. The low viscosity of polyether polyol also makes it possible to use more than 40 wt % of repolyol obtained from foam waste in the polyol mixture. In this process, di- or tricarboxylic acids or their derivatives like anhydrides and radical catalyzer can be used. Finally, it was found that it is possible to recycle post-consumer foam waste to a polyol using a similar process to that currently used at Dendro, and the polyol mixture can contain up to 100 wt % repolyol.

The recycled polyol in this way can be used for the production of rigid foam panels using 40 wt % recycled polyol and 60 wt % of aromatic polyester polyol or polyether polyol. The produced rigid foam with recycled polyol up to 40 wt % showed good performance in the foaming process, foam structure and dimensional stability, similar to traditional PUR rigid foam.

Flexible foams prepared with various contents of repolyol were obtained. The physical and mechanical properties of these foams were investigated and listed in Table 3.

Economic and ecological benefits

An industrially suitable chemical procedure including process technology and system concept for producing recycling polyols from PUR waste mattresses foam is available for the first time – this is a process offering economic and ecological benefits. The costs to manufacture recovered polyol are about 40 % percent lower than the market price of the original polyol. An exemplary calculation is shown in Table 4.

This simple calculation shows an extremely attractive price for the product. The price of polyol for rigid foams production starts at 1400 €/t.

The new procedure proves its ecological worth through increased material efficiency and sparing of resources as polyols can be replaced partially by recycled polyols. Both productivity and energy efficiency are increased, because the reaction can be carried out using a comparably low temperature in a relatively short time.

T a b l e 3. Physical and mechanical properties of standard flexible foam

Property	Standard	Foam obtained with repolyol content		
		20 wt %	30 wt %	100 wt %
Density, kg/m^3	PN-EN ISO 845	27.52 ± 0.03	24.51 ± 0.03	27.54 ± 0.03
Resilience, %	PN-EN ISO 8307	42.8 ± 0.3	45.1 ± 0.3	31.6 ± 0.3
Hardness, N	PN-ISO 2439 Method B (40 %)	140.5 ± 0.5	133.2 ± 0.5	121.3 ± 0.5
Support factor	PN-ISO 2439	2.3	2.3	3.5
Tensile strength, kPa	PN-EN ISO 1798	151 ± 1	154 ± 1	103 ± 1
Elongation at break, %	PN-EN ISO 1798	237 ± 5	224 ± 5	171 ± 5

T a b l e 4. Calculation of repolyols mixture production cost per 1 t

Cost component	Quantity	Unit	Price, € per 1 t	Cost, €/t
Chemical components:				
foam scraps	42.2	%	150	63
polyester polyol	31.0	%	1400	434
acid	10.0	%	1100	110
short diol	13.8	%	1400	193
catalyst	1.0	%	600	6
additive	2.0	%	1600	32
Water removal by distillation	4.0	%	150	6
Electricity, per 1 t polyol mixture	700	kWh	–	60
Nitrogen, per 1 t polyol mixture	35	m^3	–	24
Labor cost, per 1 t polyol mixture	1	–	55	55
Administration cost, per 1 t polyol mixture	1	–	35	35
Total price of 1 t of repolyols mixture				1018

CONCLUSIONS

Our study shows that it is possible to recycle post-consumer PUR-PIR foam waste to a repolyol with a similar process to that currently used at Dendro Poland. Repolyols prepared in this way can be successfully used for flexible, as well as rigid foam production. During the processing of flexible PUR foam for mattress production, up to 40 wt % of repolyols can be used. The most suitable application for recycled polyols, from post-consumer foam waste was identified as rigid foam for thermo insulation. The produced rigid foams showed good performance in the foaming process, foam structure and dimensional stability.

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