

*Paulina Kosmela¹, Lukasz Zedler¹, Krzysztof Formela¹, Jozef Haponiuk^{1,2}
and Lukasz Piszczyk^{1,2}*

RECENT DEVELOPMENTS IN POLYURETHANE FOAMS CONTAINING LOW-COST AND PRO-ECOLOGICAL MODIFIERS

¹ *Gdansk University of Technology, Faculty of Chemistry, Department of Polymer Technology,
11/12 Narutowicza St., 80-233 Gdansk, Poland*

² *NovaPUR Sp. z o.o.; jozef.haponiuk@pg.gda.pl*

Received: September 12, 2016 / Revised: September 20, 2016 / Accepted: October 01, 2016

© Kosmela P., Zedler L., Formela K., Haponiuk J., Piszczyk L., 2016

Abstract. Diversity of the polyurethane (PU) foams applications cause that investigation of the relationships between their structure and properties is currently very popular topic among the many research institutions and companies. At the turn of the last years many scientific papers about PU foams and their composites were published. The one of the main research trends in this field is related to the reduction of production costs of PU foams. This aim can be successfully achieved through the incorporation of raw materials of natural origin or the utilization of waste materials. This work reviews the progress and recent developments in area of PU foams containing low-cost and pro-ecological modifiers, such as crude glycerol, liquefied biomass, ground tire rubber, *etc.*

Keywords: polyurethane foams, crude glycerol, liquefied biomass, ground tire rubber.

1. Introduction

Estimated data indicates that the level of global production of polyurethane (PU) materials in 2016 will reach 18 million tonnes, from which about 10 million stands for PU foams [1]. A growing interest in these polymeric materials and their increased popularity are both related to the simplicity of the manufacturing process and a wide spectrum of properties, which can be freely customized, *e.g.* by changing the chemical structure of PU or adding specific modifiers.

Components used in polyurethane industry based mainly on the fossil-fuels and petroleum products. On the other hand, ongoing trends related to sustainable development and provisions of Kyoto Protocol regarding the reduction of the fossil-fuels application result in the increased interest of chemical industry in alternative, more environmental friendly components. The recently announced by European Union, Energy and Climate

Change Package set explicit targets for 3x30, which means that the emission of greenhouse gases emissions in 2030 should be 40 % lower than in 1990; the share of renewable energy should reach 27 %; and consumption of energy should be decreased by 27 % [2]. Law regulations, economic and environmental aspects enforced the industry and academic society to search and develop of environmentally friendly technologies based on low-cost and pro-ecological, mainly renewable raw materials and recycled materials.

Nowadays, polyurethanes industry uses renewable materials for the production of biopolyols, which in terms of their chemical structure, are generally esters of glycerol and unsaturated fatty acids. Depending on the location, the most common oils used in biopolyols manufacturing are: in Europe – castor, rapeseed and sunflower oils, in Asia – palm and coconut oil, and in USA – soybean oil. Natural oils, which are currently the primary compounds used in production of PU, are mainly used in food industry. Incorporation of the natural oils into polymer production could unfavorably affect their price and cost of resulting food products. Therefore, research conducted in this field are focused mainly on the use of other materials, being by-products of the renewable materials processing, such as lignocellulose biomass and crude glycerol or waste materials, *e.g.* ground tire rubber. In the present work, a short review about current research in these fields is presented.

2. Application of Crude Glycerol in Polyurethane Foams Technology

Unstable situation in the petroleum market and ecological aspects obligated European Union countries to save traditional diesel and partially substitute it for biodiesel. The producers are required to achieve the

carbon dioxide emission at the level of 95 g/km in 2021 (there are also proposals for further reduction of CO₂ emission to 68–78 g/km in 2025) [3]. According to the European Biodiesel Board and Ecofys the use of biodiesel results in the reduction of the carbon dioxide emission by 65–90 % comparing to conventional diesel [4].

Current production capacity of biodiesel in European Union is about 11 million tonnes and forecasts indicate that in 2020 it will exceed 15 million tonnes per year [5]. Such trend is not observed only in European Union, from 2006 there has been observed great enlargement of the global biodiesel market. According to prognosis value of global biofuels market will rise by more than 12 % per year till 2017 and it will be still concentrated in Europe (67 % of global production). It is worth to mention, that for each ton of produced biodiesel, from 90 to 110 kg of crude glycerol is obtained. Before its discharge, transesterification catalyst (acidic or basic) and alcohol (usually methanol) have to be removed, which increase the biodiesel production costs. Comparing to pure glycerol, crude one also contains free fatty acids, fatty acid methyl esters (FAME) and glycerides. Detailed composition obviously depends on the type of used oils, type and amount of catalyst and potential treatment applied to final product [6].

The simplest application of crude glycerol is energy recovery through combustion as alternative for conventional fuels. Although there has been a lot of concern about highly toxic acrolein formed during this process, the recent studies proved that its emission is not very high and with a little effort can be reduced to acceptable level. However, this method of crude glycerol utilization does not use the whole potential of this component, which can be used in other applications. Glycerol is a valuable material for many branches of chemical industry (used, for example, in pharmaceutical, food, cosmetic, tobacco, explosives, etc.), so the development of the purification methods in order to obtain high-purity product is very important. Therefore, various methods and techniques are nowadays used to purify crude glycerol, such as filtration, microfiltration, ultrafiltration with polymer membranes, ion exchange or absorption. All of the mentioned processes are very expensive and economically unavailable for the smaller biodiesel producers, which reduces the profitability of glycerol production from crude glycerol. Elimination of the time and cost consuming processes of purification may be very beneficial for the profitability of biodiesel production.

At present, very interesting and promising route is the incorporation of biodiesel-based glycerol into polymer technology, while among the various plastics produced or modified with crude glycerol, the most popular are

polyurethanes. A comprehensive review work about application of crude glycerol in polymer was recently published by Hejna *et al.* [7].

Glycerol obtained from biodiesel production might be incorporated into polyols and PU production by many different ways, indirectly, by the use of materials derived from glycerol, or directly, by incorporation glycerol or its polymeric form into processes.

Another way of crude glycerol utilization could be its oligomerization and polymerization, also often called etherification, resulting in polyglycerols. Oligomerization of glycerol resulting in di- and triglycerol has been described in comprehensive review by Martin and Richter [8]. However in plastics industry, more popular is polyglycerol, highly branched compound, which should be soluble in water and other polar solvents and should be non-volatile at room temperature [9]. Its high functionality and reactivity of hydroxyl groups allow its application in the production of polyurethanes, polyesters, epoxy resins and different copolymers. Number of polyglycerols are commercially available, however traditionally they are produced through anionic polymerization of glycidol in rapid cation exchange equilibrium [10, 11]. Incorporation of crude glycerol could eliminate the use of glycidol, which is considered carcinogenic to humans [12]. Moreover, glycidol is rather expensive compound, which utilization leads to high cost of the final product, that noticeably limits the wider utilization of resulting polyglycerols [13].

Polymerization process of glycerol can be performed using different types of catalysts (preferably base catalysts) and resulting polyglycerol may be successfully used in preparation of polymeric materials [14]. Potential structure of polyglycerol prepared by crude glycerol polymerization can be seen in Fig. 1. Generally oligomerization of glycerol results in the mixture of linear and branched polyglycerol, as well as some cyclic compounds. These mixtures are obtained using different types of catalysts such as zeolites, mesoporous materials, acids, ion-exchange resins or different metal hydroxides, oxides and carbonates. Acidic catalysis results in high degree of polymerization, which affects color properties of obtained products. Also the selectivity of the reaction is affected and noticeable amount of cyclic polyglycerols is formed. Among basic catalysts, carbonates were found out to be more active than hydroxides and oxides, because of the better solubility in the glycerol.

Apart from catalysts, the process conditions affect significantly final properties of polyglycerols. Lower reaction temperatures and low pH values lead to the formation of cyclic isomers, while at elevated temperatures side reactions show unfavourable influence on color and smell of the product [15].

Nowadays researchers focus on the development of the polycondensation process parameters and catalysts leading to high molecular weight products with satisfactory efficiency and selectivity of final product, which will definitely lower the production costs, due to the elimination of complex purification processes [16, 17]. Obviously researchers are very interested in heterogeneous catalysts, which are easier to separate and recover after the reaction, and generally provide higher activity, selectivity and longer lifetime [18-20]. There have been also attempts of microwave irradiation incorporation into polymerization of crude glycerol in order to eliminate the use of catalysts [21].

Wirpsza and Banasiak [22] patented the method of crude glycerol distillation resulting in oligoetherols. Glycerol contained also various impurities, such as water, free fatty acids, natural oils, methanol, glycerides and residual catalyst. Process was performed at 533–573 K under atmospheric pressure and neutralized with sulfuric acid until pH reached 4-8. Then, mixture was heated up once again. Depending on specific reaction conditions, resulting polyols were characterized by hydroxyl number of 250–430 mg KOH/g and molecular weight of 1500–1700 g/mol.

Soi *et al.* [23] in their patent described the production of polyglycerol through polymerization of crude glycerol, containing residues of soaps, which were used as catalysts. Crude glycerol should contain at least 10 wt % of soaps produced during transesterification. As in previously mentioned patent of Wirpsza and Banasiak [24], presented process includes heating the crude glycerol at elevated temperature (473–563 K) under atmospheric pressure. According to the results of HPLC (high-performance liquid chromatography) analysis, there is very little evidence of cyclic diglycerol, so process can be claimed to be selective for linear polyglycerols.

Polyglycerols, because of their branched structure can be considered very interesting substrates for synthesis of highly crosslinked PU materials, such as adhesives or rigid PU foams. Because of their bio-based character they can also be incorporated into production of potentially biodegradable materials [24]. These compounds have been repeatedly analyzed as polyols for polyurethanes [25-27].

During our own research [28], two types of commercially available polyglycerols from Eco Innova, produced according to previously mentioned patent [22] were used. In Table 1 there are presented properties of foams obtained by replacement of 35 and 70 wt % of commercial Rokopol RF551 by polyglycerols Pole and PGK. It can be seen that incorporation of 35 wt % results in maintenance of structure and thermal properties of foams, simultaneously enhancing compressive strength of foams, without addition of modifiers, which was related to increase of apparent density of material. Moreover, incorporation of biopolyols resulted in the enhancement of thermal stability, even by 288 K.

Glycolysis is the most widely used recycling process for PU. It consists of a transesterification reaction, in which the ester group joined to the carbonyl carbon of the urethane is interchanged by the hydroxyl group of a glycol. With a large molar glycol excess condition, the reaction product splits in two phases, where the upper layer is mainly formed by the recovered polyol, with a higher purity than in the case of single phase glycolysis processes, and the bottom layer by the excess of glycolysis agent and reaction byproducts. However, this huge molar excess causes an important increasing of the operation costs what makes almost impossible the implantation of industrial glycolysis plants.

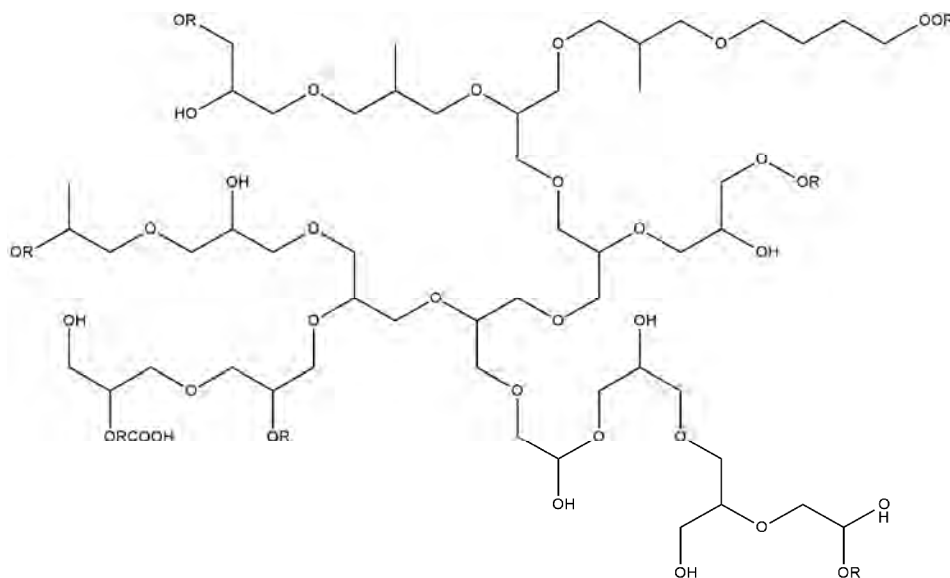


Fig. 1. Potential structure of polyglycerol prepared by crude glycerol polymerization

Table 1

Properties of rigid polyurethane foams prepared with crude glycerol-based polyglycerol [28]

Properties	Foam symbol				
	P ₀	P _{Pole 35}	P _{Pole 70}	P _{PGK 35}	P _{PGK 70}
Apparent density, kg/m ³	21.7 ± 1.2	30.3 ± 0.9	36.1 ± 1.3	25.5 ± 1.2	28.1 ± 1.1
Compressive strength at 20 % deformation, kPa	140 ± 3	170 ± 4	180 ± 4	164 ± 3	168 ± 4
Thermal conductivity coefficient, mW/m-K	26.1 ± 0.8	25.8 ± 0.7	32.6 ± 0.6	26.3 ± 0.8	28.1 ± 0.8
Closed cell content, %	82	83	65	82	77
Average pore diameter, μm	110 ± 9	111 ± 8	121 ± 9	107 ± 8	109 ± 8

Nikje *et al.* [29] presented glycolysis of isocyanate derived cold cure foams, with glycerin as a new glycolysing agent. The reaction was performed under atmospheric pressure in a stirred flask at the temperature of 443–463 K. Glycerin and NaOH were used as solvent and catalyst in the glycolysis system, respectively. The reaction was followed by using spectroscopic methods. The obtained results from Fourier transform infrared spectroscopy (FT-IR) and gel permeation chromatography (GPC) showed the similarity of recycled and virgin polyols. Authors found that glycerin could be used as glycolysis agent to recovering of high quality polyol, which can be reused for production of new flexible PU foams.

Simon *et al.* [30] showed in their work the feasibility of the glycolysis process of flexible PU foam scraps by means of using crude glycerol, a waste of the biodiesel production. Transesterification reactions have been carried out using a molar excess of crude glycerol and have provided an split phase product, where the glycolysis upper phase mainly consists of the recovered polyol and the bottom one of several reaction byproducts, such as low weight carbamates and aromatic amines similar, and of the excess of crude glycerol employed to displace the transesterification equilibrium to the polyol release. It has been demonstrated that crude glycerol provides a glycolysis upper phase with a lower content of byproducts and transesterification agent than in the case of using the best transesterification agent described until this moment, as a consequence of its higher dielectric constant. Furthermore, as a result of crude glycerol higher dielectric constant it has been obtained a glycolysis bottom phase free of polyol, increasing of this way the total yield of the glycolysis process.

Kopczyńska and Datta [31] presented a method of polyurethane thermo-chemical recycling, glycerolysis by means of crude glycerol. Authors used the crude glycerol as a decomposing agent for PU recycling. In the work they reported the influence of polyurethane-to-glycerol mass ratio on chemical structure, using FT-IR, GPC and proton nuclear magnetic resonance spectroscopy (¹H NMR), also an analysis of the thermal and rheological

properties. Based on the received results, the authors concluded that the chemical structure of glycerolysates is quite similar to that of virgin polyol. It was established that using crude glycerol in the glycerolysis process is suitable for PU recycling.

In another work Kopczyńska *et al.* [32] received PU elastomers by using different mixtures of petrochemical and glycerolysate polyols and 4,4-diphenylmethane diisocyanate (MDI). Glycerolysate polyol was produced from PU foam decomposition using crude glycerine as a decomposition agent. Glycerolysate polyol was incorporated into PU formulation as soft segment. Authors found that thermal properties did not worsen after using glycerolysate into PU formulation and observed a slight increase in glass transition temperature with the incorporation of glycerolysate polyol. Authors observed the improvement of mechanical properties with increasing recycled polyol content.

3. Liquefaction of Lignocellulose Biomass

Lignocellulose biomass is the oldest renewable source of energy, lately gaining more and more attention. It involves all types of animal and plant materials, which are prone to biodegradation, such as agricultural, forestry, communal and industrial wastes. Because of the complex composition, there are various possibilities of biomass processing. Its main ingredients are cellulose and lignin. In Fig. 2 the basic scheme of biomass composition is presented.

Increase of the biomass share in energy production can be observed in developing and industrialized countries. For purposes of organic industry there are used mainly materials rich in carbon. Significant potential, possible to extract in biorefineries, can be found in renewable plant-based materials, such as root crops, cereals, wood, fiber crops, oilseeds, vegetable oils, natural rubber, vegetable proteins or waxes [33].

Lignocellulose biomass is promising alternative for production of biopolyols, which could find application in

production of plastics, mainly because of their renewable character. In order to obtain high quality product, biomass needs to be subjected to one of the following thermochemical transformations: direct combustion, pyrolysis, gasification or liquefaction. The last one is low-temperature and high pressure thermochemical process based on solvolysis reactions. This process leads to generation of smaller particles or fragments soluble in water or other solvents. Such low molecular weight fragments are characterized by low stability and high reactivity, which allows their re-polymerization and preparation of oil compounds with vast range of molecular weight. Materials prepared by this way can be applied in production of PU, epoxy resins, phenolic resins, polyesters and others [34-37]. In lignocellulose biomass one can find many compounds containing hydroxyl groups, which can be used, among others, in reactions with isocyanates.

Yamada *et al.* [38, 39] showed the similarities in reaction pathways of acid catalyzed liquefaction reactions with different alcohols containing multiple hydroxyl groups used as solvents (ethylene glycol, polyethylene glycol, glycerol). Authors noticed that cellulose is decomposed through solvolysis into glucose particles and other low molecular weight derivatives. These compounds can subsequently react with solvent leading to glycoside derivatives, which can further react and create levulinic acid and its derivatives.

The highest rate of liquefaction is observed for amorphous biomass ingredients, such as lignin, hemicellulose or amorphous cellulose. Liquefaction of crystalline cellulose is considered the slowest phase, limiting the velocity of the whole process. This is related to organization of structure in crystalline cellulose, which limits availability for solvents. Selection of proper solvent is very important, because it has significant impact on efficiency of liquefaction of biomass and final physico-chemical properties of obtained polyol. Obviously, other important factor is the cost of solvent; therefore nowadays

many researchers focus on utilization of waste materials for this purpose. Characteristics of the process implicate the necessity of using the solvent excess with respect to biomass. The content of used solvent in final product is usually significant and has great impact on the properties and possibilities of biopolyol application. Polyols used in PU production are prepared from alcohols containing multiple hydroxyl groups, such as polyethylene glycol or glycerol. Course of the reaction and chemical structure of obtained polyols depend on the parameters of the process, such as temperature, time, applied catalyst, but mainly type of biomass and solvent. Moreover, as mentioned before, the liquefaction process itself is very complicated and still remaining unclear, because of the competition between various reactions leading to liquefaction. Complexity of the process was proved by Zhang *et al.* [40], who showed the variety of the products of liquefaction with ethylene glycol assisted by acidic catalysts. Except cellulose and lignin derivatives, and obviously solvent molecules, among the final products were saccharides, alcohols, aldehydes, ketones, phenols and organic acids. The properties of biopolyols prepared by biomass liquefaction are shown in Table 2.

According to literature reports, including cited above, so far, the main substance used as solvents in liquefaction of biomass were phenolic compounds [41-43] and alcohols containing multiple hydroxyl groups, however researchers are still looking for other possibilities [44]. Recently there has been conducted research related to incorporation of more complicated substances, such as crude glycerol [45], supercritical ethanol [46] or subcritical water [47]. Further research focused on the application of other, unconventional solvents are associated with ongoing trend related to incorporation of renewable raw materials and law regulations, such as directives of European Union. It is essential to use the materials, which would meet the requirements mentioned above, therefore the material, which attracts a lot of attention is crude glycerol generated during biodiesel production.

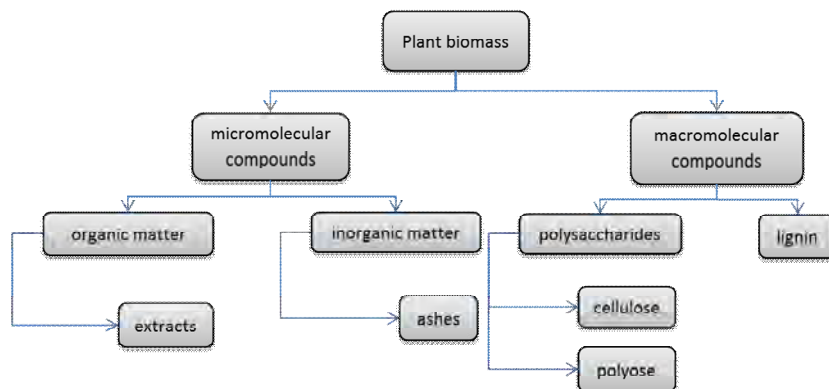


Fig. 2. The chemical composition of plant biomass

Table 2

General properties of bioolygomerols derived from lignocellulosic biomass [48-54]

	Polyol properties				
	Biomass conversion, %	Hydroxyl value, KOH/g	Acid value, KOH/g	Viscosity, mPa·s	Molecular weight, g/mol
Acid catalysis liquefaction					
Enzymatic hydrolysis of lignin	98	249	–	–	–
Cellulose or waste paper	55–99	360–396	19–30	2.6–3.9	650–900
Residues from agriculture	60–95	109–430	15–30	1.0–1.7	1050–4000
Industrial waste	84–98	137–586	28–34	0.4–3.0	250–2000
Wood	80–98	200–435	12–38	0.3–31.6	583–667
Basic catalysis liquefaction					
Birch wood	>99	112–204	24–41	–	1500–7900
Soybean straw	65–75	440–540	<5	16–45	–

Table 3

Effect of glycerol / corn stover ratio on the liquefaction process [65]

Item	Glycerol/straw ratio	% of insoluble solid residues	Liquefaction extent, %	Hydroxyl value, mgKOH/g
Pure glycerol	2/1	7.22	78.34	267
	3/1	4.36	82.56	290
	4/1	3.24	83.80	360
	5/1	1.98	88.12	346
Waste glycerol	2/1	not determined	not determined	not determined
	3/1	11.91	52.36	278
	4/1	9.75	51.25	307
	5/1	8.17	50.98	309

Different types of biomass have been studied for production of biopolyols, such as wood, corn bran, corn stover or corncobs, wheat straw, cork or soybean straw [48-56]. In many cases, obtained polyols showed promising, comparable properties for the PU production with their petroleum analogs. Nevertheless, traditional liquefaction of lignocellulosic biomass require high volumes of solvents, in order to provide satisfactory yield of the process [57], so use of petroleum-based solvents does not decrease significantly the final cost of process. As mentioned before, nowadays, the material, which attracts a lot of attention is crude glycerol generated during biodiesel production.

There have been a lot of published research works, where glycerol was used as a solvent for biomass liquefaction together with other bi-functional alcohols in order to provide the moderate degree of branching of resulting polyols [58]. Authors often used combination of glycerol especially with polyethylene glycol [59]. Many of them incorporated also microwave radiation in order to accelerate the process [60]. One step further to produce totally eco-friendly biopolyols is incorporation of crude glycerol without any other alcohols. Recently, several researchers published their works presenting liquefaction of biomass with crude glycerol [61].

Hu and Li [62] presented two-stage process of biomass liquefaction resulting in preparation of biopolyols

used in polyurethane synthesis, using crude glycerol as solvent. Content of impurities in used glycerol was from 26 to 40 wt %. First step of acid catalyzed reaction showed high yield of liquefaction and esterification of fatty acids and glycerol or other hydroxyl compounds. During second stage, base catalyzed reaction, there have been observed mainly condensation reactions, such as transesterification or etherification. Method proposed by Hu and Li was supposed to combine the advantages of application of both catalysts. Acid catalysis leads to high yield of biomass conversion, while following base catalysis allows the reduction of fatty acids and fatty acids methyl esters content, the increase of molecular weight of resulting polyol and the decrease of its acid value. Obvious disadvantage of presented process is the necessity application of two different catalysts on different stages of process.

In other research work Hu and Li [63] characterized the influence of the crude glycerol impurities on the properties of resulting polyols and PU foams. Authors found out that free fatty acids and fatty acids methyl esters contained in crude glycerol exhibited positive impact on resulting products, despite of the negative effects on biomass conversions. Prepared polyols showed hydroxyl numbers from 405 to 794 mgKOH/g and molecular weights from 400 to 1000 g/mol, while

resulting PU foams showed densities and compressive strength from 37 to 48 kg/m³ and from 140 to 188 kPa, respectively. Results suggest that crude glycerol containing impurities may be potentially applied in PU industry.

The same authors [64] prepared biopolyols and PU foams through liquefaction of soybean straw with crude glycerol. Polyols prepared under preferential conditions (513 K, 3 h, 3 % of sulfuric acid as catalyst) showed hydroxyl numbers from 440 to 540 mgKOH/g, acid numbers below 5 mgKOH/g and viscosities from 16 to 45 Pa·s, which is comparable to some commercially available products. Resulting PU foams had apparent density from 33 to 37 kg/m³ and compressive strength values from 148 to 227 kPa. Presented results suggest that materials obtained through lignocellulosic biomass liquefaction with crude glycerol can be promising alternative for petroleum-based polyols.

Wang *et al.* [65] successfully liquefied corn stover using an industrial biodiesel glycerol as a solvent. Process was conducted under atmospheric pressure at 433 K. Prepared polyols were compared to those obtained using pure glycerol. Results of performed analysis are presented in Table 3. In case of biodiesel glycerol insoluble biomass residues ratio was higher comparing to pure glycerol, which can be related to the presence of impurities contained in crude glycerol. Also yield of liquefaction was lower (~52 % for different crude glycerol/corn stover ratio, ~83 % for pure glycerol), however this problem could be solved by the differences in the price of used solvents. Polyols prepared from crude glycerol showed slightly lower values of hydroxyl number, which still allow the preparation of PU materials. FT-IR analysis also revealed that corn stover has beneficial structure for liquefaction process and can be valuable resource for polyol production.

Kosmela *et al.* [66] synthesized biopolyols from cellulosic biomass. Authors characterized the effect of time and temperature on the effectiveness of liquefaction and the parameters of resulting biopolyols. The prepared materials were analyzed in terms of their chemical structure, rheology, thermal and oxidative stability, and basic physical and mechanical properties that are important from the point of view of PU manufacturing. The optimal parameters for the biopolyol production with 94 % yield were achieved at 423 K for 6 h. The obtained polyols were characterized by the hydroxyl number of 643 mgKOH/g and enhanced thermal and oxidative stability compared to the polyols obtained at lower temperatures, which is associated with the altered mechanism of liquefaction.

The object of the invention by Piszczyk *et al.* [67] is a method for producing polyols from lignocellulosic biomass that is applicable to manufacturing of environment-friendly PU foams which could be used in

different branches of industry such as construction, furniture and automotive industries. The invention relates to the method of obtaining polyols from lignocellulosic biomass (*e.g.* brewer's spent grain) *via* biomass liquefaction in an excessive amount of solvent (*e.g.* crude glycerol), using a chemical process or by means of microwave irradiation within the temperature range of 373–573 K for 1–600 min.

4. Application of Ground Tire Rubber and Other Low-Cost Fillers

The usage of such cross-linked material as ground tire rubber (GTR) as a filler for PU foams leads to creation of a new material with potentially interesting properties and applications. Cachaco *et al.* [68] carried out experiments to investigate the influence of GTR on PU foams in order to obtain floating trays and compression-absorbing buoys. They proved that utilization of GTR in this application can be very promising and their product shows properties similar to commercial buoys, although the main problem of implementation these results lies in scale-up of the production process. Zhang *et al.* [69] found out that the incorporation of mechano-chemically devulcanized GTR into PU foams imparts excellent acoustic absorption properties. The treatment was carried out in pan-mill reactor at ambient temperature. Also the influence of untreated GTR was tested. However, untreated filler does not lead to any enhancement of the final material. It is ascribed to the poor adhesion between untreated rubber and PU matrix. Piszczyk *et al.* [70] also investigated the modification of PU foams by two kinds of GTR, untreated and thermo-mechanically reclaimed with the exception that the whole process were carried out using a co-rotating twin screw extruder. It was proven that usage of GTR as a filler in PU foams leads to improvement of the thermal stability and compressive strength. Moreover, scientists proved that reaction between groups in PU foams and active groups on the GTR surface took place. In another study [71] during the synthesis of rigid PU foams polyglycerol was used instead of petrochemical polyol. As a filler two types of GTR were used. Fig. 3 shows the samples of modified PU foams.

It can be observed that the sample with reclaimed GTR shows high interaction between polymer matrix and rubber particles in comparison with sample containing untreated GTR. Also the difference in appearance of both samples can be explained by the migration of a carbon black between components. The study proves that the addition of GTR can enhance mechanical and thermal properties of modified foam. Moreover, utilization of GTR leads to lowering the cost of final product by shortening the production time and reducing the

temperature during synthesis. Fig. 4 presents FT-IR spectra of three kinds of foams: neat PU foam (A), PU foam with addition of unmodified GTR (B) and PU foam with devulcanized GTR (C).

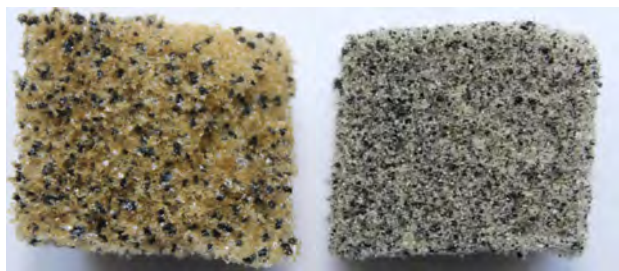


Fig. 3. Rigid PU foams modified with untreated (left) and thermomechanically reclaimed GTR (right) [71]

As it is shown in Fig. 4 the incorporation of GTR into PU foam matrix caused reaction between isocyanate group and reactive functional groups present on the surface of devulcanized GTR. Signals (a), (d), (f) and (i) are assigned consecutively to N–H group, C=O bonds, C–N bonds and O–C=O group. The intensity of those signals respond to the amount of urethane groups. The difference in intensity of those signals between neat PU foam and modified PU foams is related to the chemical interactions between isocyanate group and functional groups on GTR surface. Moreover, signals (c) and (g) are characteristic for isocyanate group and rings. The weaker signal means that the reactive groups on GTR surface react with those groups. Additionally, it can be observed that the material with devulcanized GTR has more significant influence on chemical structure of newly created material. Fig. 5 shows the schematic reactions between isocyanate group and reactive groups on GTR surface.

In Table 4 apparent density and compressive strength were summarized. Higher density and compressive stress value are achieved by devulcanized GTR modified PU foam. It proves that devulcanization of GTR and its implementation into PU foam matrix leads to better interaction between components.

Gayathri *et al.* [72] investigated the influence of different filler types (nanosilica, crumb rubber and nanoclay) on sound absorption characteristics, thermal stability and mechanical properties. The PU foams were prepared by the free rising foaming method. It was shown that the addition of 1.4 % of any filler improves the acoustic property. Additionally, thermal and mechanical properties were also improved.

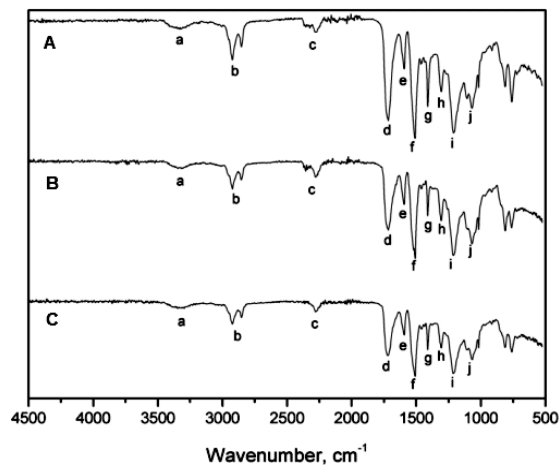


Fig. 4. FT-IR spectra for neat PU foam (A), PU foam with unmodified GTR (B) and PU foam with devulcanized GTR (C) [71]

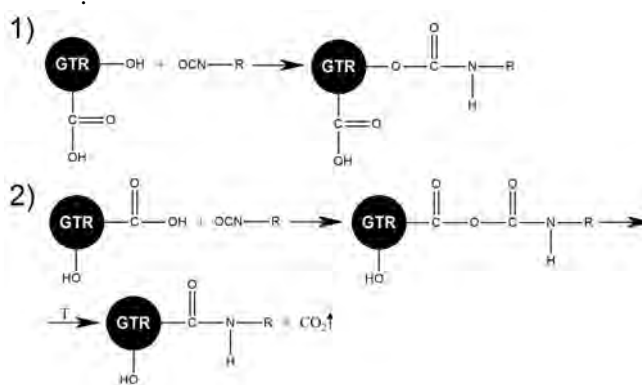


Fig. 5. Reaction scheme between isocyanate groups and reactive groups on GTR surface

Table 4

Comparison of compressive strength of PU foams with GTR [71]

Filler type	Filler content, pbw	Density, kg/m ³	Compressive strength, kPa	
			at 20 % deformation	at 40 % deformation
–	0	68.8 ± 2.1	195 ± 5	207 ± 4
Unmodified GTR	10	76.6 ± 3.1	201 ± 7	223 ± 10
	20	82.2 ± 3.3	207 ± 7	240 ± 5
	30	101.5 ± 2.5	213 ± 9	257 ± 13
Devulcanized GTR	10	83.6 ± 3.2	214 ± 6	232 ± 8
	20	90.3 ± 5.0	245 ± 13	254 ± 10
	30	108.2 ± 2.6	274 ± 12	291 ± 18

Furthermore, the final properties and price of PU foams could be tailored using other fillers as low cost modifiers, for example, Bryskiewicz *et al.* [73]. Prepared and characterized the flexible PU with addition of walnut shells and hazelnut shells as natural fillers. Tests like thermal gravimetric analysis (TGA), differential scanning calorimetry(DCS), dynamic mechanical analysis(DMA), FT-IR physical and mechanical properties were carried out in order to examine the influence of this type of modification on the properties and structure of PU foams. It was observed that addition of nut shells improves the thermal properties of studied composites. Furthermore, surprisingly the addition of walnut and hazelnut shells has influence on physical and mechanical properties. In any case apparent density increased. However, the higher quantity of walnut shells results in higher irreversible strain. The addition of 13.5 wt % of hazelnut shells led to obtaining material with the best parameters. Kuranska *et al.* [74] proposed using of flax and hemp fibers as a filler in PU foams based on rapeseed oil derivative as biopolyol. The presented results indicate that application of the flax fibers and the rapeseed oil derivative has positive influence on thermal and mechanical properties of final product. Zieleniewska *et al.* [75] decided to utilize egg shells as a filler in rigid PU foams. The natural filler was mechanically grounded and after that dried in order to remove water and deactivate organic substances. The foam was prepared using the one-step mechanism. The obtained results show that application of egg shells has significant influence on the material physico-mechanical and biological properties. The addition of 20 pbw of natural fiber results in 13 % growth of compressive strength value, compared to the PU reference sample. However, the higher amount of egg shells in composition led to higher structural anisotropy and lower closed cell content what results in lower compressive strength. Interesting implementation of natural fiber was developed by Wrzesniewska-Tosik *et al.* [76]. The elastic PU foam was modified by poultry feathers. In order to obtain keratin fibers wet feathers were disintegrated several times, centrifuged, dried and grounded. It was proven that the addition of pretreated feathers increase the value of inflammability. The limiting oxygen index increase with the growing content of keratin fibers. Moreover, the lack of droplets during combustion test prevents the chance of secondary self-ignition. The isolation properties changed insignificantly and the ability to absorb sound stay at the level of 20 %.

5. Conclusions

Increasing the share of renewable raw materials and recycled materials in plastics technology is a

permanent trend related to the protection of the environment and sustainable development.

In this regard, it is important that developed technologies ensure an appropriate level of quality products, which is often difficult because of the frequent heterogeneity of these materials

Presented results achieved in the field of polyurethane foams suggest a number of possible solutions to this problem, especially when applying polyols obtained by liquefaction of the biomass.

References

- [1] Prociak A., Rokicki G., Ryszkowska J.: *Materiały Poliuretanowe*, PWN, Warszawa 2014.
- [2] Commission implementing decision (EU) 2016/1362 of 9 August 2016 on recognition of the 'Roundtable on Sustainable Biomaterials EU RED' for demonstrating compliance with the sustainability criteria under Directives 98/70/EC and 2009/28/EC of the European Parliament and of the Council.
- [3] <http://www.theicct.org/issues/co2-standards>.
- [4] <http://ebb-eu.org/>.
- [5] <http://www.eia.gov/biofuels/issuestrends/pdf/bit.pdf>.
- [6] Pott R., Howe C. and Dennis J.: *Bioresource Technol.*, 2014, **152**, 464.
- [7] Hejna A., Kosmela P., Formela K. *et al.*: *Renew. Sust. Energ. Rev.*, 2016, **66**, 449.
- [8] Martin A. and Richter M.: *Eur. J. Lipid. Sci. Tech.*, 2011, **113**, 100.
- [9] Marion H. *et al.*: *Biomaterials*, 2006, **27**, 5471.
- [10] Gholami Z., Abdulla A. and Lee K.: *Renew. Sus. Energ. Rev.*, 2014, **39**, 327.
- [11] Frey H. nad Haag R.: *Mol. Biotechnol.*, 2002, **90**, 257.
- [12] Sunder A., Hanselmann R., Frey H. and Mulhaupt R.: *Macromolecules*, 1992, **32**, 4240.
- [13] Criminna R., Katrynio B., Paul S. *et al.*: *Org. Procoess Res. Dev.*, 2015, **19**, 748.
- [14] Barrault J., Clacens J. and Pouilloux Y. : EP1292557, 2006.
- [15] Hasenhuettl G.: *Food Emulsifiers and Their Application*, 2008, 11.
- [16] Gandini A. and Lacerda T.: *Prog. Polym. Sci.*, 2015, **48**, 1.
- [17] Lemke D. and Nivens S.: Pat. US 20080306211, Publ. Dec. 11, 2008.
- [18] Mat R., Samsudin R., Mohamed M. and Johari A.: *B. Chem. React. Eng. Catalysis*, 2012, **7**, 142.
- [19] Helwani Z., Othman M., Aziz N. *et al.*: *Appl. Catal. A*, 2009, **363**, 1.
- [20] Chopade S., Kulkarni K., Kulkarni A. and Topare N.: *Acta Chimica Pharmac. Indica*, 2012, **2**, 8.
- [21] Din N., Idris Z., Kian Y. and Hassan H.: *J. Oil. Palm. Res.*, 2013, **25**, 289.
- [22] Wirpsza Z. and Banasiak S.: Pat. PL 210779, Publ. Feb. 29, 2012.
- [23] Soi H., Bakar Z., Nik Siti M. *et al.*: Pat. US 8816132 B2, Publ. Aug. 26, 2014.
- [24] Guerrero-Perez M. and Banares M.: *Chem. Sus. Chem.*, 2008, **1**, 511.
- [25] Chai S., Wang H., Liang Y. and Xu B.: *Green Chem.*, 2008, **10**, 1087.

- [26] Chai S., Wang H., Liang Y. and Xu B.: Appl. Catal. A, 2009, **353**, 213.
- [27] Ning L., Ding Y., Chen W. et al.: Chin. J. Catal., 2009, **29**, 212.
- [28] Piszczyk L., Strankowski M., Danowska M. et al.: Eur. Polym. J., 2014, **57**, 143.
- [29] Nikje M. and Nikrah M.: Polym. Bull., 2007, **58**, 411.
- [30] Simon D., Borreguero A., de Lucas A. and Rodriguez J.: Polym. Degrad. Stabil., 2015, **121**, 126.
- [31] Kopczyńska P. and Datta J.: Polym. Int., 2016, **65**, 946.
- [32] Kopczyńska P., Calvo-Correas T., Eceiza A. and Datta J.: Eur. Polym. J., 2016, **85**, 26.
- [33] Bogoczek R. and Kociolek-Balawejder E.: Technologia Chemiczna Organiczna, Wrocław 1992.
- [34] Wang H., Chen H.Z.: J. Chin. Inst. Chem. Eng., 2007, **38**, 95.
- [35] Zhang H., Pang H., Zhang L. et al.: J. Polym. Environ., 2013, **21**, 329.
- [36] Yoshioka M., Nishio Y., Saito D. et al.: J. Appl. Polym. Sci., 2013, **130**, 622.
- [37] Hu S., Wan C. and Li W.: Bioresource Technol., 2012, **103**, 227.
- [38] Yamada T. and Ono H.: J. Wood Sci., 2001, **47**, 458.
- [39] Yamada T., Aratani M., Kubo S. and Ono H.: J. Wood Sci., 2007, **53**, 487.
- [40] Zhang T., Zhou Y., Liu D. and Petrus L.: Bioresource Technol., 2007, **98**, 1454.
- [41] Ono H., Yamada T., Hatano Y. and Motohashi K.: J. Adhesion, 1996, **59**, 135.
- [42] Muna S. and Jang J.: J. Ind. Eng. Chem., 2009, **15**, 743.
- [43] Jin Y., Ruan X., Cheng X. and Lu Q.: Bioresource Technol., 2011, **102**, 3581.
- [44] Zhang T., Zhou Y., Liu D. and Petrus L.: Bioresour. Technol., 2007, **98**, 1454.
- [45] Hu S.: Production and Characterization of Bio-based Polyols and Polyurethanes from Biodiesel-derived Crude Glycerol and Lignocellulosic Biomass. Doctor of Philosophy, Ohio State University, 2013.
- [46] Brand S., Susanti R., Kim S. et al.: Energy, 2013, **59**, 173.
- [47] Harry I., Ibrahim H., Thring R. and Idem R.: Biomass Bioenerg., 2014, **71**, 381.
- [48] Alma M., Basturk M. and Digrak M.: J. Mater. Sci. Lett., 2003, **22**, 1225.
- [49] Zhang H., Pang H., Zhang L. et al.: J. Polym. Environ., 2013, **21**, 329.
- [50] Xu J., Jiang J., Hse C. and Shupe T.: J. Appl. Polym. Sci., 2014, **131**, 400.
- [51] Lee S., Yoshioka M. and Shiraishi N.: J. Appl. Polym. Sci., 2000, **78**, 319.
- [52] Zhang H., Ding F., Luo C. et al.: Ind. Crop. Prod., 2012, **39**, 47.
- [53] Wang Y., Wu J., Wan Y. et al.: Int. J. Agric. Biol. Eng., 2009, **2**, 32.
- [54] Wang H. and Chen H.: J. Chin. Inst. Chem. Eng., 2007, **38**, 95.
- [55] Chen F. and Lu Z.: J. Appl. Polym. Sci., 2009, **111**, 508.
- [56] Soares B., Gama N., Freire C. et al.: ACS Sustain. Chem. Eng., 2014, **2**, 846.
- [57] Hassan E. and Shukry N.: Ind. Crop. Prod., 2008, **27**, 33.
- [58] Briones R., Serrano L., Llano-Ponte R. and Labidi J.: Chem. Eng. J., 2011, **175**, 169.
- [59] Jo Y., Ly H., Kim J. et al.: J. Ind. Eng. Chem., 2015, **29**, 304.
- [60] Xie J., Hse C., Shupe T. et al.: J. Appl. Polym. Sci., 2014, **131**, 40207.
- [61] Cheng D., Wang L., Shahbazi A. et al.: Fuel, 2014, **130**, 251.
- [62] Hu S. and Li Y.: Bio.Tech., 2014, **161**, 410.
- [63] Hu S. and Li Y.: Ind. Crop. Prod., 2014, **57**, 188.
- [64] Hu S., Wan C. and Li Y.: Bioresource Technol., 2012, **103**, 227.
- [65] Wang Y., Wu J., Wan Y. et al.: Int. J. Agric. Biol. Eng., 2009, **2**, 32.
- [66] Kosmela P., Hejna A., Formela K. et al.: Cellulose, 2016, **23**, 2929.
- [67] Piszczyk L., Danowska M., Kosmela P. et al.: Pat. EP. 15460078.7. Publ. Sept. 02, 2015
- [68] Cachaco A., Afonso M. and Pinto M.: J. Appl. Polym. Sci., 2013, **129**, 2873.
- [69] Zhang X., Lu Z., Tian D. et al.: J. Appl. Polym. Sci., 2013, **127**, 4006.
- [70] Piszczyk L., Hejna A., Formela K. et al.: Iran. Polym. J., 2014, **24**, 75.
- [71] Piszczyk L., Hejna A., Danowska M. et al.: J. Reinf. Plast. Comp., 2015, **34**, 708.
- [72] Gayathri R., Vasanthakumari R. and Padmanabhan C.: Int. J. Eng. Sci., 2013, **4**, 302.
- [73] Bryskiewicz A., Zieleniewska M., Przyjemka K. et al.: Polym. Degrad. Stabil., 2016, **132**, 32.
- [74] Kuranska M. and Prociak A.: Compos. Sci. Technol., 2012, **72**, 299.
- [75] Zieleniewska M., Leszczynski M., Szczepkowski L. et al.: Polym. Degrad. Stabil., 2016, **132**, 78.
- [76] Wrzesniewska-Tosik K., Zajchowski S., Bryskiewicz A. and Ryszkowska J.: Fibers. Text. East. Eur., 2014, **22**, 119.

НОВІТНІ РОЗРОБКИ В ОБЛАСТІ ПІНОПОЛІУРЕТАНІВ, ЩО МІСТЯТЬ НЕДОРОГІ ТА ПРОЕКОЛОГІЧНІ МОДИФІКАТОРИ

Анотація. Різноманітність застосування пінополіуретанів (ППУ) є причиною того, що вивчення зв'язків між їх структурою і властивостями в даний час є дуже популярною темою досліджень серед багатьох науково-дослідних інститутів і компаній. На рубежі останніх років опубліковано багато наукових робіт щодо ППУ та їх композитів. Одна з основних тенденцій в цій області досліджень пов'язана зі скороченням витрат на виробництво пінополіуретанів. Досягти такої мети можливо внаслідок залучення сировини природного походження або утилізації відходів. В роботі проведено огляд досягнень і новітніх розробок в області ППУ, що містять недорогі і проекологічні модифікатори, такі як сирий гліцерин, зріджена біомаса, молота шинна гума, тощо.

Ключові слова: пінополіуретани, сирий гліцерин, зріджена біомаса, молота шинна гума.