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Application of Vegetable Oil-based Biopolyols in Manufacturing of Rigid Polyurethane Foams – Short Review

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ABSTRACT

The development of polyurethane foams' market, as well as ongoing trends associated with sustainable development cause increasingly growing interest in the utilization of materials from renewable resources. Great example of such phenomenon is the use of vegetable oils in manufacturing of foamed polyurethanes. These materials can be applied directly or after previous modifications in production of biopolyols, main constituents of polyurethanes. In this paper, analysis of polyurethane foams' market was presented and forecasts pointing to the potentially increasing position of so-called bio-polyurethanes in the future. Moreover, this paper summarizes previously published reports related to the manufacturing of vegetable oil-based biopolyols and their further incorporation into formulations of rigid polyurethane foams.

Keywords: Vegetable oils; Biopolyols; Rigid polyurethane foams

1. Polyurethane foam industry – general information

Plastics industry is developing very dynamically, due to the variety of potential applications of plastics and the possibility of selection of the right material with the desired properties for almost every application. Over the last decades, noticeable increase of global plastics' production was noted, which can be seen in the **Figure 1**[1]. Presented data does not include production of various fibers obtained from polymeric materials, such as PET, PP or PA fibers[2].

Dynamic development of European plastics market has been slightly inhibited by the global economic crisis and the fact that some companies moved their production to Asia, due to lower production costs. Because of that, European share in global plastics production decreased from 23 to 20 % in 2006-2014[3].

According to the reports of PlasticsEurope, the biggest consumer of plastics is packaging industry, which stands for almost 40% of total production. Around 20% of European production accounts for construction and building materials. In case of packaging, the most popular are polyethylene, polypropylene and poly(ethylene terephthalate), while on construction market dominate poly(vinyl chloride), high density polyethylene, expanded polystyrene and polyurethanes (PUR).

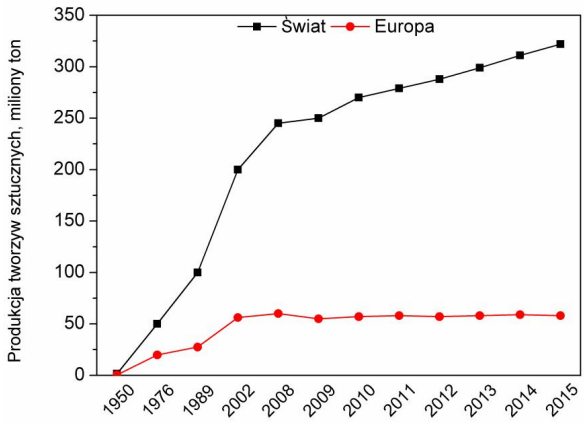


Figure 1; Global and European production of plastics from 1950 to 2015[1].

In case of polyurethanes, the biggest producers are located in Asia. In 2012, Asian production of PUR was around 10 million tonnes, while Europe produced 4,8 million tonnes[4].Prognosis indicate that European production will reach 5,4 million tonnes in 2018, which is associated with the increase of production in Eastern Europe[5]. It can be noticed that economic growth in many regions of the world causes that both, production and demand, for PUR are constantly growing. In Asia,

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driving force for the polyurethane industry is significant increase in the demand for materials used in construction[6]. In other regions, demand for PUR is also very large, polyurethanes are ranked 5th in Europe among all plastics (7.5%)[7].

Polyurethanes, due to their versatility and possibility of adjusting their parameters in very wide range are used in many branches of industry. Nearly 50% of the entire polyurethane market consists of adhesives and sealants as well as elastomers (CASE – PUR coatings, adhesives, sealants and elastomers). Polyurethane coatings are used to improve the durability and appearance of the products. In the automotive industry, they provide high gloss and a resistance to corrosion and scratches. Polyurethane adhesives and sealants provide durability and high resistance to water, biological and chemical factors. They are mainly used in construction and automotive industry. Polyurethane elastomers show high resistance to abrasion, good impact resistance, low brittleness and resistance to aging and mold. Their use is very wide, for example in manufacturing of wheels or containers.

Second half of PUR production stands for flexible and rigid foams. Flexible foams are used mainly in clothing, furniture and automotive industry, while rigid are applied in manufacturing of thermal insulation materials and structural foams for refrigerators and construction materials. Advantages of rigid foams are related to their low apparent density, high content of closed cells, rigidity, relatively high mechanical strength, low moisture absorption, high chemical resistance and, above all, excellent thermal insulation properties. The use of polyurethane foams as thermal insulation materials is very important issue due to the energy saving. It is estimated that on a global scale about 40% of the energy consumed is used to maintain the proper temperature in buildings, both through heating and air conditioning. It allows to imagine how important from the energetical point of view is good thermal insulation in buildings[8]. An undeniable advantage of using PUR spray foams is the possibility of thermal insulation without joints, which sufficiently reduces the head loss caused by breaks or welds. This results in higher energy efficiency and lowering the costs of heating/air conditioning of buildings. Spray foams can by also used in hard-to-reach places, without the additional cutting. Application of rigid PUR foam results in additional stiffening of roof structure, which can increase the lifetime of buildings. Moreover, PUR foams are safer than for example mineral wool. It is good barrier for dust and pollen. Also, appropriate application of spray foam can increase the corrosion resistance of metal elements[9].

The value of polyurethane foam market in 2012 was 40.1 billion USD, while the forecasts indicate achievement of 61.9 billion USD in 2018. Also in Europe, PUR marked is growing very rapidly. European production in 2012 was 4.8 million tonnes, while it should reach 5.4 million tonnes in 2018[10].

Nowadays, PUR industry is dependent on crude oil, because the most important substrates for their production, i.e. polyols, are mainly petroleum-based products. Nevertheless, bot in case of foams and solid plastics, very popular direction of research are so-called bio-polyurethanes. These are mostly materials prepared using biopolyols, i.e. polyols based on renewable raw materials. As a result, final products contain from 30 to 70% of raw materials from renewable resources, depending on the application and used materials. Currently, bio-polyurethane market is not very large comparing to the entire PUR market. In 2013, global market of so-called ecological polyurethanes reached 1634 tonnes, 75% of which were flexible and rigid PUR foams. About 30% of the ecological polyurethanes' production are materials used in construction, in particular thermal insulation materials. Dynamic development of the economy and urbanization in such countries as India, China or Brazil can significantly contribute to the growth of bio-polyurethanes production. By 2020, production of bio-PUR is expected to exceed 2540 tonnes, which will account for 0.07% of the total market[11]. The increased interest in bio-polyurethanes is mainly related to the current trends of sustainable development and provisions of the Kyoto Protocol on limiting the use of fossil fuels. In addition, there are also regional regulations related to the content of raw materials of natural origin in plastics, e.g. in countries like USA, China or Great Britain. By relevant directives and

climate packages, European Union (EU) obligates Member States to direct their industry towards renewable resources. Directive EU 2009/28/WE requires Member States to achieve 10% share of biofuels in transport sector[12]. Climate Package 3x20 obliges to reduce CO_2 emission by 20% comparing to 1990, acquire 20% of energy from renewable sources and reduce energy consumption by 20%[13].

2. Biopolyols

2.1 General information

Having in mind law regulations described above, industrial and academic community show increased interest in the development of eco-friendly technologies based on raw materials from renewable resources. These materials are relatively cheap comparing to petroleum-based raw materials and their availability is definitely their advantage, because they are basically regenerating every year. In terms of chemical structure, biopolyols used in polyurethane industry are most often esters of glycerol and higher unsaturated fatty acids[14]. To their production are often used vegetable oils. To the most popular and most commonly used oils, depending on the gheological location, belong: for Europe – rapeseed and sunflower oil[15, 16], for Asia – palm and coconut oil[17, 18], for US – soybean oil[19, 20]. Moreover, the subject of research was also the use of other oils such as linseed oil or Ceylon ironwood oil[21-23].

As mentioned above, in Europe the most popular oil used for polyols' manufacturing is rapeseed oil, which is triglyceride of unsaturated fatty acids, containing on average 61% of oleic acid residues, 21% of linoleic acid residues, 10% of -linolenic acid and 8% of saturated fatty acid residues. Main constituents of rapeseed oil are shown in the **Figure 2**. Derivatives of rapeseed oil can be applied as reactive substrates for manufacturing of polyesters, polyamides or polyurethanes[24].

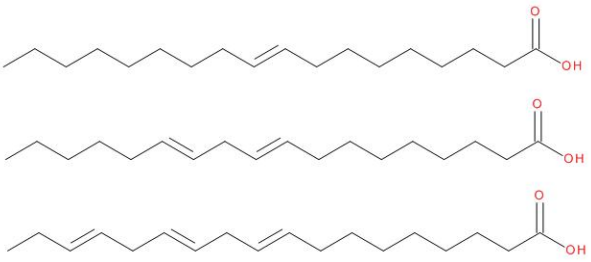


Figure 2; Main fatty acid constituents of rapeseed oil: oleic acid, linoleic acid and -linolenic acid.

2.2 Manufacturing of biopolyols from vegetable oils

Manufacturing of polyols from vegetable oils can take place in several ways. As it can be seen on the example of rapeseed oil (**Figure 2**), fatty acid particles present in the structure of vegetable oils have no hydroxyl groups in their structure. Therefore, in order to be useful in production of polyurethane materials, vegetable oils need to be modified. An exception is castor oil, which could be directly applied, due to the very high content of ricinoleic acid, possessing in its structure both carboxyl and hydroxyl groups, as well as unsaturated bond (structure presented in the **Figure 3**)[25]. Nevertheless, for the most effective application of castor oil it is also most often modified physically or chemically.

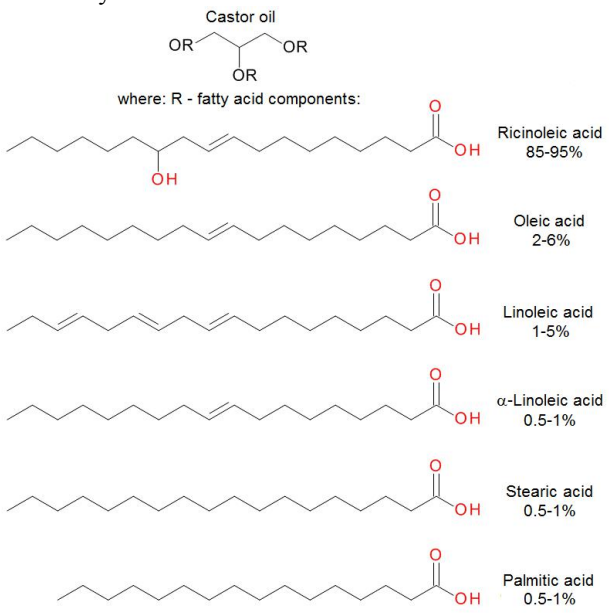


Figure 3; Chemical structure of castor oil.

One of the methods od production of biopolyols from vegetable oils is based on the oxidation of unsaturated fatty acids. However, this process has its drawbacks. It is difficult to control in such a way that the effect would be obtaining products containing only hydroxyl groups as functional groups[15]. Instead, significant content of other oxidation products can be expected, e.g. peroxides, aldehydes, ketones or carboxylic compounds, whose presence may cause various defects in finished materials such as discoloration, unpleasant odor or variation in mechanical

properties caused by inhomogeneous structure of polyol[26].

Better process control can be obtained by epoxidation of unsaturated bonds in fatty acids, followed by the opening of epoxide rings by reaction with hydrogen donors, which leads to the formation of hydroxyl groups[27, 28]. General scheme of vegetable oil epoxidation with hydrogen peroxide and methanol is shown in the **Figure 4**. Epoxidation of vegetable oils can be also carried out by in situ reaction with acetic acid and hydrogen peroxide or other oxidizing agents[29]. As a result of vegetable oils' modification can be obtained polyols with hydroxyl value from several dozen to over 400 mg KOH/g and viscosity from several hundred to over 10000 mPa·s[30-32]. Polyols produced by the epoxide ring opening are characterized by a low content of unsaturated bonds, which noticeably enhances their resistance to oxidation and environmental factors[33,34]. However, it is often related to the increased viscosity, which may be considered problematic from the technological point of view[35].

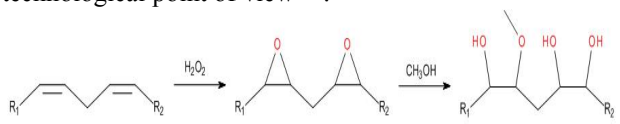


Figure 4; General scheme of vegetable oils' epoxidation with hydrogen peroxide and further ring opening with methanol.

Campanella *et al*.[36] studied epoxidation of soybean oil with hydrogen peroxide and formic acid, further ring opening with methanol and compared results with those for hydroxylated and esterified soybean oil. Polyols obtained via epoxidation showed the highest hydroxyl value and highest viscosity comparing to other samples, which make them the most suitable for the further manufacturing of rigid PUR foams.

Guo *et al*.[37] obtained biopolyol by ring opening in epoxidized soybean oil. The ring was opened with methanol, hydrochloric acid, hydrobromic acid an hydrogen. When HBr was used, prepared polyol showed the lowest hydroxyl value, the highest functionality and molecular weight. Authors observed the aforementioned problem with elevated viscosity, because among the four obtained biopolyols, only one, prepared with methanol was a liquid at room temperature. Similar effect was noted by Pawlik *et al*.[38], who prepared biopolyols by ring opening in epoxidized palm oil with diethylene glycol. Moreover, they incorporated microwave radiation to shorten reaction time. Nevertheless, obtained biopolyols were not liquids at room temperature.

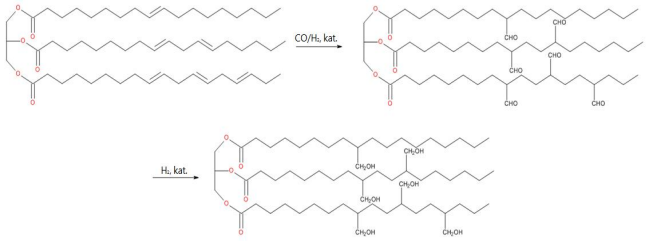


Figure 5; General scheme of hydroformylation of triglyceride consisting of oleic, linoleic and -linolenic acid.

Another method of manufacturing of polyols from vegetable oils is their hydroformylation [39-41]. This process involves treating of oils with a mixture of carbon monoxide and hydrogen, followed by further conversion of aldehyde groups to hydroxyls by hydrogenation. Scheme of the process is shown in the **Figure 5**. Drawback of this method is the necessity of using often expensive catalysts[42,43].

Guo *et al*.[44] investigated production of biopolyols by hydroformylation of soybean oil. They analyze the influence of catalyst on the process and properties of obtained materials. When using an expensive rhodium catalyst, conversion reached 95%, while cobalt catalyst allowed only 67% conversion. In addition, in the first case polyol showed higher hydroxyl value, functionality and molecular weight. Nevertheless, for the use of rhodium catalysts to be cost-effective, it would require their full recovery from the process, which would engage very costly methods.

Biopolyols can be also obtained by ozonolysis of vegetable oils[45]. This process enables qualitative conversion of unsaturated bonds into hydroxyl groups. However, the products of this process include also low molecular weight glycols and monohydric alcohols. Alternatively, ozonolysis can be performed in presence of glycols, which cause simultaneous esterification of generated low molecular weight compounds with polyol[46,47]. Polyols prepared by ozonolysis are characterized by the noticeably lower molecular weight in comparison to products of epoxidation or hydroformylation, which results in lower values of viscosity.

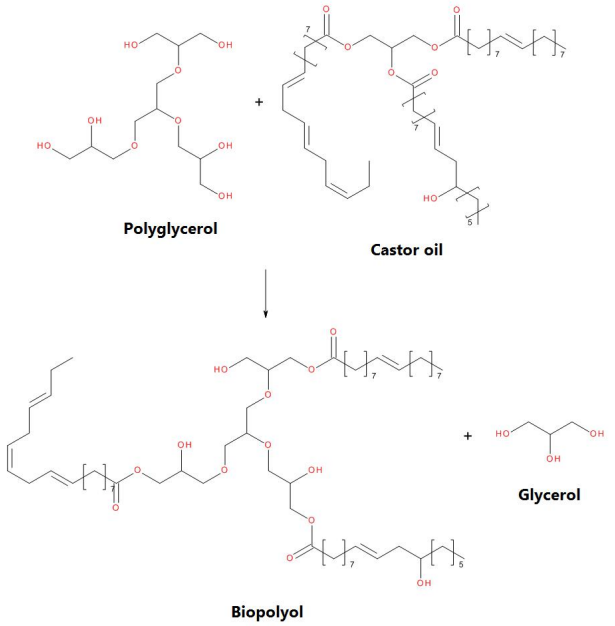


Figure 6; Exemplary scheme of transesterification of castor oil with polyglycerol.

Other popular method of manufacturing biopolyols is the esterification process[48]. It involves reacting vegetable oils with polyhydric alcohols, often with modified glycerol[49,50]. Exemplary scheme of transesterification of castor oil with polyglycerol is shown in the **Figure 6**. This process requires the use of catalysts to achieve high yield, however, low-cost ant readily available inorganic acids and bases can be applied[51,52]. Polyols obtained by the esterification of glycerol with vegetable oils are most often characterized by high hydroxyl values, which is beneficial for the preparation of polyurethane materials with high crosslink density. Obviously, it is also possible to use various glycols, which will lead to difunctional polyols, that can be applied in manufacturing of thermoplastic polyurethane elastomers[53].

Tanaka *et al.*[54] prepared biopolyols by transesterification of palm oil with glycerol. Authors obviously obtained mixture of compounds, where predominant species were monoglycerides of palmitic and oleic acid. Increasing of palm oil/glycerol ratio resulted in the decrease of conversion rate and yield of synthesis.

Manufacturing of biopolyols via transesterification of castor oil with condensed crude glycerol was lately described by Hejna *et al.*[55]. Authors presented two-step process based on the condensation of crude glycerol and further reaction with castor oil. Obtained biopolyols were characterized by the hydroxyl values similar to those of petrochemical polyols, conventionally applied in production of rigid polyurethane foams.

2.3 Incorporation of vegetable oil-based polyols into manufacturing of rigid polyurethane foams

In the literature, there are many examples related to the use of polyols prepared by aforementioned processes in the manufacturing of foamed polyurethane materials.

Pielichowski *et al.*[56] used soybean oil and glycerol for the production of polyurethane foams. Glycerol was applied as crosslinking agent, because applied soybean oil showed too low hydroxyl value and did not provide the appropriate degree of crosslinking. Authors found out that foam containing 50% of polyol synthesized from soybean oil and glycerol (used as a substitute for petrochemical polyol) showed slightly worse, but still satisfactory mechanical and thermal insulation properties, comparing to reference sample. Similar effect, related to comparable properties of soybean oil-based PUR foams comparing to petrochemical-based ones were observed by Guo *et al.*[57].

Malewska *et al.*[58] incorporated biopolyols prepared via epoxidation of rapeseed oil and opening of oxirane rings with isopropanol and diethylene glycol into formulations of PUR foams. As a result, mechanical performance of foams was enhanced due to simultaneous increase of hard segments' content (due to higher hydroxyl value of polyols) and plasticization of polyurethane matrix (due to long dangling chains of fatty acids).

Rapeseed oil-based polyols were also incorporated into formulations of rigid polyurethane foams by Zieleniewska *et al.*[59]. Applications of biopolyol resulted in enhancement of thermal stability by almost 7% and decreased amount of easily volatilized products. Compressive strength was slightly decreased due to decrease in physical crosslinking in the material and lowered glass transition temperature. Increasing content of plant-based polyol resulted in the enhancement of biological properties and decreased water absorption.

Prociak[60] obtained rigid PUR foams from vegetable oil-based biopolyols and analyzed their thermal insulation properties. He used rapeseed, soybean,

sunflower and linseed oils. Application of prepared biopolyols allowed to obtain better thermal insulation properties, than for foams prepared solely with petrochemical raw materials. The most beneficial properties were observed for samples containing rapeseed and sunflower oils, however other oil also enhanced insulation properties comparing to reference sample. According to author, vegetable oil-based polyols should not be used in the amount exceeding 30% of total polyols mass, because it leads to creation of open-cell structure, which deteriorates thermal insulation properties of foam.

Tu *et al*.[61] analyzed 15 polyols based on esterified, oxidized, epoxidized and hydrolyzed soybean and castor oil in preparation of water-blown rigid PUR foams. Authors noticed that incorporation of polyols with secondary hydroxyl groups into formulations of foams led to the increase of thermal conductivity coefficient and reduction of compressive strength.

Narine *et al*. [62] prepared rigid polyurethane foams using polyols synthesized from rapeseed, soybean and castor oil, whose content in the polyol mixture varied from 12 to 15 wt%. Incorporation of vegetable oils into formulation of polyurethane foams resulted in the shortening of foaming process, which should be considered beneficial from the technological point of view. Similar effects were observed by Septevani *et al*.[63], who applied palm oil-based biopolyol in preparation of rigid PUR foams. Except shortening of the manufacturing process, they observed other advantages of biopolyol's application. Its incorporation up to 20 wt% caused decrease of the average cell size by 7%, which resulted in the drop of thermal conductivity coefficient from 26.6 to 24.8 mW/(m·K). Analyzed modification lead to the enhancement of mechanical properties – increase of compressive strength by more than 15% was noted.

Zhang *et al*.[64] modified castor oil with organophosphorous in order to obtain biopolyol simultaneously acting as flame retardant of PUR foams. Incorporation of modified polyol to formulation resulted in the enhancement of foams' fire resistance. Authors noted decrease of total heat released during combustion by more than 30% and increase of char residue from 2.5 to 10.0 wt%, which was caused by effective inhibition of combustion process in gas phase. Moreover, prepared modifications resulted in the enhancement of mechanical performance.

Application of modified castor oil in manufacturing of PUR foams was also investigated by Li *et al*.[65]. Oil was modified via transesterification with glycerol. Substitution of 50 wt% of conventional, petrochemical polyols with prepared bio-based one in formulation of foams resulted in maintaining of beneficial cellular structure and slightly deteriorated mechanical performance of material.

Hejna *et al*.[66,67] in their research works applied crude glycerol and castor oil-based polyol, which preparation was described in other paper[55] in manufacturing of polyurethane-polyisocyanurate foams, which could be used as thermal insulation materials. Incorporation of up to 35 wt% of analyzed biopolyol resulted in the reduction of average cell size and increase of closed cell content, which decreased thermal conductivity coefficient by ~10%. Additionally, over 90% increase of compressive strength was noted due to the enhanced crosslink density. Similar effects were observed by Ionescu *et al*.[68] who also applied castor oil-based polyols in preparation of rigid PUR foams.

Basing on the presented literature reports, it can be noted that research works related to the incorporation of vegetable oils into manufacturing of biopolyols and polyurethane foams are very popular over the last years. Complexity of these works is still growing, at the beginning researchers applied unmodified oils, nowadays they are conducting advanced modification processes, aimed at providing additional effects, such as reduction of flammability.

3. Conclusions

Presented analysis of polyurethane market, as well as the literature reports, allows to state that PUR market is very perspective for innovations, because demand for PUR materials is constantly growing, e.g. due to the economic growth in many regions of the world. Current trends and law regulations are directing market towards application of raw materials from renewable resources, such as biopolyols, which can be considered very interesting alternative for conventionally used petrochemical polyols. Such solutions are very beneficial from the economic and ecological point of view.

Therefore, many research groups are focused on the development of biopolyols for polyurethanes based on vegetable oils. Many examples have been already described in the literature and considering increasing share of bio-polyurethanes in the market, the number of industrially applied biopolyols will be growing in the near future. Nevertheless, for successful application of developed materials more emphasis should be put on the very important from the technological point of view thermal and rheological properties of biopolyols, which have not been as comprehensively described as e.g. their chemical structure.

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