STUDY ON THERMAL PROPERTIES OF SYNTHETIC AND BIO-BASED POLYURETHANE

by

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Polymers that are created by the chemical polymerization of naturally occurring monomers are attracting considerable commercial interest in the last few years because of their non-toxicity, biodegradability and biocompatibility, and use of feedstock that is renewable. The development of specialized lignin compounds, such as electrically conducting polymers, engineering plastics, and polyurethane, is an area of highest interest and growth. The paper will present the comparison of the mechanical and thermal properties of conventional polyurethane and bio-based polyurethane, i. e. polyurethane based on polyols produced by liquefaction of waste wood biomass.

Key words: *polyurethane, bio-based polyol, thermal conductivity*

Introduction

Each year, tremendous amounts of lignocellulosic residues are generated from agricultural and forestry industries, of which only a very small portion has been utilized, and most being wasted. The focus of the project E!3611 – BIOPUR Development of Biopolymers from Waste Wood Biomass [1] was to develop a technology that will enable preparation of a controlled composition of lignin from waste wood biomass and transform it to polymer. The results of the project are biopolymers produced by the liquefaction of wood in the presence of polyvalent alcohols or phenols and a suitable catalyst. By liquefaction of wood biomass in the presence of polyvalent alcohol (mainly glycerol) and suitable catalyst, rigid, flexible or foamed polyurethane foams can be made.

Polyurethane foams

Polyurethane (PU) foams are used widely in many fields as heat-insulating, packaging, structural, flotation and load bearing materials, due to their ease of processing and unique combination of excellent thermal insulation and mechanical properties [2]. Polyurethanes are one of the most useful 3-D polymers because they can be used in various forms of materials such as sheets, foams, elastomers, adhesives, paints, *etc*. About 80% of all polyurethanes are used in the form of foams, 20% in the form of non-cellular products [3].

Rigid foams are characterized by excellent insulating properties, moisture resistance and mechanical strength. Flexible foams show a relatively low resistance to deformation when

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exposed to pressure. Integral skin foams are structural foams that are chemically homogeneous, but whose density continuously decreases from the outside to the inside. They are characterized by a soft or porous core and tough outer skin [4].

There are two ways to achieve a typical foam structure [4]:

- by using a 'chemical' blowing agent that directly forms during the polymerisation process. An example of this is the foaming process for polyurethane, where water or carboxylic acids react during the polyaddition process with isocyanates forming CO_2 that has a blowing and foaming effect, and
- by adding a 'physical' blowing agent which evaporates during the polymerisation process from the liquid solution or decomposes at a certain temperature to form gas (CO_2, N_2). Suitable physical blowing agents include volatile organic compounds (VOC) such as pentane, but also CFC, HCFC or HFC.

Rigid polyurethane (PUR) insulating materials are closed-cell, rigid plastic foams made of PU. They have excellent thermal insulation performance. In the building and construction industry, rigid PUR foam panels are mostly used to insulate flat roofs, saddle roofs, ceilings, floors (also in combination with floor heating systems), and walls. Another area of application is insulation for low energy houses. Compared to rigid foams, flexible foams offer less resistance to deformation when exposed to pressure. They have a very wide spectrum of applications: it ranges from cushions and mattresses, foam cushions used in the fabrication of furniture or automotive industry to the production of toys, sports equipment, noise absorbers or packaging materials. Flexible foams are open-cell foams [3].

Despite these differing properties, polyurethanes have one common characteristic in that they all incorporate the urethane group (-NH-CO-O-) into their structure. However, they differ from simple thermoplastic polymers, such as the polyolefins, in that they are not sold as ready-made polymers but as precursors that are mixed at the conversion stage. These precursors are commonly polyols (compounds containing multiple -OH groups) and isocyanates (compounds containing -NCO groups) [5].

Production of bio-based polyurethane

Traditional PU foams are prepared by the polymerization of polyol with isocyanate simultaneously occurring with gas generation resulting from the chemical reaction of water of blowing agent evaporation by the exothermic reaction itself. However, the raw materials for preparing PU foams, based on polyol (polyether or polyester polyols) and isocyanate, are obtained mainly from fossil resources. With increasing concern of the shortages of fossil resources and the impetus for reducing costs of polyurethane, preparation of polyols from renewable biomass resources has been an interesting subject in the polyurethane industry. Biomass as natural polymer contains more than one hydroxyl group in the molecular chains, and can be used as polyol for preparing polyurethane materials [2].

With the conversion to “cleaner” blowing agents firmly in place for PU foam production, there is now a strong movement under way to use bio-based renewable resources as raw-material feedstocks. The goals are to reduce demand for non-renewable fossil fuels and to cut production of carbon dioxide “greenhouse gas” to fend off global warming [6].

Natural oils, including oil from soybeans, have favourable characteristics when processed into polyols. One challenge with natural oil-based polyols is that high-volume production of natural oil-based polyols would inevitably compete with food supplies. Therefore, despite the extensive research and commercialization efforts relating to development of bio-based polyols or "biopolyols" from natural oil alternatives, petroleum-based polyols still dominate the global polyol market [7].

Lignocellulosic biomass, such as wood and crop residues, is composed primarily of cellulose, hemicellulose, and lignin. It is renewable, abundantly available at low prices, and does not compete directly with food supplies. The conversion of lignocellulosic biomass to biopolyols is typically achieved by a liquefaction process where wood or lignocellulosic materials, such as waste paper, starch, *etc*., reacts with phenol or multifunctional alcohols to yield low molecular mass, liquid products that can be used for polymer synthesis. Liquefied wood can be considered to be a polyhydric alcohol. After the liquefaction process, the presence of hydroxyl group-containing species in the wood components can be used as polyols for several different purposes [7, 8].

The raw material in this project is chestnut wood. After processing wood, remains of biomass, so called cellulignin is available which contains above all cellulose, lignin and smaller amounts of hemicellulose. Currently is cellulignin used mainly for fuel, but it can be also used as a raw material for the production of new materials with higher added value. It is very suitable for further chemical processing because of its homogeneity and chemical pre-treatment.

The approach is to use a unique liquefying reagent to chemically break down the lignocellulosics under mild conditions. Lignin is a polymer found in woody and herbaceous plants. Its principal function is to provide structural support in plant cell walls; it consists of phenylpropane building blocks and belongs to the polyphenol family of polymers. Along with cellulose and hemicellulose, lignin is one of the three chemically distinct components occurring in plant tissue. The liquefaction process partially decomposes the macromolecules of lignin and hemicellulose in the lignocellulosic materials, and thus converts the lignocellulosic materials into a homogeneous viscous liquid. The liquefied mixture contains large amounts of polyols. These polyols can be directly used without further purification and separation since they are rich in accessible reactive groups that can react with other chemicals to produce polymers, namely polyurethane and polyester [1].

Materials

Two types of PU foams were investigated in the paper – PU foams made of conventional, synthetic polyol and PU foams made of bio-based polyol made by liquefaction of wood biomass. PUR foam plates were made in the company PLAST-A, Sapjane, Croatia.

Table 1 presents the composition of tested PU foams. The PU foam plates, marked with the letter A, were made of synthetic polyol, whilst the ones marked with the letter B were made of bio-based polyol. The blowing agent used for the production of rigid PU foams was water.

Table 1. Tested polyurethane foams

PUR foam plate	Polyol [mass %]	Isocyanate [mass %]	Water [mass %]
A 0/B 0	100.0	110.0	0.0
A 2/B 2	100.0	113.4	0.2
A 4/B 4	100.0	116.8	0.4
A 6/B 6	100.0	120.2	0.6
A 8/B 8	100.0	123.6	0.8
A 10/B 10	100.0	127.0	1.0
A 12/B 12	100.0	130.4	1.2
A 14/B 14	100.0	133.8	1.4
A 16/B 16	100.0	137.2	1.6
A 18/B 18	100.0	140.6	1.8
A 20/B 20	100.0	144.0	2.0
A 22/B 22	100.0	147.4	2.2
A 24/B 24	100.0	150.8	2.4
A 26/B 26	100.0	154.2	2.6

Methodology

The object of the study was to compare the thermal conductivity of polyurethane foam made of synthetic polyol and the one made of bio-based polyol.

Determination of steady state thermal transmission properties for thermal insulation and prefabricated insulating products, such as sandwich insulating panels or pipe/in/pipe assemblies, is of a great importance. In conformity assessment procedures of such construction products the value of its thermal conductivity must be given to enable the designer to perform correct and efficient calculations and design [9].

The coefficients of thermal conductivity were measured for 14 specimen couples of series A and 14 specimen couples of series B. The dimensions of all specimens have been measured and weighed on a precision scales in order to determine the density for every final specimen couple (tab. 2 and 3).

Table 2. Dimensions, mass, and average densities of PUR foam specimens made of synthetic polyol

Test specimen	Dimensions [mm]		Mass [kg]		Average density [kgm^{-3}]
	Specimen 1	Specimen 2	Specimen 1	Specimen 2	
A 0	504 × 504 × 38	504 × 504 × 42	0.60	0.63	62.98
A 2	506 × 506 × 40	506 × 505 × 39	0.54	0.52	52.45
A 4	505 × 505 × 40	507 × 507 × 40	0.50	0.50	48.82
A 6	504 × 504 × 41	505 × 505 × 40	0.47	0.45	45.85
A 8	503 × 503 × 40	503 × 503 × 40	0.44	0.44	43.48
A 10	505 × 505 × 40	504 × 504 × 40	0.41	0.41	40.27
A 12	506 × 504 × 39	505 × 503 × 39	0.35	0.39	38.23
A 14	505 × 502 × 40	504 × 502 × 38	0.39	0.37	38.47
A 16	503 × 503 × 39	503 × 503 × 38	0.36	0.35	36.44
A 18	503 × 503 × 41	503 × 503 × 41	0.33	0.35	32.78
A 20	501 × 507 × 38	504 × 507 × 40	0.35	0.34	34.76
A 22	504 × 504 × 40	505 × 504 × 40	0.31	0.31	30.51
A 24	504 × 503 × 40	503 × 503 × 40	0.32	0.32	31.59
A 26	507 × 506 × 41	507 × 508 × 40	0.30	0.31	29.31

The measurement was carried out according to the standard HRN ISO 8302:1998 (Thermal insulation – Determination of steady-state thermal resistance and related properties – Guarded hot plate apparatus), in the guarded hot plate apparatus with two specimens [10].

In two specimen apparatuses a central flat plate consists of a heater and metal surface plates and this heating unit is sandwiched between two nearly identical specimens. The heat flow rate is transferred through the specimen to separate isothermal flat assemblies called the cooling units or to outer specimen surfaces (fig. 1).

Test specimens are placed on both sides of the heater and thermocouples placed on the required positions (fig. 2). For temperature measurement 8 thermocouples of the type T were used and temperatures indicating the heat equilibrium between the main and the guard plates was measured with 16 thermopiles. The data were collected by an A/D converter type AGILEND and processed later.

Table 3. Dimensions, mass, and average densities of PUR foam specimens made of bio-based polyol

Test specimen	Dimensions [mm]		Mass [kg]		Average density [kgm^{-3}]
	Specimen 1	Specimen 2	Specimen 1	Specimen 2	
B 0	503 × 506 × 40	504 × 506 × 39	0.60	0.58	58.63
B 2	501 × 503 × 39	501 × 502 × 40	0.49	0.59	54.25
B 4	500 × 503 × 40	503 × 502 × 38	0.49	0.48	49.37
B 6	500 × 503 × 40	500 × 504 × 40	0.46	0.46	45.68
B 8	502 × 502 × 40	503 × 500 × 40	0.40	0.42	40.72
B 10	500 × 500 × 40	495 × 496 × 40	0.37	0.39	38.36
B 12	502 × 500 × 39	500 × 500 × 40	0.35	0.35	35.38
B 14	502 × 501 × 40	505 × 503 × 38	0.36	0.35	36.02
B 16	503 × 503 × 40	500 × 500 × 39	0.34	0.35	34.75
B 18	502 × 501 × 40	498 × 500 × 40	0.34	0.36	34.97
B 20	503 × 502 × 40	498 × 503 × 40	0.33	0.33	32.80
B 22	498 × 500 × 40	499 × 500 × 39	0.32	0.32	32.51
B 24	502 × 500 × 39	493 × 490 × 38	0.30	0.31	32.21
B 26	502 × 502 × 38	495 × 495 × 40	0.28	0.30	29.92

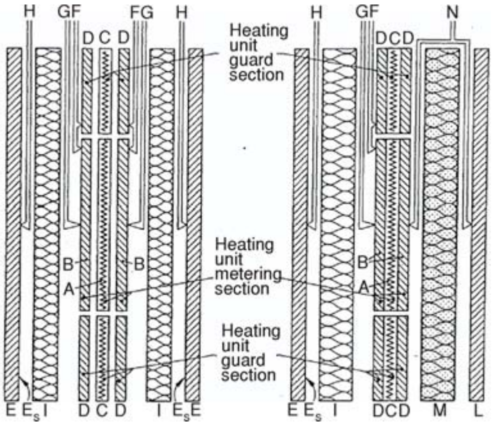

Figure 1. Schematic presentation of test configuration for prefabricated insulating panels

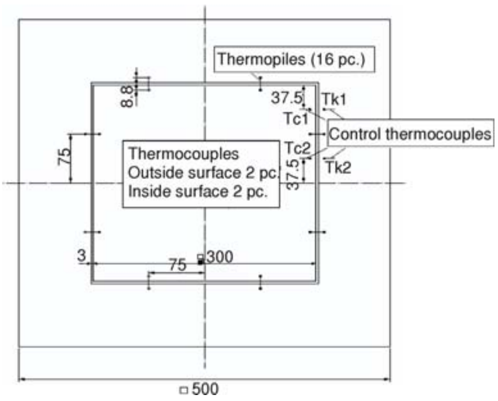

Figure 2. Position of thermocouples and thermopiles in the testing apparatus

All the measurements were carried out in stationary conditions, with the time necessary to achieve the stationary condition taking on the average about 39 hours. Only one measurement was carried out for every couple of specimens.

The thermal conductivity of the specimens is calculated as:

$$\lambda = \frac{\Phi d}{A(T_1 - T_2)} [\mathrm{Wm^{-1}K^{-1}}] \tag{1}$$

where Φ [W] is the average power of central heating unit, T_1 [K] – the average temperature of inner sample surface, T_2 [K] – the average temperature of outer sample surface, A [$\mathrm{m^2}$] – the surface area of central section according to standard, and d [m] – the average sample thickness.

Results and discussion

The differences in the measured values of thermal conductivity for both specimens are minimal and below the limit of 2% which has been stipulated by the HRN ISO 8302 standard. Therefore an average of measured values for both specimens is used as a single experimental result.

The diagrams of the density as a function of mass percentage of isocyanate for PUR plates made of synthetic and bio-based polyol are presented in the figs. 3 and 4, and the diagrams of thermal conductivity as a function of mass percentage of isocyanate for PUR foam plates made of synthetic and bio-based polyol are presented in figs. 5 and 6. It was found that PUR foam plate density highly correlates with the mass percentage of isocyanate in both cases, for PUR plates made of synthetic as well as bio-based polyol. Experimental data can be modelled by two-parameter rational function:

$$y = \frac{ab}{b + x} [\mathrm{kgm^{-3}}] \tag{2}$$

where y [$\mathrm{kgm^{-3}}$] is the density of PUR foam, x [mass %] – the mass share of isocyanate, and a and b – the parameters.

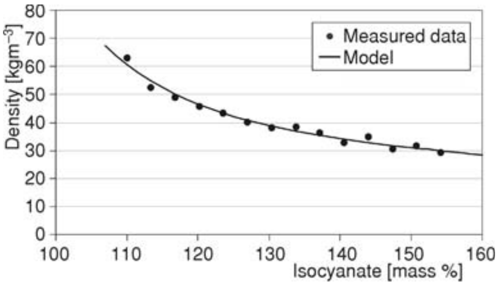

Figure 3. Density as a function of the mass percentage of isocyanate (PUR plates made of synthetic polyol)

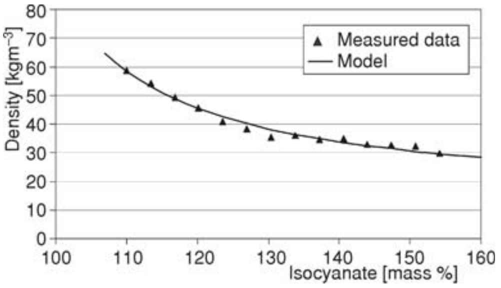

Figure 4. Density as a function of the mass percentage of isocyanate (PUR plates made of bio-based polyol)

In the case of PUR plates made of synthetic polyol, parameters obtained by ordinary least square method are: $a = 13.1512$ kg/m^3, $b = -0.8612$, with high correlation coefficient $r = 0.9895$ (shown as a curve in fig. 3).

In the case of PUR plates made of bio-based polyol, the obtained parameters are: $a = 13.258$ kg/m^3, $b = -0.8507$, with high correlation coefficient $r = 0.9888$ (shown as a curve in fig. 4).

Modelling of the relationships between the thermal conductivity and the density as well as the thermal conductivity and the mass percentage of isocyanate yielded for all the examined models a very low correlation coefficient ($r < 0.6$). On the other hand, regardless of the ex-

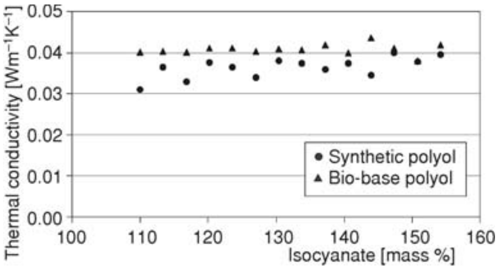

Figure 5. Thermal conductivity as a function of the mass percentage of isocyanate of PUR plates made of synthetic and bio-based polyol

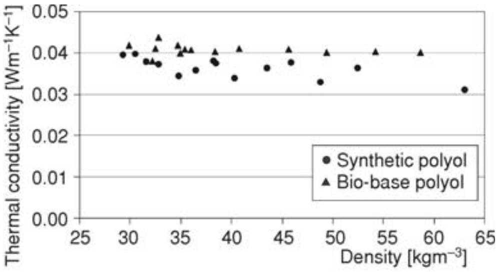

Figure 6. Thermal conductivity as a function of PUR foam density of PUR plates made of synthetic and bio-based polyol

perimental value of the density and the mass percentage of isocyanate, the thermal conductivity remained in a relatively narrow interval. For PUR foam plates made of bio-polyol, standard deviation is around half of the value of PUR foam plates made of synthetic polyol, *i. e*. the dispersion of the thermal conductivity values for PUR foam plates made of synthetic polyol is greater than the dispersion of the thermal conductivity values for PUR foam plates made of bio-based polyol. In addition, values of the thermal conductivity of PUR foam plates made of bio-polyol were greater than the corresponding values of the thermal conductivity of PUR foam plates made of synthetic polyol (tab. 4).

Table 4. Basic statistical data (thermal conductivity of synthetic and bio-based polyol)

Value [Wm^{-1}K^{-1}]	PUR plate made of synthetic polyol	PUR plate made of bio-based polyol
Mean	0.03633	0.04078
Min	0.03098	0.03802
Max	0.03985	0.04366
Standard deviation	0.00251	0.00125

For all examined values of mass percentage of isocyanate, the thermal conductivity remained in a relatively narrow interval around average level: ±13% for PUR foam made of synthetic polyol and ±7% for PUR foam made of bio-based polyol. The average value of thermal conductivity for PUR foam made of bio-based polyol is approximately 12% higher than the one of PUR foam made of synthetic polyol.

Since all the specimens were not prepared with sufficient quality (referring to the quality of specimen cutting), it may happen that some measurement results are affected by the lack of uniformity in the specimen thickness.

Conclusions

Cellulose and lignin are one of the most abundant constituents of biological matter. It is the principal component of plant cell walls, so the methods that enable the transformation of lignins from waste wood biomass were developed that enable them to be applied as a raw material for production of polyurethanes.

The object of the study was to compare thermal conductivity of polyurethane foam made of synthetic polyol and the one made of bio-based polyol. The strong correlation between the density and a share of isocyanate was found, and two-parameter rational function was proposed as a suitable model.

In all the cases, density of PUR foam made of bio-based polyol is smaller than the one of PUR foam made of synthetic polyol for the same share of isocyanate. There is no significant correlation between the mass percentage of isocyanate and the thermal conductivity and therefore there is no significant correlation between the density and the thermal conductivity as well.

It can be concluded that the PUR foam made from bio-based polyol according to the thermal conductivity does not differ from PUR foam made of synthetic polyol, *i. e*. cellulignin that is available after processing wood is suitable for the production of polyol by liquefaction process.

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