

Influence of Isocyanate Index on Selected Properties of Flexible Polyurethane Foams Modified with Various Bio-Components

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ABSTRACT: In this article, the results of the foaming process analysis of flexible polyurethane with different isocyanate indexes are presented. Two types of flexible polyurethane foams (FPURF) were obtained: (1) by using petrochemical components and a rapeseed-oil-based polyol (used in the amount of 20 wt%), (2) by using petrochemical components and cellulose as a natural filler in the amount of 3 php (per hundred parts of polyol). The characteristic parameters of the foaming process, such as the foam's growth velocity, the core temperature and dielectric polarization, were measured using a Foamate device. Moreover, the following properties of flexible polyurethane foams were determined: apparent density, resilience, compressive strength, hardness, hysteresis and support factor, in order to determine the influence of isocyanate index on selected properties of the foams modified with bio-polyol and bio-filler.

KEYWORDS: Flexible polyurethane foam, bio-polyols, natural filler, foaming process, mechanical properties, isocyanate index

1 INTRODUCTION

Nowadays, biobased polymers are much more popular due to the economic situation in the world. Among renewable raw materials that may be used in polyurethane (PUR) synthesis are vegetable oils [1]. In the world market, such oils as palm, soybean, rapeseed, sunflower and coconut oil are produced in the highest amounts [2]. The modification of vegetable oils in order to introduce reactive hydroxyl groups can be carried out by means of various methods. These methods are mostly based on the conversion of double bonds into hydroxyl groups [3, 4] or transesterification and transamidation reactions [5, 6]. However, the addition of such bio-polyols may affect the selected properties of obtained foams. For example, the addition of bio-polyols may change the structure and mechanical properties of final foams [7–9].

Renewable components may also be introduced into flexible PUR foams by an addition of fillers such as wood pulp, linen or sisal. Natural fillers contain mainly cellulose, hemicellulose and lignin. Several

researchers have attempted to apply them directly into flexible and rigid polyurethane foams. Such fillers are not expensive but the problem lies in their repetitive properties and stability. Another approach is to isolate one of the main components such as lignin or cellulose. On the basis of lignin it is possible to obtain polyols which can substitute petrochemical polyols. On the other hand, it is possible to obtain cellulose powder (Figure 1) and apply it as a filler, which can reinforce porous three-dimensional structure of open-cell polyurethane foams [10, 11].

In most cases, the application of bio-polyols and bio-fillers in the synthesis of polyurethane foams needs a modification of formulation in order to obtain porous products with desired properties. Among other components of PUR formulation in which the type and/or content has to be changed are: catalysts, surfactants and water as the most popular chemical blowing agent. A change in the amount of blowing agent directly influences the resulting apparent density of synthesized foams. The higher the water content in the formulation, the lower was their apparent density [8, 12].

The water content in polyurethane formulation as well as the applied isocyanate index may significantly affect the foaming process and the chemical structure

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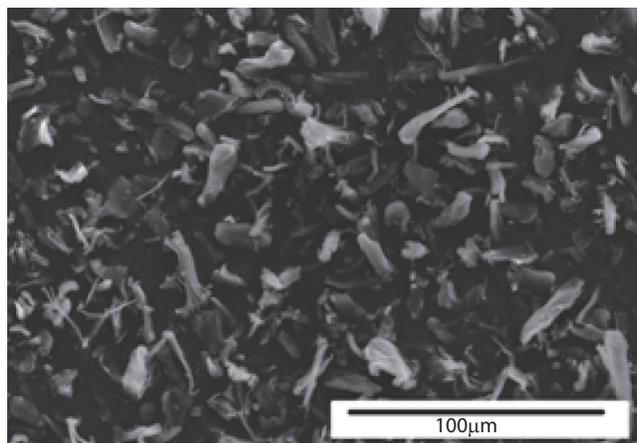


Figure 1 SEM microphotography of cellulose filler ARBOCEL® UFC100 under 500x magnification.

of obtained PUR materials and, as a consequence, the foam's cellular structure and mechanical properties, including cell size and foam hardness, as well as hysteresis value [8, 9, 13, 14].

Generally, PUR are made by the reaction of a polyol with a diisocyanate. The isocyanates form the major part of the hard or rigid phase of the polyurethane. Polyols provide the soft segment of the polymer and are end-capped with a hydroxyl group [15]. The amount of isocyanate used in relation to the theoretical equivalent amount is known as the isocyanate (NCO) index. The index value can have a significant impact on the foaming process and properties of the materials. Increasing the value of the NCO index may affect the gelling and curing time, as well as the foam's growth rate, because blowing efficiency increases. This is due to the additional blowing by the CO₂ produced in the reactions between the isocyanate groups [16, 17]. In addition, the isocyanate index value affects the amount of rigid segments in the polyurethane and, therefore, also affects the mechanical properties like compressive and tensile strength. It is caused by forming more urea and biuret groups [18]. As a consequence, the foam with higher isocyanate index has lower elasticity [17].

In this article, the effect of different isocyanate indexes on selected properties of flexible polyurethane foams modified with rapeseed oil-based polyol or ultrafine cellulose is shown and discussed. The NCO index is an important parameter which determines the amount of isocyanate groups in polyurethane formulation. Synthesis of flexible PUR foams with the use of natural resources is a complex process. That is why determining the effects of basic parameters, such as the isocyanate index of the foaming process and mechanical properties of final foams, is vital [19].

2 EXPERIMENTAL

In PUR formulations the following raw materials were used:

- F3600, polyether polyol, obtained on the basis of glycerol having LOH = 48 mg KOH g⁻¹ and a water content of 0.10% by mass. The polyol is produced by PCC Rokita SA (Poland).
- M6000, polyether polyol, obtained on the basis of glycerol having LOH = 28 mg KOH g⁻¹ and a water content of 0.10% by mass. The polyol is produced by PCC Rokita SA (Poland).
- Rz/iP, rapeseeds-oil-based polyol having LOH = 84 mg KOH g⁻¹ and a water content of 0.02% by mass. The polyol was produced by ZD Organika Sp. z o.o. (Poland).
- TDI, toluene diisocyanate (80:20 by mass mixture of 2.4- and 2.6-isomers) produced by BASF (Germany).
- Dabco T-9 (stannous octoate), a strong, metal-based catalyst produced by Air Products and Chemicals Inc. (Netherlands).
- Dabco BLV, a composition of a gel and a blow tertiary amine catalyst, providing a balanced reactivity, produced by Air Products and Chemicals Inc. (Netherlands).
- Niox Silicone L-618, surfactant produced by Momentive Performance Materials Inc. (Germany).
- Carbon dioxide as a chemical blowing agent, a product of water and TDI reaction.
- UFC100, ARBOCEL®, an ultrafine cellulose, unmodified natural filler that contains 6.0% of moisture, produced by JRS Rettenmaier (Germany).

The molded polyurethane foams were obtained using two different formulations. In the case of the first formulation (ROP), 20 wt% of petrochemical polyol was replaced with the bio-polyol synthesized in a two-step method of epoxidation and oxirane ring opening by isopropanol. Three different isocyanate indexes were applied in order to prepare the PUR foams. The second formulation was modified by the addition of cellulose fibers in 3 php concentration. Firstly, polyol premixes were prepared by stirring polyols with catalyst, surfactants, with water as a chemical blowing agent and filler. Next, toluene diisocyanate (TDI) as component B was added to component A and the mixture was stirred. In the first case of mixtures modified with rapeseed oil-based polyol, mixing with an overhead stirrer was applied for 10 seconds. In the second case of foams containing natural filler, a mixing-dosing device equipped with a static-dynamic mixer, type

MR 10–12 produced by Sulzer (Germany) was used. Time of mixing was 3.75 s and the whole volume of the reaction mixture was 90 cm³. Finally, the prepared mixtures were dropped into an open mold to obtain foams. Table 1 shows the used foam formulations.

After the foaming process (3 min), samples in molds were seasoned for 30 min at a temperature of 70 °C. Foams were taken out of the molds on the next day after synthesis and cut into samples. In the study of the foaming process, a Foamate device was used for conducting measurements of such characteristic parameters as the velocity of foam growth, reaction mixture temperature, pressure, as well as changes in dielectric polarizations which represent the reaction progress.

The morphology of foam's cellular structure was analyzed using a scanning electron microscope (Hitachi S-4700). The samples were sputter-coated with gold before testing to avoid charging. Apparent density of synthesized foams was determined according to ISO 845. Their mechanical properties were measured using Zwick Z005 TH AllroundLine equipment according to ISO 3386 and the rebound elasticity was determined according to ISO 8307. Each sample was compressed four times to 75% of their initial height. Between the successive measurements, there were 5 min intervals in order to allow the sample to return to its initial dimensions. The program records the values of compressive stress during loading and unloading of samples. The loops of stress-strain characteristics were the basis on which compression strength at 40% (foam hardness) and 75% deformation were determined, as well as the calculation of the hysteresis loss and support factor. Tensile strength and elongation at break was determined according to EN ISO 1798:2008.

3 RESULTS AND DISCUSSION

Measuring the foam formation parameters gives an insight into how the reaction is proceeding. Analysis

of the foaming process enables the evaluation of the impact of different additives on the polyurethane system's reactivity. The application of different isocyanate indexes resulted in some changes to the foaming process. The increase of the isocyanate amount in the reaction mixture caused a temperature rise inside the material's core (Figure 2). This is due to the fact that the isocyanate-water reaction is highly exothermic. In addition, the velocity of foams rising was also changed (Figure 3a). In the compositions with a higher isocyanate index, the reaction of isocyanate with water was strongly promoted, which resulted in a greater volume of carbon dioxide gas generation in a shorter time. Powder fillers in PUR systems sometimes act as nucleic agents and can delay the foaming process. However, in the analyzed formulations with various isocyanate indexes, their increase resulted in a similar effect as observed for foams modified with rapeseed oil-based polyol (Figure 3b).

The higher reactivity of PUR formulation is followed by shorter gelling and curing time. Gelling time for foams with 0.95 index was 26 s and for foam with 1.05 index was only 17 s. A similar dependency occurs for curing time, which for foam with the lowest isocyanate index was 460 s, and for foam with the highest index was 270 s. Increase of the amount of isocyanate in the reaction mixture increases the rate of reaction.

SEM images showed that depending on the direction of growth of the foam, the shape of cells was different. There is no visible correlation between the isocyanate index value and cellular structure parameters. Cells had the same shape and size in all analyzed foams. Figures 4 and 5 show the SEM images of the surface of flexible polyurethane foams in the cross section perpendicular and parallel, respectively, to the direction of foam rise.

Changes in the foaming process also had an impact on the apparent density of obtained foams. The higher the isocyanate index, the lower the foams apparent density was (Figure 3). Foam density decreased,

Table 1 Foam formulations.

Symbol	ROP 95 [g]	ROP 100 [g]	ROP 105 [g]	CEL 90 [g]	CEL 105 [g]	CEL 115 [g]
F3600	80	80	80	70	70	70
M6000	0	0	0	30	30	30
Rz/iP	20	20	20	0	0	0
Additives*	2.00	2.00	2.00	1.94	1.94	1.94
Water	4.2	4.2	4.2	5	5	5
UFC 100	0	0	0	3	3	3
TDI	47.6	50.1	52.6	48.2	56.3	61.6
Isocyanate index	0.95	1.00	1.05	0.90	1.05	1.15

* A mixture of catalysts and surfactant.

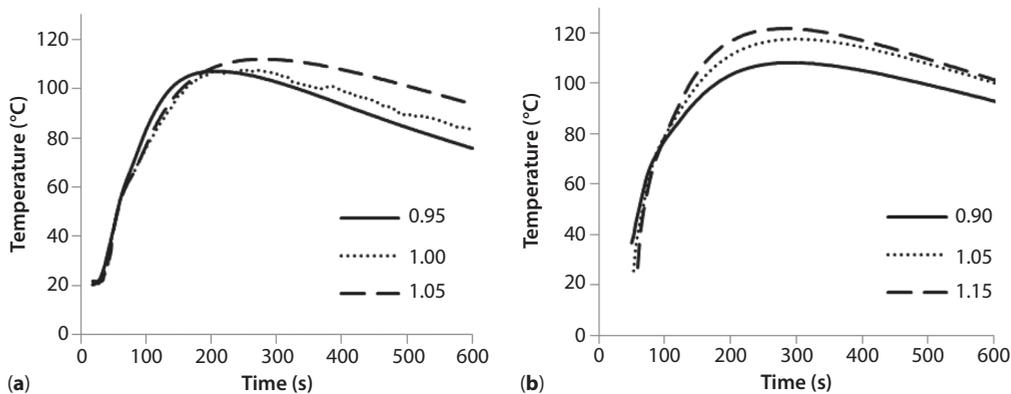


Figure 2 Core temperature profiles of foams with 20 wt% of ROP (a) and 3 php of cellulose filler (b) for formulations with various isocyanate indexes.

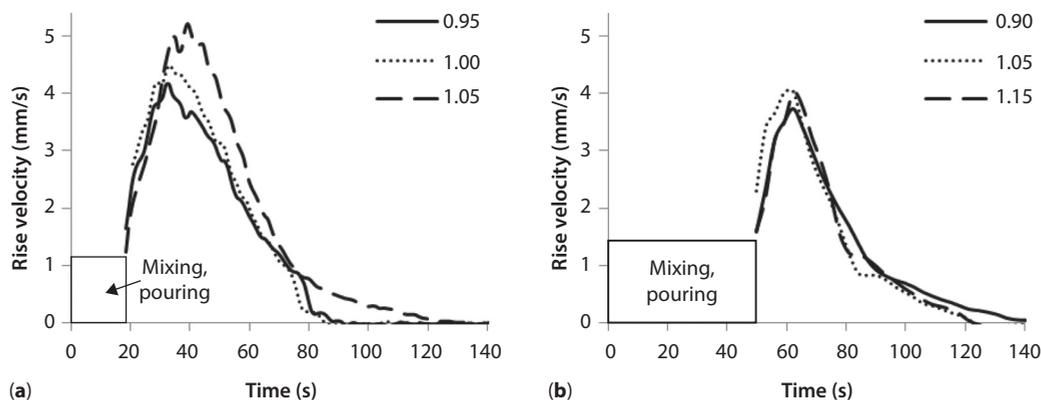


Figure 3 The velocity of rising of foams with 20 wt% of ROP (a) and 3 php of a cellulose filler (b) for formulations with various isocyanate indexes.

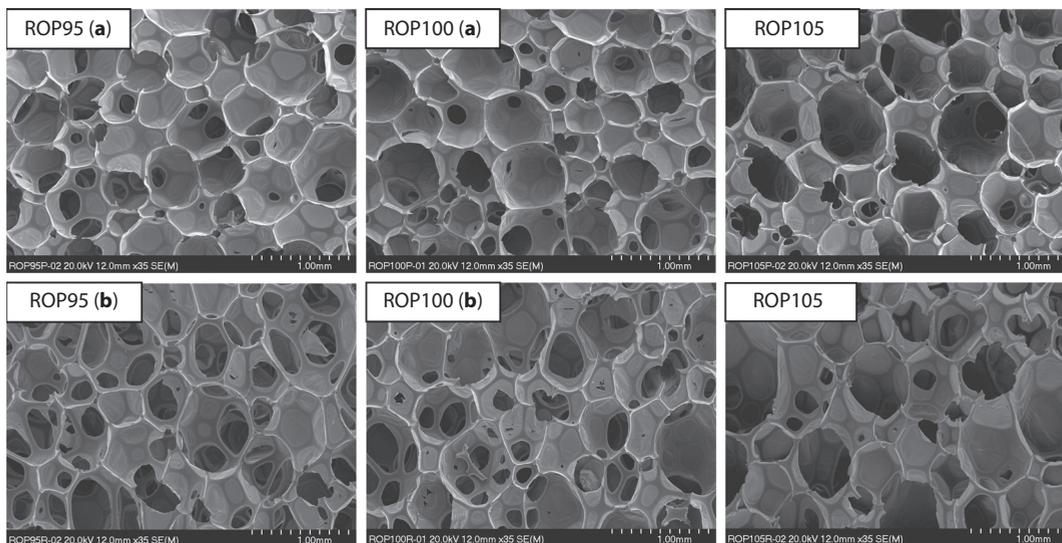


Figure 4 SEM images of ROP-foam cross section: (a) perpendicular and (b) parallel to foam rise direction.

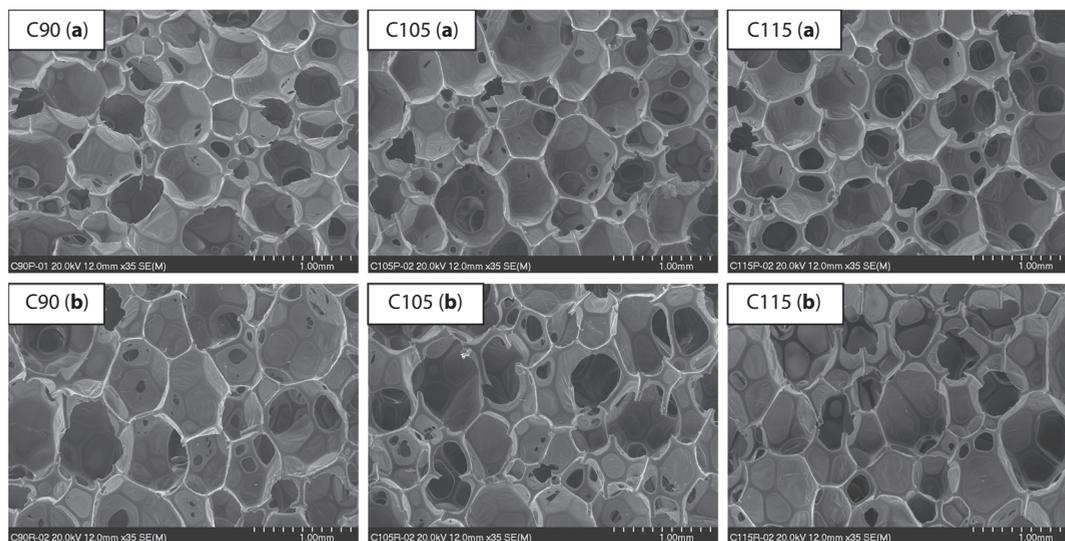


Figure 5 SEM images of foam with cellulose cross section: (a) perpendicular and (b) parallel to foam rise direction.

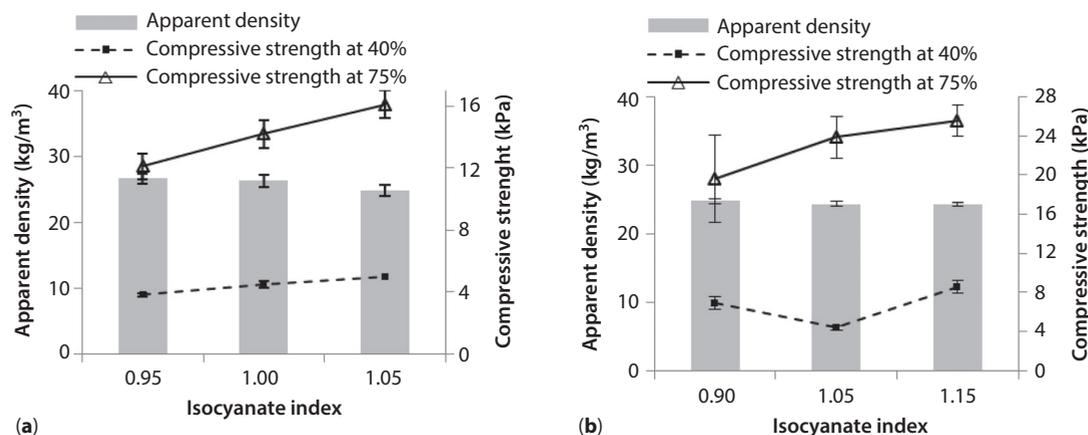


Figure 6 Apparent density and compressive strength of foams with 20 wt% of ROP (a) and 3 php of cellulose filler (b) for formulations with various isocyanate indexes.

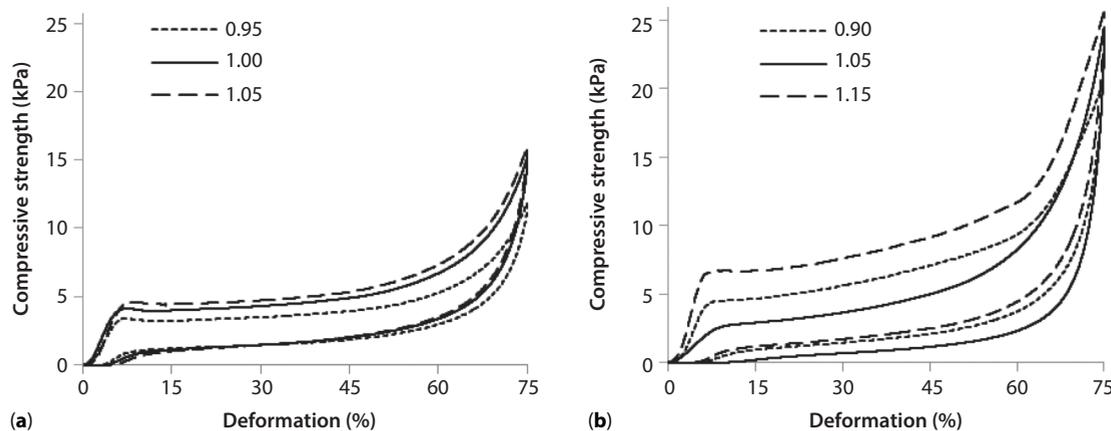
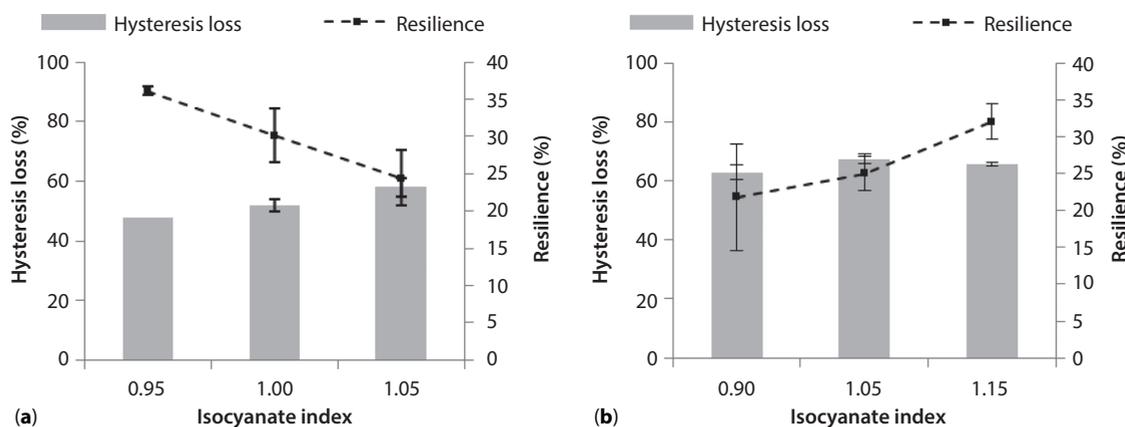
because blowing agent generation increased along with the increase of NCO index. This was also due to the additional blowing by the CO_2 produced in reactions between the isocyanate groups [15, 16]. With the increase of NCO content in the PUR formulation, the resulting standard deviations of apparent density decreased. It suggests that the foaming process of PUR formulations with high NCO index is more repeatable.

The apparent density affects the mechanical strength of foams. Typically, with higher values of apparent density, the foam's mechanical strength is also higher. In this study, the result is the opposite. It was found that with the slight decrease of apparent density (due to the increase of the isocyanate index), hardness and strength at 75% strain increased (Figure 6). This can be explained by the fact that the mechanical strength was

influenced not only by the characteristics of the porous structure but also by the hard segment content in the polyurethane foam. In the case of NCO index value below 1.0, there are not enough isocyanate groups, which results in slower gelling and unreacted -OH groups left in the foamed material. This results in a low level of crosslinking of PUR material. In comparison, when the value of NCO index is above 1.0, there are unreacted -NCO groups present in the foam. In this case it results in the formation of a higher amount of urea and biuret groups in the polymer structure [17]. The excess isocyanate used in the foam formulation should result in a more complete conversion of -OH groups from the polyol, as well as in the additional reaction with moisture from the air during seasoning time, leading to more polyurea and also allophanate crosslinked, rigid structures in the PUR foam [18].

Table 2 Characteristic data collected during foam compression tests.

Parameter	Unit	ROP 95	ROP 100	ROP 105	CEL 90	CEL 105	CEL 115
ΔW	Nmm	806 ± 38	1036 ± 75	1281 ± 99	1755 ± 409	1374 ± 135	2393 ± 186
$W_{\text{compression}}$	Nmm	1668 ± 73	1977 ± 98	2201 ± 47	2774 ± 543	2034 ± 159	3642 ± 255
F(25%)	kPa	3.47 ± 0.14	4.12 ± 0.14	4.51 ± 0.09	5.7 ± 0.7	3.3 ± 0.2	7.2 ± 0.5
F(65%)	kPa	6.49 ± 0.31	7.65 ± 0.44	8.79 ± 0.49	12.2 ± 0.9	10.5 ± 1.0	13.8 ± 0.8

**Figure 7** The hysteresis loop of foams with 20 wt% of ROP (a) and 3 php of cellulose filler (b) for formulations with various isocyanate indexes.**Figure 8** Hysteresis and resilience of foams with 20 wt% of ROP (a) and 3 php of cellulose filler (b) for formulations with various isocyanate index.

During the compression tests, data like compression strength during deformation was measured, in particular at 25, 40, 65 and 75% of deformation. Hysteresis was calculated as the value of the difference between the work during compression and decompression (ΔW), divided by work during compression ($W_{\text{compression}}$). These results are presented in Table 2.

In the graph presenting the hysteresis loops of materials with different isocyanate indexes, a certain change in the compression strength was also visible. The foams with higher isocyanate index had a greater

surface area of the hysteresis loop, which indicates a greater ability of these materials to absorb energy (Figure 7). Greater ability to absorb and dissipate energy is reflected by the decrease in resilience of the material (Figure 8a). The resilience of foams modified with ROP was reduced proportionally with the increase of isocyanate index. It can be explained as the effect of higher hard segment content in the foams with higher isocyanate index. As a consequence, the foam with higher isocyanate index had lower elasticity [16]. However, the presence of a cellulose filler

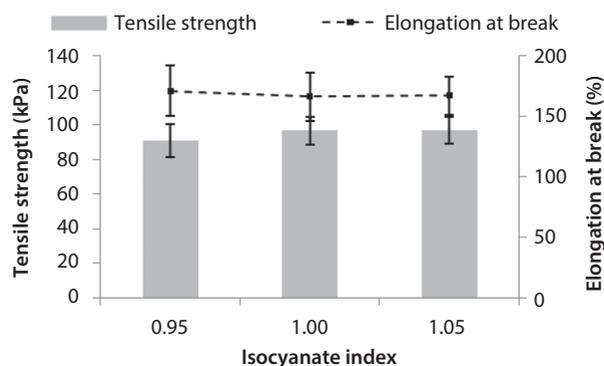


Figure 9 Tensile strength and elongation at break of foams with different isocyanate indexes and 20 wt% of ROP.

can reinforce the porous structure of flexible foams and with the increase of NCO it may give a synergistic effect with the polyurethane matrix, so that the material acts like a spring. Energy that was absorbed partially is reflected during the ball rebound test, which results in an increase of resilience in reference to the increase of isocyanate amount (Figure 8b).

The modification of polyurethane systems by the change of isocyanate index did not significantly influence tensile strength and elongation at break values of synthesized flexible foams (Figure 9).

4 CONCLUSIONS

In order to achieve a high quality synthesis of porous materials containing two different natural components, various methods of component mixing were applied. Natural fillers, such as powder like cellulose, always present an issue in obtaining proper homogenization of the the product. That is why static-dynamic mixers can successfully be used in the synthesis of polyurethane foams. Physical-mechanical properties of flexible polyurethane foams depend on a large number of factors and processing parameters. The introduction of new components to polyurethane formulation may cause unexpected changes in its processing and the properties of final foams.

The isocyanate index is one of the important factors that influence the physical-mechanical properties of flexible polyurethane foams by changing the polymer matrix properties. In most cases, the formation of the high content of hard segments in the polyurethane matrix increases compressive strength and decreases resilience. The modification of polyurethane formulation with biobased components may cause changes in the dependence of various properties of foam on the isocyanate index. Along with the increase of NCO index, foam's apparent density decreases and hardness

is higher, while tensile properties are unchanged. In the case of foams with ROP, their resilience decreased in contrast to the foams with cellulose filler, in which case the increase of resilience was observed. That is why further study should be applied in order to assess how the foam's properties may change when higher concentrations of renewable components are applied. The foam's mechanical properties can be adjusted by regulating the amount of isocyanate in the PUR foam formulation.

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