

Flexible Polyurethane Foams Modified with New Bio-Polyol Based on Rapeseed Oil

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Received November 29, 2014; Accepted January 7, 2015

ABSTRACT: This article describes the effects of the modification of polyurethane system with rapeseed oil-based polyol on the cell structure and physical-mechanical properties of conventional flexible polyurethane foams. The foams were prepared by substituting a part of the petrochemical polyether-polyols mixture with the bio-polyol based on rapeseed oil. Selected physical-mechanical properties of these foams were examined and compared to the properties of reference foam. The properties such as apparent density, resilience, comfort factor and stress-strain characteristics were analyzed in compression tests. It was found that the modification of polyurethane formulation with rapeseed oil-based polyol improves the selected properties of the final products.

KEYWORDS: Bio-polyol, physical-mechanical properties, polyurethane flexible foams, rapeseed oil

1 INTRODUCTION

Polyurethanes (PUs) are a class of polymers with a broad range of properties and applications. Their applications vary from flexible foams in the furniture industry to rigid foams as heat insulating materials, and from thermoplastic polyurethanes used in medical devices and footwear, to coatings, adhesives, sealants and elastomers used in the building and automotive industries. Polyurethanes have increasingly been used during the past thirty years in a variety of applications due to their comfort, cost benefits, energy savings and potential environmental soundness. The extensions of product life cycle and resource conservation are important environmental considerations that often favor the selection of PUs [1–3].

The use of natural oil-based polyols (NOPs) in the synthesis of flexible foams can be very promising due to such foams have the largest share in the market of PU products. Additional advantages of NOPs are their environmental benefits, which are confirmed by life cycle assessment (LCA). Vegetable polyols generate very low greenhouse gas emissions [4]. Nowadays, soy oil-based polyols are the NOPs most often used in PU materials [5,6]. However, flexible and viscoelastic foams are also modified with palm [7,8] and rapeseed

oil-based polyols [6,9]. In the case of PU foams synthesized using such entirely oil-derived polyols, the final products have not been of sufficient quality. However, partial incorporation of NOPs has been much more successful [10–12].

Recently, it was found that the addition of 20–30 wt% vegetable oil-based polyols into a foam formulation achieves similar mechanical and physical properties as those foams containing solely 100% petroleum-based polyols [11,13]. For selected foams with petrochemical polyols partially replaced with NOPs, higher hardness and compressive modulus are observed. Moreover, a significant load bearing increase measured by indentation force deflection test (IFD) was reported [11,14].

The characteristic of flexible foams depends on the structure of the polyols used. The reactivity of NOPs may be higher in comparison to the typical polyether polyols used in the synthesis of flexible foams [12,15]. The influence of the hydroxyl groups type and position on the PU system reactivity and foaming process was investigated using soybean and rapeseed oil-based polyols. It was found that NOPs containing primary OH-groups were more reactive and allowed for the obtainment of foams with smaller and more uniform cells [16]. However, such polyols show a lower tendency for cell opening [15].

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DOI: 10.7569/JRM.2014.634131

In this article, PU formulation was modified using rapeseed oil-based polyol with secondary hydroxyl groups. The influence of the replacement of petrochemical polyol with rapeseed oil-based polyol up to 50 wt% on cell structure and selected properties of final flexible foams were analyzed.

2 EXPERIMENTAL

The polyurethane foams were obtained in a two-step mixing process. Firstly, a mixture of polyols F 3600 and M 6000 (PCC Rokita S.A.) was stirred with two catalysts, Dabco T-9 and Dabco BL-11 (Air Products), water as a chemical blowing agent and surfactant Niax Silicone L-627 (Momentive Performance Materials Inc.) in order to prepare the polyol premix (component A). Next, toluene diisocyanate (TDI) (Ciech Pianki) as component B was added to component A and the mixture was stirred for 10 seconds with an overhead stirrer. Finally, the prepared mixtures were poured into an open mold. The reference polyurethane foam contained only petrochemical polyols, while the modified foams were obtained by replacing petrochemical polyols with the bio-polyol (RISO) based on rapeseed oil (ZD Organika). The same amount of both catalysts was used in all formulations. However, different amounts of isocyanate had to be used in order to keep the same level of isocyanate index. The formulations of the compared foams are shown in Table 1.

In this work, an oil-based bio-polyol was used, which has been synthesized on an industrial scale (ZD Organika) by epoxidation of rapeseed-oil, followed by oxirane ring-opening with isopropanol. The bio-polyol with hydroxyl value 75 mg KOH/g, desired for its flexible foam formulations, was obtained on an industrial scale. In the first step the desired part of the double bonds in fatty acid chains of rapeseed triglycerides

was oxidized and then oxirane rings were converted into hydroxyl groups. Using this method, bio-polyol with only secondary hydroxyl groups (Figure 1) was obtained and successfully applied as a replacement for the petrochemical polyols in the formulations of the PU system to prepare flexible foams. The petrochemical polyols were replaced with the amount of bio-polyol RISO from 10 to 50 wt% and the influence of such a modification on the cell structure and selected physical-mechanical properties of the obtained foams was analyzed.

Apparent density of synthesized foams was determined according to ISO 845. Mechanical properties were measured by using the Zwick Z005 TH Allround-Line equipment according to ISO 3386. During the measurement the samples of foams were loaded (compressed) up to 75% and next unloaded. The strength at 40% strain was defined as foam hardness. The area under the loading curves and hysteresis loop were used to determine the ability of the foams to absorb energy. The hysteresis loss was calculated as the ratio of loop area and area below the loading curve. Another interesting parameter is comfort factor (CF), which gives an indication of cushioning quality. The CF is also known as the sag factor. The CF was calculated as the ratio of strengths at 65% and 25% of strain. Higher CF indicates better cushioning quality.

The resilience of foams was determined according to ISO 8307. All mechanical properties of obtained foams were measured in the direction parallel to the direction (vertical) of the foam rise. Aphelion™ software was used to analyze average cells parameters such as the number of cells per surface unit, cell cross-section surface and anisotropy index. These parameters were analyzed in two foam cross sections, parallel and perpendicular to the foam rise direction. The anisotropy index was calculated as the ratio of cell height and width. All cell parameters were evaluated on the basis of more than 100 cells.

Table 1 Formulations of obtained foams.

Raw materials	REF	M 1	M 2	M 3
Petrochemical mixture of polyol, g	100	90	70	50
Bio-polyol RISO, g	–	10	30	50
Catalysts, g		1.0		
Surfactant, g		1.5		
Water, g		4.0		
TDI, NCO Index		1.0		

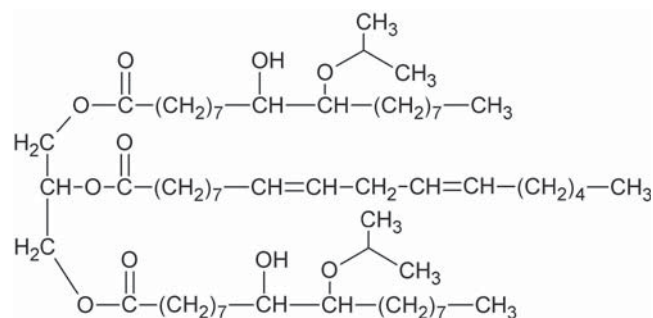


Figure 1 Suppositious chemical structure of bio-polyol RISO.

3 RESULTS AND DISCUSSION

The incorporation of RISO bio-polyol into the PU system caused slight changes in apparent density of obtained flexible polyurethane foams. The apparent density of foams modified with RISO bio-polyol has a tendency to increase up to ca. 10%. However, all obtained foams have apparent density ca. 30 kg/m³, which allows comparison of their mechanical properties. Generally, the modification of applied polyurethane system with RISO polyol resulted in the improvement of mechanical properties of the obtained foams (Table 2). The compression strength of the foams modified with bio-polyol RISO were higher, which is reflected by a significant increase of foam hardness at 40% compressive strain as well as by the character of the changes of the hysteresis loops, which are shown in Figure 2.

Much more energy is required during the loading of the foams that contain a higher amount of RISO bio-polyol. The higher area of hysteresis loop, as a consequence higher values of hysteresis loss (HL), means that the foams have a better energy-absorbing ability, enabling them to absorb and dissipate shock and impact. The foams containing RISO bio-polyol have higher HL values in comparison to the reference materials (Table 2). This is probably due to the effect of good mixing of hard and soft segments, as well as their more beneficial ratio.

It was also found that RISO bio-polyol improves the comfort factor. Increasing the amounts of bio-polyol in the polyurethane system allowed for an increase ca. 20% in the so-called comfort factor of modified foams. However, foam resilience was reduced by ca. 20% with an increasing amount of bio-polyol RISO up to 50 wt%

Table 2 Physical-mechanical properties of obtained foams.

Properties	REF	M 1 (10% RISO)*	M 2 (30% RISO)*	M 3 (50% RISO)*
Apparent density, kg/m ³	28.8	28.7	30.2	31.8
Resilience, %	30.3	23.4	24.6	23.9
Hysteresis loss, %	42.9	52.9	58.2	63.3
Hardness at 40%, kPa	5.1	6.6	7.8	8.9
Comfort factor	1.76	1.64	1.83	2.04

* - % wt. in relation to the mass of polyol mixture.

in the polyols premix. Such effects can be explained by the chemical structure of polyurethane matrix. The bio-polyol used has hydroxyl groups introduced at the positions of double bonds. The higher hardness and lower resilience of modified foams can be correlated with an effect of shorter chains between branching points and an increase of hard segments content. Higher hydroxyl value of the bio-polyol in comparison to the applied petrochemical polyols was the cause for the necessity of using a higher amount of isocyanate component and an increase of hard segment content in the modified foams. However, the bio-polyol has no terminal hydroxyl groups and dangling chains in such structure to play the role of a plasticizer.

The cell structure has an important influence on the physical-mechanical properties of flexible foams. Due to the possible anisotropy of cell structure, resulting from the forced rise of the prepared foams, they were characterized in cross sections both parallel and perpendicular to the vertical rise direction of the foams (Table 3).

Generally, the cells in compared foams were spherical, which is confirmed by the results of the anisotropy index, which have values in the frame 0.9–1.0. The cell structures of modified and reference foams are compared in Figures 3 and 4. It can be seen that the increase of rapeseed oil-based polyol in PU formulation gives more regular cell structure of modified foams.

The incorporation of RISO bio-polyol into the PU system also resulted in a lower number of cells with higher dimensions in the cross section parallel to the foam rise direction. However, an opposite trend was noticed

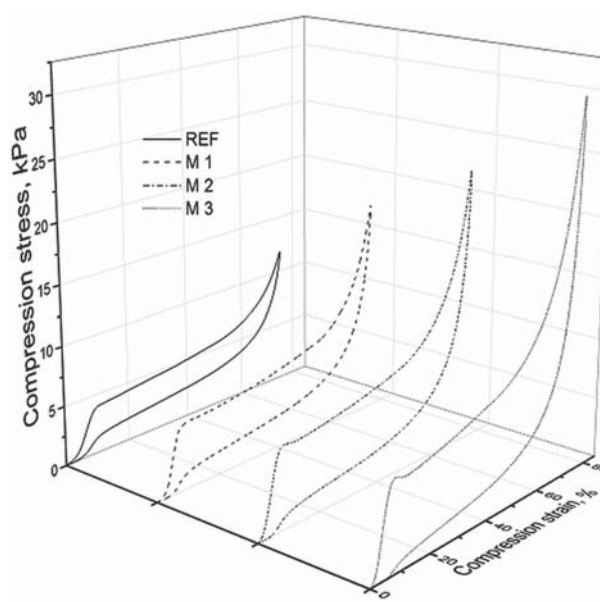
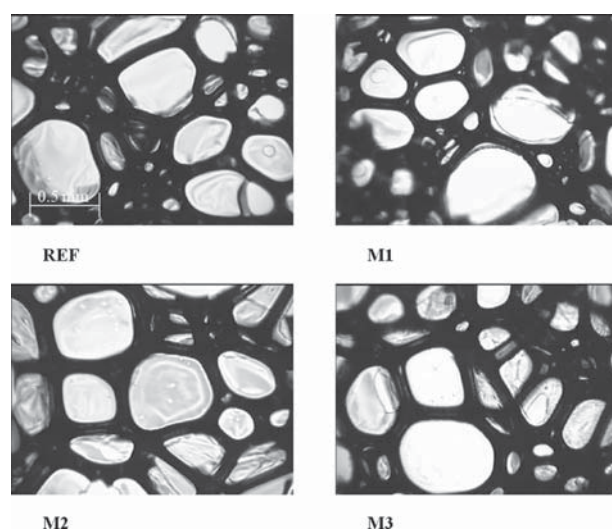
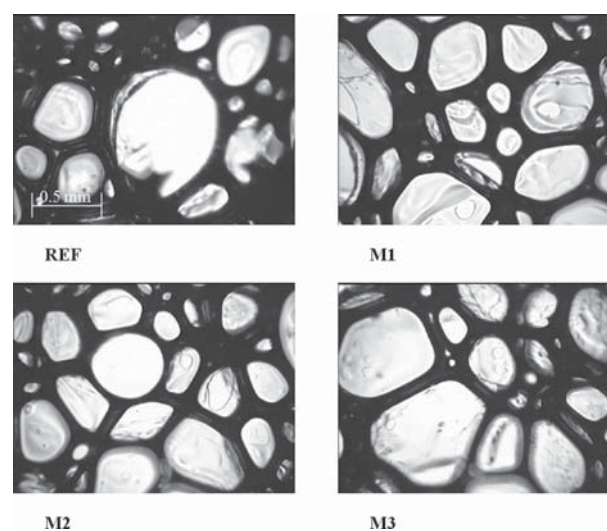


Figure 2 Hysteresis loops of obtained foams.

Table 3 Parameters of cell structure of obtained foams.

Average values of parameters of the cells	Cross-section	REF	M 1	M 2	M 3
Number of cells/mm ²	parallel	17	20	14	15
	perpendicular	14	14	19	17
Cell cross-section surface, mm ²	parallel	0.024	0.020	0.030	0.026
	perpendicular	0.033	0.030	0.023	0.024
Anisotropy index	parallel	0.93	0.92	1.00	0.86
	perpendicular	0.92	0.97	0.91	0.91

**Figure 3** Cellular structure of polyurethane foams (parallel cross section): REF (reference foam), M1, M2, M3 (foams modified with 10, 30 and 50 wt% of rapeseed oil polyol in polyol premix).**Figure 4** Cellular structure of polyurethane foams (perpendicular cross section): REF (reference foam), M1, M2, M3 (foams modified with 10, 30 and 50 wt% of rapeseed oil polyol in polyol premix).

when the cell structure was analyzed in the cross sections perpendicular to the foam rise direction (Table 3).

The increase of RISO bio-polyol content allowed the creation of cells with more uniform size, which is confirmed by a subtle lower average number of cells per surface unit. This can be explained by the chemical structure of rapeseed oil-based polyol that allows for the effects similar to the case of surfactants.

4 CONCLUSIONS

The results of this work have confirmed the possibility of modifying polyurethane systems with new bio-polyol containing only secondary hydroxyl groups based on rapeseed oil in order to obtain flexible foams with more uniform cell structure and beneficial selected mechanical properties.

Replacing 50 wt% of petrochemical polyol with new rapeseed oil-based polyol makes it possible to obtain more comfortable foams with higher hardness at 40% compressive strain, as well as with a higher energy-absorbing ability.

However, an effect of such a replacement of petrochemical polyols with rapeseed oil-based polyol also decreases foam resilience.

ACKNOWLEDGMENT

The research leading to the results presented had financial support from the National Centre for Research and Development in the frame of ERA-Net MATERA project 'Bio-Based Polyurethane Materials.'

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