

# The effect of different palm oil-based bio-polyols on foaming process and selected properties of porous polyurethanes

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## Abstract

Rigid polyurethane foams were successfully prepared by blending up to 70 wt% of two different palm oil-based bio-polyols with a petrochemical polyether polyol. The bio-polyols were synthesized by epoxidation–oxirane ring-opening process using water (PP102) and diethylene glycol (PP147), respectively. Due to the high viscosity of both bio-polyols the reactive mixture was heated to start the foaming reaction at about 50 °C. Under these conditions, the gelling reactions speed up as the amount of PP147 increases but slow down to a great extent when PP102 is used. The thermal conductivity of modified foams is higher and the closed cell content lower compared to reference ones, even when the bio-foams present a lower apparent density. However, all foams exhibit reduced water absorption, excellent dimensional stability and better thermal stability at temperatures up to 400 °C than the control foam. Conversely, their mechanical and dynamic mechanical properties become poorer as the PP147 concentration increases and even more so if PP102 is used instead. PP147 foams containing up to 50% bio-polyol could be used as a green replacement of petroleum-based ones in applications where excellent behaviour in compression (the most affected properties) is not fundamental, with the additional advantages of reduced density and increased content of bio-derived components.

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**Keywords:** rigid polyurethane foams; palm oil-based polyol; heat-insulating materials; cellular structure

## INTRODUCTION

Polyurethane (PU) rigid foam, an indispensable material in the construction industry, accounts for approximately 23% of all PU production because of such features as excellent insulation, good adhesion, high strength-to-weight ratio and durability.<sup>1,2</sup>

The rigid polyurethane foams (RPFs) currently available on the market are usually made from petroleum-based polyether or polyester polyols and polyisocyanates, in the presence of blowing agents, surfactants and catalysts.<sup>3,4</sup> In the case of water-blown PU foams, the reaction of water and isocyanate produces carbon dioxide gas which forms into small air bubbles.<sup>5</sup> One of the problems related to the production of PU foams is their dependence on petroleum-derived products,<sup>2,4</sup> as the petrochemical resources used worldwide in large-scale production for the chemical and building industries are gradually being depleted.<sup>6,7</sup>

Natural oils have great potential to compete with petroleum in producing polyols used to make PU<sup>1,2,4</sup> since they are non-toxic, non-volatile, non-depletable, domestically abundant, relatively inexpensive and biodegradable.<sup>1,2,4,8</sup> However, except for a few oils like castor and lesquerella oils,<sup>1,9</sup> the majority of natural oils do not contain the hydroxyl groups that are needed to form urethane links with isocyanate.<sup>1,10</sup> The unsaturated sites in natural oils can be used to introduce hydroxyl groups, and thus a number of methods, such as hydroformylation followed by hydrogenation, epoxidation followed by oxirane opening, ozonolysis followed by hydrogenation, and microbial conversion,<sup>4,10–15</sup> have been developed for the synthesis of natural oil-based bio-polyols.

These different methods allow one to obtain hydroxyl derivatives characterized by differentiated structures. The structure of polyols has a significant influence on properties of resultant PU foams, which also depend on the foaming process.<sup>16,17</sup> Nevertheless, the most important and frequently used reaction route for producing polyols is to epoxidize the double bonds and then react the epoxy groups with various ring-opening reagents,<sup>2,4,13,18–20</sup> probably due to the variety of polyols that can be obtained by opening of the epoxide groups using different agents, as well as its simplicity, safety and economy.<sup>11</sup> Furthermore, commercial products based on this methodology have become available.<sup>21</sup>

At present, several plant bio-polyols are being used predominantly in the manufacturing of PU foams due to their relatively high functionality.<sup>22</sup> However, challenges still remain in terms of properties and performance compared to PU foams based on polyether polyols. For example, RPFs based on vegetable oil polyester polyols exhibit poor dimensional stability (excessive

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shrinkage) at higher loadings of the bio-based polyols,<sup>23</sup> unfortunately limiting the potential savings of these cheaper and renewable polyols. Also, other studies have raised concerns over the low reactivity of oil-derived polyols and difficulties associated with foam density control.<sup>10</sup>

Oil palm (*Elaeis guineensis*) is an abundant and renewable resource that is largely cultivated in Indonesia and Malaysia,<sup>23</sup> giving one of the most important vegetable oils due to its price and production efficiency in comparison to any of the other commercial oils.<sup>17,24</sup> Nevertheless, the chemical modification of palm oil is not easy because of a relatively high content of saturated fatty acids that limits the degree to which such oils can be functionalized, leading to low-hydroxyl-value polyols as compared to other highly unsaturated vegetable oils such as soybean oil.<sup>5</sup> Additionally, as its double bonds are internal, the obtained polyols have secondary hydroxyl groups and dangling chains,<sup>5</sup> the former being not only less reactive in polymerization reactions, but also known to cause incomplete crosslinking and imperfections in the polymer network.<sup>5,25</sup> The dangling chains, which result from saturated fatty acids and the portion of the fatty acids between the functional group (usually at the ninth or tenth carbon atom) and the chain end, act as plasticizers that reduce PU rigidity and lower the glass transition temperature.<sup>2,26</sup> According to Pillai et al.,<sup>5</sup> the molecular weight and hydroxyl value of the polyol, the occurrence of dangling chains and the position of the hydroxyl groups in the fatty chain are the most important factors affecting the properties of modified PU materials.

In a previous work,<sup>17</sup> we proved the feasibility and potential of preparing RPFs from a palm-based polyol (PP102) obtained by epoxidation followed by ring opening with water, which is the cheapest ring-opening reagent.<sup>13</sup> Although this procedure has the advantage that both epoxidation and water ring-opening reactions could be conducted in one pot, it led to a bio-polyol with only secondary hydroxyl groups and low hydroxyl number, and thus the foams derived from it did not exhibit outstanding properties. In the study reported here, diethylene glycol was selected as a ring-opening reagent for the chemical modification of palm oil. The resulting bio-polyol was used to modify a commercial formulation to produce RPFs. Both the foaming process and the properties of the modified PU foams are discussed and compared with those of foams produced using PP102.

## EXPERIMENTAL

### Materials and methods

In this study, for the preparation of RPFs, the following materials were used: three different polyols, diisocyanate, catalysts, surfactant and water as a chemical blowing agent. Reference foams were obtained using only one petrochemical polyol with trade name Rokopol RF-551, supplied by PCC Rokita SA. Rokopol RF-551 is a polyether polyol characterized by hydroxyl value (OHval) of 449 mg KOH g<sup>-1</sup>. Modified PU foams were obtained using two different bio-polyols based on palm oil as additives. These bio-polyols were prepared on a laboratory scale in the Department of Chemistry and Technology of Polymers of Cracow University of Technology according to patent PL 205405B1. The epoxidation of palm oil in both cases was performed using peracetic acid generated *in situ* from the reaction of H<sub>2</sub>O<sub>2</sub> and glacial acetic acid. The synthesis method has been previously described.<sup>4,27</sup> The palm oil-based bio-polyols used in the foam synthesis were denoted PP102 and PP147, respectively. Bio-polyol PP102 was obtained in a one-pot synthesis. The epoxidation of palm oil was carried out at 60 °C. The

oxirane rings were opened using a stoichiometric amount of water. Bio-polyol PP147 was synthesized in a two-step method. In the first step, the epoxidation of the double bonds of palm oil was carried out at 55 °C. The second step involved the opening of the oxirane rings using a stoichiometric amount of diethylene glycol at 80 °C.

For the synthesis of foams, polymeric methylene diphenyldiisocyanate (PMDI) was used as the diisocyanate component to react with polyols and water. PMDI contained 31.5 wt% of free isocyanate groups and was supplied by Minova Ekochem SA. Polycat-9 was used as an amine-based catalyst (produced by Air Products). Niax Silicone L-6915 is a silicone surfactant, which was used as a stabilizer of the foam structure (produced by Momentive Performance Materials Inc.).

### Foam synthesis

RPFs with different contents of PP147 or PP102 and petrochemical polyol were prepared using a one-step method. Surfactant (1.5 wt% with respect to total polyol content), water (4.5 wt% with respect to total polyol content) and polyols were mechanically stirred for 15 s to ensure their complete homogenization and then the mixture (named 'polyol premix') was heated at 60 °C in a convective oven to reduce its viscosity. Amine catalyst (1.8 wt% with respect to total polyol content) and PMDI were immediately added to the polyol premix, at a NCO/OH ratio of 1.1:1.0 (the contributions of the polyols and water were considered in the OH calculation) and the whole mixture was mechanically stirred for 5 s and then poured into a plastic container (25 × 25 × 10 cm<sup>3</sup>).

In the notation of modified PU foams, the following information is included: F, foams; PP147 or PP102, type of bio-polyol; and content of bio-polyols (30, 50 or 70) in the polyol premix. An example is FPP147-30. The reference foam based only on the petrochemical polyol was named as REF.

### Characterization of bio-polyols

The polyols used to prepare the foams were characterized using gel permeation chromatography. Measurements were performed using a Knauer chromatograph equipped with a PLgel MIXED-E column for the analysis of oligomers and a refractometric detector. Calibration was performed using polystyrene standards. Tetrahydrofuran was used as an eluent at 0.8 mL min<sup>-1</sup> flow rate. Moreover, OHval and water content (using a Karl Fischer method) in the palm oil-based bio-polyols were determined according to PN-93/C-89052/03 and PN-81/C-04959 standards, respectively. Number-average functionalities ( $f_n$ ) of polyols were calculated based on OHval and experimentally determined number-average molecular weight ( $M_n$ ), according to the equation<sup>28</sup>

$$f_n = \frac{M_n \times \text{OHval}}{56\ 110} \quad (1)$$

Additionally, Fourier transform infrared (FTIR) spectroscopy was performed for palm oil, epoxidized palm oils and polyols. The FTIR spectra were recorded with a Genesis II FTIR spectrometer in transmission mode with NaCl plates. The spectra were recorded at a resolution of 2 cm<sup>-1</sup>, and the reported results are the average of 32 scans.

### Characterization of foaming process

Foaming process analysis involved measurements of foam core temperature, pressure, height of growth and dielectric polarization of reactive mixture. The measurements were carried out using FOAMAT<sup>®</sup> apparatus during 1800 s after mixing the PU-forming

components. On the basis of the results, the following parameters were calculated: start time as the time at which the ratio between the instantaneous rise velocity and the maximum rise velocity was 0.15, rise time as the time in which the height of the sample reached 98% of the maximum height, gel time as the time at which the dielectric polarization reaches 85% of its maximum value, maximum temperature reached in the system, etc.

### Characterization of foam properties

#### Apparent density

One of the basic properties of PU foams is the apparent density. It has been determined on the basis of the measurements of sample weight and volume (ISO 845).<sup>29,30</sup> For these measurements, foam samples with a size of  $ca\ 5 \times 20 \times 20\text{ cm}^3$  were used.

#### Foam morphology

The cellular structure was analysed on the basis of images taken using a microscope coupled to a camera. Images of the parallel and perpendicular cross-sections to the direction of foam growth were obtained. Cell structure images were analysed using the ImageJ program. The height, width, area and number of cells were set. Cell density was calculated using the following equation:<sup>31,32</sup>

$$N = \left(\frac{n}{A}\right)^{3/2} \quad (2)$$

where  $N$  is cell density in number of cells per  $\text{cm}^3$ ,  $n$  is the number of cells and  $A$  is area in the image of foam cross-section (in the present case it corresponds to  $0.00182\text{ cm}^2$ ).

Additionally, the closed cell content in foams was measured according to the ISO 4590 standard.

#### Thermal conductivity

Thermal conductivity was measured with a LaserComp heat flow meter. In order to measure thermal conductivity at an average temperature of  $10\text{ }^\circ\text{C}$ , the temperature on the bottom plate was set at  $20\text{ }^\circ\text{C}$  and on the top plate was set at  $0\text{ }^\circ\text{C}$ . The study involved samples of size  $5 \times 20 \times 20\text{ cm}^3$ .

#### Mechanical properties

In order to determine the mechanical properties of the foams, appropriate samples (ISO 844) were subjected to compression tests using a Zwick 1445 instrument. Compressive strength at 10% deformation was investigated in two directions: parallel and perpendicular to the direction of foam rise.<sup>29,30</sup>

Moreover the dynamic mechanical properties of the samples were determined using an Anton Paar Physica MCR rheometer. Torsion geometry was used for solid samples with a rectangular shape, whose dimensions were length = 30 mm, width = 10 mm, thickness = 3 mm. Measurements were performed as temperature sweeps, in the temperature range  $-50$  to  $250\text{ }^\circ\text{C}$  at a heating rate of  $5\text{ }^\circ\text{C min}^{-1}$ . The frequency was kept at 1 Hz, and the applied deformation at 1%, to ensure working in the linear viscoelastic range. The thermal transition temperature was arbitrarily selected as the temperature of the maximum in the  $\tan\delta$  curves.

#### Water absorption

Water absorption was measured (PN-93/C-89084) and calculated using the following equation and expressed as % water volume absorbed by the sample:<sup>29,30</sup>

$$X_w = 100 \times \frac{V_w}{V} \quad (3)$$

**Table 1.** Selected properties of petrochemical polyol and bio-polyols

Property	PP147	PP102	Petrochemical polyol RF-551
Hydroxyl value (OHval, mg KOH $\text{g}^{-1}$ )	147.1	102.0	449
Acid number (LK, mg KOH $\text{g}^{-1}$ )	2.4	9.0	< 0.1
Iodine number (LI, g $\text{I}_2$ (100 g) $^{-1}$ )	17.1	7.8	0
Water content (wt%)	0.07	0.12	0.10
Number-average molecular weight ( $\text{g mol}^{-1}$ )	1155	1648	542
Dispersity	2.54	3.57	1.5
Number-average functionality	3.0	3.0	4.3

where  $X_w$  is the water absorption,  $V_w$  the volume of absorbed water and  $V$  the volume of the sample.

#### Dimensional stability

Dimensions of samples of  $ca\ 100\text{ mm} \times 100\text{ mm} \times 25\text{ mm}$  were measured in specific positions before and after conditioning in an oven at  $70\text{ }^\circ\text{C}$  for 24 h. The dimensional stability was calculated using the following equation according to ISO 2796-1986 standard:

$$DS = 100 \times \left(\frac{l_f - l_i}{l_i}\right) \quad (4)$$

where DS is the dimensional stability,  $l_i$  is the initial measured size and  $l_f$  is the size after thermal treatment.

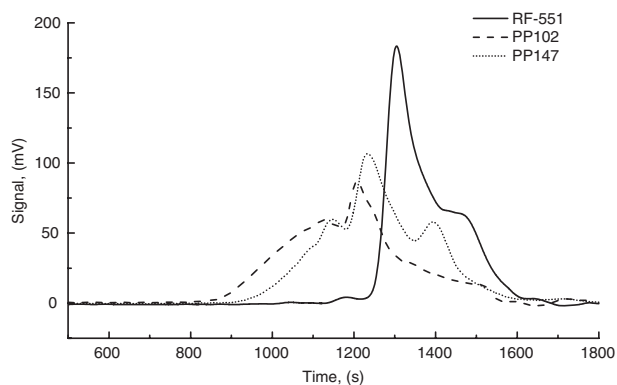
#### Thermogravimetric analysis

Thermal decomposition curves were obtained using a Shimadzu TGA-50 thermogravimetric analyser at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ , from 25 up to  $800\text{ }^\circ\text{C}$  under nitrogen atmosphere.

## RESULTS AND DISCUSSION

### Characterization of bio-polyols

The obtained bio-polyols were very viscous (almost solids) at room temperature due to the presence of crystals with crystallization temperature slightly over room temperature, like most bio-based polyols.<sup>12</sup> In contrast, the petrochemical polyol was liquid under the same conditions. The chemical characterization and gel permeation chromatograms of petrochemical polyol and palm oil-based polyols are summarized in Table 1 and shown in Fig. 1, respectively. It is clear that the number-average molecular weights of both bio-polyols are larger than that of the petrochemical one, although palm oil-based bio-polyols have lower dispersity. The iodine values of the bio-polyols are low but not zero, which indicates that not all the C=C bonds had reacted during bio-polyol synthesis, this being more marked for PP147. Moreover, bio-polyol PP102 has the lowest OHval and only secondary hydroxyl groups, because oxirane rings were opened using water. On the other hand, the bio-polyols present wider distributions of molecular weights compared to the petrochemical one (Fig. 1), which is a proof of oligomerization side reactions occurring



**Figure 1.** Chromatograms of polyols used in the synthesis of porous PU materials.

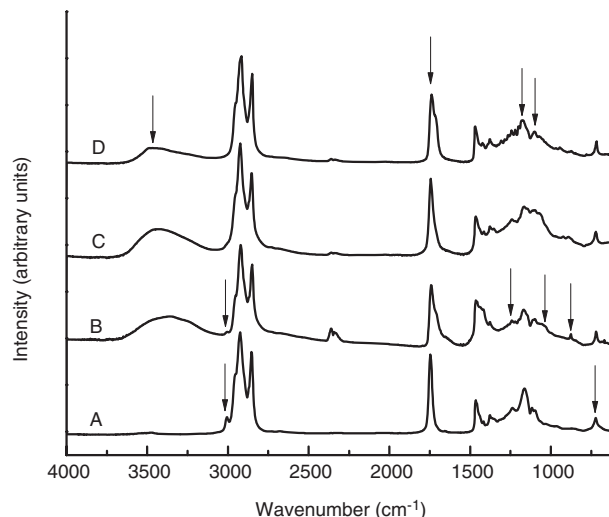
during the ring-opening reactions. These oligomerization side reactions occur when recently formed hydroxyl derivatives of the vegetable oil react with other epoxy groups, as indicated in related work.<sup>28</sup>

The FTIR spectra of palm oil, epoxidized palm oil and both palm oil-based polyols PP147 and PP102 are shown in Fig. 2. Bands at approximately 2925 and 2850  $\text{cm}^{-1}$ , associated with the asymmetric and symmetric stretching vibrations of C—H bonds in methylene groups present in aliphatic chains and methyl end groups,<sup>30,31</sup> are observed for all samples, as expected. The absorption bands characteristic for  $\text{CH}_2$  and C—OH in-plane bending vibrations are also observed at 1380 and 1465  $\text{cm}^{-1}$  in all spectra.<sup>33,34</sup> It is clear that the peak related to carbon-carbon double bonds of palm oil, at 3007  $\text{cm}^{-1}$ ,<sup>11,35</sup> is reduced to a great extent upon epoxidation. According to the literature,<sup>11</sup> the epoxy group is characterized for having three absorption bands<sup>35</sup> around 1250, 860–950 and 785–865  $\text{cm}^{-1}$ . In this sense the appearance of the epoxy group absorption band at 875  $\text{cm}^{-1}$  can be observed in the spectrum of the epoxidized oil. The band at 1236  $\text{cm}^{-1}$  is related to symmetric axial bending of the oxirane ring, in which all the ring bonds expand and contract in phase.<sup>35</sup> The band at 1043  $\text{cm}^{-1}$  is due to oxirane ring stretching.<sup>35</sup> However, it is clear that all epoxy bands are of small intensity and that the most noticeable change in the spectrum from epoxidized oil is the very large increase in the 3200–3400  $\text{cm}^{-1}$  band, corresponding to O—H stretching in hydrogen-bonded hydroxyls,<sup>36</sup> which are clear indications of the instability of the formed epoxy groups. All these characteristics indicate that most of the carbon-carbon double bonds were turned into epoxy or OH groups during epoxidation reaction.

After the ring-opening reaction, the characteristic peaks of epoxidized palm oil weakened and the hydroxyl band became the most noticeable difference with respect to the palm oil spectrum.<sup>11</sup> Thus, in the bio-polyol spectra, a strong stretching band at 3470  $\text{cm}^{-1}$  (O—H group), a stretching band at 1740  $\text{cm}^{-1}$  (C=O group), an antisymmetric stretching band at 1180  $\text{cm}^{-1}$  (C—O—C group) and a stretching band at 1100  $\text{cm}^{-1}$  (secondary O—H group) can be seen.<sup>12</sup> The higher O—H group content of PP147 with respect to that of PP102 is clearly visible as a more intense band in the 3400–3500  $\text{cm}^{-1}$  zone (Fig. 2).

### Foaming kinetics

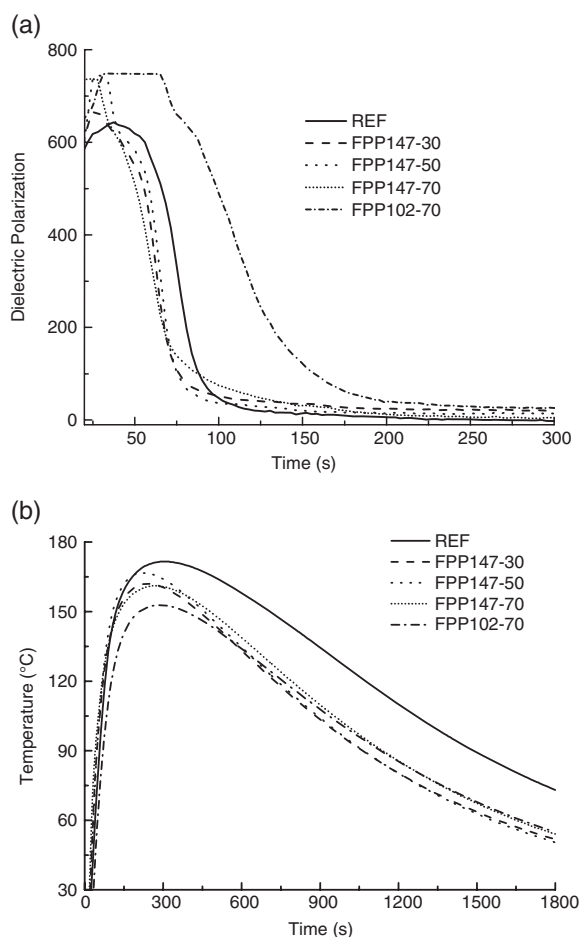
The obtained palm oil-derived bio-polyols were solid at room temperature; thus the so-called polyol premix became more viscous as the content of palm oil-based bio-polyols increased. Moreover,



**Figure 2.** FTIR spectra: (A) palm oil; (B) epoxidized palm oil; (C) PP147; (D) PP102.

these mixtures separate quickly into solid and liquid phases at room temperature if high concentrations of bio-polyols are used. Therefore, to ensure not only homogeneity but also to reduce the viscosity of the blend, the polyol premix was preheated at 60 °C before compounding with catalyst (volatile liquid) and isocyanate component.

The reactivity of the PU system can be computed by measuring the dielectric polarization, which decreases as an effect of the progress of the reaction.<sup>28</sup> Figure 3(a) shows the dielectric polarization as a function of reaction time for all samples prepared with PP147 in addition to that corresponding to the foam prepared with 70% PP102. The complete characterization of foams based on PP102 was discussed in a previous publication<sup>17</sup> and thus only selected properties are considered in this paper for comparison. As can be seen in Fig. 3(a), the bio-based PUs modified with bio-polyol PP147 are characterized by the fastest decrease of the dielectric polarization indicating a similar, or even higher, reactivity as compared with the reference foam (REF) regardless of their bio-polyol content. On the other hand, FPP102-70 exhibits a noticeably lower reactivity. Such an effect could be associated with the chemical structure of the bio-polyols. PP102 has lower OHval and only secondary hydroxyl groups because oxirane rings during synthesis were opened using water. In the case of PP147, diethylene glycol was used as the agent for opening epoxy groups and thus it led to the formation of both primary and secondary hydroxyl groups. It is known that primary hydroxyl groups have higher reactivity than secondary ones due to the strong steric hindrance caused by the latter.<sup>28,37</sup> According to Kurańska and Prociak,<sup>28</sup> in a reaction with an aromatic isocyanate, primary hydroxyl groups are about three times more reactive than secondary hydroxyl groups. Moreover, the features discussed previously have a direct correlation with the temperature profile developed during the reaction (Fig. 3(b)). In this case, it is observed that foams based on PP147 reach high temperatures of the reaction mixture during foaming, only surpassed by the corresponding reference sample, and in shorter times. Foam based on PP102, on the other hand, reaches the lowest reaction temperature. The averaged start, gel and rise times reported in Table 2 confirm the previous observations. This behaviour is in agreement with similar results reported in the literature.<sup>36,38</sup>



**Figure 3.** (a) Dielectric polarization and (b) temperature profiles during reaction of different PU systems modified with bio-polyols as a function of reaction time.

### Physical properties and foam structure

The apparent density, content of closed cells and thermal conductivity of the foams modified with bio-polyols are reported in Table 3. The replacement of petrochemical polyol with PP147 bio-polyol causes a decrease of the apparent density of obtained foams, which could be associated with lower reactivity of systems modified with the bio-polyol that retards the gelling of the foam and thus the cells could increase their volume during a longer time. This effect is even more pronounced for the foam made from PP102, which exhibits the longest gel and rise times (i.e. the lowest reactivity). Moreover, a longer foam expansion time could also cause cracking of cells. A confirmation of such an effect is the significantly low content of closed cells of foams modified with 70% palm oil-based bio-polyols that decreases to a great extent in both cases. Kuránska and Prociak<sup>28</sup> also found this behaviour for their PU foams based on two different rapeseed oil-based

**Table 3.** Apparent density, content of closed cells and thermal conductivity of reference sample and foams modified with palm oil-based polyols

Foam	Apparent density (kg m <sup>-3</sup> )	Content of closed cells (%)	Thermal conductivity (mW m <sup>-1</sup> · K <sup>-1</sup> )
REF	34.9 ± 0.8	83.4 ± 4.0	24.9 ± 1.4
FPP147-30	32.7 ± 0.5	68.9 ± 3.5	29.0 ± 1.3
FPP147-50	31.0 ± 0.1	83.0 ± 2.2	27.3 ± 1.6
FPP147-70	30.1 ± 0.1	37.7 ± 10.2	31.3 ± 1.5
FPP102-70	29.4 ± 1.8	8.9 ± 1.5	35.5 ± 1.1

bio-polyols and attributed the effect of cell opening to a reduced degree of crosslinking owing to the decreased functionality of the bio-polyols, as compared to the petrochemical one.

Regarding thermal conductivity, it is essential to keep this value as low as possible since the main use of rigid foams is for heat-insulating applications.<sup>1,23</sup> Thermal conductivity of the foam is affected by the conductivity of PU phase (solid phase) as well as the gas trapped (CO<sub>2</sub> in this case because water was used as a blowing agent) within the closed cell structure,<sup>1,8,9</sup> but also by the heat transport by radiation between cells.<sup>23,39</sup> According to Septevani *et al.*,<sup>23</sup> thermal conductivity of foams increases with increasing cell size but decreases with increasing closed cell content because open cells allow more convection, and even air to enter the foam, which has much higher conductivity (24.9 mW m<sup>-1</sup> K<sup>-1</sup>) than CO<sub>2</sub> (15.3 mW m<sup>-1</sup> K<sup>-1</sup>).<sup>1</sup> Tan *et al.*<sup>1</sup> also indicated that thermal conductivity is closely related to foam density and cell morphology. Hejna *et al.*<sup>34</sup> clearly indicated that an increase of cell size causes a simultaneous increase of the radiation contribution to the foam thermal conductivity. Thus, it is concluded that low conductivity results from low foam density, small average cell size and high closed cell content. In fact, the results found in this work show such a strong and reverse correlation of the thermal conductivity with the closed cell content that masks the dependence on density and cell size, especially for the foams containing high amounts of natural polyols. In fact, if the reference sample is not taken into account, a linear inverse relationship can be drawn, thermal conductivity = 36.043 – 0.106 × closed cell content (%), with *R* = 0.97.

Characteristics such as cell number, cell size (cross-sectional surface), cell density and cell anisotropy were determined using image analysis of optical micrographs (Table 4). The number of cells per area and the cell density calculated for the cross-section parallel to the rise direction of the foams modified with bio-polyols are higher than those of the reference sample. They also increase with the content of PP147 up to 50% and then decrease somewhat. In all cases, FPP102-70 exhibits noticeably lower values than FPP147-70. Accordingly, the cross-sectional surface of the cells shows the opposite trend. In the transverse direction the contrary tendency for these characteristics is observed, including the 50% PP147 content as the limit for reversing the trend. Moreover, the

**Table 2.** Characteristic times of foaming reaction (premix at 60 °C)

Characteristic time (s)	REF	FPP147-30	FPP147-50	FPP147-70	FPP102-70
Start time	14.7 ± 1.8	15.5 ± 0.1	15.5 ± 0.1	15.5 ± 0.1	15.5 ± 0.1
Gel time	23.8 ± 2.1	18.9 ± 2.9	17.4 ± 1.6	16.1 ± 1.0	27.0 ± 4.1
Rise time	70.1 ± 2.5	53.3 ± 3.3	48.0 ± 1.6	39.8 ± 1.8	78.2 ± 7.4

**Table 4.** Foam morphology<sup>a</sup>

Foam	Transverse direction				Rise direction			
	NC	CC ( $\times 10^3$ )	An	$N (\times 10^{-5})$	NC	CC ( $\times 10^3$ )	An	$N (\times 10^{-5})$
REF	43.96 $\pm$ 8.35	4.53 $\pm$ 1.09	1.02 $\pm$ 0.06	2.95 $\pm$ 0.83	22.3 $\pm$ 3.95	11.81 $\pm$ 2.79	1.13 $\pm$ 0.07	1.06 $\pm$ 0.29
FPP147-30	42.36 $\pm$ 6.70	5.59 $\pm$ 0.74	1.06 $\pm$ 0.03	2.78 $\pm$ 0.65	32.47 $\pm$ 5.76	7.58 $\pm$ 1.18	1.60 $\pm$ 0.08	1.87 $\pm$ 0.49
FPP147-50	21.63 $\pm$ 3.81	9.14 $\pm$ 1.17	1.48 $\pm$ 0.07	1.02 $\pm$ 0.27	56.54 $\pm$ 5.27	3.46 $\pm$ 0.59	1.25 $\pm$ 0.04	4.26 $\pm$ 0.58
FPP147-70	32.42 $\pm$ 2.97	6.86 $\pm$ 0.97	1.05 $\pm$ 0.10	1.85 $\pm$ 0.25	40.90 $\pm$ 8.81	6.18 $\pm$ 1.80	1.24 $\pm$ 0.04	2.65 $\pm$ 0.87
FPP102-70	38.03 $\pm$ 4.72	4.80 $\pm$ 0.80	1.66 $\pm$ 0.07	2.36 $\pm$ 0.44	24.79 $\pm$ 3.77	6.01 $\pm$ 2.29	1.25 $\pm$ 0.12	1.24 $\pm$ 0.28

<sup>a</sup> NC, number of cells per mm<sup>2</sup>; CC, cell cross-sectional surface (mm<sup>2</sup>); An, anisotropy index; N, cell density (number of cells per cm<sup>3</sup>).

anisotropy of the cells is in general higher for the modified foams in comparison with the reference one. As was also pointed out in a previous publication,<sup>17</sup> the replacement of the petrochemical polyol by the bio-derived ones led to less homogeneous and more anisotropic foams even when the initial viscosity of the reactive mixture was kept relatively low by preheating the polyol premix. This reflects the effect of the lower reactivity of the bio-polyols that have higher molecular weight but also only secondary (PP102) or both primary and secondary (PP147) hydroxyls as compared with the commercial polyol RF-551.

Regarding dimensional stability, it is evident from Table 5 that the variations in sample dimensions after the thermal treatment are random, showing an increase in the linear dimensions as well as a decrease. Although these changes are more noticeable for the foams prepared with PP147 and PP102, their magnitude is very low and the variations in the measurements (i.e. standard deviation) are high if compared to the value of the dimensional change, indicating that the dimensional stability of the modified foams is not a problem. This last fact is attributed to the methodology used, i.e. measurement after the thermal treatment could not be done exactly in the same specific positions used initially but near those. On the other hand, it is interesting to notice that the foams modified with both bio-polyols absorb less water than the reference material, even if the amount of water absorbed per unit volume is also low (in absolute values) in all cases. In this sense, it should be mentioned that the amount of water absorbed by a cellular material mainly depends on the cell structure of the foam, whether it is closed or open, and also on cell wall (strut) thickness.<sup>40</sup> Additionally, according to Kairyte and Vėjelis,<sup>41</sup> the open and closed cell content as well as apparent density are the main factors affecting foam water absorption, just in a way contrary to what is observed in this work, i.e. water absorption increases as closed cell content<sup>41</sup> and foam apparent density decrease.<sup>40</sup> However, those authors explained the effect of foam apparent density on water absorption considering that the decrease of the foam apparent density is due to an increase in the cell size and the consequent decrease in the cell-wall thickness,<sup>40</sup> while in this work it is found that the number of cells per area and cell density (calculated in the previous section) for the foams modified with bio-polyols are higher than those of the reference sample. Thus, it can be concluded that in this case the heterogeneity of the cell structure of the bio-foams is the dominating factor affecting water sorption.

### Compression properties

The compression properties of the foams are presented in Table 6. As expected, both the modulus and compressive strength decrease as the content of palm oil-based bio-polyol in the

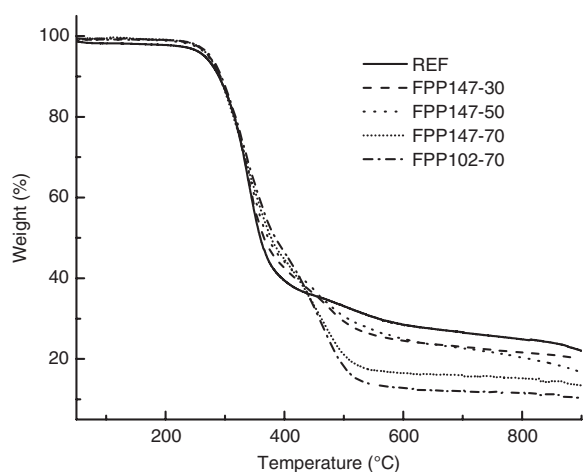
**Table 5.** Water absorption (WA) and dimensional stability (DS) of rigid foams modified with palm oil-based polyols

Foam	DSy (%)	DSx (%)	DSz (%)	WA (vol%)
REF	0.08 $\pm$ 0.14	0.08 $\pm$ 0.18	-0.03 $\pm$ 0.39	1.12 $\pm$ 0.37
FPP147-30	-0.27 $\pm$ 0.10	-0.42 $\pm$ 0.24	-0.04 $\pm$ 0.51	0.90 $\pm$ 0.23
FPP147-50	0.16 $\pm$ 0.08	0.13 $\pm$ 0.08	-0.36 $\pm$ 0.44	0.54 $\pm$ 0.04
FPP147-70	-0.22 $\pm$ 0.11	-0.14 $\pm$ 0.14	0.02 $\pm$ 0.44	0.39 $\pm$ 0.12
FPP102-70	-0.27 $\pm$ 0.20	-0.28 $\pm$ 0.12	0.01 $\pm$ 0.36	0.53 $\pm$ 0.27

**Table 6.** Compression properties of rigid foams modified with palm oil-based bio-polyols

Foam	Parallel		Transverse	
	Modulus (MPa)	Strength at 10% deformation (kPa)	Modulus (MPa)	Strength at 10% deformation (kPa)
REF	5.54 $\pm$ 0.76	187.2 $\pm$ 16.7	3.34 $\pm$ 0.36	125.2 $\pm$ 9.9
FPP147-30	4.92 $\pm$ 0.42	146.6 $\pm$ 12.0	2.65 $\pm$ 0.20	117.2 $\pm$ 8.2
FPP147-50	4.44 $\pm$ 0.64	143.3 $\pm$ 7.3	2.07 $\pm$ 0.16	87.4 $\pm$ 12.1
FPP147-70	5.11 $\pm$ 0.51	117.4 $\pm$ 8.4	1.46 $\pm$ 0.14	61.8 $\pm$ 2.5
FPP102-70	3.80 $\pm$ 0.20	100.5 $\pm$ 37.6	1.22 $\pm$ 0.16	59.3 $\pm$ 5.9

PU formulation increases. Moreover, lower values are exhibited by the foam prepared with PP102 polyol. In addition, mechanical property values measured perpendicular to the foam rise direction (transverse) are lower than the corresponding values measured parallel to the foam rise direction, which is a consequence of the anisotropic character of the obtained foams. As is clearly stated in the literature, mechanical properties of RPFs are closely correlated to their apparent density,<sup>9,23</sup> due to an increase in the cell wall thickness and/or a decrease in the cell size; according to Euler–Bernoulli beam theory, this gives rise to an increase in the bending moment of the cell wall.<sup>33</sup> And this correlation can be clearly noticed for both foams modified with the bio-polyols that exhibit systematic decreases as their apparent density decreases (increasing concentration of the bio-polyol). The compressive modulus was calculated from the linear elastic region of the stress versus strain compression curve and thus is controlled by cell wall bending and stretching. On the other hand, the compressive strength was calculated at 10% deformation, and thus could include the contributions of cell buckling.<sup>42</sup> Thus, the increasing amounts of dangling chains added to the reduction of the primary

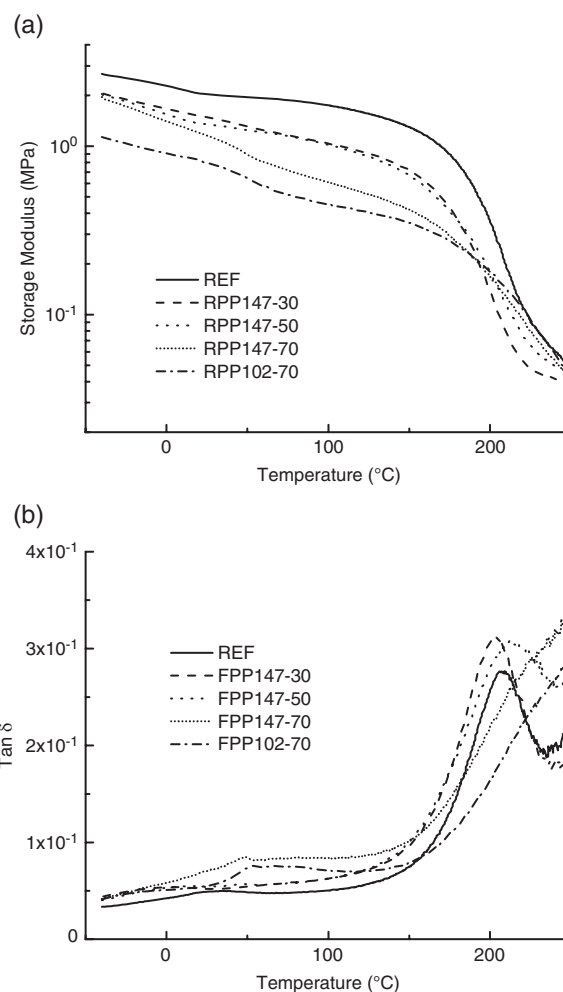


**Figure 4.** Thermal degradation profiles of synthesized foams.

hydroxyl groups as the concentration of the bio-polyols increases lead to weaker cell walls, as was pointed out in previously,<sup>23</sup> resulting in lower modulus and strength. The reduction of the content of closed cells with increasing addition of palm oil-based bio-polyols also contributes to these results due to the contribution to the modulus coming from the stretching of the closed cell walls, which is decreased with bio-polyol addition. Nevertheless, the green foams obtained in this study show apparent density values of 29–35 kg m<sup>-3</sup> and compressive strengths of 59–187 kPa, which are well in the range exhibited by conventional commercial foams that present densities in the 15–130 kg m<sup>-3</sup> range<sup>33</sup> and compressive strength values in the range 100–150 kPa (rigid foams at a density of 30 kg m<sup>-3</sup>).<sup>43</sup> Based on these results, the foams produced from palm oil-derived bio-polyols can potentially be used on an industrial scale in the construction and packaging industries.

### Thermal degradation

The thermal stability of the prepared foams is shown in Figure 4. Up to 250 °C, the foams only lose adsorbed water, and thus the mass lost in this temperature range is negligible, as indicated previously. For higher temperatures, two stages of thermal degradation can be clearly identified, with maximum degradation rates occurring between 341 °C (REF) and 334 °C (FPP147-70 and FPP102-70), first degradation stage, and 453 °C (REF) to 446 °C (FPP147-70 and FPP102-70), second stage, as identified from the derivative curves (not shown). The temperatures at which both maximum degradation rates take place decrease steadily as the amount of bio-polyol increases with no obvious differences noticed between FPP147-70 and FPP102-70 samples. Moreover, the char yield at 900 °C changes from 22% (REF) to 20, 16, 13 and 10% for FPP147-30, FPP147-50, FPP147-70 and FPP102-70, respectively. This clearly indicates that bio-based foams are less thermally stable at high temperature than the reference foam, with the poorer behaviour exhibited by the foams based on PP102. However, if we take into account that foams are usually used up to a temperature range of 110–150 °C, these differences are not significant since all modified foams lose less mass than the reference foam until 435 °C. The weight loss due to thermal degradation of PU foams is attributed to the degradation of the urethane linkages<sup>12,23</sup> followed by polyol decomposition.<sup>23,44</sup> Urethane linkage degradation involves three competing mechanisms: the dissociation of the original isocyanates and polyol precursors, the formation of



**Figure 5.** Dynamic mechanical behaviour of obtained foams: (a) storage modulus versus temperature; (b) tan  $\delta$  versus temperature.

carbamic acid and olefin with subsequent carbamic acid dissociation to primary amine and carbon dioxide, and the formation of secondary amine and carbon dioxide.<sup>23</sup> At higher temperatures the degradation of the isocyanate component of the foams takes place, as reported by Zhou *et al.*,<sup>44</sup> in association with depolycondensation and polyol degradation.<sup>23</sup>

### Dynamic mechanical behaviour

The dynamic mechanical behaviour of the foams as a function of temperature is presented in Fig. 5. It can be noticed that the storage modulus ( $G'$ ) decreases as the content of natural polyol increases, being noticeably influenced by the type of bio-polyol. The higher  $G'$  for the 100% petrochemical polyol sample is attributed to its higher foam density, as well as higher crosslinking density (a result of both low molecular weight that means less steric hindrance and higher hydroxyl content) than those modified with the palm oil-based bio-polyols. As the polyol substitution increases, glassy to rubbery transition shifts gradually to higher temperatures, although almost no changes are observed for bio-polyol concentrations lower than 50%. No rubbery plateau is observed for any of the foams in the range of temperature analysed. The main thermal glass-to-rubbery transitions, determined from the peak in tan  $\delta$ , increase from ca 205 °C (REF and FPP147-30) to 212 °C (FPP147-50) and 224 °C (FPP147-70)

and about 226 °C for the FPP102-70 sample. With increasing polyol substitution, the  $\tan \delta$  peak broadens, indicating increasing amounts of non-homogeneous network zones, which is consistent with the heterogeneity of the palm oil-based bio-polyols employed. Similar results were reported by Tan *et al.*,<sup>1</sup> Ribeiro da Silva *et al.*<sup>45</sup> and Septevani *et al.*,<sup>23</sup> among others. Moreover, the magnitude of the  $\tan \delta$  peak is strictly correlated with the nature of polymeric material and the ability of the material to dissipate energy by internal friction and molecular motions. High value of loss tangent is characteristic for materials with a high, non-elastic strain component, while a low value indicates a material that is more elastic.<sup>34</sup> From Fig. 5(b) it is noted that the  $\tan \delta$  peak is slightly higher for modified foams, as compared to the reference sample, which can be associated with the enhanced mobility of polymer chains in the foam structure.

## CONCLUSIONS

In summary, RPFs were successfully prepared by blending up to 70% of palm oil-based bio-polyols with petrochemical polyether polyol. Due to the high viscosity of the bio-polyols derived from palm oil (solids at room temperature), the reactive mixture had to be heated, and thus the foaming reactions started at ca 50 °C. However, the analysis of selected parameters of foaming processes showed a slightly and noticeable deceleration in foaming gelling reactions as an effect of the increase of the content of PP147 or PP102. In general, the hydroxyl value, functionality, molecular weight and chemical structure of polyols used in the synthesis of PU foams have a significant influence on the foaming process, leading to differences in cell structure and density that influence mechanical and thermal properties. In this work it was found that thermal conductivity, compression, dynamic mechanical properties and thermal stability deteriorate with an increase of the P147 bio-polyol content. However, PP147 proved to be a much better alternative than PP102 due to its higher hydroxyl content and lower molecular weight, but mainly due to the presence of primary hydroxyls in its chains that lead to a higher reactivity, reflected in the lower gel times of the FPP147 series. What is more, PP147 foams containing up to 50% palm oil-based bio-polyol could be used as a green replacement of petrochemical polyols in the synthesis of PU foams for various applications where excellent mechanical properties are not fundamental. The obtained bio-foams showed low thermal conductivity, very good dimensional stability and very low water absorption.

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