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Waste-Cooking-Oil-Derived Polyols to Produce New Sustainable Rigid Polyurethane Foams

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Abstract: Polyurethanes (PUs) are one of the most versatile polymeric materials, making them suitable for a wide range of applications. Currently, petroleum is still the main source of polyols and isocyanates, the two primary feedstocks used in the PU industry. However, due to future petroleum price uncertainties and the need for eco-friendly alternatives, recent efforts have focused on replacing petrol-based polyols and isocyanates with counterparts derived from renewable resources. In this study, waste cooking oil was used as feedstock to obtain polyols (POs) for new sustainable polyurethane foams (PUFs). POs with various hydroxyl numbers were synthesized through epoxidation followed by oxirane ring opening with diethylene glycol. By adjusting reagent amounts (acetic acid and H_2O_2), epoxidized oils (EOs) with different epoxidation degrees (50–90%) and, consequently, POs with different OH numbers (200–300 mg KOH/g) were obtained. Sustainable PUFs with high bio-based content were produced by mixing the bio-based POs with a commercial partially bio-based aliphatic isocyanate and using water as the blowing agent in the presence of a gelling catalyst and additives. Various water (4, 8, 15 php) and gelling catalyst (0, 1, 2 php) amounts were tested to assess their effect on foam properties. PUFs were also prepared using EOs instead of POs to investigate the potential use of EOs directly in PUF production. Characterization included morphological, chemical, physical, thermal, and mechanical analyses. The rigid PUFs exhibited high density (150–300 kg/m^3) and stability up to 200 °C. The combined use of bio-based polyols with partially bio-based isocyanate and water enabled PUFs with a bio-based content of up to 77 wt.%. EOs demonstrated potential in PUF production by bypassing the second synthesis step, enhancing sustainability, and significantly reducing energy and costs; however, PUF formulations with EOs require optimization due to lower epoxy ring reactivity.

Keywords: waste cooking oil; epoxidized oil; bio-based polyol; bio-based polyurethanes; rigid foams; sustainable materials; green polymers

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1. Introduction

Polyurethanes (PUs) are one of the most versatile polymeric materials, making them suitable for a wide range of applications, such as coatings, sealants, adhesives, flexible and rigid foams, elastomers, adsorbents, and thermoplastic polymers. The global market volume of polyurethanes reached nearly 26 million metric tons in 2022, and it is forecasted to grow to about 32 million tons by 2030 [1].

Although many studies on the production of non-isocyanate polyurethanes (NIPU) have been reported in the literature [2–6], PUs are still mostly produced by the reaction of OH groups of polyols and NCO groups of isocyanates. At present, petroleum remains the primary source of polyols and isocyanates. The United States, China, and Russia

are the three countries with the highest oil-refining capacity. As a result, the majority of polyols needed for polyurethane production are exported from these countries to the rest of the world. Additionally, the gradual depletion of oil reserves will inevitably lead to a petrochemical crisis. Therefore, it is time to focus more on developing new sustainable materials that can be produced domestically. This is an opportunity for scientists and industries to develop bio-based polyols, eliminating dependence on fossil resources and promoting sustainability. Switching to bio-based polyols can decrease reliance on limited fossil resources and potentially reduce carbon emissions, thus increasing the sustainability of PU production.

The most common way to incorporate renewable materials into PUs is using bio-based polyols, typically obtained from plant-based feedstocks [7]. These included lignocellulosic biomass [8–10], vegetable oils [11–26], macro- and microalgae [24,27–32], and, more recently, genetically modified oil plants [33]. Among these raw materials, vegetable oils are particularly promising for the production of polyols due to their chemical structure. Vegetable oils are triglycerides composed of glycerol and fatty acids, such as palmitic, stearic, oleic, linoleic, and ricinoleic acid [34]. They typically contain carbon–carbon double bonds, which are highly reactive, making them suitable for taking part in different reactions, such as epoxidation and ozonolysis, to introduce functional groups into their chemical structure. For this reason, in recent years, vegetable oils have been widely used as precursors for synthesizing polyols with different functionalities even at an industrial level [35,36].

Castor oil, an inedible oil, was selected by many authors as a component in polyurethane foam (PUF) production without additional modification as it already contains the OH functionality required by the polyurethane reaction [37–43]. However, its hydroxyl content, typically around 160 mg KOH/g, is suitable for flexible foams but insufficient for rigid PUFs, resulting in weak materials. Additionally, the low reactivity due to the secondary hydroxyl groups necessitates long processing times, limiting its applications [44]. To address these issues, chemical modifications are needed to increase the hydroxyl content and reactivity of castor oil, thereby improving the performance of the resultant castor-oil-based PUFs. Thiol-ene reactions, for instance, were used to modify castor oil introducing primary OH groups into its molecules, achieving high hydroxyl numbers and increased reactivity. Rigid PUFs produced by these bio-based polyols, pure or mixed with castor oil, exhibited good mechanical and physical properties [45,46]. An ultra-high hydroxyl value (463 mg KOH/g) was obtained by Su et al. through the reaction of castor oil and 1-thioglycerol [47]. Hejna et al. [48] produced castor-oil-based polyols by glycerol polymerization and subsequent polycondensation with castor oil. The resulting polyurethane foams showed good mechanical properties and excellent thermal stability. To reduce costs and environmental impact, Carriço et al. [42] used a simple mix of castor oil (90%) and crude glycerol (10%), producing rigid PUFs with comparable mechanical and physical properties with the other study. Omani et al. [49] increased the hydroxyl number of castor oil by epoxidation followed by ring opening with water to obtain rigid PUFs with high performance. More recently, to enhance the mechanical properties of PUFs from castor oil, Pinto et al. introduced Kimberlite clay as a filler in PUFs derived from castor oil polyols [50].

Also, polyols derived from rapeseed, palm, soybean, olive, sunflower, and canola oils needed chemical treatments to introduce the hydroxyl groups into their structure, such as hydroformylation, ozonolysis/reduction, and epoxidation/ring opening [2,7]. Among these, the most efficient procedure to introduce hydroxyl groups into the oily structure consists of a two-step synthetic route: epoxidation of the unsaturated bonds followed by the opening of the oxirane ring with a mono- or difunctional alcohol [2,51,52]. Depending on the ring-opening agent used, polyols with varying reactivity toward isocyanates, related to their primary and/or secondary OH group content, can be synthesized.

Extensive research has been conducted into PUFs synthesized from polyols derived from rapeseed [53–57], palm [13,24,58–60], soybean [22,23,61–63], canola, sunflower, and linseed oil [64]. However, to avoid competition with food and feed production and to reduce the environmental impact and production costs, inedible oils, waste cooking oils

(WCOs), or vegetable oil derived from biomasses are preferred as raw materials to produce bio-polyols [16,19,25,63,65–68].

Currently, about 0.6 million tons of WCO are collected in Europe from households, restaurants, and food-processing industries, but it is estimated that 4 million tons per year will be reached in the next decade due to the huge amount of vegetable oils consumed worldwide (about 21.8 million tons in 2024) [69,70]. Governmental authorities worldwide strongly encourage the collection of waste cooking oils for their potential valorization into value-added products, preventing environmental concerns such as water pollution and clogged sewer systems that can result from improper disposal [71]. One major application is the production of biodiesel, a renewable energy source alternative to fossil fuels. However, the decline in demand for biodiesel due to its polluting impact on diesel engines is driving the search for alternative uses for its valorization. For instance, WCO can be utilized as feedstock in the manufacture of high-value chemicals, such as bio-based polyols used in polyurethane foams, contributing to more sustainable materials' production. An interesting review on renewable polymeric materials, such as acrylic, alkyd, polyurethane, and epoxy polymers, as well as polyhydroxyalkanoates derived from waste cooking oil, was recently published by Onn et al. [72]. Moreover, it has been found that WCOs exhibit similar chemical characteristics to fresh vegetable oils; thus, they can replace virgin oils in polyol production, as reported by Kurańska et al. [52]. Bio-based polyols derived from WCOs offer a promising solution for their recovery and conversion, avoiding the use of fossil resources, reducing WCO management costs and environmental impacts associated with improper disposal, and creating economic value from what would otherwise be waste.

The synthesis of bio-based polyols derived from WCO and their influence on the final properties of rigid PUFs have been thoroughly investigated by many authors [19,25,65,73,74]. Asare et al. [25] prepared rigid polyurethane foams by modifying WCO through epoxidation followed by ring opening with methanol, resulting in PUFs with densities ranging from 28 to 42 kg/m^3. Polaczek et al. [19] synthesized various polyols from epoxidized used cooking oil and subsequent ring opening with diethylene glycol (DEG) to produce open-cell polyurethane foams with a low density (12.4–13.3 kg/m^3). The authors investigated the effect of different parameters, such as molecular weight, viscosity, and hydroxyl number, on the final properties of PUFs. Bio-based polyols can also be synthesized from WCO via transesterification reactions, as reported by some authors [65,74]. Enderus and Tahir [65] prepared WCO-derived polyols to produce green rigid polyurethane foams with a density of 208.4 kg/m^3 and a compression strength of 0.03 MPa. Kurańska and Malewska prepared bio-polyol by transesterification of used cooking oil with several agents, such as ethylene glycol, propylene glycol, glycerine, and triethanolamine [74]. The same authors also studied their influence on the final properties of open-cell PUFs, observing that an increase in the bio-based content of up to 60% led to an increase in closed cells. Conversely, a higher amount of bio-based polyol in the PUF formulation resulted in cell opening [75].

Many authors have investigated the effect of bio-based polyols by partially or completely replacing petrol-based counterparts. For instance, Zhang and Kessler [76] synthesized a bio-based polyol by reacting epoxidized soybean oil with castor oil, aiming to replace up to 80% of petrol-based polyol in rigid PUFs for thermal insulation. Their results indicated that as the bio-based polyol content increased, the foams exhibited higher density and thermal conductivity. This was due to faster blowing compared to gelling, resulting in a weak PU network and a higher content of open cells. Additionally, the compression strength decreased, tending toward the mechanical behavior of flexible foams. The increase in open-cell content was also reported by Prociak when more than 30% of a petrol-based polyol was replaced by polyols derived from rapeseed, soybean, sunflower, or linseed oil [64]. Nevertheless, the reduced reactivity of the polyurethane systems, as also reported in other studies [53,77,78], suggested that when bio-based polyols are employed in place of conventional ones, the PUF formulation needed to be optimized to achieve comparable physical and mechanical properties. Furthermore, since the final properties of polyurethane

foams depend on the chemical structure of their components, it would be more accurate to compare the performance of the final PUFs rather than just polyols.

Another important aspect related to materials' sustainability is their end of life, as recyclability and/or degradability positively impact the environment by potentially lowering the carbon footprint. Kurańska et al. [79] chemically recycled PUFs synthesized by vegetable-oil-based polyol, recovering new polyols that were reused in the PUF production with satisfactory results, aligning with the circular economy approach. As expected, the chemical structure of the foam components affected the recycling process. Polo et al. [80] investigated the potential degradation of bio-based PUF by two fungi, *Aspergillus niger* and *Aspergillus clavatus*. Since the ester bonds can be attacked by these microorganisms, the authors tested polyester–polyurethane foams prepared from castor-oil-based polyols and, after 60 days of treatment, observed weight losses 4–6 times greater than the control sample, ascribed to biodegradation processes. According to this result, PUFs containing vegetable oil segments in their structure could potentially be biodegraded.

As reported above, numerous studies have been published on bio-polyols derived from WCO. However, most of these works have focused on the production and characterization of low-density open-cell rigid PUFs [15,16,19,75]. Conversely, to the best of our knowledge, there are no papers in the literature on the use of WCO-derived polyols for producing rigid PUFs with a closed-cell morphology and medium–high density (150–300 kg/m^3). In this context, in the present study, waste cooking oil was employed as feedstock to produce polyols through epoxidation and subsequent ring opening with diethylene glycol (DEG). Epoxidized oils (EOs) with different degrees of epoxidation were obtained and, consequently, polyols (POs) with a range of hydroxyl numbers were synthesized and used in the production of rigid polyurethane foams (PUFs).

Compared to other studies [16,19,25,65], a partially bio-based isocyanate was used as an alternative to petrol-based isocyanates in order to increase the bio-based content of the PUFs. In addition, PUFs were also produced by directly using EOs in place of POs to investigate the reactivity of epoxy rings, which, to the best of our knowledge, has not yet been explored in the literature. Tu et al. produced foams replacing up to 50% of the polyol with an epoxidized soybean oil [61,81], but no studies have been reported in the literature on the use of epoxidized oil to fully substitute polyols in the formulation of rigid polyurethane foams. The direct use of EOs, bypassing the ring-opening step, would simplify the polyol production process with obvious economic benefits from an industrial point of view and increase the sustainability of the overall PUF production. Finally, the effects of the content of the blowing agent (water) and the gelling catalyst on the cross-linking structure and macroscopic properties of the PUFs were examined.

All of the produced PUFs were characterized in terms of morphology by stereomicroscopic and scanning electron microscopic (SEM) analysis. Fourier-Transform Infrared (FTIR) spectroscopy was used to examine their chemical structure. Finally, the thermal behavior of the PUFs was investigated by thermogravimetric (TGA) and Differential Scanning Calorimetric (DSC) analysis. Compression tests were also performed to investigate the mechanical properties of PUFs.

2. Materials and Methods

2.1. Materials

Waste cooking oil (WCO), collected from local Italian restaurants and purified by decantation, was supplied by Physis srl (Pisa, Italy), with a viscosity of 78 mPa·s at 25 °C. WCO fatty acids composition included 9.3% palmitic acid (C16:0), 3.1% stearic acid (C18:0), 44.9% oleic acid (C18:1), and 41.9 linoleic acid (C18:2), reflecting a blend of vegetable oils commonly used in Italian cuisine, such as olive, sunflower, and corn oil [82]. WCO has a molecular weight of 882 g/mol and 3.67 mol of carbon double bonds per mol of oil, determined using a procedure based on a method reported in the literature [83] and described in a previous work [84].

The epoxidation and the ring-opening reactions were performed using the following chemicals: glacial acetic acid (99.8%), hydrogen peroxide (30%), tetrafluoroboric acid (48% in H_2O), and diethylene glycol (99%) provided by Sigma-Aldrich (St. Louis, MO, USA); Ion Exchanger Amberlite® IR-120 and chloroform (ACS Reagent) by Supelco (St. Louis, MO, USA); and $NaHCO_3$ by Solvay (Livorno, Italy).

For the synthesis of rigid PUFs, a partially bio-based aliphatic polyisocyanate, Desmodur® CQ N7300 (NCO content 21.9%, bio-based carbon 68%), supplied by Covestro (Leverkusen, Germany), and the following additives, kindly furnished by Evonik Industries (Essen, Germany), a blowing catalyst (Polycat® 37), a surfactant (Tegostab® B 8870), and a gelling catalyst (Kosmos® 19) were used. Distilled water was used as the chemical blowing agent.

2.2. Synthesis of Bio-Based Polyols

POs were synthesized through a two-step method: epoxidation of WCO followed by the opening reaction of the oxirane ring, as shown in the scheme reported in Figure 1.

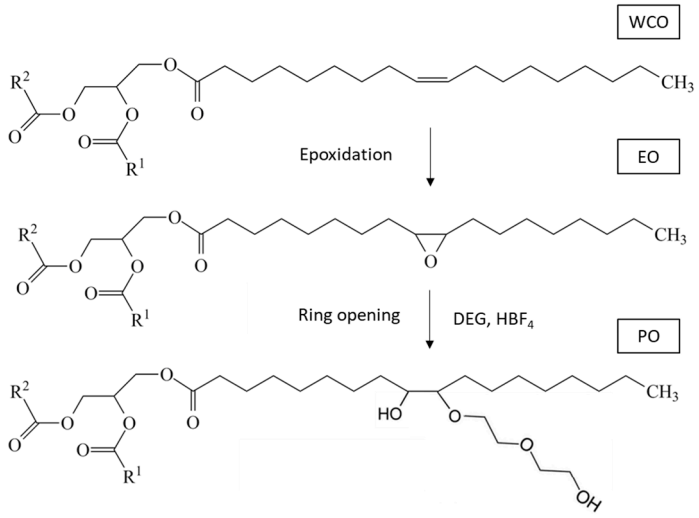


Figure 1. Scheme of conversion of WCO in EO and PO.

2.2.1. Epoxidation

Epoxidation was carried out by heterogeneously catalyzed oxidation of the double bonds of WCO, following a procedure reported in the literature [85]. As an example, epoxidized oil with a theoretic conversion of 100% of carbon double bonds was prepared as follows: a 500 mL round-bottom flask was filled with about 100 g (0.113 mol) of WCO and 15 g of Amberlite® IR-120 (catalyst, 15% by weight of oil). The flask was equipped with a reflux condenser, a mechanical stirrer, and a dropping funnel. A mix of 12.4 g of glacial acetic acid and 93.8 g of hydrogen peroxide (30 wt.%), corresponding to a molar ratio of C=C/acetic acid/H_2O_2 equal to 1/0.5/2, was prepared and placed into the dropping funnel. The system was heated to 70 °C, and then the mix was added dropwise into the flask over 30 min. The reaction was maintained at 70 °C for 6.5 h under mechanical stirring. At the end of the reaction, the mixture was cooled to room temperature, separated from the catalyst, and neutralized by an aqueous saturated solution of $NaHCO_3$. The organic phase was recovered and washed three times with deionized water. The residual water in the synthesized EOs was removed by a rotary evaporator under vacuum.

Three epoxidized oils (EOs), hereafter referred to as EO1, EO2, and EO3, were synthesized by varying the amount of acetic acid and hydrogen peroxide to obtain different epoxidation degrees (from 50 to 90%). For this purpose, the quantity of the reagents was calculated based on the desired conversion of unsaturated bonds.

2.2.2. Oxirane Rings' Opening

After epoxidation, POs were synthesized by the reaction of EOs and diethylene glycol (DEG), using tetrafluoroboric acid as a homogeneous catalyst. The reaction was carried out in a 500 mL round-bottom reactor equipped with a dropping funnel, a reflux condenser, and a mechanical stirrer. The reactor was filled with an amount of DEG corresponding to a molar ratio of oxirane rings/DEG equal to 1/5.5 and tetrafluoroboric acid (0.4% by weight of EO) and heated up to 90 °C. Then, 100 g of EO was added dropwise to the DEG mixture. The reaction was conducted at 90 °C for 2.5 h under stirring. Then, a saturated aqueous solution of $NaHCO_3$ was added to neutralize the mixture. The synthesized product was extracted by chloroform and washed with deionized water three times [58]. The solvent was removed under vacuum by a rotary evaporator [62,86,87].

In this work, three polyols, PO1, PO2, and PO3, were produced from EO1, EO2, and EO3, respectively.

2.3. Polyurethane Foam Production

PUFs were produced by a one-step method at room temperature. The different components were added in the following order: PO, surfactant (Tegostab B 8870), blowing catalyst (Polycat 34), blowing agent (water), isocyanate (Desmodur N7300), and gelling catalyst (Kosmos 19). The mix was homogenized after each addition. The formulations of the PUF are detailed in Table 1.

Table 1. PUF formulations for 100 g of PO or EO.

Sample	Polyol	Water (g)	Polycat 34 (g)	Tegostab 8870 (g)	Kosmos 19 (g)	Desmodur N7300 (g)	Bio-Based Content (%)
PUF-1	PO1	15	5	1.5	-	402.2	74.1
PUF-2	PO2	15	5	1.5	-	424.6	74.2
PUF-3	PO3	15	5	1.5	-	432.0	73.9
PUF-4	PO3	15	5	1.5	1	432.0	73.7
PUF-5	PO3	15	5	1.5	2	432.0	73.6
PUF-6	PO3	8	5	1.5	1	282.8	75.4
PUF-7	PO3	4	5	1.5	1	197.6	77.1
PUF-8	EO3	15	5	1.5	1	432.0	73.7

A weighted quantity of mixture was poured into a mold and the foaming process was carried out using a closed mold to reach the desired density and uniform morphology. The curing was conducted at room temperature for 24 hours.

Different formulations were tested using a molar ratio NCO/OH of 1, and by varying the quantity of water (from 4 to 15 php, percentage by weight of polyol) and the gelling catalyst (from 0 to 2 php). PUFs with various densities were produced by changing the amount of mixture poured into the mold.

In addition, to study the reactivity of oxirane rings in the foam's production, PUFs were also produced using EO3 at the highest epoxidation degree in place of POs.

2.4. Characterization

2.4.1. H-NMR Analysis

The ^{1}H-NMR spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer (Billerica, MA, USA). Chemical shifts (δ) are reported in parts per million.

The analysis was carried out on EOs to calculate their epoxidation degree, EP, defined as the ratio between the number of epoxy rings, n_{EP}, to the number of C=C of WCO, $n_{C=C,WCO}$, and expressed by Equation (1).

$$EP = n_{EP}/n_{C=C,WCO} \quad (1)$$

As an example, the chemical structure of EO1 and its ^{1}H-NMR spectrum are reported in Figure 2.

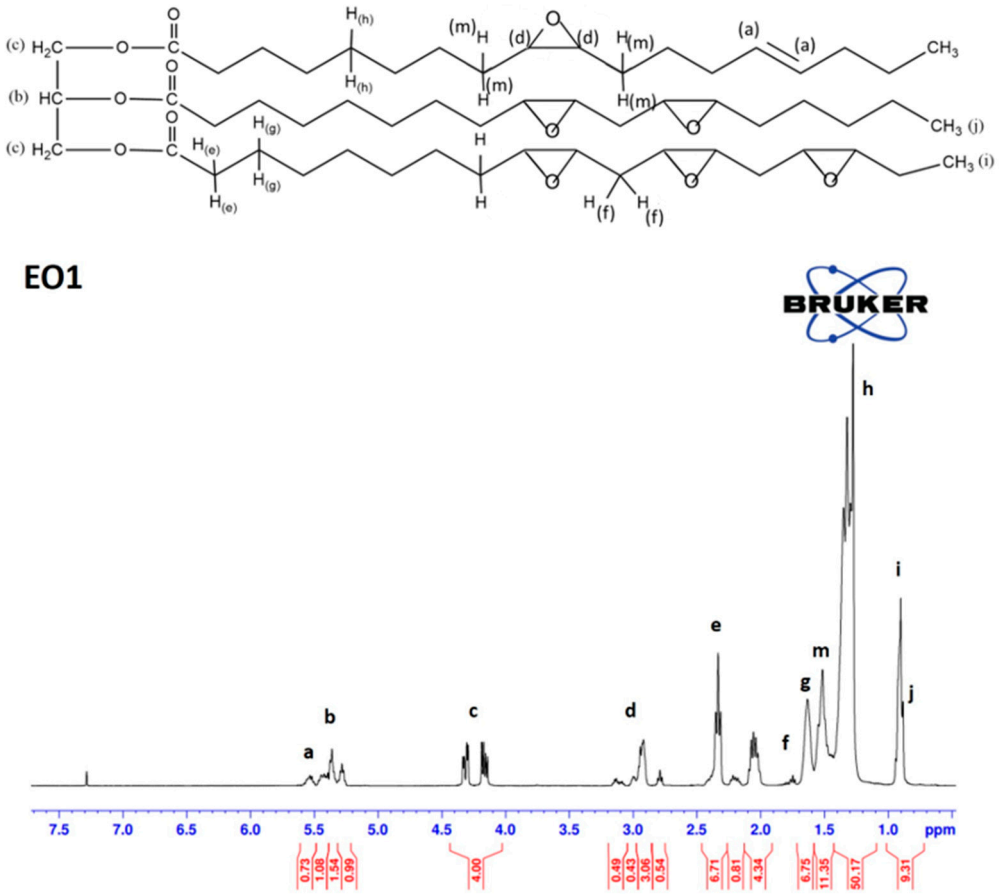


Figure 2. Chemical structure (top) and ^{1}H-NMR spectrum of EO1 (bottom).

Considering the normalized areas of the signals, the ^{1}H-NMR analysis allowed for the calculation of n_{EP}, the average number of residual double-bonded carbons, $n_{C=C,EO}$, and the molecular weight of EO, $M_{w,EO}$, by using a method reported in the literature [83]. Based on this method, n_{EP}, $n_{C=C,EO}$, and $M_{w,EO}$ were provided by Equations (2), (3), and (4), respectively.

$$n_{EP} = d/2 \quad (2)$$

$$n_{C=C,EO} = \frac{1}{2}\cdot(a + b - c/4) \quad (3)$$

$$M_{w,EO} = \frac{15.034}{3}\cdot(i + j) + \frac{14.026}{2}\cdot(d + e + f + g + h) + \frac{173.100}{4}\cdot(c) + 26.016\cdot n_{C=C,EO} + 42.037\cdot n_{EP} \quad (4)$$

where *a*-*j* are the normalized areas of the signals reported in Figure 2.

The ^{1}H-NMR was also performed on the POs to evaluate the presence of unreacted DEG.

2.4.2. Fourier-Transform Infrared Spectroscopy

All the samples (WCO, EOs, POs, and PUFs) were chemically characterized by FTIR spectroscopy. FTIR analysis was carried out in ATR mode by an Agilent Cary 630 FTIR Spectrometer (Agilent, US). Spectra were recorded in the wavenumber range of 4000–400 cm^{-1} at a scanning resolution of 4 cm^{-1}.

2.4.3. Gel Permeation Chromatography

Gel Permeation Chromatography (GPC) was used to determine the amount of unreacted DEG in the produced POs. Solutions at a concentration of 4 mg/mL were prepared by dissolving PO samples or DEG in THF. The analysis was conducted with a Jasco apparatus (Jasco Europe srl, Cremella, Italy) equipped with RI and UV detectors. The tests were performed using a Phenomenex column (Phenogel: 5 μm, pore size 10^4 Å, 300 × 7.8 mm^2, 100–5000 Da) at the following conditions: 50 μL of injected volume, THF rate of 1 mL/min, and 30 °C.

2.4.4. Morphological Analysis

A stereomicroscope Leica S9i (Leica microsystem, Wetzlar, Germany) was used to investigate the morphology of the produced bio-based foams. Additionally, the most performing PUFs were analyzed by a Scanning Electron Microscope (SEM) using a COXEM EM-30N SEM (COXEM Co., Ltd., Daejeo, Republic of Korea). The analysis was conducted on surfaces coated with a thin gold layer.

2.4.5. Density Measurement

The apparent density of the produced foams was measured according to ASTM D 1622. The size of the cylindrical specimen was 75 × 30 mm (length × diameter). The apparent densities of five specimens per sample were measured, and then the average values were reported.

2.4.6. Thermal Analysis

Thermal gravimetric analysis (TGA) was performed by an STA 2500 Regulus Netzsch (NETZSCH-Gerätebau GmbH, Selb, Germany). An alumina pan was filled with about 8 mg of PUF sample and heated from room temperature to 850 °C with a heating rate of 10 °C/min under nitrogen flow (20 mL/min). In addition, Differential Scanning Calorimetry (DSC) was used to examine the curing reaction and to obtain qualitative information on the glass transition temperatures of the samples. The analysis was carried out by a DSC 6000 Perkin Elmer Instrument (Waltham, MA, E.S.). About 4 mg of foam samples were subjected to a first run of heating from −40 to 120 °C followed by a cooling run from 120 to −40 °C and a second heating from −40 to 120 °C, with a heating/cooling rate of 10 °C/min under nitrogen flow of 20 mL/min.

2.4.7. Compression Tests

Compression tests were carried out according to ISO 844-A on cylindrical samples with a diameter of 25.4 mm and a height of 25.4 mm. Tests were performed using a Galdabini Quasar 10 (Galdabini, Varese, Italy). The compression strength was measured at a compression speed of 5 mm/min and a strain of 10%.

3. Results and Discussions

3.1. Characterization of EOs and POs

To semi-qualitatively estimate the epoxidation degree of EOs, their FTIR spectra were recorded and compared to the WCO ones. As can be seen in Figure 3, WCO showed two peaks at 3008 and 1651 cm^{-1}, related to the carbon–carbon double bonds. In the spectra of EOs, a reduction in the intensity of these peaks and a contemporary appearance of peaks at 840 and 820 cm^{-1}, ascribed to the C-O-C of the epoxy rings can be observed, thus confirming the conversion of C=C into oxirane rings. Based on the intensity of the peaks, the epoxidation degrees varied as follows: EO3 > EO2 > EO1.

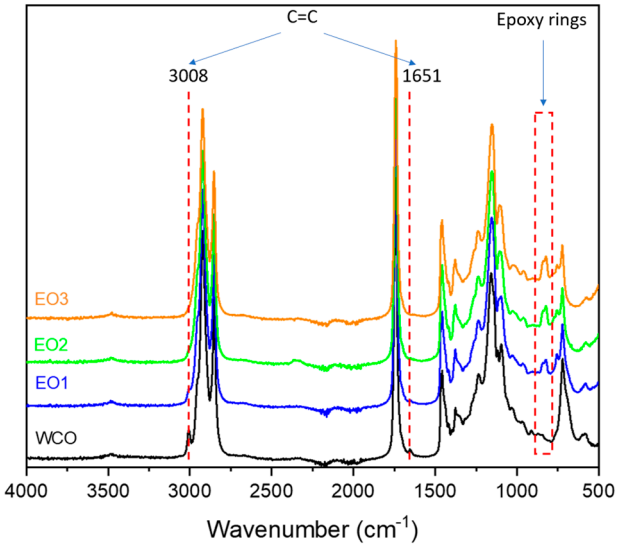


Figure 3. FTIR spectra of WCO and the synthesized EOs.

To calculate the epoxidation degree (*EP*) more accurately and the molecular weight of produced EOs, an ^{1}H-NMR analysis was conducted. The obtained values of $n_{C=C}$, n_{EP}, *EP*, and M_w of EOs samples are reported in Table 2. As shown, three EOs were synthetized by converting 54, 79, and 88% of unsaturated bonds of starting WCO to epoxy rings.

Table 2. Double-bonded content ($n_{C=C}$), epoxy rings content (n_{EP}), epoxidation degree (*EP*), and molecular weight (M_w) of WCO and EOs.

Sample	$n_{C=C}$ (mol/mol)	n_{EP} (mol/mol)	EP (%)	M_w (g/mol)
WCO	3.67	-	-	882.0
EO1	1.66	1.99	54	906.9
EO2	0.77	2.90	79	922.1
EO3	0.40	3.24	88	932.7

These data were used to properly dose the reagents for the synthesis of the corresponding polyols PO1, PO2, and PO3.

As can be observed in Figure 4, FTIR spectra of POs showed a broad peak at 3460–3470 cm^{-1} related to the presence of OH groups in the chemical structure of the samples. As expected, PO3 showed the highest content of OH due to the highest epoxidation degree of the corresponding epoxidized oil, EO3. Moreover, it can be observed that there was a disappearance of the peaks at 840 and 821 cm^{-1}, thus suggesting a complete reaction of the oxirane rings.

However, FITR was not sufficient to quantify the hydroxyl number of POs. Therefore, POs were subjected to ^{1}H-NMR analysis. The same analysis was also carried out on DEG. As can be observed in Figure 5, the analysis of POs confirmed the complete reaction of oxirane rings, indicated by the absence of signals at 3.0 ppm. Moreover, the appearance of signals in the range of 3.5–4.0 ppm revealed the presence of DEG molecules in the samples. Unfortunately, the signal of the proton of the OH group is strongly affected by many factors, such as the solvent and the sample concentration; so, it was not possible to calculate the hydroxyl number directly from the ^{1}H-NMR analysis. Nevertheless, the OH number could be estimated considering the epoxidation degree of the starting EO and the quantity of DEG in the final product.

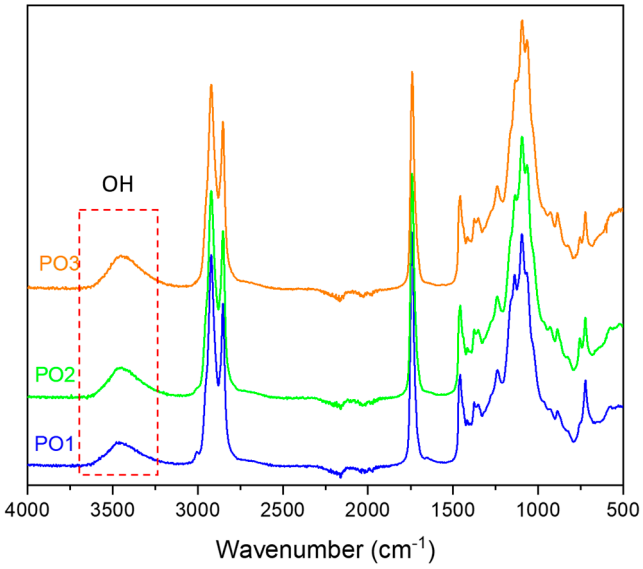


Figure 4. FTIR spectra of the produced POs.

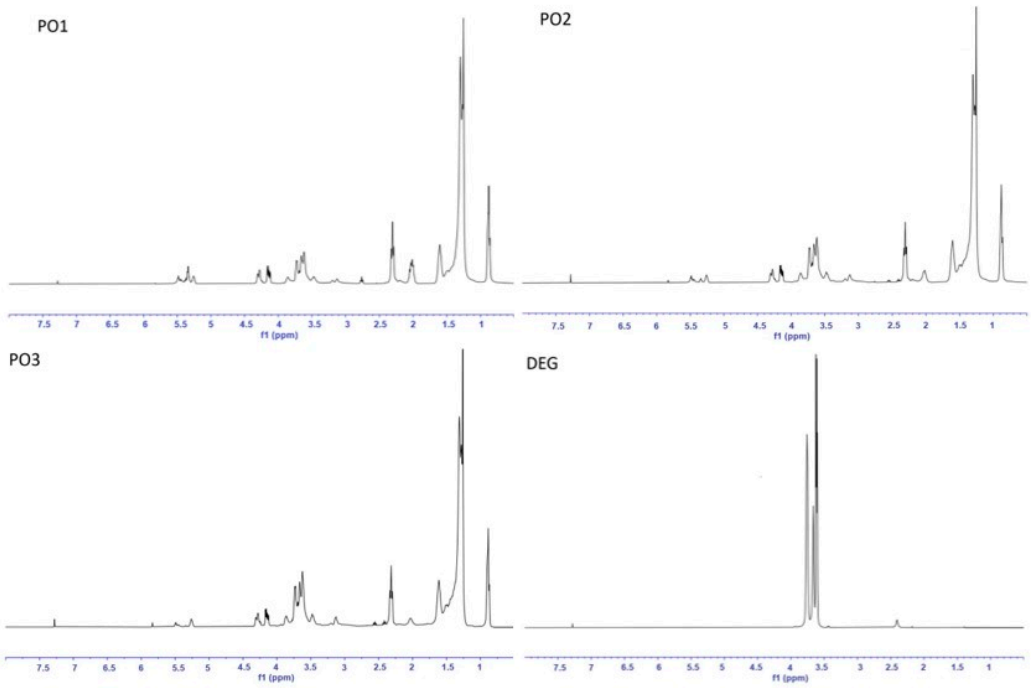


Figure 5. ^{1}H-NMR spectra of the produced POs and DEG.

To quantify the unreacted DEG molecules that remained in the products after the POs synthesis reaction, GPC analysis was also carried out on POs. As shown in Figure 6, all the molecules of the PO samples showed a retention time in the range of 6.5–9.5 min and no peaks were present in the range of DEG molecules (10.5 min), thus indicating that no unreacted molecules of DEG remained in the final product recovered at the end of the PO synthesis.

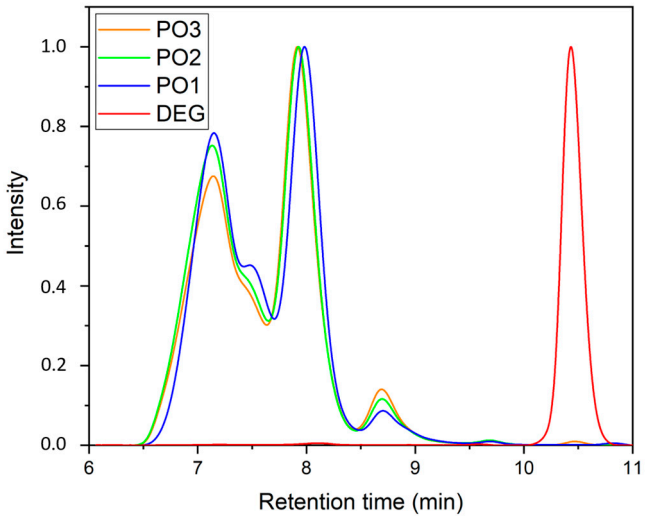


Figure 6. GPC chromatograms of the produced POs and DEG.

Considering the complete reaction of epoxy rings, suggested by ^{1}H-NMR analysis, and the absence of molecules of unreacted DEG, indicated by GPC results, it can be supposed that 1 mol of DEG was added to each mol of oxirane rings of EO.

Based on these results, the molecular weight, $M_{w,PO}$, and the hydroxyl number, expressed as *mol OH per mol of polyol* (n_{OH}), *mol OH per grams of polyol* (OH_v), and *mg of KOH per grams of polyol* (OH'_v), of POs were calculated by Equations (5), (6), (7), and (8), respectively. The obtained values are reported in Table 3.

$$M_{w,PO} = M_{w,EO} + 106.2\ g/mol \cdot n_{DEG} \quad (5)$$

$$n_{OH} = 2n_{DEG} = 2n_{EP} \quad (6)$$

$$OH_v = n_{OH}/M_{w,PO} \quad (7)$$

$$OH'_v = 56100 \cdot OH_v \quad (8)$$

Table 3. Molecular weight (M_w) and hydroxyl number of POs.

Sample	M_w (g/mol)	n_{OH} (mol OH/mol)	OH_v (mol OH/g)	OH'_v (mg KOH/g)
PO1	1113	3.98	3.58×10^{-3}	200.7
PO2	1224	5.80	4.75×10^{-3}	266.2
PO3	1266	6.48	5.13×10^{-3}	287.6

3.2. Foam Characterization

3.2.1. Morphological Analysis

All the PUFs synthesized in this study were rigid types Figure 7 reports the microscopic images of some PUFs produced without the gelling catalyst, using PO1, PO2, or PO3 as polyols. As is well known, cell morphology strictly depends on the balance between the blowing and the gelling rates [88]. PUF-1, PUF-2, and PUF-3 showed the typical structure formed when the blowing occurs faster than the gelling. In this case, gas bubbles expanded rapidly, causing breaks in the cell walls and resulting in large and coarse open cells [88]. Among the three foams, PUF-1 displayed cells with the biggest dimension. This can be related to the lower hydroxyl number of PO1. In fact, one of the factors that influence the balance between blowing and gelling is the hydroxyl number of the polyol. Polyols with lower functionalities require a higher conversion to reach the gel point.

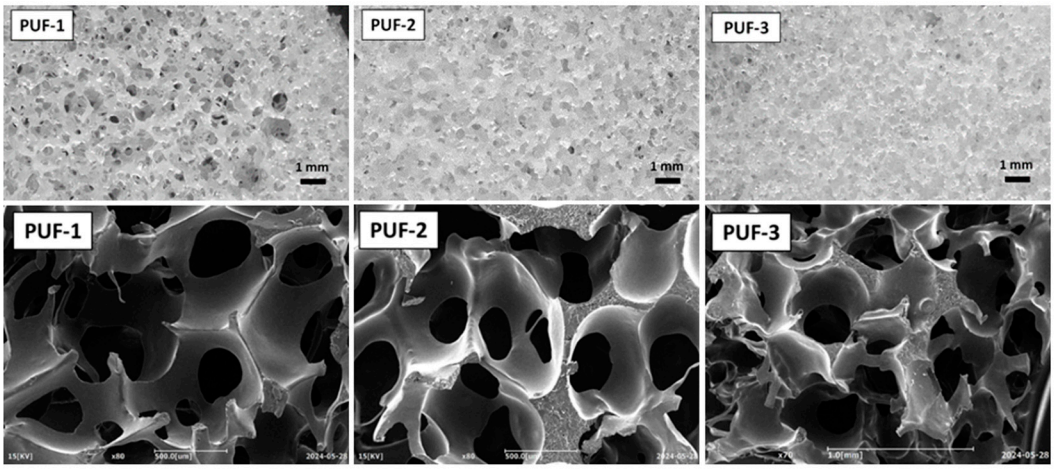


Figure 7. Stereomicroscopic (top) and SEM (bottom) images of PUFs prepared using PO1 (PUF-1), PO2 (PUF-2), and PO3 (PUF-3) as polyol.

To increase the gelling rate, a gelling catalyst (Kosmos 19) was added to the formulation PUF-3, based on PO3. Specifically, PUF-4 and PUF-5 were prepared by adding 1 and 2 php of gelling catalyst, respectively. The stereomicroscopic and SEM images of PUF-4 and PUF-5 are reported in Figure 8. Compared to PUF-3, PUF-4 and PUF-5 showed a quite homogeneous closed-cell structure, indicating a good blowing/gelling balance. As can be observed, 1 php of gelling catalyst was enough to reach an equilibrium between blowing and gelling, thus producing fine cells with a diameter of up to approximately 500 μm. For this reason, 1 php was selected as the suitable quantity of gelling catalyst for the production of PUFs based on PO3 using different amounts of water, 8 php for PUF-6 and 4 php for PUF-7, to investigate the effect of the quantity of the blowing agent.

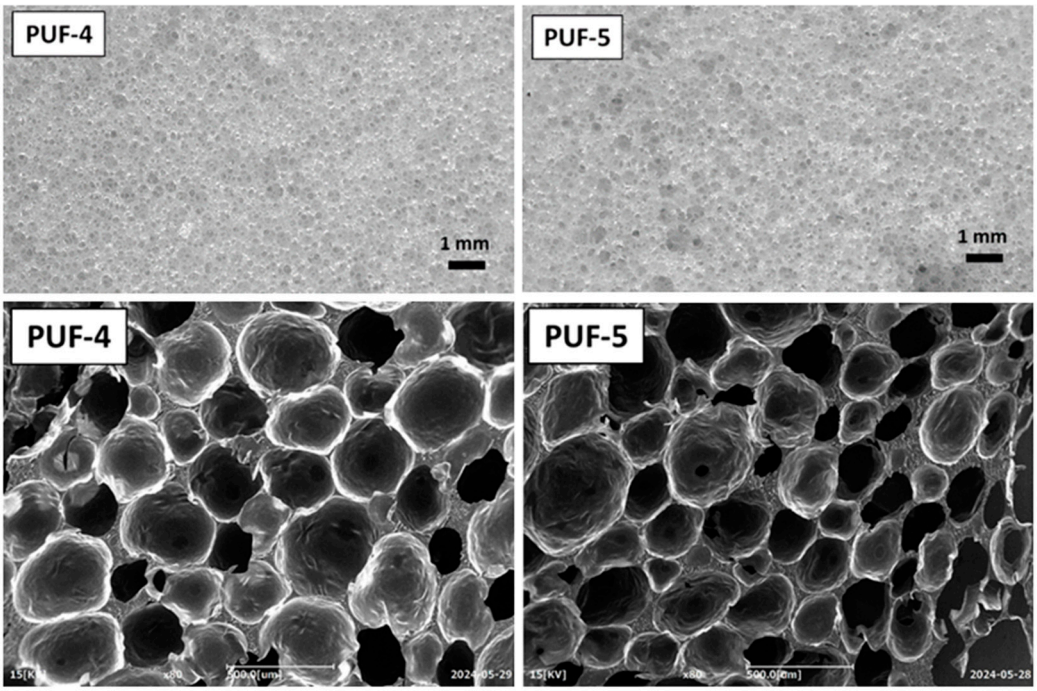


Figure 8. Stereomicroscopic (top) and SEM (bottom) images of PUFs prepared using PO3 as the polyol and 1 php (PUF-4) or 2 php (PUF-5) of gelling catalyst.

As expected, lowering the amount of water resulted in foams with finer cells and thicker struts, as can be seen in the microscopic images of PUF-6 and PUF-7, reported in

Figure 9. This is because the decreased CO2 production during the blowing reaction led to the formation of smaller bubbles within the matrix.

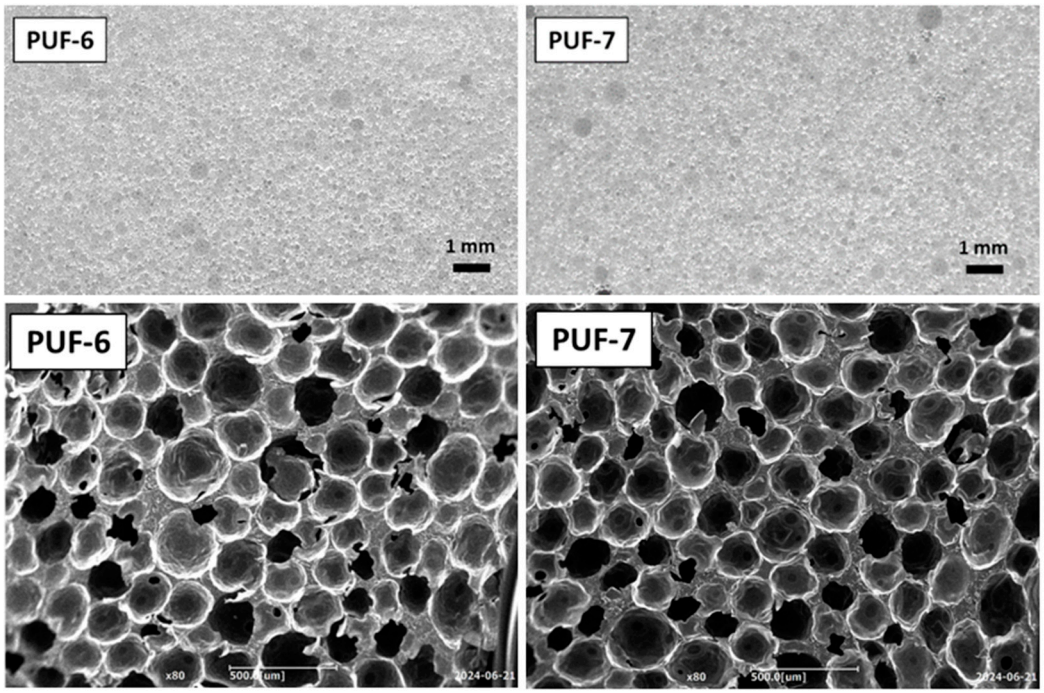


Figure 9. Stereomicroscopic (top) and SEM (bottom) images of PUFs produced using 8 php (PUF-6) and 4 php (PUF-7) of water.

As expected, larger cells with thinner walls were obtained using the same formu-lation of PUF-4 but reducing the amount loaded in the mould by 40 (PUF-9) and 60% (PUF-10) compared to PUF-4 (Figure 10). It is important to remember that the foams were produced in a closed mold, thus limiting the rise of the foam while still allowing the escape of gas.

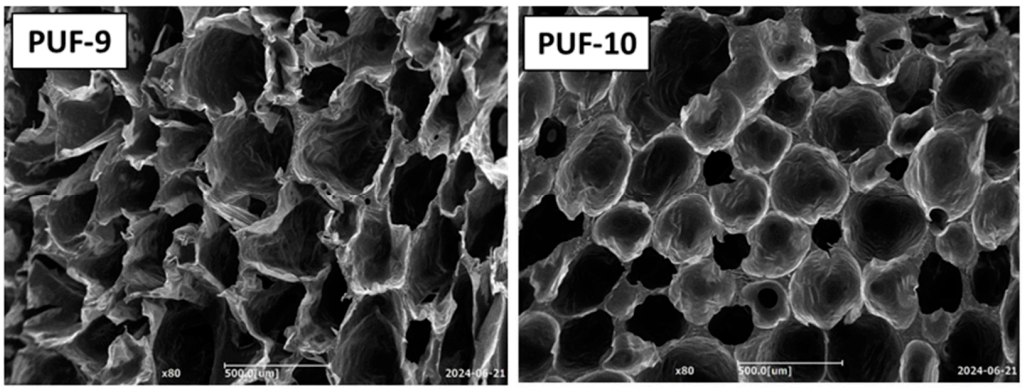


Figure 10. SEM (right) images of PUF-9 and PUF-10.

Finally, to study the reactivity of the epoxy ring in the PUF formulation, Figure 11 reports microscopic images of the foams produced using EO3 in place of PO3. PUF-8 exhibited large cells with broken walls, similar to the cellular structure of the foams prepared without the gelling catalyst (Figure 7) indicating a balance in favour of the blowing. In addition, PUF-8 showed larger cells (up to 1–1.5 mm in diameter) and struts with greater thickness compared to PUF-4, as shown in Figure 12. This can be related to the lower reactivity of the epoxy rings than OH groups leading to a slower gelling reaction with a coalescence of cells [89]. Nevertheless, it is worth noting that the epoxidized oil reacted with the other components of the mixture leading to a solid cellular structure. This

was an interesting finding because indicated that oxirane rings present in the chemical structure of the polyol can participate in the foaming process.

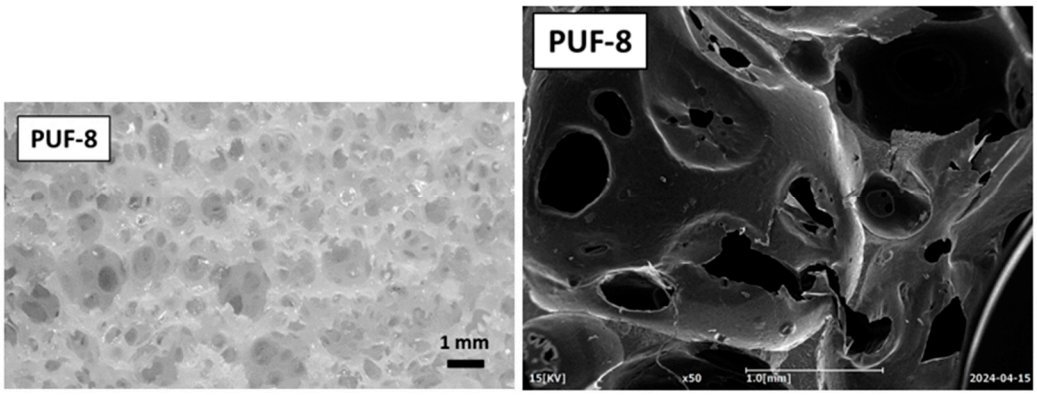


Figure 11. Stereomicroscopic (top) and SEM (bottom) images of PUF prepared using EO3 as the polyol (PUF-8).

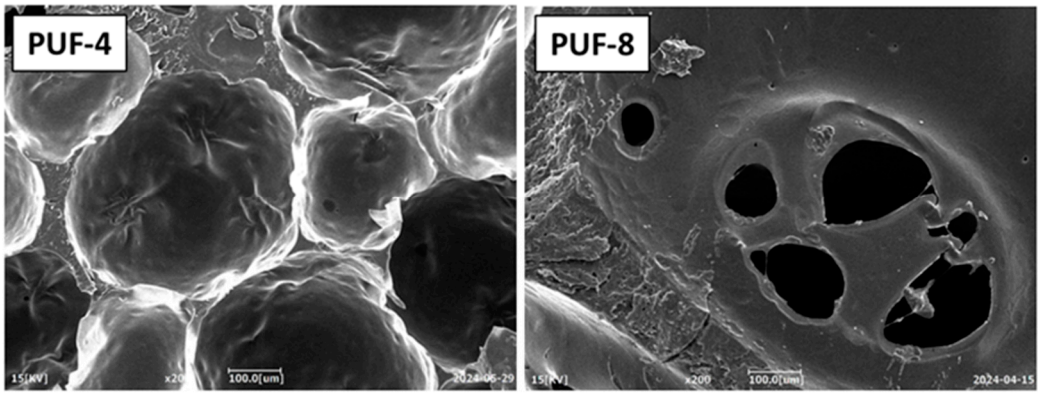


Figure 12. SEM images of PUF-4 and PUF-8 at 200× magnification.

3.2.2. Density Measurement

The produced bio-based foams showed a density in the range of 179–297 kg/m^3 (Table 4). It is worth noting that PUFs containing PO1 and PO2 showed lower expansions compared to PO3, leading to higher apparent densities. As an example, PUF-2 did not fill the mold during the foaming process and showed the highest density (297.2 kg/m^3). This can be related to the slower gelling rate due to the lower OH number, as better explained above. Moreover, the greater content of unmodified oily chains in the polyols derived from epoxidized oil with lower epoxidation degrees probably also reduced the miscibility between POs and the other components of the mixture. For this reason, PO3 was selected as the suitable polyol to produce the bio-based PUFs.

As expected, lowering the blowing agent increased the density of the produced foams obtaining 297 and 301 kg/m^3 when 8 and 4 php were used, respectively. The higher density was due to the lower quantity of CO_2 produced during the blowing reaction.

Nevertheless, some applications require inferior density. Therefore, PUF-9 and PUF-10 were produced using the same formulation of PUF-4 but by pouring into the closed mold about 40 and 60% by weight of the mixture, respectively. PUF-10 showed a density of 145.2 kg/m^3. In contrast, 40% by weight (PUF-9) was not enough to fill the mold and obtain a homogenous foam; thus, the density was not measured.

A lower density was also shown by the foam containing the epoxidized oil (PUF-8). This result suggested that PUFs can be produced using EO, even if the reactivity of the oxirane ring is lower than that of hydroxyl groups.

Table 4. Density of the bio-based PUFs measured at 25 °C.

Sample	Polyol	Density (kg/m^{-3})
PUF-1	PO1	207.5
PUF-2	PO2	297.2
PUF-3	PO3	179.3
PUF-4	PO3	230.0
PUF-5	PO3	179.6
PUF-6	PO3	296.7
PUF-7	PO3	300.8
PUF-8	EO3	184.1
PUF-9	PO3	n.d.
PUF-10	PO3	145.2

3.2.3. FTIR Analysis

The FTIR spectra of the produced foams were analyzed to study the success of the polyaddition reaction between polyol and isocyanate, highlighted by the appearance of urethane bonds. However, when water is used as the blowing agent, the chemical structure of the foams also includes urea bonds deriving from the reaction between NCO and water. Figure 13 reports the FTIR spectra of PUFs produced using the three POs with 15 php of water. As can be seen, in addition to the characteristic bands due to the asymmetric and symmetric vibrations of CH and CH_2 (3000–2800 cm^{-1}) present in the aliphatic chains of both polyol and isocyanate components, FTIR spectra showed three peaks at 3350, 1543, and 760 cm^{-1} related to the stretching, in-plane bending, and wagging of N-H, respectively, and a signal at 1241 cm^{-1} due to the C-N stretching [89–91]. A multiplet in the range 1630–1780 cm^{-1} can also be observed, which is the carbonyl stretching region. These signals can be ascribed to the C=O bonds present in the urethane and urea groups, as well as in the carbonyl groups of the PO chemical structure. In these systems, carbonyls can be hydrogen-bonded or non-hydrogen-bonded ("free") [92]. As reported in the literature, the carbonyl bonds in the urea groups vibrate at 1619–1686 cm^{-1} and 1690–1702 cm^{-1} if linked by hydrogen bonds or unbonded, respectively [91]. Analogously, peaks at 1705–1727 and 1736–1760 cm^{-1} can be attributed to C=O in the urethane groups hydrogen-bonded and unbonded, respectively [91]. As can be noted, the dominating peak is located at 1677 cm^{-1} and can be associated with the overlapping of the signals of the C=O in the triglyceride of the polyol and the urea groups. Moreover, the intensity of the shoulder at 1636 cm^{-1} is greater than that of the ones at 1714 and 1740 cm^{-1}, suggesting that carbonyls are mainly present in the urea groups. This result is not surprising given that the water reacted with approximately 70–75% of the NCO groups of the isocyanate. Additionally, this is in agreement with what was reported in the literature on rigid polyurethane foams produced by using water as the blowing agent [91,93].

These results confirmed that the polyurethane reaction occurred between the NCO functionality of the isocyanate and the hydroxyl groups of the polyol and additives. Nevertheless, the presence of a weak peak at 2270 cm^{-1} associated with NCO groups indicated a non-complete reaction. This agrees with the DSC results reported below. This could be related to the lower reactivity of secondary hydroxyl groups compared to primary ones.

To evaluate the effect of water, a comparison of the spectra of PUF-4, PUF-6, and PUF-7 is reported in Figure 14. As can be noted, a lower quantity of water led to a reduction in the intensity of the signals ascribed to urea bonds (1677 and 1636 cm^{-1}) and an increase in the bands at 1740 and 1714 cm^{-1} related to urethane bonds. Thus, the lower the quantity of water as a blowing agent, the higher the urethane/urea bonds' ratio [91,93].

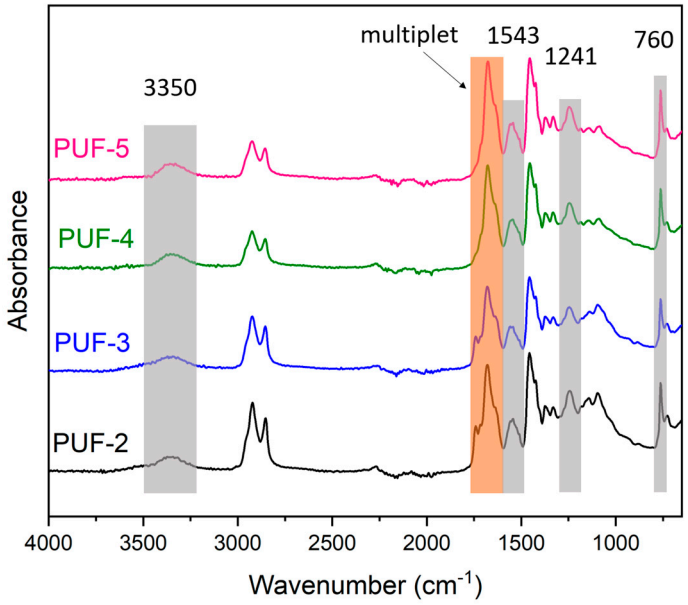


Figure 13. FTIR spectra of PUFs synthesized using PO3 with 15 php of water.

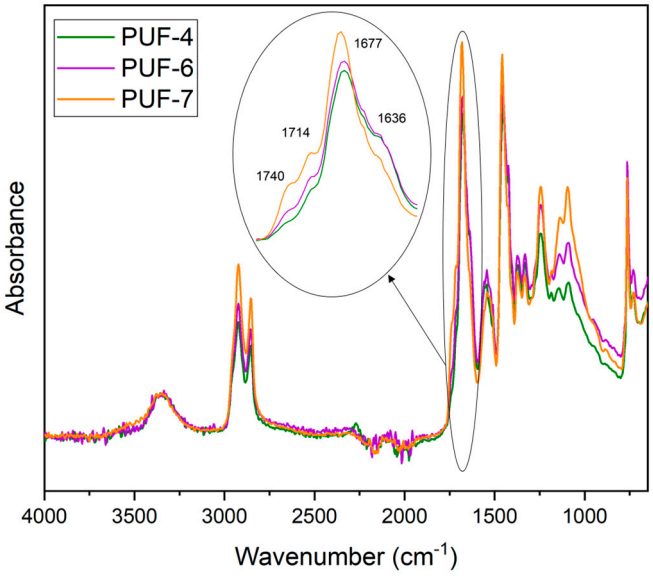


Figure 14. FTIR spectra of PUFs synthesized using PO3 with different amounts of water: 4 php (PUF-7); 8 php (PUF-6) and 15 php (PUF-4).

As previously mentioned, in this study, the chemical behavior of epoxy rings in the formulation of polyurethane foams was analyzed. Figure 15 reports the FTIR spectra of PUF-3 and PUF-8, produced using PO3 and EO3, respectively, and the same additives. Notably, the spectra were almost superimposed, indicating that PUF-8 exhibited absorption bands associated with N-H, C-N, and C=O bonds. The differences observed were due to the presence of diethylene glycol molecules in the chemical structure of PO3, with peaks at 1100 cm^{-1} attributed to C-O-C ether bonds. This suggested that PUFs can be potentially produced using directly epoxidized oil in place of polyol in the PUF formulation. This implies that the second step of polyol synthesis, the ring-opening step, could be bypassed, leading to substantial cost and time savings, lower carbon footprint, and improved sustainability.

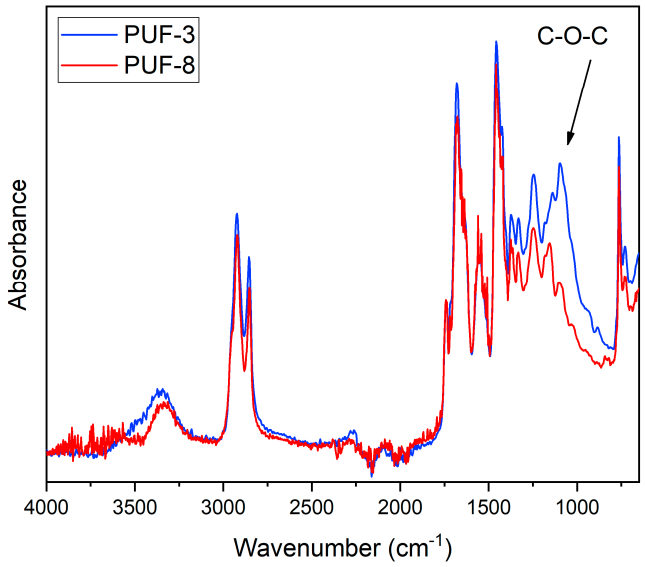


Figure 15. Comparison of FTIR spectra of PUFs synthesized using PO3 (PUF-3) and EO3 (PUF-8).

3.2.4. Thermal Analysis

Table 5 and Figure 16 report the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves and the thermal stability properties of the synthesized foams, respectively. All the PUFs showed thermal stability up to 200 °C, as shown by T_{onset}, with an initial very small mass loss, between 50 and 120 °C, ascribed to the evaporation of residual moisture, and the release of unreacted isocyanate and/or polyols and other volatile additives. Then, three major thermal decomposition patterns were displayed. The thermal event that occurred in the range of 200–290 °C can be attributed to the removal of the hard segment and the cleavage of urethane bonds [25,94–96]. According to this, PUFs containing a higher urethane bond content showed lower degradation temperatures ($T_{5\%}$). The main weight loss was displayed from 300 to 500 °C and exhibited two peaks at 375 and 440 °C. This event was due to the overlapping of the degradation of the soft segments in the foams and the aliphatic chains of both isocyanate and polyol. The slight differences in the DTG curves can be related to the different proportions of polyol and isocyanate in the formulations.

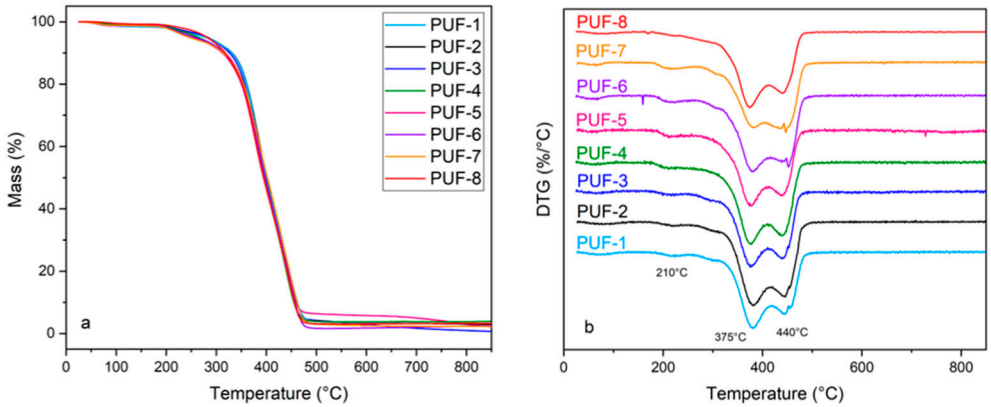


Figure 16. TG (**a**) and DTG (**b**) curves recorded under nitrogen at 10 °C/min of the synthesized PUFs.

Table 5. Thermal stability properties for bio-based PUFs.

Sample	Water (php)	T_{onset} (°C)	$T_{5\%}$ (°C)
PUF-1	15	201.2	279.2
PUF-2	15	199.6	280.2
PUF-3	15	214.2	283.2
PUF-4	15	211.1	263.7
PUF-5	15	207.7	253.2
PUF-6	8	204.2	255.7
PUF-7	4	199.2	246.2
PUF-8	15	229.6	281.7

At the end of the cure, all the foams appeared sticky with a slight smell of oil, suggesting that some oil-derived molecules were still present in the final product. Therefore, DSC analysis was performed on the foams to examine the completion of the cross-linking reactions. Figure 17 reports the DSC curves of PFUs from PO3 related to the first heating (I Run), the second heating, and the cooling runs. As shown, all the PUFs exhibited an endothermic peak during the first heating, which disappeared in the second one, confirming that the cross-linking reactions were not complete, as supported by the FTIR results. Repeating the analysis over extended curing times at room temperature did not result in a finalized reaction. Thus, curing at around 60 °C is necessary to accomplish the curing reactions. Unlike the other foams, PUF-8 showed a peak at low temperatures in the second heating run, which also appeared in the cooling curve, indicating the presence of unreacted EO3 molecules in the final product. This result suggested that even if EO3 can be potentially used in the PUF preparation, the formulation should be optimized in this case due to the lower reactivity of the epoxy rings compared to OH groups.

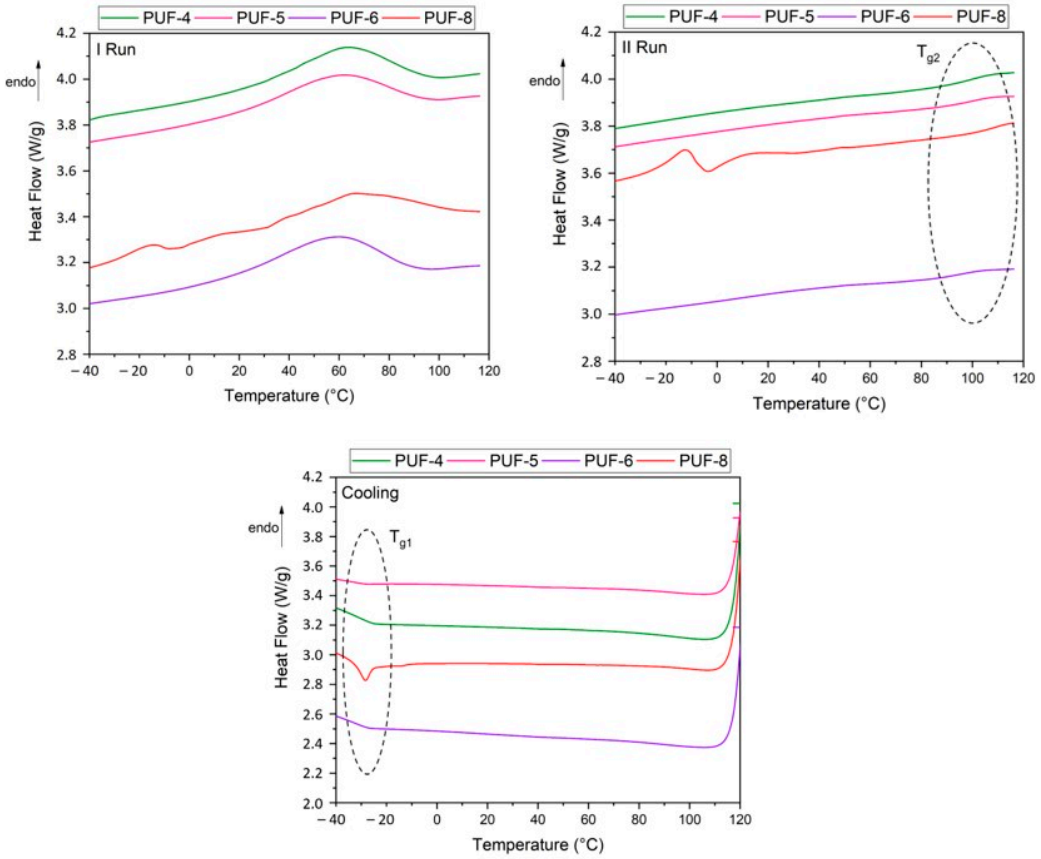


Figure 17. DSC thermograms of the first heating (I Run), second (II Run) heating, and cooling runs.

DSC analysis also provided qualitative insights into the glass transition temperatures. Typically, polyurethanes exhibit two glass transition temperatures, related to the soft and hard segments of their structure [97]. Consistent with reports in the literature, the PUFs produced showed two glass transition temperatures: T_{g1}, ranging from −28 to −25 °C [98]; and T_{g2}, ranging from 96 to 110 °C. T_{g1} is associated with the motion of the soft domains consisting of the aliphatic chains of the polyol and isocyanate, and it remained unaffected by the ratio of these components in the mixture. In contrast, T_{g2} showed a greater variation. Specifically, PUF-6 displayed a lower T_{g2} (compared to PUF-4 and PUF-5, suggesting that a higher concentration of urethane bonds enhances the mobility of the hard-segment molecules.

3.2.5. Compression Tests

Compression strength measured at a strain of 10% and Young's modulus are reported in Table 6. PUFs showed compression strength ranging from 0.586 to 1.09 MPa. Compression properties are usually correlated with density. The higher the density, the greater the compression strength and the Young's modulus values. Nevertheless, compression strength is influenced by polyol functionality, foam density, and cell size and cell walls. Thus, to better correlate PUF compression strength with these parameters, specific compression strength, defined as the ratio of compression strength to density, was considered [99]. Figure 18 presents the calculated values of specific compression strength. According to the literature, polyol with a higher hydroxyl number (PO3) led to foam with higher specific compression strength due to the increased cross-linking density. An increase in this mechanical property was also observed when the gelling agent was used and smaller cell sizes were displayed. Furthermore, it is interesting to note that specific compression strength tends to decrease when a lower quantity of water is employed. This can be attributed to a decrease in urea bonds and a corresponding increase in urethane linkage content, leading to a less rigid structure.

Analyzing the mechanical properties of PUFs derived from similar polyols reported in the literature, PUFs produced in the present study showed comparable values to foams with a density of around 70–80 kg/m^3. These values were quite lower than those reported by Kirplusk et al. (1.97–2.72 MPa) for rigid PUFs with a density of 200 kg/m^3 [93]. This can be related to the chemical structure of the isocyanate employed in the formulation. Mostly, aromatic isocyanates are employed for rigid PUF production because aromatic rings confer rigidity to the hard segments. In this study, an aliphatic partially bio-based isocyanate was selected to improve the material sustainability and reduce the environmental impact of the process. Nevertheless, mechanical properties could be improved by adding fillers, as reported by Zhang et al. [100]. In this work, the authors prepared rigid bio-based polyurethane foams with enhanced compressive strength using coconut-palm-derived polyol and coconut shells, coconut palm, and seaweed as fillers to achieve a low carbon footprint and high sustainability. The compression strength increased from 140 to 284, 290, and 288 kPa when 5% of seaweed, 15% of coconut shells, and 10% of coconut palm were added, respectively.

Table 6. Compression properties of the bio-based PUFs.

Sample	Polyol	Density (kg/m^{-3})	Young's Modulus (MPa)	Compression Strength (MPa)
PUF-1	PO1	207.5	8.59	0.586
PUF-2	PO2	297.2	9.42	0.873
PUF-3	PO3	179.3	12.38	0.723
PUF-4	PO3	230.0	13.77	0.980
PUF-5	PO3	179.6	9.36	0.782
PUF-6	PO3	296.7	10.83	1.091
PUF-7	PO3	300.8	12.98	0.908

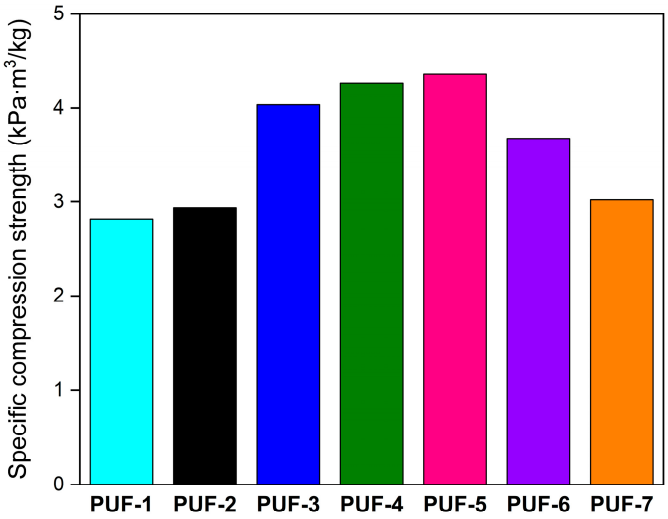


Figure 18. Specific compression strength of bio-based PUFs.

4. Conclusions

Rigid closed-cell polyurethane foams were produced using polyols derived exclusively from waste cooking oil through heterogeneously catalyzed epoxidation followed by oxirane ring-opening with DEG. Epoxidized oils, EOs, with different epoxidation degrees (from 54 to 88%), were synthesized, resulting in POs with hydroxyl numbers ranging from 200 to 288 mg KOH/g. The combined use of 100% bio-based POs with a commercial partially bio-based isocyanate (bio-based carbon 68%) and water as a green chemical agent enabled rigid PUFs at medium–high density (145–300 kg·m^{-3}) with a bio-based content of 73–77 wt.%.

Morphological analysis showed that polyols with a lower hydroxyl content (PO1 and PO2) led to us obtaining foams with larger and coarse open cells compared to those with higher OH content (PO3), indicating lower gelling rates. At least 1 php of gelling catalyst was necessary to reach the right equilibrium of gelling/blowing to achieve the closed-cell structure typical of the rigid foams. By reducing the amount of water, from 15 to 4 php, foams with smaller closed-cell sizes and a higher density were obtained. FTIR analysis confirmed the reaction between the OH and NCO functionalities, forming urethane linkages. Urea bonds were also present in the produced PUFs, derived by the reaction of water and NCO during the blowing reaction. TGA analysis showed that all the foams are thermally stable up to 200 °C. PUFs showed compression strength ranging from 0.59 to 1.1 MPa. As the urethane linkage content increased, the mechanical properties decreased due to the lower rigidity of urethane bonds compared to urea ones. Nevertheless, new sustainable rigid PUFs with enhanced mechanical properties could be improved by adding fillers derived from biomass wastes.

PUFs were also produced by replacing POs with EO3 in the formulation to study the chemical behavior of epoxy rings with isocyanate and additives. Morphological analysis revealed that EOs led us to obtaining rigid foams with a similar chemical structure and thermal behavior to those produced with POs but with larger and coarse open cells, suggesting a balance in favor of blowing. This finding indicated that oxirane rings can react with isocyanate functionalities and other components of the foaming mixture. However, due to the lower reactivity of epoxy rings compared to hydroxyl groups, unreacted EO3 molecules were still present in the final product. Therefore, the operating conditions and the formulations should be optimized in this case to ensure complete cross-linking reactions.

In conclusion, the synthesis of polyols from waste cooking oil presents a promising alternative to produce rigid polyurethane foams. This approach not only enhances the sustainability of foam production by utilizing renewable resources but also contributes to waste reduction, aligning with the principles of a circular economy. The bio-based polyurethane foams exhibit comparable physical and mechanical properties to traditional petroleum-based foams, making them a viable option for various industrial applications. In

addition to the applications planned for traditional PUFs, the rigid foams produced, with a bio-based content of up to 77%, could be incorporated into green building projects for insulating and sound-absorbing panels, thereby contributing to sustainability certifications and eco-friendly construction practices. By embracing these innovative materials, a more sustainable future in the polyurethane industry can be fostered, ultimately benefiting both the environment and the economy.

Author Contributions: Conceptualization, S.F., M.C. and M.S.; methodology, M.C. and S.F.; validation, M.C., I.A. and D.R.; formal analysis, M.C.; investigation, C.C., I.A. and M.C.; resources, I.A. and D.R.; data curation, M.C. and I.A.; writing—original draft preparation, M.C., D.R., I.A. and M.S.; writing—review and editing, P.C., S.F., G.P. and E.O.; visualization, M.C. and D.R.; supervision, M.S.; project administration, M.S.; funding acquisition, M.S. All authors have read and agreed to the published version of the manuscript.

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References

1. Polyurethane Global Market Volume 2015–2030. Available online: https://www.statista.com/statistics/720341/global-polyurethane-market-size-forecast/ (accessed on 9 October 2024).
2. Khatoon, H.; Iqbal, S.; Irfan, M.; Darda, A.; Rawat, N.K. A Review on the Production, Properties and Applications of Non-Isocyanate Polyurethane: A Greener Perspective. *Prog. Org. Coat.* **2021**, *154*, 106124. [CrossRef]
3. Werlinger, F.; Caballero, M.P.; Trofymchuk, O.S.; Flores, M.E.; Moreno-Villoslada, I.; Cruz-Martínez, F.D.L.; Castro-Osma, J.A.; Tejeda, J.; Martínez, J.; Lara-Sánchez, A. Turning Waste into Resources. Efficient Synthesis of Biopolyurethanes from Used Cooking Oils and CO2. *J. CO2 Util.* **2024**, *79*, 102659. [CrossRef]
4. Campana, F.; Brufani, G.; Mauriello, F.; Luque, R.; Vaccaro, L. Green Polyurethanes from Bio-Based Building Blocks: Recent Advances and Applications. *Green Synth. Catal.* **2024**, S2666554924000875. [CrossRef]
5. Delavarde, A.; Savin, G.; Derkenne, P.; Boursier, M.; Morales-Cerrada, R.; Nottelet, B.; Pinaud, J.; Caillol, S. Sustainable Polyurethanes: Toward New Cutting-Edge Opportunities. *Prog. Polym. Sci.* **2024**, *151*, 101805. [CrossRef]
6. Rayung, M.; Ghani, N.A.; Hasanudin, N. A Review on Vegetable Oil-Based Non Isocyanate Polyurethane: Towards a Greener and Sustainable Production Route. *RSC Adv.* **2024**, *14*, 9273–9299. [CrossRef] [PubMed]
7. Phung Hai, T.A.; Tessman, M.; Neelakantan, N.; Samoylov, A.A.; Ito, Y.; Rajput, B.S.; Pourahmady, N.; Burkart, M.D. Renewable Polyurethanes from Sustainable Biological Precursors. *Biomacromolecules* **2021**, *22*, 1770–1794. [CrossRef] [PubMed]
8. Huang, X.; De Hoop, C.F.; Xie, J.; Wu, Q.; Boldor, D.; Qi, J. High Bio-Content Polyurethane (PU) Foam Made from Bio-Polyol and Cellulose Nanocrystals (CNCs) via Microwave Liquefaction. *Mater. Des.* **2018**, *138*, 11–20. [CrossRef]
9. Szpiłyk, M.; Lubczak, R.; Walczak, M.; Lubczak, J. Polyol and Polyurethane Foam from Cellulose Hydrolysate. *J. Chem. Technol. Biotechnol.* **2021**, *96*, 881–889. [CrossRef]
10. Szpiłyk, M.; Lubczak, R.; Lubczak, J. The Biodegradable Cellulose-Derived Polyol and Polyurethane Foam. *Polym. Test.* **2021**, *100*, 107250. [CrossRef]
11. Prociak, A.; Rojek, P.; Pawlik, H. Flexible Polyurethane Foams Modified with Natural Oil Based Polyols. *J. Cell. Plast.* **2012**, *48*, 489–499. [CrossRef]
12. Kong, X.; Zhao, L.; Curtis, J.M. Polyurethane Nanocomposites Incorporating Biobased Polyols and Reinforced with a Low Fraction of Cellulose Nanocrystals. *Carbohydr. Polym.* **2016**, *152*, 487–495. [CrossRef] [PubMed]

13. Marcovich, N.E.; Kurańska, M.; Prociak, A.; Malewska, E.; Kulpa, K. Open Cell Semi-Rigid Polyurethane Foams Synthesized Using Palm Oil-Based Bio-Polyol. *Ind. Crops Prod.* **2017**, *102*, 88–96. [CrossRef]
14. Prociak, A.; Kurańska, M.; Cabulis, U.; Ryszkowska, J.; Leszczyńska, M.; Uram, K.; Kirpluks, M. Effect of Bio-Polyols with Different Chemical Structures on Foaming of Polyurethane Systems and Foam Properties. *Ind. Crops Prod.* **2018**, *120*, 262–270. [CrossRef]
15. Kurańska, M.; Polaczek, K.; Auguścik-Królikowska, M.; Prociak, A.; Ryszkowska, J. Open-Cell Rigid Polyurethane Bio-Foams Based on Modified Used Cooking Oil. *Polymer* **2020**, *190*, 122164. [CrossRef]
16. Kurańska, M.; Leszczyńska, M.; Kubacka, J.; Prociak, A.; Ryszkowska, J. Effects of Modified Used Cooking Oil on Structure and Properties of Closed-Cell Polyurethane Foams. *J. Polym. Env.* **2020**, *28*, 2780–2788. [CrossRef]
17. Prociak, A.; Kurańska, M.; Uram, K.; Wójtowicz, M. Bio-Polyurethane Foams Modified with a Mixture of Bio-Polyols of Different Chemical Structures. *Polymers* **2021**, *13*, 2469. [CrossRef] [PubMed]
18. Coman, A.E.; Peyrton, J.; Hubca, G.; Sarbu, A.; Gabor, A.R.; Nicolae, C.A.; Iordache, T.V.; Averous, L. Synthesis and Characterization of Renewable Polyurethane Foams Using Different Biobased Polyols from Olive Oil. *Eur. Polym. J.* **2021**, *149*, 110363. [CrossRef]
19. Polaczek, K.; Kurańska, M.; Prociak, A. Open-Cell Bio-Polyurethane Foams Based on Bio-Polyols from Used Cooking Oil. *J. Clean. Prod.* **2022**, *359*, 132107. [CrossRef]
20. Doke, R.B.; Paraskar, P.M.; Rajput, Y.N.; Kulkarni, R.D. Synthesis and Characterization of Green Polyurethane Coatings Derived from Niger-Seed-Oil-Based Polyesteramide Polyols. *Eur. J. Lipid Sci. Technol.* **2022**, *124*, 2100171. [CrossRef]
21. Vijayan, J.G.; Chandrashekar, A.; Ag, J.; Prabhu, T.N.; Kalappa, P. Polyurethane and Its Composites Derived from Bio-Sources: Synthesis, Characterization and Adsorption Studies. *Polym. Polym. Compos.* **2022**, *30*, 096739112211103. [CrossRef]
22. Xu, Q.; Lin, J.; Jiang, G. Synthesis, Characterization and Properties of Soybean Oil-Based Polyurethane. *Polymers* **2022**, *14*, 2201. [CrossRef] [PubMed]
23. Das, S.; Dave, M.; Wilkes, G.L. Characterization of Flexible Polyurethane Foams Based on Soybean-based Polyols. *J. Appl. Polym. Sci.* **2009**, *112*, 299–308. [CrossRef]
24. Chavarro Gomez, J.; Zakaria, R.; Aung, M.M.; Mokhtar, M.N.; Yunus, R.B. Characterization of Novel Rigid-Foam Polyurethanes from Residual Palm Oil and Algae Oil. *J. Mater. Res. Technol.* **2020**, *9*, 16303–16316. [CrossRef]
25. Asare, M.A.; De Souza, F.M.; Gupta, R.K. Waste to Resource: Synthesis of Polyurethanes from Waste Cooking Oil. *Ind. Eng. Chem. Res.* **2022**, *61*, 18400–18411. [CrossRef]
26. Kaikade, D.S.; Sabnis, A.S. Polyurethane Foams from Vegetable Oil-Based Polyols: A Review. *Polym. Bull.* **2023**, *80*, 2239–2261. [CrossRef] [PubMed]
27. Petrović, Z.S.; Wan, X.; Bilić, O.; Zlatanić, A.; Hong, J.; Javni, I.; Ionescu, M.; Milić, J.; Degruson, D. Polyols and Polyurethanes from Crude Algal Oil. *J. Am. Oil Chem. Soc.* **2013**, *90*, 1073–1078. [CrossRef]
28. Kumar, S.; Hablot, E.; Moscoso, J.L.G.; Obeid, W.; Hatcher, P.G.; DuQuette, B.M.; Graiver, D.; Narayan, R.; Balan, V. Polyurethanes Preparation Using Proteins Obtained from Microalgae. *J. Mater. Sci.* **2014**, *49*, 7824–7833. [CrossRef]
29. Patil, C.K.; Jirimali, H.D.; Paradeshi, J.S.; Chaudhari, B.L.; Alagi, P.K.; Hong, S.C.; Gite, V.V. Synthesis of Biobased Polyols Using Algae Oil for Multifunctional Polyurethane Coatings. *Green Mater.* **2018**, *6*, 165–177. [CrossRef]
30. Patil, C.K.; Jirimali, H.D.; Paradeshi, J.S.; Chaudhari, B.L.; Alagi, P.K.; Mahulikar, P.P.; Hong, S.C.; Gite, V.V. Chemical Transformation of Renewable Algae Oil to Polyetheramide Polyols for Polyurethane Coatings. *Prog. Org. Coat.* **2021**, *151*, 106084. [CrossRef]
31. Phung Hai, T.A.; Neelakantan, N.; Tessman, M.; Sherman, S.D.; Griffin, G.; Pomeroy, R.; Mayfield, S.P.; Burkart, M.D. Flexible Polyurethanes, Renewable Fuels, and Flavorings from a Microalgae Oil Waste Stream. *Green Chem.* **2020**, *22*, 3088–3094. [CrossRef]
32. Peyrton, J.; Chambaretaud, C.; Sarbu, A.; Avérous, L. Biobased Polyurethane Foams Based on New Polyol Architectures from Microalgae Oil. *ACS Sustain. Chem. Eng.* **2020**, *8*, 12187–12196. [CrossRef]
33. Ranjbar, S.; Malcata, F.X. Challenges and Prospects for Sustainable Microalga-Based Oil: A Comprehensive Review, with a Focus on Metabolic and Genetic Engineering. *Fuel* **2022**, *324*, 124567. [CrossRef]
34. Sawpan, M.A. Polyurethanes from Vegetable Oils and Applications: A Review. *J Polym. Res.* **2018**, *25*, 184. [CrossRef]
35. Cargill. BiOH Soy-Based Polyols and Polymers. Available online: https://www.cargill.com/bioindustrial/foams (accessed on 24 August 2024).
36. BASF. Sovermol, Natural-Oil Polyols. Available online: https://www.basf.com/us/en/products/General-Business-Topics/dispersions/Products/sovermol (accessed on 24 August 2024).
37. Macalino, A.; Salen, V.; Reyes, L. Castor Oil Based Polyurethanes: Synthesis and Characterization. *IOP Conf. Ser. Mater. Sci. Eng.* **2017**, *229*, 012016. [CrossRef]
38. Bresolin, D.; Valério, A.; De Oliveira, D.; Lenzi, M.K.; Sayer, C.; De Araújo, P.H.H. Polyurethane Foams Based on Biopolyols from Castor Oil and Glycerol. *J. Polym. Environ.* **2018**, *26*, 2467–2475. [CrossRef]
39. Saha, P.; Khomlaem, C.; Aloui, H.; Kim, B.S. Biodegradable Polyurethanes Based on Castor Oil and Poly (3-Hydroxybutyrate). *Polymers* **2021**, *13*, 1387. [CrossRef]
40. De Oliveira, B.P.; Balieiro, L.C.S.; Maia, L.S.; Zanini, N.C.; Teixeira, E.J.O.; Da Conceição, M.O.T.; Medeiros, S.F.; Mulinari, D.R. Eco-Friendly Polyurethane Foams Based on Castor Polyol Reinforced with Açaí Residues for Building Insulation. *J. Mater. Cycles Waste Manag.* **2022**, *24*, 553–568. [CrossRef]

41. Emeka-Chioke, E.A.; Orie, K.J.; Nsude, O.P.; Udeozo, P.I.; Onyia, S. Comparative Studies on the Physico-Mechanical Properties of Polyurethane Foams Derived from Bio-Based Polyols. *Asian Res. J. Curr. Sci.* **2024**, *6*, 13–22.
42. Carriço, C.; Fraga, T.; Carvalho, V.; Pasa, V. Polyurethane Foams for Thermal Insulation Uses Produced from Castor Oil and Crude Glycerol Biopolyols. *Molecules* **2017**, *22*, 1091. [CrossRef]
43. Kim, H.J.; Jin, X.; Choi, J.W. Investigation of Bio-Based Rigid Polyurethane Foams Synthesized with Lignin and Castor Oil. *Sci. Rep.* **2024**, *14*, 13490. [CrossRef]
44. Repecka Alves, L.; Miraveti Carriello, G.; Manassés Pegoraro, G.; Moraes, C.E.; De Lourdes Rezende, M.; De Menezes, A.J. Green Polyurethane Foams: Replacing Petrochemical Polyol with Castor Oil through Factorial Design. *J. Polym. Res.* **2024**, *31*, 227. [CrossRef]
45. Ionescu, M.; Radojčić, D.; Wan, X.; Shrestha, M.L.; Petrović, Z.S.; Upshaw, T.A. Highly Functional Polyols from Castor Oil for Rigid Polyurethanes. *Eur. Polym. J.* **2016**, *84*, 736–749. [CrossRef]
46. Lee, J.H.; Kim, S.H.; Oh, K.W. Bio-Based Polyurethane Foams with Castor Oil Based Multifunctional Polyols for Improved Compressive Properties. *Polymers* **2021**, *13*, 576. [CrossRef]
47. Su, Y.; Ma, S.; Wang, B.; Xu, X.; Feng, H.; Hu, K.; Zhang, W.; Zhou, S.; Weng, G.; Zhu, J. High-Performance Castor Oil-Based Polyurethane Thermosets: Facile Synthesis and Properties. *React. Funct. Polym.* **2023**, *183*, 105496. [CrossRef]
48. Hejna, A.; Kirpluks, M.; Kosmela, P.; Cabulis, U.; Haponiuk, J.; Piszczyk, Ł. The Influence of Crude Glycerol and Castor Oil-Based Polyol on the Structure and Performance of Rigid Polyurethane-Polyisocyanurate Foams. *Ind. Crops Prod.* **2017**, *95*, 113–125. [CrossRef]
49. Omrani, I. High Performance Biobased Pour-in-Place Rigid Polyurethane Foams from Facile Prepared Castor Oil-Based Polyol: Good Compatibility with Pentane Series Blowing Agent. *J. Cell. Plast.* **2022**, *58*, 449–466. [CrossRef]
50. Pinto, R.C.; Pereira, P.H.F.; Maia, L.S.; Silva, T.L.S.E.; Faria, M.I.S.D.; Rosa, D.S.; Mulinari, D.R. A Promising Use of Kimberlite Clay on Sustainable Polyurethane Foams. *Appl. Clay Sci.* **2024**, *258*, 107472. [CrossRef]
51. Desroches, M.; Escouvois, M.; Auvergne, R.; Caillol, S.; Boutevin, B. From Vegetable Oils to Polyurethanes: Synthetic Routes to Polyols and Main Industrial Products. *Polym. Rev.* **2012**, *52*, 38–79. [CrossRef]
52. Kurańska, M.; Benes, H.; Polaczek, K.; Trhlikova, O.; Walterova, Z.; Prociak, A. Effect of Homogeneous Catalysts on Ring Opening Reactions of Epoxidized Cooking Oils. *J. Clean. Prod.* **2019**, *230*, 162–169. [CrossRef]
53. Kurańska, M.; Prociak, A. The Influence of Rapeseed Oil-Based Polyols on the Foaming Process of Rigid Polyurethane Foams. *Ind. Crops Prod.* **2016**, *89*, 182–187. [CrossRef]
54. Zieleniewska, M.; Leszczyński, M.K.; Kurańska, M.; Prociak, A.; Szczepkowski, L.; Krzyżowska, M.; Ryszkowska, J. Preparation and Characterisation of Rigid Polyurethane Foams Using a Rapeseed Oil-Based Polyol. *Ind. Crops Prod.* **2015**, *74*, 887–897. [CrossRef]
55. Uram, K.; Prociak, A.; Kuranska, M. Influence of the Chemical Structure of Rapeseed Oil-Based Polyols on Selected Properties of Polyurethane Foams. *Polimery* **2020**, *65*, 698–707. [CrossRef]
56. Leszczyńska, M.; Malewska, E.; Ryszkowska, J.; Kurańska, M.; Gloc, M.; Leszczyński, M.K.; Prociak, A. Vegetable Fillers and Rapeseed Oil-Based Polyol as Natural Raw Materials for the Production of Rigid Polyurethane Foams. *Materials* **2021**, *14*, 1772. [CrossRef]
57. Kairytė, A.; Vaitkus, S.; Vėjelis, S.; Pundienė, I. A Study of Rapeseed Oil-Based Polyol Substitution with Bio-Based Products to Obtain Dimensionally and Structurally Stable Rigid Polyurethane Foam. *J. Polym. Env.* **2018**, *26*, 3834–3847. [CrossRef]
58. Soloi, S.; Majid, R.A.; Rahmat, A.R. Novel Palm Oil Based Polyols with Amide Functionality. *Int. J. Sci.* **2018**, *37*, 74–86.
59. Jin, Y.; Hu, X.; Wu, C.; Zong, R.; Liu, S.; Shentu, B. Influence of Palm Oil-Based Polyols on the Microstructure and Properties of Bio-Based Flexible Polyurethane Foams. *Biomass Conv. Bioref.* **2023**, *13*, 987–999. [CrossRef]
60. Lee, C.S.; Ooi, T.L.; Chuah, C.H.; Ahmad, S. Rigid Polyurethane Foam Production from Palm Oil-Based Epoxidized Diethanolamides. *J. Am. Oil Chem. Soc.* **2007**, *84*, 1161–1167. [CrossRef]
61. Tu, Y.; Suppes, G.J.; Hsieh, F. Water-blown Rigid and Flexible Polyurethane Foams Containing Epoxidized Soybean Oil Triglycerides. *J. Appl. Polym. Sci.* **2008**, *109*, 537–544. [CrossRef]
62. Yang, F.; Yu, H.; Deng, Y.; Xu, X. Synthesis and Characterization of Different Soybean Oil-Based Polyols with Fatty Alcohol and Aromatic Alcohol. *e-Polymers* **2021**, *21*, 491–499. [CrossRef]
63. Zhang, Y.; Zhang, W.; Deng, J.; Zhong, Y.; Zhao, P.; Li, H.; Zhang, T. Synthesis of Waste Soybean Oil-Based Waterborne Polyurethane for Exploration of Its Green and Various Application. *Ind. Crops Prod.* **2024**, *216*, 118733. [CrossRef]
64. Prociak, A. Heat-insulating properties of rigid polyurethane foams synthesized with use of vegetable oils—based polyols. *Polimery* **2008**, *53*, 195–200. [CrossRef]
65. Enderus, N.F.; Tahir, S.M. Green Waste Cooking Oil-Based Rigid Polyurethane Foam. *IOP Conf. Ser Mater. Sci. Eng.* **2017**, *271*, 012062. [CrossRef]
66. Cabulis, U.; Ivdre, A. Recent Developments in the Sustainability of the Production of Polyurethane Foams from Polyols Based on the First- to the Fourth-Generation of Biomass Feedstock. *Curr. Opin. Green Sustain. Chem.* **2023**, *44*, 100866. [CrossRef]
67. Malewska, E.; Kurańska, M.; Tenczyńska, M.; Prociak, A. Application of Modified Seed Oils of Selected Fruits in the Synthesis of Polyurethane Thermal Insulating Materials. *Materials* **2023**, *17*, 158. [CrossRef]

68. Qin, Z.-H.; Fridrihsone, A.; Mou, J.-H.; Pomilovskis, R.; Godina, D.; Miao, Y.; Liu, Z.; Tsang, C.-W.; Zhang, L.; Xu, C.; et al. Valorisation of Food Waste into Bio-Based Polyurethane Rigid Foams: From Experimental Investigation to Techno-Economic Analysis. *Chem. Eng. J.* **2024**, *493*, 152680. [CrossRef]
69. Vegetable Oils Consumption Worldwide. 2023/2024. Available online: https://www.statista.com/statistics/263937/vegetable-oils-global-consumption/ (accessed on 24 August 2024).
70. European Biomass Industry Association Used Cooking Oil. Available online: https://www.eubia.org/cms/wiki-biomass/biomass-resources/challenges-related-to-biomass/used-cooking-oil-recycling/ (accessed on 24 August 2024).
71. Lopresto, C.G.; De Paola, M.G.; Calabrò, V. Importance of the Properties, Collection, and Storage of Waste Cooking Oils to Produce High-Quality Biodiesel—An Overview. *Biomass Bioenergy* **2024**, *189*, 107363. [CrossRef]
72. Onn, M.; Jalil, M.J.; Mohd Yusoff, N.I.S.; Edward, E.B.; Wahit, M.U. A Comprehensive Review on Chemical Route to Convert Waste Cooking Oils to Renewable Polymeric Materials. *Ind. Crops Prod.* **2024**, *211*, 118194. [CrossRef]
73. Kuranska, M.; Polaczek, K.; Auguscik-Krolikowska, M.; Prociak, A.; Ryszkowska, J. Open-Cell Polyurethane Foams Based on Modified Used Cooking Oil. *Polimery* **2020**, *65*, 216–225. [CrossRef]
74. Kurańska, M.; Malewska, E. Waste Cooking Oil as Starting Resource to Produce Bio-Polyol—Analysis of Transesteryfication Process Using Gel Permeation Chromatography. *Ind. Crops Prod.* **2021**, *162*, 113294. [CrossRef]
75. Kurańska, M.; Malewska, E.; Polaczek, K.; Prociak, A.; Kubacka, J. A Pathway toward a New Era of Open-Cell Polyurethane Foams—Influence of Bio-Polyols Derived from Used Cooking Oil on Foams Properties. *Materials* **2020**, *13*, 5161. [CrossRef] [PubMed]
76. Zhang, C.; Kessler, M.R. Bio-Based Polyurethane Foam Made from Compatible Blends of Vegetable-Oil-Based Polyol and Petroleum-Based Polyol. *ACS Sustain. Chem. Eng.* **2015**, *3*, 743–749. [CrossRef]
77. Hu, Y.H.; Gao, Y.; Wang, D.N.; Hu, C.P.; Zu, S.; Vanoverloop, L.; Randall, D. Rigid Polyurethane Foam Prepared from a Rape Seed Oil Based Polyol. *J. Appl. Polym. Sci.* **2002**, *84*, 591–597. [CrossRef]
78. Fan, H.; Tekeei, A.; Suppes, G.J.; Hsieh, F. Rigid Polyurethane Foams Made from High Viscosity Soy-polyols. *J. Appl. Polym. Sci.* **2013**, *127*, 1623–1629. [CrossRef]
79. Kurańska, M.; Benes, H.; Kockova, O.; Kucała, M.; Malewska, E.; Schmidt, B.; Michałowski, S.; Zemła, M.; Prociak, A. Rebiopolyols—New Components for the Synthesis of Polyurethane Biofoams in Line with the Circular Economy Concept. *Chem. Eng. J.* **2024**, *490*, 151504. [CrossRef]
80. Polo, M.L.; Russell-White, K.; Vaillard, S.E.; Ríos, L.; Meira, G.R.; Estenoz, D.A.; Spontón, M.E. Bio-Based Polyester-Polyurethane Foams: Synthesis and Degradability by Aspergillus Niger and Aspergillus Clavatus. *Biodegradation* **2024**, *35*, 315–327. [CrossRef]
81. Tu, Y.; Kiatsimkul, P.; Suppes, G.; Hsieh, F. Physical Properties of Water-blown Rigid Polyurethane Foams from Vegetable Oil-based Polyols. *J Appl. Polym. Sci* **2007**, *105*, 453–459. [CrossRef]
82. Annisa, A.N.; Widayat, W. A Review of Bio-Lubricant Production from Vegetable Oils Using Esterification Transesterification Process. *MATEC Web Conf.* **2018**, *156*, 06007. [CrossRef]
83. Miyake, Y.; Yokomizo, K.; Matsuzaki, N. Rapid Determination of Iodine Value by 1H Nuclear Magnetic Resonance Spectroscopy. *J. Am. Oil Chem. Soc.* **1998**, *75*, 15–19. [CrossRef]
84. Cappello, M.; Strangis, G.; Cinelli, P.; Camodeca, C.; Filippi, S.; Polacco, G.; Seggiani, M. From Waste Vegetable Oil to a Green Compatibilizer for HDPE/PA6 Blends. *Polymers* **2023**, *15*, 4178. [CrossRef] [PubMed]
85. Kurańska, M.; Beneš, H.; Prociak, A.; Trhlíková, O.; Walterová, Z.; Stochlińska, W. Investigation of Epoxidation of Used Cooking Oils with Homogeneous and Heterogeneous Catalysts. *J. Clean. Prod.* **2019**, *236*, 117615. [CrossRef]
86. Zhang, J.; Tang, J.J.; Zhang, J.X. Polyols Prepared from Ring-Opening Epoxidized Soybean Oil by a Castor Oil-Based Fatty Diol. *Int. J. Polym. Sci.* **2015**, *2015*, 529235. [CrossRef]
87. Dai, H.; Yang, L.; Lin, B.; Wang, C.; Shi, G. Synthesis and Characterization of the Different Soy-Based Polyols by Ring Opening of Epoxidized Soybean Oil with Methanol, 1,2-Ethanediol and 1,2-Propanediol. *J. Am. Oil Chem. Soc.* **2009**, *86*, 261–267. [CrossRef]
88. Peyrton, J.; Avérous, L. Structure-Properties Relationships of Cellular Materials from Biobased Polyurethane Foams. *Mater. Sci. Eng. R Rep.* **2021**, *145*, 100608. [CrossRef]
89. Caddeo, S.; Baino, F.; Ferreira, A.M.; Sartori, S.; Novajra, G.; Ciardelli, G.; Vitale-Brovarone, C. Collagen/Polyurethane-Coated Bioactive Glass: Early Achievements towards the Modelling of Healthy and Osteoporotic Bone. *Key Eng. Mater.* **2014**, *631*, 184–189. [CrossRef]
90. Kirpluks, M.; Cabulis, U.; Avots, A. Flammability of Bio-Based Rigid Polyurethane Foam as Sustainable Thermal Insulation Material. In *Insulation Materials in Context of Sustainability*; Almusaed, A., Almssad, A., Eds.; InTech: Rijeka, Croatia, 2016; ISBN 978-953-51-2624-9.
91. Zieleniewska, M.; Auguścik, M.; Prociak, A.; Rojek, P.; Ryszkowska, J. Polyurethane-Urea Substrates from Rapeseed Oil-Based Polyol for Bone Tissue Cultures Intended for Application in Tissue Engineering. *Polym. Degrad. Stab.* **2014**, *108*, 241–249. [CrossRef]
92. Pretsch, T.; Jakob, I.; Müller, W. Hydrolytic Degradation and Functional Stability of a Segmented Shape Memory Poly(Ester Urethane). *Polym. Degrad. Stab.* **2009**, *94*, 61–73. [CrossRef]
93. Kirpluks, M.; Cabulis, U.; Ivdre, A.; Kuranska, M.; Zieleniewska, M.; Auguscik, M. Mechanical and Thermal Properties of High-Density Rigid Polyurethane Foams from Renewable Resources. *J. Renew. Mater.* **2016**, *4*, 86–100. [CrossRef]

94. Askari, F.; Barikani, M.; Barmar, M.; Shokrolahi, F.; Vafayan, M. Study of Thermal Stability and Degradation Kinetics of Polyurethane–Ureas by Thermogravimetry. *Iran. Polym. J.* **2015**, *24*, 783–789. [CrossRef]
95. Chattopadhyay, D.K.; Webster, D.C. Thermal Stability and Flame Retardancy of Polyurethanes. *Prog. Polym. Sci.* **2009**, *34*, 1068–1133. [CrossRef]
96. Gondaliya, A.; Nejad, M. Lignin as a Partial Polyol Replacement in Polyurethane Flexible Foam. *Molecules* **2021**, *26*, 2302. [CrossRef]
97. Hatakeyama, H.; Matsumura, H.; Hatakeyama, T. Glass Transition and Thermal Degradation of Rigid Polyurethane Foams Derived from Castor Oil–Molasses Polyols. *J. Therm. Anal. Calorim.* **2013**, *111*, 1545–1552. [CrossRef]
98. Morales-Cerrada, R.; Tavernier, R.; Caillol, S. Fully Bio-Based Thermosetting Polyurethanes from Bio-Based Polyols and Isocyanates. *Polymers* **2021**, *13*, 1255. [CrossRef]
99. Ji, D.; Fang, Z.; He, W.; Luo, Z.; Jiang, X.; Wang, T.; Guo, K. Polyurethane Rigid Foams Formed from Different Soy-Based Polyols by the Ring Opening of Epoxidised Soybean Oil with Methanol, Phenol, and Cyclohexanol. *Ind. Crops Prod.* **2015**, *74*, 76–82. [CrossRef]
100. Zhang, T.; Lin, C.; Li, J.; Li, Y.-J.; Xu, S. Fabricating Coconut Palm-Based Rigid Polyurethane Foam with Enhanced Compressive Strength Using Biomass Waste. *Polymer* **2024**, *310*, 127472. [CrossRef]

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