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Research Article

Fabrication and Characterization of Green Polyurethane Foams with Enhanced Vibration Damping Capability

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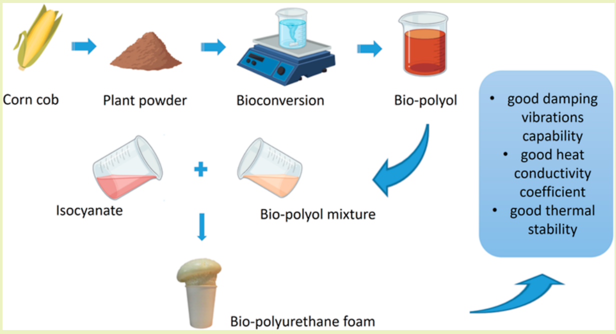

ABSTRACT: Over the past decades, there has been an intensive development of the technologies and innovations aimed at increasing the quality of life. This development largely concerns the comfort of use of everyday products that, among others, are products of the automotive, construction, or furniture industries. Considering the increase in the comfort of using products such as cars, houses, and flats, one of the comfort features of their use is the ability to dampen the sounds coming from the outside. Currently, in addition to wood-based boards, mineral wool, or glass wool fillings, polyurethane foams are more often used as soundproofing materials. This article describes the method of obtaining selected mechanical and thermal properties in flexible polyurethane foams with the ability to dampen vibrations, which were obtained with the use of raw materials of natural origin. The results of the tests of thermal stability and the vibration damping coefficient confirmed the possibility of using flexible polyurethane foams of natural origin as an alternative to the previously used vibration damping materials in the construction or the automotive industry.

KEYWORDS: *polyurethane foams, damping vibration capability, natural resource, sustainable production, environmental attitudes*

■ INTRODUCTION

Polyurethanes (PUs) are a very important group of polymer materials. Due to the possibility of their production in the form of foams, elastomers, coatings, adhesives, and fibers, PUs have been used in a wide range of applications. The global PU market in 2022 was valued at USD 73.84 billion. It is projected to reach USD 101.04 billion by 2030 with a compound annual growth rate of 4.00%.[1] The size of the global PU market in 2021 was estimated at 24.72 million metric tons and is expected to reach 29.19 million metric tons by 2029.[1] The largest share in the global PU market is constituted by flexible and rigid PU foams as their production amounts to 65% of the production of PU materials.[2]

PU foams are the products of the polyaddition reaction between polyisocyanates and polyols, containing at least two isocyanate groups and two hydroxyl groups, respectively. These compounds react with each other to form a characteristic urethane bond. In the production of foamed PU materials, blowing agents, catalysts, surfactants (SAA), chain extenders, fillers, and other auxiliaries are also used. PU foams are usually manufactured using a one-step method from a two-component system consisting of a polyol mixture and a polyisocyanate. The polyol mixture consisted of a polyol (petrochemical or natural), blowing agent, catalyst, surfactant, and other additives.

Currently, flexible PU (FPU) foams are the most developed and widespread group of porous materials. Due to their irreplaceable properties, the ease of production, and the ability to obtain various forms of the product, FPU has been used in many industries, including the automotive, furniture, construction, electrical engineering, and textile and footwear industries. Moreover, by combining the unique mechanical and acoustic properties of mainly FPU foams, they have been used as vibration damping materials. They are used, among others, for soundproofing cars, construction and industrial machines, work vehicles, as well as soundproofing walls, ceilings, and floors. PU, thanks to its effective properties of reducing sound[3−5] and mechanical vibrations,[6,7] contributes to the improvement of comfort in the construction, automotive, aviation industries, etc. In order to improve the ability to dampen vibrations, nanofillers, e.g., graphene,[8] carbon nanotubes,[9] or composites, e.g., with mineral wool,[10,11] are often added to PU foams. The vibration absorption efficiency of PU is strongly related to the cell structure, pore morphology, and foam density. The morphology of the material is influenced by the content of open or closed cells, their homogeneous distribution, and their size. PU foams with the highest content

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of open cells are characterized by the highest damping coefficient due to their ability to convert mechanical energy into thermal energy.[10]

Hu and coauthors[12] described the damping properties of biobased PU composites. The materials were synthesized using poly(lactic acid) (PLA), 4,4′-diphenylmethane diisocyanate (MDI), and trimethylolpropane diallylether (TME) as the chain extender. In the second step, 3,9-bis-{1,1-dimethyl-2[β-(3-*tert*-butyl-4-hydroxy-5-methylphenyl-)propionyloxy] ethyl}-2,4,8,10-tetraoxaspiro [5,5]-undecane (AO-80) was added to make the composites with different amounts of AO-80. Using the dynamic mechanical analysis (DMA) method, the effective damping temperature range was determined (temperature range of $\tan\delta > 0.3$). Moreover, the glass transition temperature of the composites was close to room temperature. It was found that the obtained materials work well as vibration damping materials at room temperature. The damping properties of the composites increase with increasing AO-80 content.

Oliviero and coauthors[13] investigated the one-step synthesis of PU foam obtained from a mixture of polyether polyol (petrochemical) with a biopolyol based on succinic acid (SA), 4,4′-diphenylmethylene diisocyanate, MDI, water as a blowing agent, a carbon black filler (CB), and triethyl phosphate to improve the dispersion of CB into polyols. The ratio of the isocyanate groups to hydroxyl groups was 1:1. The foams were cured at 40 °C for 5 h. The obtained foams were characterized by an open-cell structure. It was found that the addition of the polyol based on SA increases the soundproofing properties of the foams in the high-frequency range (1000−6000 Hz). The apparent density of the synthesized foams was in the range of 49 to 83 kg/m^3.

For the production of PUs, raw materials obtained from fossil fuels are mainly used. However, due to all the principles of sustainable development, the increasing prices of fossil fuels, and inefficiency in the oil and gas market, the raw materials of natural origin are used increasingly instead of petrochemical raw materials. The use of biopolyols or bioisocyanates in the production of PU materials greatly increases the renewable carbon content of the final material. Currently, the production of biobased polyols from vegetable oils,[14−17] such as palm oil[18−20] and castor oil,[21] is the most advanced method. The second most advanced bioraw materials are dicarboxylic acids, for example, SA[22,23] or azelaic acid (AA) and natural glycols[24] like 1,3-propanediol (PDO)[25] and 1,4-butanediol (BDO).[26] Due to the importance of the PU materials, the interest in the production of biopolyurethanes, including biofoams,[27,28,34,35] especially rigid foams,[29−33] is growing. Research is still underway on the appropriate selection of the components for the synthesis of PU biomaterials that will be an alternative to petrochemical materials.

Furtwengler[26] in his publication described a PU foam obtained via a one-step method using a mixture of a polyester biopolyol based on adipic acid, sorbitol, 1,4-butanediol, and petrochemical polyether polyol, the content of which was in the range of 0−75 wt %. In addition, pure sorbitol, pure glycerol, MDI 4,4′-diphenylmethylene diisocyanate, catalyst, surfactant, flame retardant, chemical and physical blowing agent, water, and isopentane were used to obtain the PU foams. The NCO/OH molar ratio was kept constant at 1.15 in all foams. The obtained biofoams were characterized by an open-cell structure (up to 92%) and a low density (30 kg/m^3).

Sonjui and Jiratumnukul[34] obtained the PU foams from a mixture of polyether polyol of petrochemical origin and polyols based on SA and glycols: diethylene glycol, triethylene glycol, tetraethylene glycol, and glycerol used in various ratios. 4,4′-Diphenylmethylene MDI diisocyanate, catalyst, surfactant, blowing agent, and distilled water were also used to obtain the PU foams using the one-step method. The foams obtained from the polyols based on a mixture of glycols were characterized by smaller cell dimensions and an increased content of closed cells in comparison to those obtained from polyols of single glycols. The PU foam obtained from the polyol based on diethylene glycol and glycerol had a density of 40 kg/m^3.

The main purpose of this work was the synthesis and characterization of FPU foams with the ability to dampen vibrations using monomers of natural origin. The ecological PU foams are entirely synthesized from the linear biobased polyester polyols. By carrying out the synthesis of FPU foams, the influence of the amount and type of the substrate used on the properties of the obtained FPU materials was investigated. The selected measurement methods were carried out, and the results were analyzed to confirm the possibility of using the obtained FPU foams as vibration damping materials.

■ MATERIALS

The main components used for the biobased polyester polyol synthesis constitute 1,3-propanediol, PDO, and dicarboxylic acids, which were SA and AA. All the aforementioned substrates were of natural origin. PDO and SA are produced by the fermentation of glucose. AA is usually produced industrially by the ozonolysis of oleic acid. The byproduct is nonanoic acid, the bacterial degradation of which yields AA. PDO—, Susterra propanediol, was obtained from DuPont Tate&Lyle Corporation Bio Products (Loudon, Tennessee, USA). This liquid component was characterized by a purity of ca. 99.98% and a molecular weight at 76.09 g/mol. SA, Biosuccinium, was kindly supplied by Reverdia (the Netherlands). Biosuccinium was characterized as a white powder with a purity of above 98% and a molecular weight of 118.09 g/mol. AA—Emerox 1144 was obtained from Emery Oleochemicals (USA). This component was characterized as a white powder with a purity above 99% and a molecular weight of 188.22 g/mol. Tetra-*n*-butyl titanate (TnBT) obtained from TCI Chemicals (India) was used as a catalyst for the polycondensation reaction. This compound was a liquid with a purity of ca. 97% and a molecular weight of 284.22 g/mol.

The PU foams were synthesized from two main compounds: polymeric 4,4′-methylene diphenyl isocyanate (PMDI) and polyols: biobased polyester polyols (acid value, AV range: 0.73−0.92, hydroxyl value, OHV range: 58−148), and commercially available petrochemical-based polyester polyol—Polios 55/20. PMDI—Ongronat 2100 was obtained from BorsodChem (Hungary). This diisocyanate contained 29% isocyanate groups. Polios 55/20 was obtained from Purinova Sp z.o.o. (Poland) for a reference sample. Polios 55/20 was characterized as a colorless liquid with a hydroxyl number of ca. 58 mg KOH/g, an acid number below 0.5 mg KOH/g, and a viscosity of ca. 0.67 Pa s. Dabco 33-LV used as an amine catalyst for the foaming process was obtained from Sigma-Aldrich (USA). Niax Silicone L-3416 was used as a surface-active agent and was obtained from Momentive Performance Materials (USA). The other materials and solvents used for the analytical measurement methods were of analytical grade.

■ SYNTHESIS

Synthesis of Biobased Polyester Polyols. In order to obtain the biobased polyester polyols, the two-step polycondensation reaction was carried out using a mixture of dicarboxylic acids—SA and AA—with different molar ratios and 1,3-propanediol. First, esterification was carried out at a temperature of 140 °C in a nitrogen atmosphere. When the acid number of the reaction mixture was decreased by half from the initial value, the catalyst was added, and the second step, the polycondensation reaction, was started. This step was carried out at 170 °C in a vacuum atmosphere. The average molecular weights of the obtained polyester polyols were determined with the use of size exclusion chromatography (the measurements were taken on an Agilent 1260 Infinity instrument equipped with a Phenogel 10 μm Linear(2) 300 × 7.8 mm column). The substances under analysis were dissolved in tetrahydrofuran (THF). Measurement conditions: analysis time = 15 min, eluent flow (THF) = 1 mL/min, column temperature = 35 °C, refractive index (RI) detector temperature = 35 °C. The molecular weights of the analyzed substances and their dispersion were determined against the standards that are linear poly(styrenes) with masses in the range of 1000−3,500,000. The selected properties of the obtained biobased polyester polyols are presented in Table 1.

Table 1. Characteristics of the Synthesized Biobased Polyester Polyols

	BIO-1	BIO-2	BIO-3	BIO-4	BIO-5
SA/PDO molar ratio	1:1.2	1:1.2	1:1.2	1:1.2	1:1.2
SA/AA molar ratio	1:1	3:1	1:3	3:1	3:1
Mn [g/mol]	1362	1353	1652	n.d.	n.d.
Mw [g/mol]	2856	2584	3521	n.d.	n.d.
PD	2.1	1.9	2.1	n.d.	n.d.
acid number [mg KOH/g]	0.76	0.90	0.92	0.85	0.73
hydroxyl number [mg KOH/g]	148	128	120	103	58
viscosity (25°C) Pa s	4.8	6.2	5.7	n.d.	n.d.

Synthesis of FPU Foams. The PU foams were obtained by a one-step method from a two-component system consisting of a polyol mixture and a diisocyanate. The molar ratio of the −NCO isocyanate groups to the hydroxyl groups to −OH was 0.8 (for each foam). The polyol mixture consisted of a polyol (petrochemical or natural), a chemical blowing agent which was distilled water, an amine catalyst, Dabco 33-LV, and a surfactant, Niax Silicone L-3416. The surfactant was added in amounts of 0.5, 1.0, and 2.0 wt % of the polyol mass. In order to prepare it, all of the above-mentioned ingredients were added in appropriate amounts and then mixed. A successively weighed amount of PMDI diisocyanate was added to the polyol mixture, and the mixture was mixed again for a few seconds. After mixing, the mixtures were poured into a closed mold and foamed. Then, the foams were removed from the mold and left for 24 h for maturing. Moreover, in order to study the course of the foaming process and the properties of the prepared foams, they were additionally synthesized in open forms. Table 2 presents the type and quantity of the substrates used for the synthesis of the petrochemical foam (FPU-REF, reference foam) and biobased foams (FPU-BP1, FPU-BP2, FPU-BP3, FPU-BP4-0.5SAA, FPU-BP4-2.0SAA, and FPU-BP5-1.0SAA). In addition, Table S1 in the Supporting Information presents the characteristics of the process of foaming the PU foams.

MEASUREMENTS

Fourier Transform Infrared Spectroscopy. Fourier transform infrared spectroscopy (FTIR) was used to obtain the spectra of the biobased PU foams and confirm the chemical structure of the synthesized materials. The measurements were recorded using a Nicolet 8700 FTIR spectrometer (Thermo Electron Corporation, USA) with the use of the attenuated total reflectance technique in a wavelength range between 4500 and 500 cm^{-1} as an average of 64 scans at the resolution of 4 cm^{-1}.

Open Cell Content. The open cell content (OCC) was determined using a single-component gas pycnometer: Ultrapyc 5000 (Anton Pear, Austria). This device determined the number of open cells according to the ASTM D6226 standard. The measurements were carried out in an inert atmosphere of nitrogen at room temperature.

Thermogravimetric Analysis. The thermal stability of the obtained PU foams was tested using a NETZSCH TG 209F3 apparatus (Netzsch, Germany). The samples weighing approximately 10 mg were placed on the crucible and heated in the temperature range 35−800 °C at a rate equal to 10 °C/min. The test was carried out in an inert nitrogen gas atmosphere. As a result of the study, a thermogravimetric curve was obtained, which is the dependence of mass loss on the temperature. The temperatures for 2, 5, 10, 50, and 90% weight loss were determined from the thermogravimetric curve. A differential thermogravimetric curve (DTG) was also obtained, which is the first derivative of the TG curve. The DTG curve made it possible to determine the temperatures at which the maximum rate of weight loss occurred ($T_{\max1}$, $T_{\max2}$).

Dynamic Mechanical Analysis. The dynamic mechanical tests were performed using a DMA Q 800 analyzer (TA Instruments, USA). The specimens with dimensions 35 × 12 × 3 mm were analyzed at a heating rate of 4 °C/min in the temperature range from −130 to 100 °C. The samples were analyzed in the single cantilever mode with a frequency of 1 Hz in the atmosphere of air. The study provided information on the storage modulus, loss modulus, and the delta tangent. On the basis of the last one, it was possible to determine the temperature range in which the foams showed the ability to insulate acoustic vibrations as a temperature range for the tan delta above 0.3.

Table 2. Formulations of the Synthesized FPU Foams

	amount of substrates [wt %]						
substrate	FPU-REF	FPU-BP1	FPU-BP2	FPU-BP3	FPU-BP4-0.5SAA	FPU-BP4-2.0SAA	FPU-BP5-1.0SAA
polyol name	Polios 55/20	BIO-1	BIO-2	BIO-3	BIO-4	BIO-4	BIO-5
polyol mass	78.4	68.4	70.1	70.7	72.6	71.8	77.5
PMDI	20.0	30.2	28.5	27.9	25.6	25.3	20.2
Dabco 33-LV	0.8	0.7	0.7	0.7	0.7	0.7	0.8
distilled water	0.8	0.7	0.7	0.7	0.7	0.7	0.8
Niax Silicone L-3416	0	0	0	0	0.4	1.4	0.8

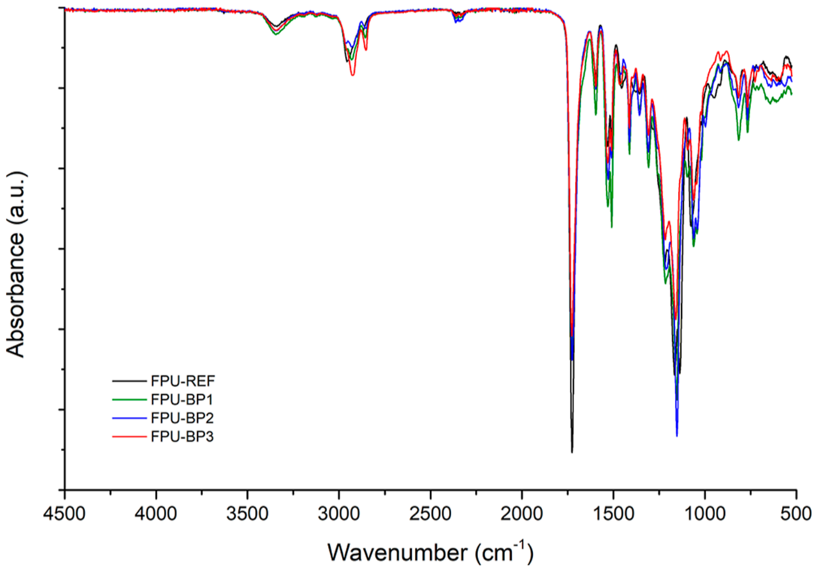

Figure 1. FTIR spectroscopy spectra of the selected synthesized FPU foams.

Table 3. Content of Open Cells in the Morphology of the Synthesized FPU Foams

type of foam	FPU-REF	FPU-BP1	FPU-BP2	FPU-BP3	FPU-BP4-0.5SAA-CM	FPU-BP4-2.0SAA-CM	FPU-BP5-1.0SAA-CM
the content of open cells [%]	80.5	76.1	59.6	71.4	74.1	81.6	78.5

Heat Conduction Coefficient. The heat conduction coefficient was measured with an HFM 446 Lambda Small Version Metrisch apparatus (Netzsch, Germany). The mean temperature of the measurement was 10 °C.

Mechanical Properties. The mechanical properties were assessed by the tensile strength measurements, which were carried out in accordance with PN-EN ISO 1798:2008 using the Zwick/Roell Z020 testing machine (Zwick Roell, Germany). The dumbbell-shaped samples were tested with an initial force of 0.5 N and a test speed of 300 mm/min. The tensile strength and tensile elongation results were averaged from at least three specimens. A graph of the relationship between the stress and relative elongation was also made for the selected samples.

■ RESULTS

Fourier Transform Infrared Spectroscopy. The analysis of the FTIR spectra allowed us to confirm the chemical structure of the synthesized PU foams. The FTIR spectra of the produced PU foams are shown in Figure 1. Moreover, the characteristic bands together with the wave numbers at which they occur are summarized in Table S2 in the Supporting Information. The spectra showed the broad absorption bands at the wavenumber in the range 3355−3345 cm^{-1}, which is related with the stretching vibrations of the N−H groups derived from the urethane groups. The signals related to the deformation vibrations of these groups were observed at 1522−1500 cm^{-1}. Two sharp absorption bands occurring in the ranges 2930−2918 and 2855−2845 cm^{-1} were assigned to the asymmetric and symmetric stretching vibrations of the C−H bonds in the −CH$_2$ groups, respectively. In the spectra, there is also a visible distinct absorption band at the wavenumber ca. 1725 cm^{-1}, which corresponds to the −C═O group stretching vibrations derived from the ester groups from the polyols' macromolecular chains. At a wavenumber of about 1250−1255 cm^{-1}, the absorption bands were observed, which are attributed to the stretching vibration of the −C−N bonds. The above signals confirm the presence of urethane bonds in the analyzed foamed materials. The signals at 1155−1130 cm^{-1} are associated with the stretching vibration of the −C−O bonds, which result from the presence of the ester groups in the structure of the polyols.

The lack of a sharp peak at ca. 2268 cm^{-1} related with the −NCO groups confirms the completion of the reaction of the free isocyanate groups and the hydroxyl groups present in the structures of the polyol mixture. Nevertheless, the results of the FTIR measurements of all the prepared FPU foams indicate the presence of an absorption band at the wavenumber range 2348−2300 cm^{-1}, which is usually related with the stretching vibration of CO$_2$, which had formed during the foaming process. The lowest intensity of this absorption band appears in the spectrum for the foam of petrochemical origin. These results are correlated with the measurements of the OCC in which the reference sample revealed the highest amount of OCC; therefore, for this sample, it was the smallest chance of entrapping the generated during foaming carbon dioxide inside the cells of the PU foam material. The biobased FPU foams prepared using biobased polyester polyols coded as BIO-1 and BIO-3 showed a similar intensity of the absorption band associated with CO$_2$, which is closely related to the open cell content in these materials. The most intensive absorption band occurring at the wavenumber range 2348−2300 cm^{-1} characterizes the sample FPU-BP2, which contains the lowest amount of open cells (59.56%), and thus, it is characterized by the highest amount of CO$_2$ trapped in the closed cells.

Open Cell Content. The synthesized FPU foams were tested to characterize the morphology. The OCC measurements of the obtained FPU foams indicate that the OCC is in the range of 59.6−81.6%. The exact list of the values for individual foams is presented in Table 3. The foams obtained with the use of biobased polyester polyols but without

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Table 4. Thermal Decomposition Characteristics of the Synthesized FPU Foams

type of foam	loss of weight [%]					T_{max1} [°C]	T_{max2} [°C]
	2	5	10	50	90		
	temperature [°C]						
FPU-REF	278.4	308.5	341.2	403.5	588.4	392.8	587.6
FPU-BP1	286.0	311.1	333.7	426.2	586.8	417.1	583.3
FPU-BP2	276.0	303.5	323.6	406.3	582.0	392.4	581.2
FPU-BP3	280.9	313.5	333.6	426.2	581.7	415.6	587.7

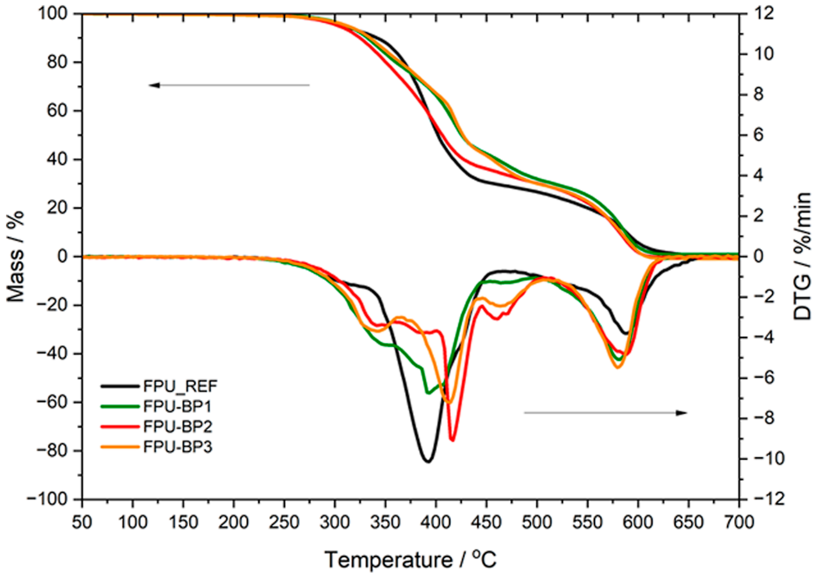

Figure 2. Dependence of the TG and DTG curves as a function of temperature for the obtained FPU foams.

surfactant usage are characterized by a lower amount of open cells compared to that of the reference foam. The FPU-BP2 foam contains the lowest amount of the open cells (59.6%). In the case of FPU, it was synthesized with the use of the surfactant. The FPU-BP4-2.0SAA foam obtained with the use of the highest amount of SAA was characterized by the highest content of the open cells (81.6%) compared to those of the reference foam and other biopolyol-based foams. It has been observed that with an increase in the amount of the surfactant in the range of 0.5−2.0% by weight of the polyol weight, the number of the open cells in biofoams increases. In their work, Peyrton and Avérous[2] specified the optimal amounts of the surfactants that should be added in order to obtain better mechanical, thermal, and morphological properties of the PU foams. They reported that for a FPU foam, the normal open cell growth increases with the increasing surfactant amounts in the range of 0.5−1.5% by weight of the polyol.

The cellular structure of the PU foams significantly affects the properties of the PU materials produced and, consequently, their applicability. The obtained PU foams are characterized by an open-cell structure, which allows them to be used as acoustic insulation materials.

Thermogravimetric Analysis. The thermal properties of PUs have a large impact on their future application and mainly depend on the type and molar ratio of the monomers used for their preparation and synthesis methods and conditions.[36] Thermogravimetric analysis (TGA) was used to determine the thermal stability characteristics of the prepared FPU foams. Table 4 presents the results of the TGA. The temperature at which there was a 2% weight loss of the FPU foams indicates the beginning of the degradation process, and for all the samples, it occurred in the range 276.0−286.0 °C. The lowest temperature value for a 2% weight loss was recorded for the FPU-BP2 foam. The temperatures for the 5 and 10% weight loss between the individual foams were similar. The temperature for the 5% weight loss was in the range of 303.5−313.5 °C. The temperature for the 10% weight loss was higher for the reference foam and amounted to 341.2 °C, while for the biobased foams, it was in the range of 323.6−333.7 °C. The temperatures at which 50% of the original weight remained was higher for the biobased foams compared to that for the reference one at about 23 °C. The temperatures for the 90% weight loss were comparable to each other.

Moreover, it was concluded from the obtained DTG curves that there are two main stages of thermal degradation of the PU foams. The first stage is associated with the degradation of the hard segments, which are mainly formed by the urethane and urea groups, which are characterized by lower thermal stability than that of the polyol bonds. This stage is a process of repeated degradation of the urethane and urea bonds, breaking down into primary amines, alkenes, secondary amines, and carbon dioxide. More than one step in this step means that the hard segments have a heterogeneous structure.[37] This step is in the temperature range of 392.8−417.1 °C (T_{max1}). The second stage is associated with the degradation of the flexible segments, which are mainly formed by the macromolecular chains derived from the polyols. This step is in the temperature range of 581.2−587.7 °C (T_{max2}).

The thermal stability of the foams of natural origin is comparable to that of the reference foams of petrochemical origin. The temperatures at which the maximum rate of weight loss occurred for individual PU foams are similar to each other.

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Table 5. DMA Results of the Prepared FPU Foams[a]

sample	T_g [°C]	tan δ_{max}	ΔT [°C]	temperature range for tan $\delta > 0.3$ [°C]	S for tan $\delta > 0.3$	$S'_{-50-75\ °C}$
FPU-REF	−12.9	0.62	38	−28−10	7.7	24.2
FPU-BP1	15.8	0.37	30	3−33	1.4	14.0
FPU-BP2	19.7	0.73	48	0−48	13.7	31.0
FPU-BP3	8.5	0.45	40	−10−30	4.0	20.8
FPU-BP4-0.5SAA-CM	13.0	0.60	50	−5−45	9.7	26.5
FPU-BP4-2.0SAA-CM	14.5	0.55	51	−5−46	8.5	22.0
FPU-BP5-1.0SAA-CM	−4.3	0.43	26	−16−11	2.2	15.3
FPU-BP4-0.5SAA-OM	11.8	0.48	28	−2−26	3.2	8.1
FPU-BP4-2.0SAA-OM	12.2	0.61	42	−5−37	8.0	24.0
FPU-BP5-1.0SAA-OM	2.1	0.47	42	−18−24	6.1	22.1

[a] T_g—glass transition from DMA results; tan δ_{max}—the maximum intensity of tan δ; ΔT—the temperature range for efficient damping (tan $\delta > 0.3$); S—the integral area for the temperature range for tan $\delta > 0.3$ in the tan δ temperature curves.

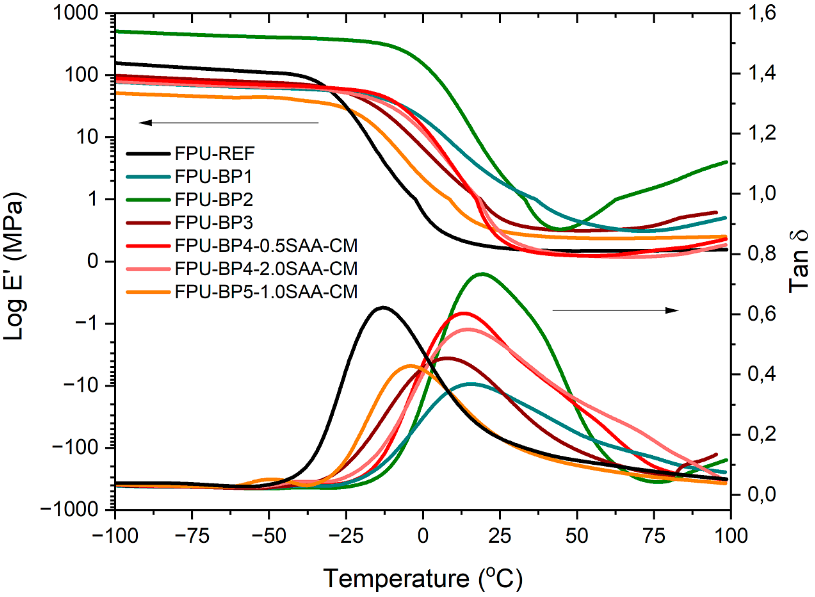

Figure 3. Storage modulus (E') and tangent delta (tan δ) as a function of temperature for FPUs synthesized in a closed mold.

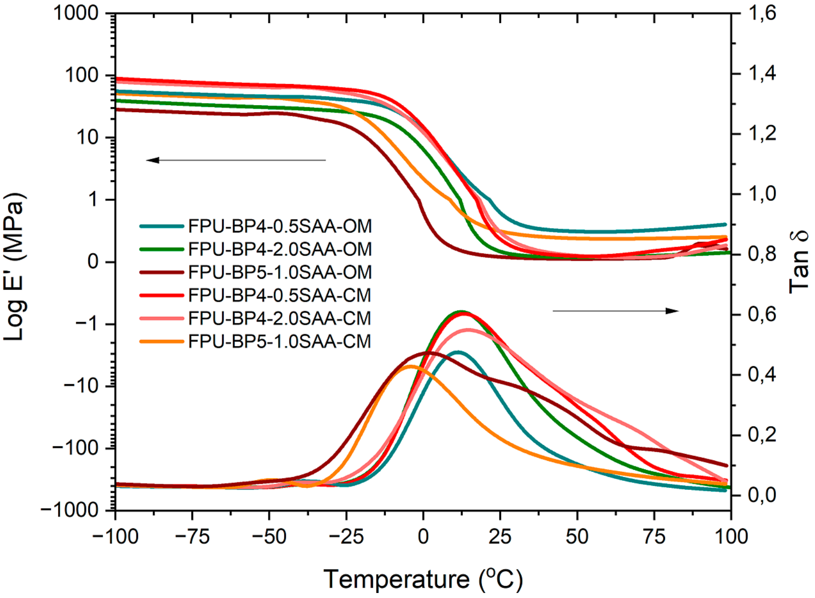

Figure 4. Comparison of the storage modulus (E') and tangent delta (tan δ) as a function of temperature for FPUs synthesized in a closed and open mold.

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Table 6. Heat Conductivity Characteristics of the Prepared FPU Foams

type of foam	FPU-REF	FPU-BP1	FPU-BP2	FPU-BP3	FPU-BP4-0.5SAA-CM	FPU-BP4-2.0SAA-CM	FPU-BP5-1.0SAA-CM
heat conductivity coefficient [W/m K]	0.056	0.061	0.067	0.065	0.053	0.054	0.048
thermal resistance [m^2 K/W]	0.21	0.19	0.16	0.18	0.22	0.19	0.21

Figure 2 shows the dependence of the mass loss as a function of temperature and shows the DTG curves for the obtained FPU foams.

Dynamic Mechanical Analysis. DMA applies an oscillatory force at a set frequency to the sample and reports the changes in the stiffness and damping; these are reported as modulus and tan δ. This allows us to record the material's response to stress, temperature, frequency, and other values. Because a sinusoidal force is applied during the DMA measurements, the modulus as an in-phase component, the storage modulus, and an out-of-phase component, the loss modulus, can be expressed. The storage modulus, E', is the measure of the sample's elastic behavior. The ratio of the loss to the storage is the tan δ, often called damping, and it is a measure of the energy dissipation of a material. It is a measure of how well a material will be at the absorbing energy and is reported as the tangent of the phase angle.[38]

DMA was used to analyze the elastic behavior and damping factor of the prepared materials. Table 5 and Figures 3 and 4 show the DMA results. Figure 3 shows the storage modulus (E') and tangent delta (tan δ) as a function of temperature for FPUs synthesized in a closed mold. The storage modulus E' curves for samples FPU-REF and FPU-BP2 differ from the others to the greatest extent. Sample FPU-REF remains in a glassy state until it reached the lowest temperature compared to that of the other measured materials. It reaches the glass transition region above ca. −35 °C, when the other samples reached this region above ca. 0 °C. Sample FPU-BP2 is characterized by the highest value of the storage modulus, which confirms the best elastic behavior for this material. Except for samples FPU-REF, FPU-BP1, and FPU-BP2, all the other samples reveal a rubbery plateau above ca. 25 °C. The reference sample reveals the rubbery plateau region from ca. 0 °C. Sample FPU-BP2 after reaching the temperature ca. 37 °C reveals the transition of the hard segments, when sample FPU-BP1 reveals a second transition above 75 °C.

The obtained DMA data allowed us to determine the temperature range in which the material damps the vibrations. When the temperature is in the glass transition region, the vibrational mechanical energy can be absorbed by the polymer to the greatest extent and converted to thermal energy by the relaxation motion of the macromolecular segment. The mechanical loss tangent (tan δ) is an important parameter for measuring the damping capacity of the material, and its maximum value can be observed in the glass transition region of the polymer. For the actual applications, the materials are considered to have effective damping properties when the tan $\delta \geq 0.3$. The larger the temperature range over which the tan delta is greater than 0.3, the better the vibration damping capacity.[36,39] Table 5 presents the collection of the DMA data obtained from the tan δ versus temperature curves courses. The results indicate that sample FPU-BP2 was characterized by the highest value of the glass temperature, 19.7 °C, the highest value of tan δ_{max}, and the highest value of the temperature range for tan $\delta > 0.3$. For more precise information about the vibration damping capability of the prepared PU foams, the value of the integral area for the temperature range for tan $\delta > 0.3$ in the tan δ temperature curves as a supplementary indicator of the damping performance, S, was defined. It allows us to confirm that sample FPU-BP2 was characterized by the highest S factor. This sample also revealed the highest value of the integral area for the temperature range from −50 to 75 °C in the tan δ temperature curves, the $S'_{-50-75\ °C}$ factor. These results are entwined with the OCC. Sample FPU-BP2 exhibits the lowest value of OCC, 59.6%. Moreover, the PU foams obtained with the addition of the surfactant are characterized by the lower vibration damping capacity than that without surfactant usage. The DMA results presented in Table 5 also confirm that with the increasing amount of the surfactant, the higher the OCC, the lower the values of the vibration damping capacity characteristics.

As shown in Table 5, the selected prepared green FPUs revealed a very efficient energy dissipation, which endowed them with the potential as a green material with high damping capacity, especially sample FPU-BP2.

The impact of the mold types (open, OM, or closed, CM, mold) on the prepared foam's damping ability was also analyzed. Figure 4 shows the storage modulus (E') and tangent delta (tan δ) as a function of temperature for FPUs synthesized with SAA in a closed and an open mold. The FPU-BP4-0.5SAA-CM foam was characterized by the highest vibration damping ability, when samples FPU-BP5-1.0SAA-OM, and FPU-BP4-0.5SAA-OM revealed the lowest values of the S factor. Although sample FPU-BP4-2.0SAA-CM exhibited the highest content of the open cells (81.6%), which should increase the damping ability, sample FPU-BP4-0.5SAA-CM exhibited a higher value for the S factor. It is related with a higher integral area for the temperature range for tan $\delta > 0.3$ in the tan δ temperature curves for sample FPU-BP4-0.5SAA-CM and a relatively high tan δ_{max} and the temperature range for efficient damping, ΔT. Moreover, it has been found that the closed-mold foams exhibit better vibration damping properties than those synthesized in open molds, except for the foam FPU-BP5-1.0SAA-CM.

Heat Conductivity Coefficient. The thermal conductivity of the material is highly dependent on the temperature gradient of the properties of the material and the path length that the heat follows. The thermal conductivity of the materials around us range from those with the lowest conductivities such as air (0.024 W/m K at 0 °C) to highly conductive metals such as copper (385 W/m K). The thermal conductivity of the materials determines how we use them. For example, those with low thermal conductivities are excellent as insulating materials for our homes, while high thermal conductivity materials are ideal for such applications as in cooking utensils and cooling systems in electronic devices, where heat must be moved quickly and efficiently from one area to another. In the case of common building insulation materials used in the exterior wall, it was confirmed that one from the best insulating materials is PU foams with a heat conductivity coefficient of around 0.02 W/m K. For comparison, the polystyrene, rock

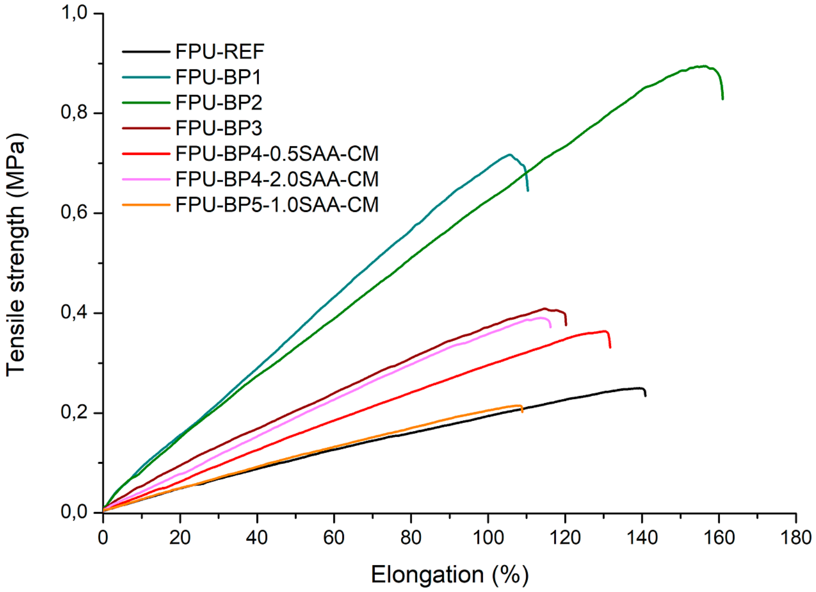

Figure 5. Dependence of the tensile strength on the elongation at break.

wool, and fiberglass are characterized by the heat conductivity coefficients above 0.03 W/m K.[40,41]

Table 6 presents the results of the heat conductivity coefficient measurements of the prepared FPU foams. The foams synthesized from the polyols of natural origin and without a surfactant have higher thermal conductivity than that of the reference foam. These differences are not significant; they fall within the range of 0.056−0.067 W/m K. For PU foams synthesized from the polyols of natural origin and containing a surfactant, the values of the thermal conductivity coefficient are lower than those for the reference foam and the foams obtained without surfactant. These values are in the range of 0.048−0.054 W/m K. The foams synthesized from the polyols of natural origin and containing a surfactant have better thermal insulation properties than the reference foam and natural walking foams without a surfactant.

Mechanical Properties. PUs are characterized by a segmented chemical structure consisting alternately of rigid segments and flexible segments. The rigid segments are composed of the isocyanate residue chain extenders, urethane groups, and urea groups. The flexible segments are formed primarily by the groups derived from the polyols: ether and ester groups. The mechanical properties of the PU materials strictly depend on the content of the individual segments in the macromolecular structure of the material.

Figure 5 shows the dependence of the tensile strength on the elongation at break. Moreover, Table S3 in the Supporting Information summarizes the mechanical properties such as tensile strength (TSb, MPa) and elongation at break (εb, %) for the obtained PU foams. All the biopolyol foams except the FPU-BP5-1.0SAA foam were characterized by a higher tensile strength compared to that of the reference foam. The poor results of the mechanical properties of the FPU-BP5-1.0SAA foam may result from the low hydroxyl number of the biopolyol used for the synthesis, which has a significant impact on the segment structure of PUs. Moreover, the natural-origin foam FPU-BP2 was characterized by the highest tensile strength (0.82 MPa) and the highest value of the relative elongation at break (153%). For the remaining foams of natural origin, the relative elongation parameter was lower, and its values were lower than that for the reference foam.

CONCLUSIONS

FPU foams were successfully synthesized using biobased polyester polyols based on a mixture of dicarboxylic acids, such as succinic and AA, and 1,3-propanediol. The research confirmed that the use of the biobased polyols allowed us to obtain PU foams characterized by similar or even better selected properties than the PU foams based on commercially available petrochemical polyester polyol. All the obtained PU foams were characterized by an open-cell structure. The values of the heat conductivity coefficients for the reference foam amounted to 0.056 W/m K, and for the obtained PU biofoams, they ranged from 0.048 to 0.067 W/m K, with the lowest value for the FPU-BP5-1.0SAA foam (0.048 W/m K), which proves its suitable thermal insulation properties. The obtained PU biofoams were characterized by proper mechanical properties; the tensile strength values were in the range of 0.22−0.82 MPa. For the synthesized foams, the vibration damping temperature range was tested as the temperature range at which tan $\delta > 0.3$. The FPU-BP4-2.0SAA foam was characterized by the widest range of vibration damping temperatures from −5 to 46 °C.

The obtained materials were characterized by appropriate vibration damping properties, which allow them to be used in the production of insulating materials. Nevertheless, there are some chemical and preparation aspects that allow improvements in the vibration damping properties of the obtained materials. First, the obtaining reproducible properties of the biopolyols allow improved also repeatability of receipt of the biobased PUs and chose the most suitable for use as insulating materials. The PU foams with the highest content of the open cells are characterized by the highest damping coefficient due to their ability to convert mechanical energy into thermal energy. The obtained results confirmed that the addition of a surfactant allows obtaining biobased PU foams characterized by a higher value of the OCC and, in consequence, better thermal insulation properties than the reference biobased PU foams (prepared without a surfactant). To improve the insulating properties of the biobased PU foams, it is necessary to determine the route to obtain the biobased polyester polyols with optimal and repeatable properties and the optimal amount of the surfactant.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.3c01751.

> Characteristics of the foaming process; characteristic absorption bands from FTIR spectroscopy of FPUs; results of the tensile strength and elongation at break of FPUs; and apparent density of the FPUs (PDF)

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Notes

The authors declare no competing financial interest.

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