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Effect of sisal fiber filler on thermal properties of bio-based polyurethane composites

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Abstract This work is mainly focused on study of thermal and thermomechanical properties of obtained bio-based polyurethane (coded as bio-PU) composites via using different types of bio-components (bio-glycol, modified soybean oil and sisal fiber) in the procedure. The chemical structure, morphology and mechanical properties were also investigated and described in this manuscript in order to know more perfect characterization of produced composites. The bio-based polyurethane matrix of composites was synthesized via prepolymer method. Bio-PU composites were produced by dispersing 5 and 15 mass% of sisal fibers into the polyurethane matrix during their synthesis. To investigate the thermal stability of sisal fibers and bio-PU composites, the thermogravimetric method (TG) was used. Thermomechanical tests were performed by means of dynamic mechanical analysis (DMA). Based on the results of thermomechanical analysis, it was found that the sisal fibers amount has the impact on storage and loss modulus. Chemical structure was confirmed by FTIR spectra. Mechanical results and scanning microscopy images of the composites showed good interfacial adhesion between sisal fibers and the bio-based PU matrix.

Keywords Sisal fiber · Silanization · Thermal stability · DMTA · Bio-polyurethane composites

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Introduction

Bio-based composites are constantly under the unremitting research attention. These materials are almost used in every sector of industry. The vegetable oil-based polyurethanes belong to these material groups, too. Vegetable oils (e.g., soybean or rapeseed oil) have become an attractive resource that can be converted to bio-based polyols to produce PU [1]. The properties of the bio-based composites including vegetable oil-based polyurethanes despite the bio-based matrix are influenced by a number of variables as form and size of fillers or processing conditions and methods. Natural fiber fillers, which consist of cellulose, hemicelluloses and lignin, are commonly used to produce bio-based composites. The most important advantages of these types of fibers are availability, environmental-friendly character, low price, good mechanical properties, biodegradability. Nevertheless, there is some weakness associated with poor compatibility and interfacial adhesion between natural fibers and polymers. The low resistance to moisture absorption made the use of natural fiber-reinforced composites less attractive. In order to eliminate these disadvantages, fibers are treating with suitable chemicals, e.g., silane, alkaline or benzyl compounds [2–4]. The knowledge about the thermal decomposition process of natural fibers could help to predict fiber-based composites process and estimate the influence on composite properties by thermal decomposition of natural fibers. The thermal stability of the fibers can be studied using thermogravimetric analysis. The kinetic modeling of the decomposition and also the knowledge about activation energy are meaningful for a proper prediction of the behavior of the materials under different working conditions and the critical energy needed to start a decomposition reaction, respectively [5]. The thermal decomposition

process of common natural fibers was described in the literature [6].

Well-known, naturally occurring fiber which can be successfully used in composites production is sisal, obtained from the Agave sisalana leaves. This fiber is produced in the tropical regions such as Mexico, Brazil, Tanzania, Kenya, Madagascar and China. Depending on the size and form, natural filler has crucial factors on the mechanical and thermal behavior of bio-composites [7, 8]. Sisal fiber represents the lignocellulosic fibers group, except such as jute, coir, pineapple, bamboo, hemp, flax, cotton, banana and straw fiber which can be used as reinforcements in different polymers. This natural fiber hydrophilic in nature and polymers which are hydrophobic are characterized by poor interfacial compatibility [9, 10]. The modification of the natural fibers surface usually leads to improving the adhesion between fiber and matrix and enhances the physical and mechanical properties of obtained composites. Treatment of natural fibers is beneficial in order to brighten the water resistance of fibers or enhance the wettability of the natural fiber surface by polymers. The investigation of sisal fibers treatment methods and sisal-based composites was subject of many research papers. Many chemical methods are used in surface modification, such as mercerization, silanization, benzylation [2, 3, 11, 12]. The physical modification methods, e.g., cold plasma treatment or corona treatment, were used as well [13].

Silanization is one of the fiber surface treatment methods, and it is conducted by using silane compounds [14, 15]. Prior used, the silanes react with water or alcohol, in order to obtain hydroxyl-silane groups (Si–OH), as coupling agent. The presence of these groups leads to direct condensation with hydroxyl groups in the natural fiber and reaction with other functional groups derived from polymer matrix [16]. Silanization does not provide to the destruction of the natural fiber. In the result, the thermally stable material with good adhesion to the polymer matrix can be obtained [17]. Overall silanes belong to the chemical compound which is efficient coupling agents extensively used in composites and adhesive formulations, e.g., in inorganic filler-reinforced polymer composites such as glass fiber or mineral fillers. The bifunctional structures of silanes have also been of interest in applying them for natural fiber/polymer composites since both glass fibers and natural fibers bear reactive hydroxyl groups [3]. Aminosilanes, especially γ-aminopropyltriethoxysilane (APS), are often used. Vinyl- or acryl-silane modifies fibers by covalent bonds in the presence of superoxide indicators [7].

Martin et al. [18] investigated the thermal degradation stability of the sisal fiber (Agave sisalana) and its constituents, cellulose, hemicellulose and lignin, exactly. The researchers indicated that depending on the atmosphere condition the exothermic peaks from DSC measurements under the nitrogen atmosphere with the maximum at 297 °C were assigned to hemicellulose degradation. The endothermal peaks at 365 °C were assigned to degradation of cellulose. Peaks indicated thermal degradation of the sisal fibers and their constituents, at air atmosphere, exhibited of two-step decomposition as visible two exothermic peaks. The first step appeared at 376 °C for raw sisal and at 351 °C for cellulose was the second step of the degradation appeared at 476 and 466 °C, respectively. TG measurements carried out under nitrogen atmosphere showed that the sisal raw sisal fiber decomposed in two steps. The first step was assigned to the hemicellulose degradation temperature, while the second step was attributed to cellulose degradation. Similar results were indicated also by Alvarez and Vazquez [19].

Kim and Netravali [20] have been investigated the chemical modification of sisal fiber (Agave sisalana) and their properties. Series of composites containing a different type of sisal fibers were prepared. The effect of the tension on the mechanical properties of the modified by mercerization sisal fibers was tested as well. First, the sisal fibers were modified by soaking in the 2 M sodium hydroxide solution under the ambient condition with desired tensions for 2 h. Moreover, the mercerized fibers without tension were also prepared. The results indicated that tensile stress and Young's modulus of the fibers increase with increasing tension weight up to 50 g per fiber. Tensile stress for untreated fibers amounted to 283.5 MPa and the Young's modulus—5.2 GPa. For the sample with mercerized fibers without tension, their parameters were: ca. 339 MPa and 6.1 GPa, respectively. Kim and Netravali [20] have used modified sisal fiber to investigate the effect of the tension on the mechanical properties of the sisal fibers-reinforced composites prepared with the use of soy protein concentration (SPC)-based resin. Composites with untreated fibers, sisal fibers mercerized with tension (50 g of mass per fiber) and slack-mercerized were prepared. Tensile strength and Young's modulus increased for mercerized fibers, and the highest parameters revealed composite containing sisal fibers mercerized with tension. The researchers explained the reinforcing effect of the mercerized sisal fiber as the impact of the solvent on the fiber chemical content, which caused the reduction in the hemicellulose and lignin. Cellulose is the polymer with the highest crystallinity level which confirms the reinforcing effect of the treated sisal fibers in the composites.

Sreekumar et al. [9] focused their work on the improvement in sisal fibers/polyester interaction by using various modifications methods including silanization. The silane treatment of fibers caused increase in the tensile strength and modulus of sisal-based composites. The SEM of silane-treated fiber shows the presence of macropores, rougher fiber surface and fibrillation.

Valadez-Gonzalez et al. [11] have been studying the effect of fiber surface treatment on the fiber–matrix bond strength of natural fiber-reinforced composites. Among tested modification methods (alkaline and preimpregnation), the silanization treatment of henequén (Agave fourcroydes) fibers was carried out. The fiber surface silanization results in a better interfacial load transfer efficiency but did not improve the wetting of the fiber. The silane treatment of the fiber surface increased the tensile strength of the analyzed composite material from 21 to 27 MPa. Depositing a silane coupling agent to henequen fibers has shown that adhesion between the natural hard fibers and matrix plays an important role on the final mechanical properties of the composite.

Barreto et al. [21] have described the properties of cardanol-based bio-composites containing sisal fibers (from Agave sisalana plant) treated by alkali solution. Based on the results, it was found that the chemical treatment improved the thermal stability of the mass loss process for sisal treated with NaOH solution (5 or 10%) when compared to non-modified sisal fiber in its raw state. A variation at 15 °C was also observed when comparing the composite reinforced by raw sisal with composite reinforced with sisal treated by NaOH 10%. Bio-composites decomposed in three stages. The first stage of thermal decomposition for bio-composites reinforced with raw fiber occurred at 341 °C, while for treated fibers with NaOH occurred at 344 °C. The second stage for bio-composites with non-modified sisal was recorded at 438 °C, and modified sisal with NaOH 5% at the range from 440 to 444 °C. The last stage reported a significant difference in temperature for non-modified sisal (527 °C) and sisal treated with NaOH solution (535 and 542 °C) which indicates the better diffusion of the resin inside the fibers treated with alkali solution.

In our previously work, effect of high hydroxylated soybean oil (H3) content on the structure and mechanical properties of polyurethane composites containing sisal fibers was described [7]. This work is mainly focused on thermal and thermomechanical characterization of composites containing non-modified and modified sisal fibers dispersed in polyurethane matrix. The reason of sisal modification was to enhance the thermal stability of fiber and, thereby, the thermal stability of bio-polyurethane composites.

Experimental

Materials and methods

Materials

The bio-based polyurethanes (bio-PU) obtained via the prepolymer method were filled with the non-modified sisal fibers (WN) and silanized (WS) sisal fibers (International Fiber Corporation, Belgium). The sisal fibers length was about 1500 μm and width 300 μm. The fibers were degreased and dried prior to use. Prepolymer was synthesized from diisocyanate MDI (BorsodChem, Hungary) and a polyol mixture consisting of 75 mass% of commercial polyether PTMG, Mn ∼2000 (Overlack, Poland) and 25 mass% of hydroxylated soybean oil H3, (Gdańsk University of Technology, Poland). The reaction was conducted at 80 °C for 1 h. During the second stage of the process, the prepolymer chains were extended by using bio-1,3-propanediol (DuPont, USA) with 0.3 mass% of 1,4-diazabicyclo[2.2.2]octane (DABCO, Merck, Germany) as a catalyst. The molar ratio $[NCO]_{prepolymer}/[OH]_{chain\ extender}$ equaled 1:1. The bio-polyurethanes were filled with 5 and 15 mass% of sisal fibers, and later samples were molded using a hydraulic press. The procedure of silanization modification was typical and was going through treatment of the vinyltriethoxysilane solution on sisal fibers. Procedure details were described in our previous work [7].

Methods

TG Thermogravimetric analysis was performed in order to characterize the thermal stability of the modified and non-modified sisal fibers and prepared bio-polyurethane composites. All specimens were tested with the use of NETZSCH TG 209F3 analyzer. Samples about ca. 7 mg were measured in the temperature range from 35 to 600 °C with the heating rate of 20 K min^{-1}. Measurements were taken under the nitrogen atmosphere. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves for sisal fibers and bio-polyurethane composites were plotted as the results of the TG analysis.

Dynamic mechanical analysis The dynamic mechanical thermal analysis of bio-polyurethane composites containing various amount of non-modified or silanized sisal fibers was performed using DMA Q800 Analyzer (TA Instruments). Rectangular samples with dimension ca. 30 × 10 × 2 mm (length × width × thickness) were measured in the temperature range from −100 to 150 °C, where the heating rate of 4 °C min^{-1} was taken. As mechanical stress during measurements, the single torsion mode was used. Tests were executed under a nitrogen atmosphere at the operating frequency of 10 Hz. In order to obtain the mechanical characteristics of the prepared bio-polyurethanes, the variation of storage modulus, E′ versus temperature, loss modulus, E″ versus temperature and Tan δ versus temperature was plotted. DMA tests were carried out for verifying the influence of the sisal fiber modification on the composites thermomechanical properties. Furthermore, this measurement

allowed to determine the glass transition temperature of the soft segments of prepared bio-PU composites, which was assumed as the transition in the Tan δ curve. The storage modulus E' is provided to information regarding the material stiffness and the stored energy. Loss modulus E'' is used to measure the energy dissipated as heat, while loss factor (Tan δ) measures the degree of molecular motion [27].

FTIR spectroscopy Spectroscopic analysis of bio-polyurethanes was carried out by means of a FTIR Nicolet 8700 spectrophotometer (Thermo Electron Corporation) and ATR technique. The Specac Heated Golden Gate single-reflection diamond ATR accessory was used. Spectra were registered at room temperature for wavenumbers ranging from 500 to 4500 cm^{-1} at 4 cm^{-1} nominal resolution with 64 scans.

SEM analysis The microscopic analysis was conducted on the cross section of samples using a Quanta FEG scanning electron microscope under the following conditions: magnification between 500 and 10,000, the Everhart–Thornley detector (ETD) and a high vacuum at 30.00 kV at a working distance of 10 mm. Samples were coated with gold prior to microscopic observation.

Tensile test The mechanical analysis in static condition was conducted by the tensile test. Tensile strength (TS_b) and elongation at break (Eb) were recorded by using Zwick Z020 tensile-testing machine according to EN ISO standard 527-1:1996 and 527-2:1996. Dumbbell-shaped samples were tested with normalized dimensions. Measurements were taken at 50 mm min^{-1} speed rate. Investigations were carried out at the room temperature.

Hardness Hardness (H) was measured according to the PN-EN ISO 868:2005 standard. The circular samples ($\Phi 56 \times 6$ mm) were placed on a flat surface, and ten measurements were taken per sample by applying a Shore A durometer for 3 s.

Rebound resilience Rebound resilience was determined by means of a rebound tester in accordance with the ISO 4662:2009 standard. Rebound resilience is measured by dropping a free-falling pendulum hammer from a given height, which impacts the sample. The amount of energy is shown on a pendulum scale. Ten measurements were recorded per sample.

Abrasion resistance Abrasion resistance (V) was tested with an Abrasion Check instrument (Gibitre instruments) in accordance with the ISO 4649:2010 standard. The value of abrasion resistance was calculated according to the following formula:

$$V = \frac{(m_1 - m_2) \times 0.2}{\rho \times \Delta m_w} \ (cm^3) \tag{1}$$

where m_1—the mass of the sample before the test (g); m_2—the mass of the sample after the test (g); 0.2—the required mass loss of the standard sample (g); ρ—the density of the analyzed material (g cm^{-3}); and Δm_w—the arithmetic mean of the mass loss of three standard samples (g).

Density Density (d) was determined according to the PN-EN ISO 1183-1:2013-06 standard. The measurements were performed in methanol at 23 ± 2 °C.

Results and discussion

Thermogravimetric analysis

Thermal properties of sisal fibers (non-modified and silanized), bio-PU composites containing 15 mass% of sisal fibers (WN or WS) and reference material (matrix) were determined by thermogravimetric analysis. Based on the obtained data, the effect of sisal fiber modification and its admixture on the thermal decomposition of the composite materials was described below (Figs. 1–4).

Thermal decomposition of sisal fibers took place in two steps (Fig. 4). Thermogravimetric analysis of the non-modified fibers (WN) and silanized fibers (WS) allowed confirming similarity in the thermal degradation curve curse. Figures 1 and 2 present the mass loss (%) and speed of the mass loss (% min^{-1}), respectively, of both of the used fibers type. Differences visible in Fig. 1 are connected with water content in the treated sisal fibers which led to gently enhanced mass loss and little faster speed of the mass loss. $T_{5\%}$, $T_{10\%}$ and $T_{50\%}$ for non-modified sisal fibers were noted at 83, 255 and 360 °C, while for silanized sisal
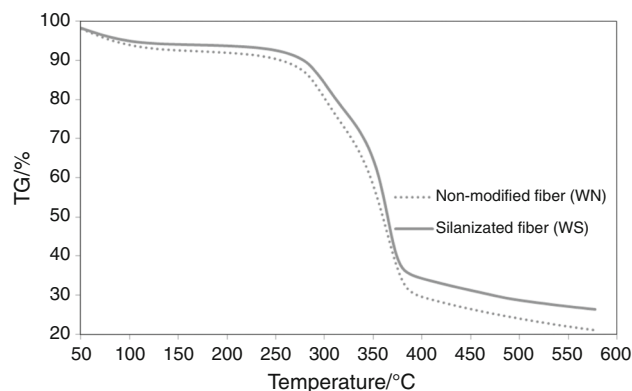

Fig. 1 Mass loss versus temperature plotted for the non-modified and silanized sisal fibers
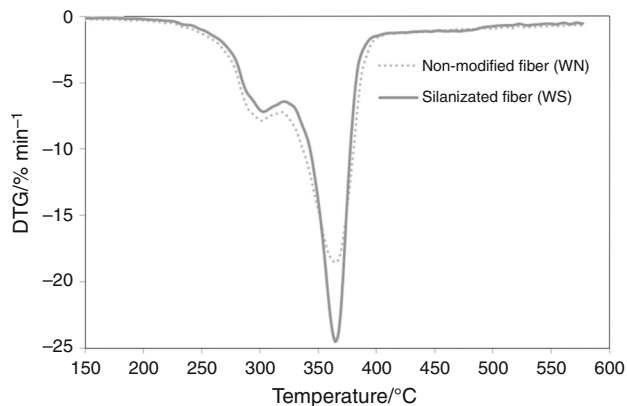
Fig. 2 DTG versus temperature plotted for the non-modified and silanized sisal fibers

Fig. 4 DTG curves of bio-PU composites containing 15 mass% of non-modified (WN) and silanized sisal fiber (WS), and reference material (REF)

fibers at 100, 278 and 365 °C, respectively. Figure 2 shows distinct peaks, where the first peak appeared at 297 °C and the second peak appeared at 365 °C. First step attributed to the hemicellulose degradation which constitutes one of the sisal fiber components. The second step corresponded to the cellulose degradation which is the sisal fiber constituent exhibited in the highest amount of the fiber. The same results were obtained by Martin et al. [18] and also by Alvarez and Vazquez [19]. Figure 2 shows speed of mass loss during thermogravimetric measurements. Silanization of the sisal fibers allowed to improve their thermal properties in bio-PU comparison with non-modified sisal fibers. Silanized sisal fibers revealed lower speed of mass loss than non-modified fibers.

Figures 3 and 4 show the TG and DTG, respectively, of the prepared bio-PU composites and reference specimen. Based on the results, it was found that composites containing chemical-modified sisal fibers revealed similarity in the thermal stability compared to non-modified sisal fiber-based composite (Fig. 3). In the case of the thermal
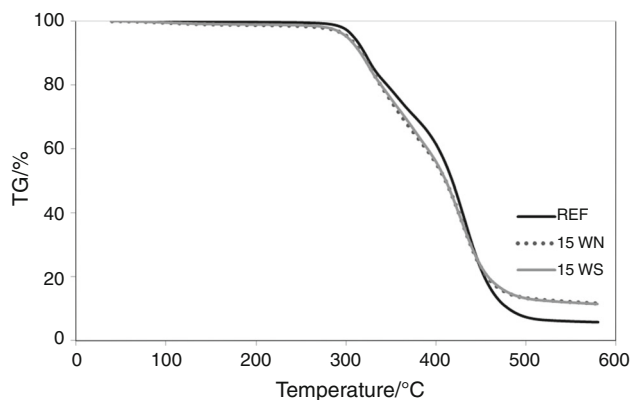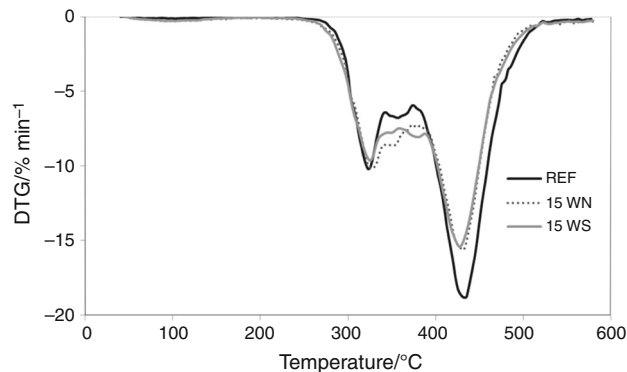
decomposition of the bio-PU composites containing sisal fibers, the processes took place in three steps. In comparison with the matrix, the difference is connected with residues after the test, which appeared with higher the value for composites containing sisal fibers. The residues at ca. 600 °C derived from ash, which constituents are organic and inorganic impurities. Figure 4 presents the DTG curves of the prepared composites. The first step appeared at ca. 325 °C is assigned to the decomposition of urethane bonds in hard segments (isocyanate component and a low molecular weight extender) [22]. The second step appeared at 353 °C for bio-polyurethane composites prepared with the use of untreated sisal fibers and at 379 °C for silanized sisal fiber-based composites. The little peaks appeared in the temperature range from 340 to 380 °C is associated with decomposition of hemicellulose, lignin and cellulose derived from the sisal fibers. In the case of the reference sample, the board peak is caused by hydroxylated soybean oil residue derived from polyol mixture. The third step appeared at ca. 430 °C for each polyurethane materials is associated with the elastic segment degradation derived from polyols polyurethanes constituents. Similar results at the peaks appearance were obtained also by Pinto et al. [23]. Although the decrease in the sisal fiber speed of mass loss by silanization, there is no visible improvement in terms of used sisal fibers-based composites speed of mass loss [24]. The admixture of fibers resulted in a slightly increasing speed of mass loss in comparison with the reference sample.

Dynamic mechanical analysis

The dynamic mechanical behavior of the bio-PU composites containing different amount and type of sisal fibers was investigated with the use of dynamic mechanical analysis. The variation of the storage modulus, E' versus temperature, variation of the loss modulus, E'' versus temperature,

Fig. 3 TG curves of bio-PU composites containing 15 mass% of non-modified (WN) and silanized sisal fiber (WS), and reference material (REF)
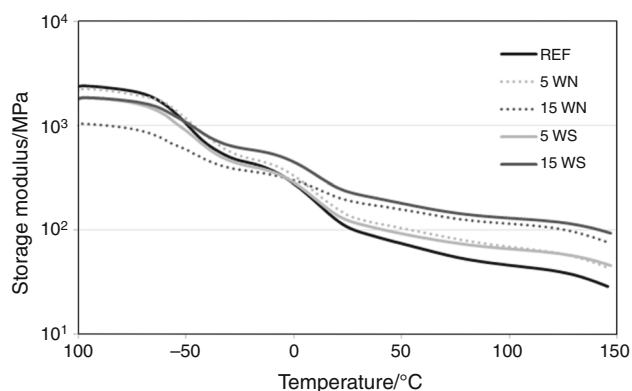
Fig. 5 Storage modulus as a function of temperature for bio-PU composites filled with non-modified (WN) and silanized sisal fiber (WS), and reference material (REF)
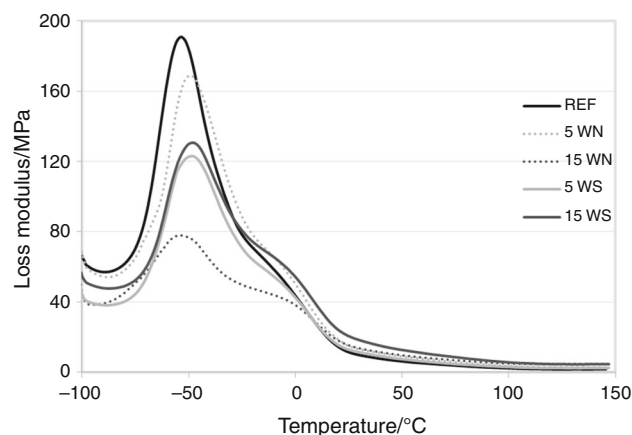

Fig. 6 Loss modulus as a function of temperature for bio-PU composites filled with non-modified (WN) and silanized sisal fiber (WS), and reference material (REF)

and variation of tangent delta, Tan δ versus temperature were recorded (Figs. 5–7). In Table 1 the determined parameters are correlated. It was observed that the sisal fibers strongly influence on thermomechanical properties of the prepared bio-PU composites. All curves indicated distinct double-peak curves. DMTA results showed that composites containing non-modified sisal fiber revealed the decrease in the storage modulus (E′), loss modulus (E″) and tangent delta (Tan δ) with increasing fiber amount. The most similar curves to the reference sample exhibited composite with 5 mass% non-modified sisal fiber content, which indicates a quite good interfacial bond strength and adhesion between the matrix and the fiber (Fig. 5). In the case of silanized sisal fiber-based composites regardless of modified sisal fiber content, the composites are characterized by similar thermomechanical behavior.

All curves indicated the linear behavior in the temperature range from −100 to −50 °C. The underlying cause of this behavior is the presence of polyurethane matrix, which occurs in the glassy state at the temperature range mentioned above. At the temperature up to −50 °C decreasing trend is observed. This tendency correlates with the alpha transition temperature [25]. The midpoint (Fig. 5) of the decreasing curve curses at the temperature range from −60 to ca. –20 °C (ca. −40 °C) is associated with the glass

transition temperature of the soft segments derived from polyols mixture contribution while the temperature peak assigned as the midpoint of the temperature range from −20 to ca. 20 °C (ca. 0 °C) indicated on the soft segments melting temperature, Tm_{SS} [26]. These points are strongly connected with peaks visible in the variation of Tan δ versus temperature graph (Fig. 6).

The storage modulus curves at the second temperature range indicated the lower values for bio-based composites correspond to reference sample. These results confirmed that there is no reinforcing effect of the sisal fibers on the composites [27].

The loss modulus (E″) strongly depended on amount and type of sisal fibers. The E″ values decreased with increasing sisal content (Fig. 6). The composite materials are characterized by the loss modulus in the range from 78 to 169 MPa. The significant differences were observed for the composite sample, with 15 mass% of non-modified sisal fiber; this value is the lowest one compared to rest materials. The elevated values of loss modulus of the obtained composites are advantageous because less energy is irreversibly lost by the materials [28]. These results confirm also the decreasing tendency in the hardness and rebound resilience properties of the prepared bio-PU composites.

Table 1 DMTA properties of bio-polyurethane composites containing non-modified (WN) and silanized sisal fiber (WS), and reference material (REF)

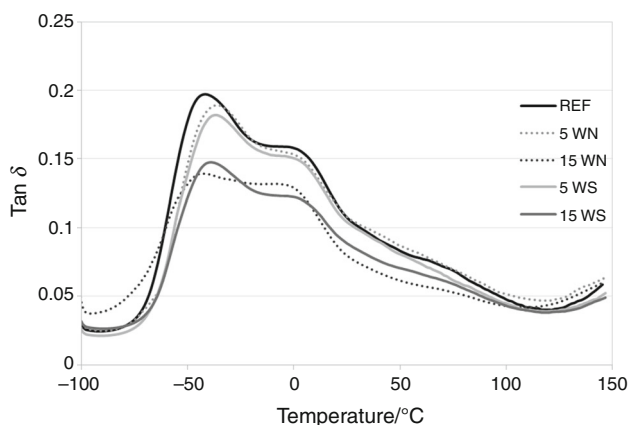| Fiber type and content/mass%	Properties				
	E′/MPa	E″/MPa	Tan δ/−	Tg_{SS}/°C	Tm_{SS}/°C
0–REF	2386	191	0.20	−42	0
WN 5	2230	169	0.19	−36	0
WN 15	1030	78	0.14	−42	−4
WS 5	1837	128	0.18	−38	0
WS 15	1839	130	0.15	−39	−0.5

Fig. 7 The Tan δ as a function of temperature for bio-PU composites filled with non-modified (WN) and silanized sisal fiber (WS), and reference material (REF)
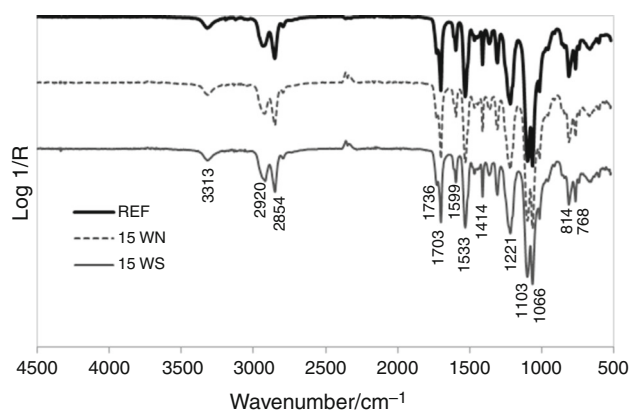

Fig. 8 FTIR-ATR spectra of bio-based polyurethane composites containing 15 mass% of non-modified (WN) and silanized sisal fiber (WS), and reference material (REF)

Table 1 shows the summary of the DMTA results of the prepared bio-PU composites. The lowest value of the glass transition temperature revealed matrix and composite with 15 mass% content of the non-modified sisal fiber (−42 °C). The highest value exhibited composite with 5 mass% content of the non-modified sisal fiber (−36 °C). The value of Tan δ is correlated with the cross-linking level between macromolecular chains (Fig. 7). The decreasing trend with growing sisal fiber content in the composites suggested the decline in the cross-linking in the prepared materials. The loss factor (Tan δ) indicates the damping ability of the material, which is the ratio of the mechanical dissipation energy and the storage energy. For good damping materials, the intensity of these peaks should be high [29]. The values of Tan δ of all investigated samples were between $0.1 \leq$ Tan $\delta \leq 0.2$, which indicates that synthesized materials have got good enough ability to damping capacity; nevertheless, with increasing sisal fiber content this ability is slightly declining [30].

Table 1 shows the DMTA properties of bio-polyurethane composites containing non-modified (WN) and silanized sisal fiber (WS) and reference material (REF).

Chemical structure

The chemical structure of bio-based polyurethane composites was investigated by FTIR-ATR analysis and is presented in Fig. 8. Registered spectra of bio-PU composites containing 15 mass% of sisal fibers (WN or WS) and bio-polyurethane matrix (REF) are similar to each other.

Characteristic for polyurethanes–urethane group vibrations registered at 3313 cm^{-1} corresponds to the stretching vibration of NH bond and at 1599 cm^{-1} is attributable to the out of plane bending of NH. The stretching vibration of CN was registered at 1533 cm^{-1} [31]. The valent vibration of carbonyl group present in the structure of synthesized bio-polyurethane matrix and composites both for free and hydrogen-bonded carbonyl groups manifests itself as a multiplet at a wavenumber range from 1703 to 1736 cm^{-1}, while the stretching vibration of C=O group occurs at 1221 cm^{-1}. The stretching vibrations of C–O–C group were registered at 1103 and 1065 cm^{-1}; the vibrations correspond to free C–O–C group and hydrogen-bonded C–O–C groups, respectively. The wavenumbers at 2854 and 2918 cm^{-1} correspond to the stretching vibrations of CH$_2$ groups, while the wavenumber value at 1414 cm^{-1} interprets as deformation vibrations of the same groups [28].

Morphology

In order to characterize the adhesion between sisal fiber and polyurethane matrix, the cross sections of the prepared bio-polyurethane composite samples were assessed by the scanning electron microscopy. It is clearly visible that the orientation of the short sisal fibers in the bio-polyurethane matrix was disordered organized. It seems that fibers were caked in polyurethanes matrix. Figure 9 shows that the non-modified sisal fibers revealed sharp edges at the matrix. These SEM images indicated on the insufficient adhesion between sisal fiber and bio-PU matrix. This
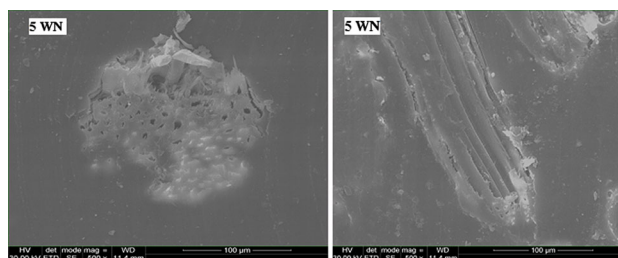

Fig. 9 Bio-PU composites containing non-modified sisal fiber (WN) in amount of 5 mass%
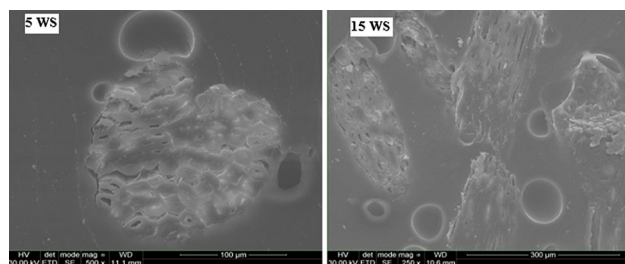
Fig. 10 Bio-PU composites containing silanized sisal fiber(WS) in amount of 5 and 15 mass%

conclusion is supported also by the free, small spaces observed along the sisal fibers. Consequently, the presence of these spaces decreases the possibility to bear the external stress by the composite. In Fig. 10 the SEM images of bio-PU composites containing 5WS and 15WS silanized sisal fiber are presented. There is clearly visible better caked sisal fiber distribution in comparison with non-modified fibers. We found that the fiber modification improved adhesion between polymer matrix and fiber. Similar results were obtained also by Manikandan Nair et al. [32], Kim and Netravali [20] and Jacob et al. [33], who investigated the modified sisal fiber adhesion with polymer matrix used the sisal fibers after such modification as benzylation, mercerization and alkali treatment, respectively. In Fig. 10 the SEM graphs exhibit bubbles which derived probably from moisture as residue from silanization or dampness from the atmosphere. The bubbles occurrence caused stress concentration which results in faster material breaking. This conclusion proved also the results of the mechanical measurements.

Mechanical properties

In order to characterize the prepared composites, their mechanical properties were investigated. The results of tensile strength and elongation at break are shown in Table 2. Moreover, hardness, rebound resilience, abrasion resistance, density were also studied. Bio-PU composites containing sisal fibers, non-modified (WN) and silanized (WS) revealed similar results in terms of tensile tests. The addition of the fibers generated the tensile strength and elongation at break reduction in compassion to reference sample (REF), bio-polyurethane matrix. Nevertheless, in the case of the bio-PU composites containing silanized sisal fiber, with increasing sisal fiber, the increasing tensile strength was noted. Bio-polyurethane composite prepared with the silanized sisal fibers usage revealed similarity in the tensile strength (ca. 9.50 MPa) to each other, despite the non-modified sisal fiber-based composites exhibited considerable distinction (12.19 and 9.43 MPa for 5 and 15 mass% fiber content, respectively). The elongation at break of the bio-polyurethanes composites was decreasing with increasing sisal content which was excepted.

Bio-polyurethane composites containing dispersed sisal fiber are characterized by lower hardness values than reference sample—bio-polyurethane matrix. Comparing the influence of sisal fiber type on the bio-polyurethane hardness, it was observed that modification slightly changed this parameter. The highest impact on the hardness reduction had addition of the 5 mass% of the non-modified sisal fibers. Overall, it was noted that with increasing fiber content hardness also increases and the bio-polyurethane composites have similar hardness to the reference sample (Table 2).

Rebound resilience decreased with growing sisal fiber addition. Some higher reduction was visible for bio-PU composites filled with silanized sisal fibers. The results are connected with the decrease in the mobility of polymer chain with the growing amount of sisal fiber. The growing fiber content resulted in harder and stiffer composites, which better assimilate the energy (Table 2).

Based on the abrasion resistance test results, it was found that the measured parameters decreased with increasing sisal fibers content, especially in the case of modified fibers. It was noted that both types of the sisal fibers (non-modified and silanized) addition caused decrease in the density, especially in the case of bio-polyurethane composites filled with silanized fibers (Table 2).

Table 2 Mechanical properties of the obtained bio-based polyurethane composites containing non-modified (WN) and silanized sisal fiber (WS), and reference material (REF)

Fiber type and content/mass%	Properties					
	TS_b/MPa	E_b/%	H/°Sh A	Rebound resilience/%	ΔV/cm^3	d/g cm^{-3}
0–REF	27.20 ± 3.13	443 ± 29	92.4 ± 0.5	48.6 ± 1.2	0.039 ± 0.005	1.064 ± 0.003
5 WN	12.19 ± 1.48	309 ± 20	86.8 ± 1.3	45.6 ± 0.9	0.055 ± 0.005	1.039 ± 0.002
15 WN	9.43 ± 0.66	48 ± 10	90.7 ± 0.5	41.6 ± 1.1	0.074 ± 0.010	1.040 ± 0.013
5 WS	9.44 ± 2.50	137 ± 50	87.0 ± 1.1	44.5 ± 1.3	0.068 ± 0.004	0.984 ± 0.001
15 WS	9.60 ± 0.47	30 ± 8	89.6 ± 0.7	38.3 ± 1.0	0.111 ± 0.007	1.040 ± 0.003

Conclusions

Series of bio-PU composites containing dispersed diverse quantity of sisal fibers (non-modified and silanized) were successfully obtained and analyzed. Based on thermogravimetric, thermomechanical and mechanical results, it was found that the sisal fibers can be added to the bio-based polyurethane matrix in the maximum quantity of 15 mass% and obtained materials characterize of good properties. Generally, thermal decomposition of bio-PU composites took place in three steps. Moreover, the chemical modification of sisal fibers slightly increases the thermal stability of sisal fibers and bio-PU composites and follows with lower rate. Overall, based on the analyzed DMA data, it can be stated that the higher silanized sisal fibers content had a quite positive effect in the whole range of temperature. Regardless of modified sisal content, the composites are characterized by similar thermomechanical properties. On the whole, sisal fibers addition to the bio-polyurethane matrix provided to decrease in the composites mechanical properties compared to reference sample. It was found that with increasing sisal fiber in the bio-PU composites, the tensile strength and elongation at break decreased. In the case of bio-PU composites containing silanized fibers, the tensile strength of these materials was similar although fibers content. In the case of comparison between both bio-PU composites types there were no significant differences in the value of hardness, rebound resilience and abrasion resistance.

References

1. Liu W, Xu K, Wang C, Qian B, Sun Y, Zhang Y, et al. Carbon nanofibers reinforced soy polyol-based polyurethane nanocomposites Thermal and mechanical characterization. J. Therm. Anal. Calorim. 2016;123:2459–68.
2. Ichazo M, Kaiser D, Albano C, Gonza J. Thermal stability of blends of polyolefins and sisal fiber. Polym Degrad Stab. 1999;66:179–90.
3. Xie Y, Hill CAS, Xiao Z, Militz H, Mai C. Silane coupling agents used for natural fiber/polymer composites: a review. Compos Part A Appl Sci Manuf. 2010;41:806–19.
4. Datta J, Kopczyńska P. Effect of kenaf fibre modification on morphology and mechanical properties of thermoplastic polyurethane materials. Ind Crop Prod. 2015;74:566–76.
5. Borsoi C, Zimmernnam MVG, Zattera AJ. Thermal degradation behavior of cellulose nanofibers and nanowhiskers. J Therm Anal Calorim. 2016;126:1867–78.
6. Yao F, Wu Q, Lei Y, Guo W, Xu Y. Thermal decomposition kinetics of natural fibers: activation energy with dynamic thermogravimetric analysis. Polym Degrad Stab. 2008;93:90–8.
7. Głowińska E, Kamerke J, Włoch M. Właściwości mechaniczne i morfologia kompozytów biopoliuretanowych wzmocnionych modyfikowanymi włóknami sizalowymi. Przem Chem. 2015;5:688–93.
8. Głowińska E, Datta J, Kamerke J. Mechanical properties of sisal fibre-reinforced soybean oil-based polyrethane biocomposites. Ph.D. Interdiscip. J. First Edit. Gdansk: Gdansk University of Technology; 2013;29–32.
9. Sreekumar PA, Joseph K, Unnikrishnan G, Thomas S. Surface-modified sisal fiber-reinforced eco-friendly composites: mechanical, thermal, and diffusion studies. Polym Compos. 2011;32:131–8.
10. Gironès J, Pimenta MTB, Vilaseca F, De Carvalho AJF, Mutjé P, Curvelo AAS. Blocked isocyanates as coupling agents for cellulose-based composites. Carbohydr Polym. 2007;68:537–43.
11. Valadez-Gonzalez A, Cervantes-Uc JM, Olayo R, Herrera-Franco PJ. Effect of fiber surface treatment on the fiber–matrix bond strength of natural fiber reinforced composites. Compos Part B Eng. 1999;30:309–20.
12. Mwaikambo LY, Ansell MP. The effect of chemical treatment on the properties of hemp, sisal, jute and kapok fibres for composite reinforcement. Macromol Mater Eng. 1999;272:108–16.
13. Wambua P, Ivens J, Verpoest I. Natural fibres: can they replace glass in fibre reinforced plastics? Compos Sci Technol. 2003;63:1259–64.
14. Gyoung J, Young S, Jin S, Hyun G, Hyeun J. Composites: part A effects of chemical treatments of hybrid fillers on the physical and thermal properties of wood plastic composites. Compos Part A. 2010;41:1491–7.
15. Belaadi A, Bezazi A, Bourchak M, Scarpa F. Tensile static and fatigue behaviour of sisal fibres. Mater Des. 2013;46:76–83.
16. Xu Y, Kawata S, Hosoi K, Kawai T, Kuroda S. Thermomechanical properties of the silanized-kenaf/polystyrene composites. Express Polym Lett. 2009;3:657–64.
17. Majeed K, Jawaid M, Hassan A, Bakar AA, Khalil HPSA, Salema AA, et al. Potential materials for food packaging from nanoclay/natural fibres filled hybrid composites. Mater Des. 2013;46:391–410.
18. Martin AR, Martins MA, Da Silva ORRF, Mattoso LHC. Studies on the thermal properties of sisal fiber and its constituents. Thermochim Acta. 2010;506:14–9.
19. Alvarez VA, Vázquez A. Thermal degradation of cellulose derivatives/starch blends and sisal fibre biocomposites. Polym Degrad Stab. 2004;84:13–21.
20. Kim JT, Netravali AN. Mercerization of sisal fibers: effect of tension on mechanical properties of sisal fiber and fiber-reinforced composites. Compos Part A Appl Sci Manuf. 2010;41:1245–52.
21. Barreto ACH, Rosa DS, Fechine PBA, Mazzetto SE. Properties of sisal fibers treated by alkali solution and their application into cardanol-based biocomposites. Compos Part A Appl Sci Manuf. 2011;42:492–500.
22. Liu L, Zhao X, Ma C, Chen X, Li S, Jiao C. Smoke suppression properties of carbon black on flame retardant thermoplastic polyurethane based on ammonium polyphosphate. J Therm Anal Calorim. 2016;126:1821–30.
23. Pinto ERP, Barud HS, Polito WL, Ribeiro SJL, Messaddeq Y. Preparation and characterization of the bacterial cellulose/polyurethane nanocomposites. J Therm Anal Calorim. 2013;114:549–55.
24. El-Shekeil YA, Sapuan SM, Khalina A, Zainudin ES, Al-Shuja'A OM. Effect of alkali treatment on mechanical and thermal properties of Kenaf fiber-reinforced thermoplastic polyurethane composite. J Therm Anal Calorim. 2012;109:1435–43.

25. Datta J, Parcheta P, Surówka J. Softwood-lignin/natural rubber composites containing novel plasticizing agent: preparation and characterization. Ind Crop Prod. 2017;95:675–85.

26. Saralegi A, Rueda L, Fernández-D'Arlas B, Mondragon I, Eceiza A, Corcuera MA. Thermoplastic polyurethanes from renewable resources: effect of soft segment chemical structure and molecular weight on morphology and final properties. Polym Int. 2013;62:106–15.

27. Głowińska E, Datta J. Structure, morphology and mechanical behaviour of novel bio-based polyurethane composites with microcrystalline cellulose. Cellulose. 2015;22:2471–81.

28. Głowińska E, Datta J. Bio polyetherurethane composites with high content of natural ingredients: hydroxylated soybean oil based polyol, bio glycol and microcrystalline cellulose. Cellulose. 2016;23:581–92.

29. Jin H, Zhang Y, Wang C, Sun Y, Yuan Z, Pan Y, et al. Thermal, mechanical, and morphological properties of soybean oil-based polyurethane/epoxy resin interpenetrating polymer networks (IPNs). J Therm Anal Calorim. 2014;117:773–81.

30. Datta J, Głowińska E. Effect of hydroxylated soybean oil and bio-based propanediol on the structure and thermal properties of synthesized bio-polyurethanes. Ind Crops Prod. 2014;61:84–91.

31. Das S, Pandey P, Mohanty S, Nayak SK. Influence of NCO/OH and transesterified castor oil on the structure and properties of polyurethane: synthesis and characterization. Mater Express. 2015;5:377–89.

32. Manikandan Nair KC, Diwan SM, Thomas S. Tensile properties of short sisal fiber reinforced polystyrene composites. J Appl Polym Sci. 1996;60:1483–97.

33. Jacob M, Thomas S, Varughese KT. Mechanical properties of sisal/oil palm hybrid fiber reinforced natural rubber composites. Compos Sci Technol. 2004;64:955–65.