Article

Processing and Properties of Wood-Plastic Composite Containing Alkali-Treated Birch Wood Shavings and Bioadditive Obtained by Biorefinery of Birch Bark

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Abstract: In the last two decades, there has been increased interest in research focused on developing innovative polymer composite materials for food packaging, obtained by compounding polymers with organic fillers, intended for the manufacture of food storage containers. Woodplastic composites (WPCs), due to high content of lignocellulosic filler, are consideredbiocomposites and can be used for the fabrication of such types of containers. Their formulations include, along with the matrix and the filler, functional additives. One of the most important considerations while developing a food packaging material is to choose eco-friendly additives. The suberinic acids (SAs), extracted from birch outer bark by hydrolysis in KOH water solution, were examined as lubricants in the formulation of recycled polypropylene/polylactic acid (rPP/PLA) composite filled with the alkali-treated milled birch shaving microparticles and proceeded by extrusion and injection molding. The incorporation of Sas in a birch wood-rPP/PLA composite was performed by treaing the wood microparticles with the SAs water suspension at the defined concentration. Their presence at the optimal content in the composite improved its processing by reducing the extruder rotor torque and injection pressure, which increased the mechanical properties and decreased the wettability of the composite.

Keywords: recycled polypropylenepolylactic composite; birch wood shavings; suberinic acids; lubricant; extrusion; rotor torque; mechanical properties

1. Introduction

According to the "Materials 2030 Roadmap" [1], the sustainable development of advanced materials is a key driver for further innovation, creating new opportunities for enhanced circularity, climate neutrality, prevention of environmental pollution, and provision of resources. In accordance with the requirements of the industry and the research communities, the development of environmentally friendly packaging from biodegradable and recycled materials is among the nine priority directions of innovation. The global market for packaging in monetary terms is huge and is around EUR 889.6 billion. There are many primary materials that are used in food packaging, including plastics, paper, cardboard, aluminum, and glass. Unfortunately, although paper and cardboard have a high recycling rate, their recycling requires significant quantities of water and heat. The production of alumina and glass takes a lot of energy. The usage of plastics in packaging grows, and today it is about 39%. This tendency in packaging will be saved in the near future due to the advantages of plastics, such as their cost, lightweight, easy production, ability to prevent gas and water vapor permeability, good mechanical properties in the solid state, etc. On the other hand, their growing application in food packaging has negative effects on the environment. To prevent pollution of the soil and aquatic environment from

plastics, the development of eco-sound plastic packaging containing, mainly, biodegradable ingredients is a challenge for packaging developers.

In the last two decades, there has been increased interest in research focused on developing innovative polymer composite materials for food packaging, obtained by compounding polymers with organic or inorganic fillers intended, for example, for the manufacture of food storage containers [2,3]. Woodplastic composites (WPCs) [4,5] can contain up to 90% lignocellulosic fibers, which, in comparison with other fillers for composite materials, have many advantages such as renewability, availability, biodegradability, light mass, high filling degree, etc. They are considered biocomposites and can be used as an eco-friendly material for such types of food packaging.

Polypropylene is indeed considered one of the most recyclable materials. In 2006, it was estimated that approximately 4.4 million tons of plastic, including polypropylene, were recycled. To mitigate the adverse environmental impact of synthetic polymers, their reuse as a polymer matrix in WPCs is a promising approach for the responsible management of polymer waste. Recycling PP has environmental benefits because it diminishes plastic waste volume and decreases carbon dioxide concentration in the atmosphere due to the absence of PP waste burning. The mechanical process of recycling PP involves several stages, namely, PP waste collection, sorting and cleaning, shredding, separation, and compounding. The obtained waste plastic mass is processed using an extruder, which melts the plastic mass at a high temperature, creating recycled PP granules [6,7].

Polylactic acid (PLA) is a biodegradable, biocompatible, and thermoplastic aliphatic polyester with significant potential use in various large-scale industrial applications ranging from packaging to consumer goods. The largest producers of PLA are NatureWorks LLC (USA), Toyota (Japan), Hitachi (Japan), DuPont (USA), Galactic (Belgium), Hisun Biomaterials (China), Total Corbion (Netherlands), etc. PLA may be considered as an alternative for replacing a thermoplastic matrix such as polyolefins in composites [8,9]. However, PLA is a brittle polymer that has poor impact strength, thermal stability, and a relatively high cost, which slows down the wide-scale application of PLA in composites.

Modification of polymers by blending is a simple, practical, and economically reasonable method for improving the properties of original polymers. To improve the poor properties of PLA and decrease the cost of end-products, it is blended with other polymers, including polypropylene (PP) [10–13]. Unfortunately, studies of binary blends of PLA with recycled PP are not enough [14]. Our investigation of the binary blends of rPP with PLA showed [15] that, when blending these polymers by extrusion, the disadvantages of each polymer were compensated by choosing the optimal weight ratio of the polymers in the blend and extrusion processing parameters. It was found that the developed hybrid rPP/PLA polymer matrix with a content of less than 10 wt% PLA in the blend was characterized by enhanced mechanical properties, improved hydrophobicity, good thermostability, a significantly lower cost compared to PLA, and supposedly improved biodegradability compared to rPP.

However, there is still an unsolved problem on how to improve the interfacial adhesion between wood fibers and the polymer matrix that significantly affects the properties of WPCs [4,5]. The adhesion affinity between polyolefins and lignocellulosic filler can be improved by the purposeful functionalization of the lignocellulosic surface or the incorporation of specific functional additives such as compatibilizers, coupling agents, adhesion enhancers, etc. in WPCs [16,17]. Several chemical methods can be employed to activate and functionalize lignocellulosic fibers, including alkalization, amination, ammoxidation, acetylation, benzylation, graft copolymerization, treatment with acids, peroxide, various anhydrides, permanganate, silane, etc., aimed at enhancing the adhesion on the polymer matrix/lignocellulosic filler interface in the composites [18–22].

The treatment of lignocellulosic fibers with alkaline water solutions is one of the simplest and most effective methods that is often used for their activation [23,24]. It is favored due to its ease of implementation and positive results achieved in terms of improved interfacial adhesion and overall composite performance. During alkalization,

the hydrogen bonding within the lignocellulosic network is disrupted or broken down. It results in a decrease in the content of amorphous cellulosic regions and an increase in the surface roughness of the fibers. The treatment also facilitates the removal of hemicelluloses, extractives, and waxes presented in the cell wall. These effects contribute to the increased availability of the lignocellulosic surface for interaction with a polymer matrix during composite processing.

There are some industrial methods for WPC processing, and extrusion is one of the most widespread ones. To improve the processing of WPCs by extrusion, special functional additives—lubricants are used in the composite formulations [5,25,26]. Lubricants reduce the melt viscosity of WPCs and positively affect energy consumption, productivity, and composite performance. They significantly improve the rheological properties of WPCs but, due to the plasticizing effect, can negatively affect the mechanical properties of the composites [27]. Fatty acids and their esters, fatty acid amides, metal salts of fatty acids (Ca, Zn, Mg, etc.), paraffin waxes, hydrocarbons, organic silicon compounds, etc., are the most known commercial lubricants used in WPCs [26,28,29]. The optimal content of a lubricant in the WPC formulations varies in the interval 2–7 wt%. Considering the application of lignocellulosic polymer composites for food packaging, using the most known synthetic lubricants in composite formulations can be harmful to man's health and pollute the environment.

Pulp and woodworking plants generate a large amount of birch bark, which is mainly used as fuel. Outer birch bark contains suberin, which is a valuable feedstock for obtaining various added-value eco-friendly products through its biorefinery. Depolymerization of suberin is the most widely exploited mode for obtaining suberinic acids (SAs) [30,31], which represent a complex of fatty acids (long-chain aliphatic saturated, unsaturated, and dicarboxylic acids) covalently bonded with aromatic structures (Figure 1).
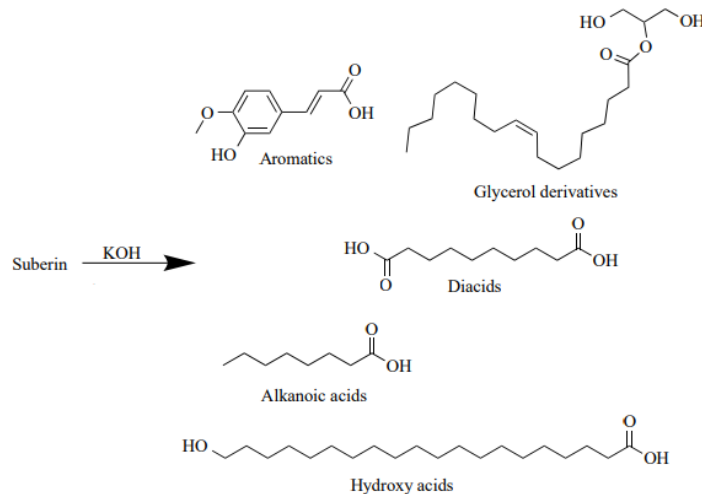

Figure 1. Suberin depolymerization fragments [32].

Due to the peculiarities of the chemical composition, SAs can be used as a formaldehyde-free adhesive for plywood [33–35], particle boards [36–38], and as a raw material for obtaining polyols for polyurethanes [32]. As mentioned, fatty acids and their esters are the most commonly used lubricants for optimizing the processing of WPCs in extrusion. The presence of fatty acids in the SAs composition allows for a high potential of SAs as a lubricant in the composite materials. The main objective of the study was to examine if suberinic acids, being the wood biorefinery product, could be used to replace a synthetic lubricant in the rPP/PLA–birch wood composite by determining the effect of the biorefinery product on the processing of the fabricated composite and its properties.

2. Materials and Methods

2.1. Materials

Birch wood shavings, which are a by-product of wood processing, were sourced from a Latvian furniture company. The wood shavings were subjected to elemental analysis (Elementar Analysensysteme GmbH, Langenselbold, Germany), and the chemical composition was determined using the Klason method for lignin (TAPPI 2002–2003) [39] and the Kürschner method for cellulose (TAPPI 1999) [40] content in birch wood, respectively. Hemicelluloses were determined according to TAPPI 1997 [41]. For the alkalization, the birch wood shavings were milled and fractioned to obtain particles $\leq$ 250 µm.

Recycled polypropylene (rPP) with the following characteristics, namely, a density of 0.9 t/m^3 and a melt flow index of 5.2 g/10 min at 230 °C and 2.16 kg, was used as the main component of the binary polymer matrix and supplied from a Latvian polymer recycling plant (Nordic Plast Ltd., Olaine, Latvia).

Polylactic acid 2002D (PLA) was purchased from NatureWorks LLC (Minneapolis, MN, USA) and had a density of 1.25 t/m^3 and a melt flow index of 5–7 g/10 min at 210 °C and 2.16 kg. PLA was used as a second component of the binary polymer matrix.

Zinc stearate (ZnSt), used as a representative of synthetic lubricants, was purchased from Sigma Aldrich (St. Louis, MO, USA). Its content in WPC samples did not exceed 2.0 wt%.

2.1.1. Suberinic Acids and Their Extraction

AS Latvijas Finieris (Riga, Latvia) supplied the isolated and fractionated wet outer birch bark, which was air-dried at room temperature to achieve a moisture content of 4–5 wt%. Subsequently, the material was milled in the SM 100 cutting mill (Retsch GmbH, Haan, Germany) to achieve particle size reduction, ensuring that it passed through a sieve with a 4 mm aperture. The milled bark underwent fractionation using an AS 200 Basic vibratory sieve shaker (Retsch GmbH, Haan, Germany). A fraction ranging from 1 to 4 mm was collected and subjected to two rounds of ethanol extraction, following the methodology described by in [42]. Following the extraction process, the residual outer birch bark was air-dried at room temperature until it reached a moisture content of 5–6 wt%. This dried residue served as the feedstock for suberin depolymerization in order to obtain suberinic acids (SAs). For the extraction of SAs, about 2.0 kg (dry basis) of the treated outer birch bark was depolymerized as described by Makars et al. [43]. The alkaline suspension obtained as a result of suberin depolymerization was gradually cooled to room temperature. Then, it was treated with HNO$_3$ to achieve a pH of 2. Following acidification, the resulting suspension underwent filtration using a polypropylene filter bag with a pore size of 100 µm. The obtained SAs were then suspended in approximately 13 L of water. The suspension was passed through a 1.5 mm mesh sieve to remove coarse particles. Subsequently, the remaining suspension was filtered again using the same filter bag to remove a significant portion of the water. The scheme for obtaining suberinic acids is shown in Figure 2.
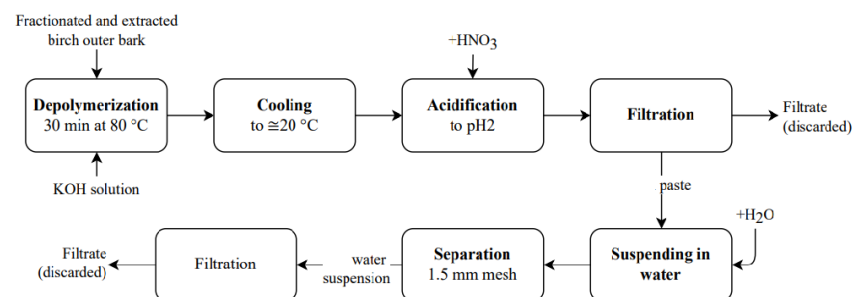

Figure 2. Scheme for obtaining SAs [43].

As a result, a SAs sample with a moisture content of 25 wt% was obtained (Figure 3). The biorefinery product contained 55.6% C, 6.8% H, and 37.6% O and was characterized by acidity—86.4 mg KOH/g, epoxy content—1.7%, and solubility in DMSO—39.3%.

Figure 3. Suberinic acids sample with 25 wt% moisture content.

2.1.2. Alkali Treatment of Milled Birch Wood Shavings

Milled shaving particles with a size smaller than 250 μm underwentalkaline treatment using a 5 L three-neck flask equipped with a return condenser, a thermometer, and a stirrer. The treatment was conducted under the following conditions: a NaOH concentration of 0.5 g/dL, a temperature of 90 °C, and a duration of 1 h, with a shavings/water weight ratio of 1/20. Subsequently, the treated shaving particles were washed until a neutral medium was achieved, dried, and then milled using a planetary ball mill (Retsch GmbH, Haan, Germany) for 15 min at 300 rpm. After sieving with a vibratory micromill "Pulverisette 0" (Frisch GmbH, Idar-Oberstein, Germany), a fraction of the birch shaving microparticles (BMS) with a size less than 100 μm was utilized as a filler in the WPC.

2.1.3. Incorporation of Suberinic Acids in the Composite

For the incorporation of SAs as a lubricant in the formulation of the composite, their water suspensions with a concentration from 2.5 to 30.0 wt% (dry basis) were prepared. A total of 100 g air-dried alkali-treated BMS particles < 100 μm were processed with 100 mL SAs suspensions having the abovementioned concentrations, and then they were carefully mixed manually for 3–5 min and dried, at first, at room temperature, then at 60 °C in a drying chamber until a constant weight. The acid content was expressed as a percentage of the weight of the composite.

2.1.4. Preparation of Composite Samples

Before fabricating the composite samples, the polymer matrix (rPP/PLA) in the form of a blend of the air-dried powdered rPP with PLA at a weight ratio of 95/5 was prepared by their mixing for 2–3 min at room temperature with a vibratory micro mill "Pulverisette 0". Then, the alkali-treated BMS microparticles, treated with SAs, were added to the rPP/PLA polymer matrix, and the obtained composite formulation was mixed for 5 min at room temperature with the same micromill and dried at 60 °C for 48 h. The extrusion and molding methods were employed using HAAKE MiniLab II and MiniJet II (Thermo Fisher Scientific, Karlsruhe, Germany) for the preparation of WPC samples for tensile, bending, and wetting tests. The samples were processed at a temperature of 175 °C and a circulation time of 5 min in a two-screw extruder. The injection molding was carried out at 120 °C. The "dogbone" samples for the tensile test had the following sizes: an overall length of 63.0 mm, an overall width of 9.4 mm, a narrow section length of 9.4 mm, a narrow section width of 3.15 mm, and a thickness of 3.15 mm. For the bending test, samples with a length of 80 mm, a width of 10.0 mm, and a thickness of 4.0 mm were prepared. Five replicates were produced, and the standard deviations of the values were determined for each mechanical test. To study contact angles, the samples were 60.0 mm in length, 10.0 mm in width, and 1.0 mm in thickness. For measuring contact angles, three replicates were performed, and

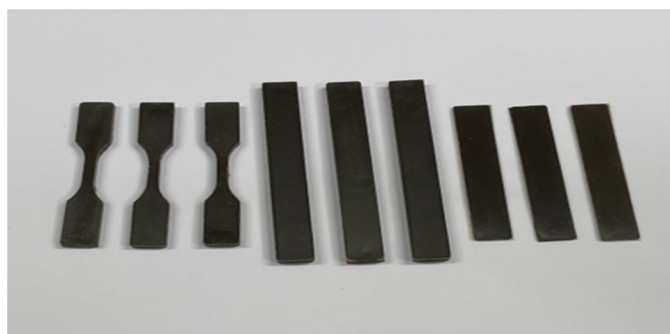the values of contact angles were arithmetic means. The samples used for the tests are presented in Figure 4.

Figure 4. Composite samples for mechanical and wetting tests.

2.2. Methods

2.2.1. Elemental Analysis

The elemental analyzer Vario MACRO CHNS (Elementar Analysensysteme GmbH, Langenselbold, Germany) with a heat conduction detector was used to determine the elemental composition of birch wood shavings before and after the alkali treatment.

2.2.2. Potentiometric and Conductometric Titration

The potentiometric and conductometric titration curves of water suspensions containing milled shaving particles (<100 μm) were generated using the InoLab level 3 Multiparameter Meter (WTW, Wissenschaftlich-Technische Werkstätten, Weilheim, Germany) equipped with a thermostat at constant stirring at 25 ± 0.1 °C. For pH adjustment, 0.1 M HCl and 0.1 M NaOH solutions were used.

2.2.3. Zeta Potential

The zeta potential (Z) of the initial and alkali-treated BMS microparticles was determined by the dynamic light scattering method using the Zetasizer Nano SZ device (Malvern Panalytical, Malvern, UK) at a temperature of 25 °C. Measurements were performed on 0.1% BMS suspensions in bi-distilled water. To ensure proper circulation of the suspension, an autotitrator MPT-2 (Malvern Panalytical, Malvern, UK) was employed. Three replicates were performed for each sample.

2.2.4. Thermogravimetric Analysis (TGA)

To evaluate the thermal stability of the initial and alkaline-treated BMS microparticles, thermogravimetric analysis (TGA) was performed using a Mettler Toledo TGA/SDTA 851e instrument (Mettler Toledo, Columbus, OH, USA) in the temperature range from 25 to 500 °C with a heating rate of 10 °C min^{-1}.

2.2.5. UV Spectroscopy

The UVspectra of water solutions of the extracted lignin, formed as a result of the treatment of initial milled shaving particles with bi-distilled water and NaOH water solutions under the same conditions, were recorded with a Genesys 10 UV/VIS spectrophotometer (Termo Fisher Scientific, San Jose, CA, USA).

2.2.6. Fourier Transform Infrared (FT-IR) Spectroscopy

The FT-IR study was performed using a Perkin Elmer Spectrum One apparatus (Perkin-Elmer Spectrum One, USA) in the range of wavenumbers from 4000 to 450 cm^{-1} at 30 scans and a resolution of 4 cm^{-1}. The tablets were prepared by mixing 20 mg of a sample with 200 mg of KBr, and then the tablet compression method was used. The differential spectrum was obtained by subtracting from the intensities of the absorption bands of the

FT-IR spectra of the alkali-treated wood sample the intensities of the absorption bands of the FT-IR spectra of the initial wood particles.

2.2.7. Water Uptake and Swelling

The water absorption capacity and swelling degree of the WPC samples were evaluated following the guidelines outlined in ASTM D 570 [44]. Prior to testing, the WPC samples were subjected to drying in an oven at 60 °C for 24 h. Subsequently, the dried samples were immersed in a desiccator containing distilled water. After 24 days, the samples were taken out, gently patted dry, and weighed. The changes in thickness were measured using a caliper. The water absorption (WA) and dimensional swelling in thickness (TS) were calculated using the following formulas:

$$WA~(\%) = (WA_t - WA_o)/WA_o \times 100, \tag{1}$$

$$TS~(\%) = (TS_t - TS_o)/TS_o \times 100, \tag{2}$$

where WA_t and WA_o were the weight of a sample after 24 days and initial time, respectively, and TS_t and TS_o were referred to as the sample thickness after 24 days and initial time, respectively. Five replicates were performed for each sample, and the standard deviation for each value was found.

2.2.8. Mechanical Tests

The mechanical properties were examined using a Zwick universal testing machine (Zwick/Roell, Ulm, Germany) with a load capacity of 0.5 kN. The tensile tests were conducted at a rate of 50 mm/min, while the bending tests were carried out at a rate of 2 mm/min. The testing procedures adhered to the ASTM D638 (2007) [45] standard for tensile testing and the ISO 178 (2010) [46] standard for bending testing. The software program TestXpert II 3.3 (Zwick/Roell, Ulm, Germany) was utilized for data analysis. Prior to testing, the samples were conditioned at 60 °C for 24 h. Five replicates were tested for each mechanical test, and the standard deviation was calculated for each parameter.

2.2.9. Torque and Injection Molding Pressure

The extruder rotor torque (T), injection pressure, and apparent viscosity of the rPP/PLA melt were measured using the HAAKE MiniLab, specially designed for compounding polymer blends and composite materials and testing their rheological properties. The device was equipped with a separate manual control box with an LCD screen for graphical data display and versatile application software. The measurements were undertaken with a rotor speed in the range of 10 rpm–130 rpm at 175 °C and a feeding weight of 5 g. For each composite formulation, the test was repeated at least three times.

2.2.10. Contact Angles

Contact angles of the WPC samples were measured with Kruss K100M (Kruss, Hamburg, Germany) using the Wilhelmy plate method. Before testing, the samples were conditioned at 60 °C for 24 h and stored at room temperature. Five replicates were performed for each sample, and the standard deviation for each value was found.

2.2.11. Milling

The birch wood shavings were milled using a planetary ball mill from Retsch (Haan, Germany). To separate the milled wood shavings into fractions, a mill "Pulverisette 0"(Frisch GmbH, Idar-Oberstein, Germany) equipped with a set of sieves was employed.

3. Results and Discussion

3.1. Characterization of Alkali-Treated Lignocellulosic Filler

It is known that the treatment of lignocellulose with an alkaline solution causes the collapse of a hydrogen bonding network and the cleavage of glycoside ether bonds in it. This reflects changes in the chemical composition of lignocellulose. Table 1 provides the chemical composition and content of the major wood components before and after the treatment of BMS with a 0.5 wt% NaOH water solution for 1 h at 90 °C. From a comparison of the chemical compositions, it follows that the alkaline treatment of the BMS particles increases the degree of oxidation of lignocellulose from 1.03 to 1.12 and decreases the hemicellulose content by 30%. At the same time, the relative content of cellulose enhances by 22%, but the content of lignin in the treated BMS enhances by 4%.

Table 1. Chemical characteristics of milled birch wood shavings before and after the alkali treatment.

Sample	C, %	H, %	O, %	N, %	O/C	Lignin, %	Cellulose, %	Hemicelluloses, %
Initial	45.9	6.2	47.5	0.4	1.03	21.5	47.9	26.1
Alkali-treated	44.1	6.3	49.3	0.3	1.12	22.3	58.3	18.2

The changes in the chemical compositions of the alkali-treated BMS particles were confirmed by the differential FT-IR spectra presented in Figure 5. The interpretation of absorption bands was performed in accordance with [47]. As can be seen, for the alkali-treated microparticles, the differential FT-IR spectrum shows a higher absorbance in the regions of 3400–2500 cm^{-1}, 1700–1290 cm^{-1}, 1220–1050 cm^{-1}, and 1050–850 cm^{-1}, and a lower absorbance within 1800–1700 cm^{-1} and 1290–1220 cm^{-1}. The absorbance peak at 3400 cm^{-1} is mainly due to O-H stretching vibration, but the peak at 2926 cm^{-1} is caused by C-H stretching vibration. The enhanced absorbance in this region can be provoked by new hydroxyl groups formed as a result of the partial oxidation of lignocellulose in the alkali-treated BMS. The remarkable decrease in absorption in the region 1800–1700 cm^{-1} with a maximum at 1738 cm^{-1} can be associated with the hydrolysis of ester bonds in hemicelluloses (xylan) in the alkaline medium and the shift of this absorption peak to the region of lower wavelengths as a result of the formation of salt bonds. This can also confirm the decrease of the absorbance peak at 1240 cm^{-1} caused by stretching vibrations in acetyl esters of hemicelluloses. The increase in absorbance at 1630 cm^{-1}, 1595 cm^{-1}, and 1507 cm^{-1} in the differential FT-IR spectra corresponds to C-C vibrations in the aromatic rings of lignin in the alkali-treated lignocellulose. A comparatively higher absorbance at a band of 1460 cm^{-1} and 1425 cm^{-1} is attributed to asymmetric C-H deformations in lignin. These findings confirm that the relative content of lignin in the alkali-treated wood microparticles in comparison with the initial BMS increases slightly. The intensity of the bands at 1374 cm^{-1}, 1331 cm^{-1}, 1162 cm^{-1}, and 898 cm^{-1}, caused by C-H and C–O-C stretching vibrations in cellulose, increases relative to the same bands in the FT-IR spectra of the initial milled shavings. This testifies that the relative content of cellulose in the alkali-treated lignocellulosic microparticles grows during the alkali treatment.

According to Table 1 and the obtained FT-IR spectra in Figure 5, the alkaline treatment of BMS does not diminish the content of lignin in the lignocellulosic matrix, although the opposite effect could be assumed. The result obtained, obviously, can be associated with the phenomenon of adsorption of the extracted lignin on the surface of the lignocellulosic particles, which can be confirmed by comparing the UV spectra of hydrolysates obtained by treating BMS in distilled water and 0.5% alkali solution at 90 °C for 1 h (Figure 6). The UV spectrum of the hydrolysate, formed as a result of the treatment of BMS in water, is characterized by pronounced absorbance bands at 238 nm (shoulder), 288 nm (maximum), and 315 nm (shoulder), which indicate the presence of biphenyl derivatives and aromatic fragments containing non-etherified hydroxyl groups, carbonyl groups, and carboxyl groups in the extracted lignin.
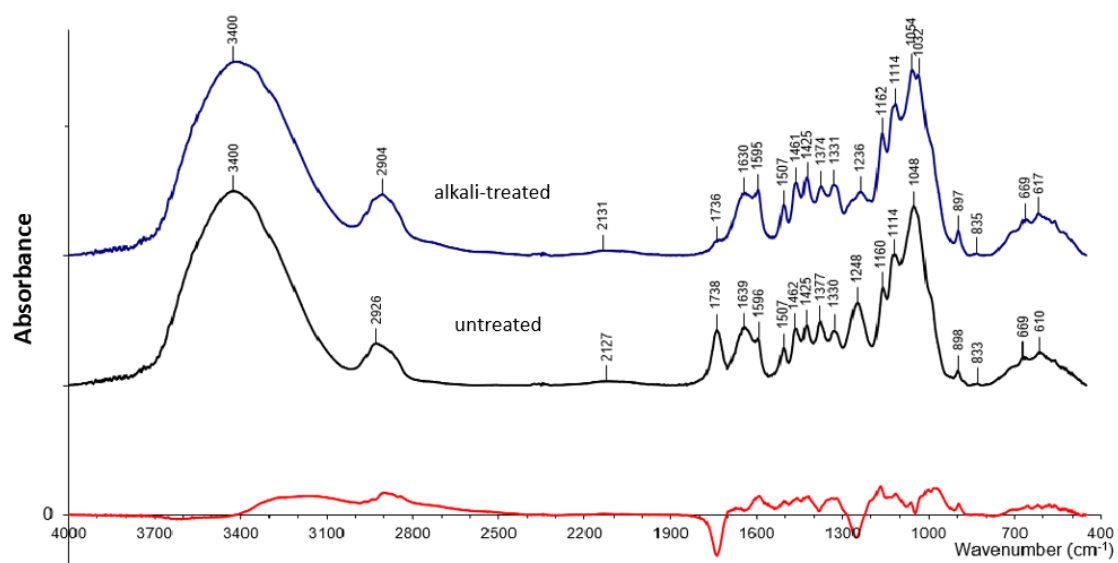
Figure 5. FT-IR spectra and differential FT-IR spectra of initial and alkali-treated BMS.
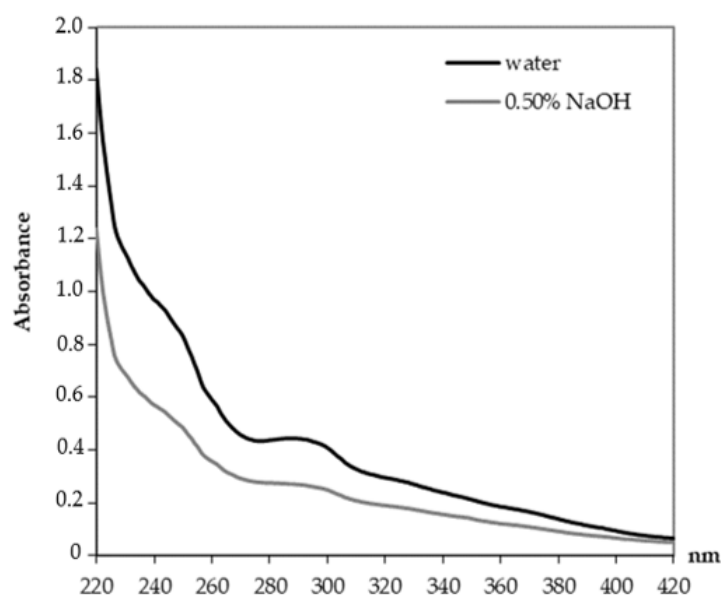

Figure 6. UV spectra of hydrolysates formed as a result of treatment of BMS with 0.5% NaOH and a bi-distilled water solution for 1 h at 90 °C.

The same bands on the UV spectrum of the extract, released as a result of the alkaline treatment of BMS, are characterized by a lower absorbance and are less pronounced. This can mean that the concentration of the extracted lignin in the alkaline hydrolysate is less than its concentration in water. This finding can indicate the partial resorption of the extracted lignin on the surface of the lignocellulosic matrix under the alkali treatment.

The changes in the functional composition of the birch shaving microparticles are reflected in the growth of the oxidation degree for the alkali-treated BMS (Table 1). The curves of potentiometric and conductometric titration of the initial and alkali-treated BMS microparticles are presented in Figure 7. As can be seen, the total content of the phenolic hydroxyl and carboxyl groups in the alkali-treated microparticles increases by almost 30%, indicating the partial oxidative degradation of the BMS particle's surface. The more charged functional groups that contain wood microparticles, the greater their zeta potential. It was confirmed by the comparison of the average values of zeta potential for the initial and alkali-treated BMS in water, which were −15.3 mV and −24.1 mV, respectively, wherein

the distribution of the zeta potential for the treated lignocellulosic particles was wider than in the case of the initial BMS.
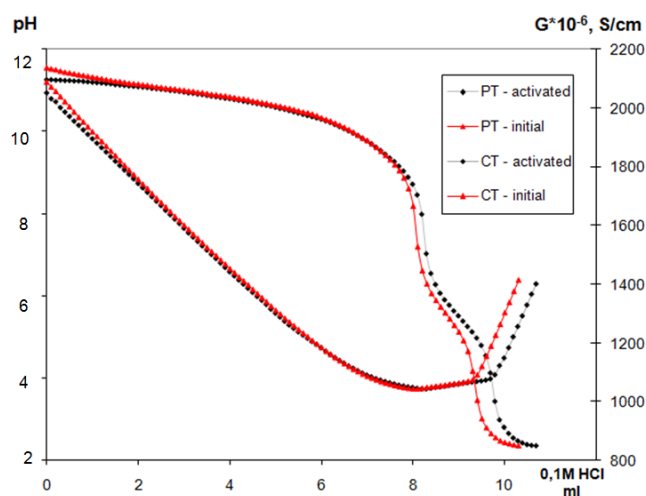

Figure 7. Potentiometric (PT) and conductometric (CT) titration curves of 0.02% water suspension of initial and alkali-treated BMS microparticles.

Considering the high processing temperature of the composite, it was necessary to compare the thermal stability of the untreated and treated birch wood microparticles, which were characterized by changes in the chemical composition. Figure 8 illustrates the thermogravimetric (TGA) and differential thermogravimetric (DTG) curves for the initial and alkali-treated BMS microparticles. As can be seen, the DTG curves of the initial and treated BMS show several decomposition regions. The first region from 50 to 115 °C corresponds to the weight losses determined by releasing water from the wood particles. The peaks at 279 °C, 320 °C, and 306 °C on the curves of the untreated and alkali-treated BMS can be associated with the thermal degradation of lignocellulosic matrix containing cellulose, hemicelluloses, and lignin, the initial degradation temperatures of which are the following: hemicelluloses—220 °C, lignin—280 °C, and cellulose—270 °C [48]. Herewith, the weight losses for the untreated and treated BMS particles vary from 40 to 45%, respectively.
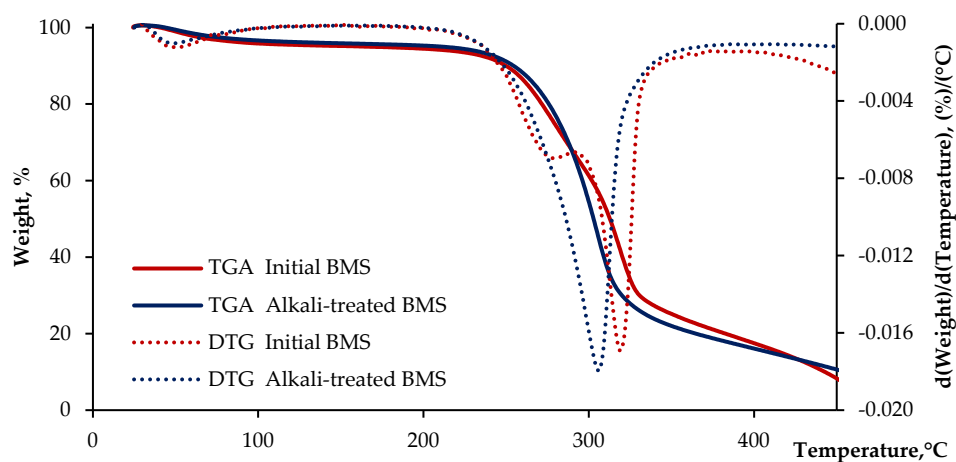

Figure 8. TGA and DTG curves for initial and alkali-treated BMS microparticles.

The shift of the peak on the DTG curve from 319 °C for the initial particles to 306 °C for the alkali-treated BMS (Figure 8) can indicate a deeper decomposition of the lignocellulosic matrix in the alkali-treated lignocellulose due to its oxidation. According to Figure 8, at a temperature of 175 °C, which is the processing temperature of the composite in the

extruder, the weight losses for the unmodified and modified BMS microparticles do not exceed 8–9 wt% and are related, mainly, to the presence of water in the samples. This means that the alkaline treatment of the BMS under the declared conditions does not reduce their thermal stability in the processing temperature region, and the alkali-treated birch shaving microparticles can be used as a filler in the biocomposite.

3.2. Processing of Composite Samples

The appearance of the added reactive sites in the form of phenolic hydroxyl and carboxyl groups on the lignocellulosic surface as a result of the alkaline treatment promoted the interaction between the lignocellulosic filler and the rPP/PLA matrix with the possible formation of a hydrogen linkage network at the interface, leading to the formation of interfacial structured adhesive layers. The formed layers favor the compatibility between the polymer matrix and the filler in the composite system and affect the processability of the developed WPC.

The rPP/PLA samples reinforced with both the initial and the alkali-treated shaving microparticles (<100 µm), containing SAs, were prepared by the extrusion and molding method. The formulations of the obtained WPC samples are given in Table 2.

Table 2. Formulation of composite samples.

rPP/PLA, wt%	MBS, wt%	SAs, wt%
50.0	50.0	0.0
50.0	48.0	1.2
50.0	47.5	2.5
50.0	45.1	4.9
50.0	43.0	7.0
50.0	40.7	9.3
50.0	38.0	12.0

According to the given formulations, the content of SAs in the composite varies from 1.2 to 12 wt%. It is known that the presence of a lignocellulosic filler in WPC increases its melt viscosity [25–28]. This is associated with the limited mobility of polymer chains in the presence of lignocellulosic particles as well as with filler particle-particle cohesive interaction that creates defined difficulties in composite processing. The main benefits from them are enhanced extruder rotor torque and enhanced injection molding pressure. The growth of the values of rotor torque and injection pressure with increasing the filling degree was also recorded by us with the HAAKE MiniLab control box during the processing of our composite samples.

The addition of a lubricant to a composite formulation can optimize the processing process by lowering the melt viscosity of the composite, thereby reducing the rotor torque. SAs were used as a potential lubricant to improve the processability of the developed WPC. Figure 9 shows the torque curves as a function of time for compounding the WPC formulation with 50 wt% untreated birch shaving microparticles (<100 µm), depending on the rotor speed. The shape of the torque curves corresponds to the typical rheological behavior of a WPC sample during the extrusion process. The first torque peak at the curves, corresponding to the start of the composite melting and compounding, is signed as a maximal torque value (T_{max}). The torque value after 5 min at the end of the compounding corresponds to a minimum torque value (T_{min}) close to a steady-state one. With a drop in the rotor speed, both the torque values decrease, and the maximal torque peak is shifted to a longer processing time.
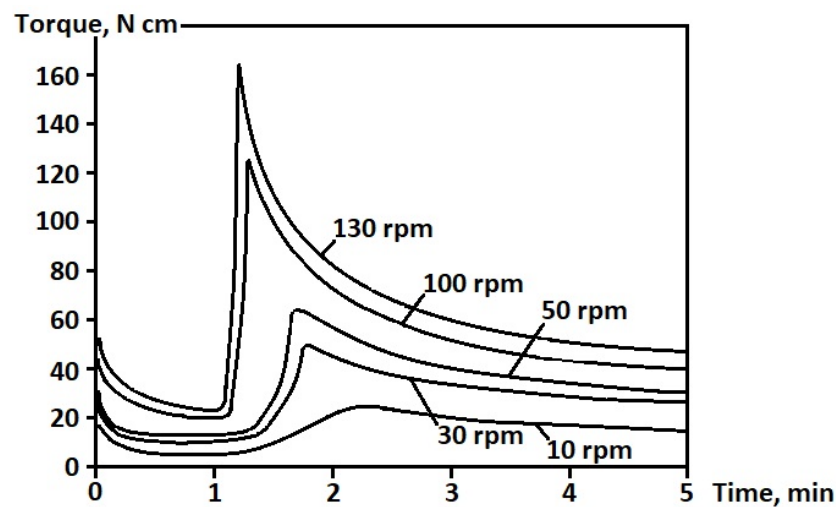
Figure 9. Torque vs. time curves for compounding WPC with a 50 wt% initial BMS at different rotor speeds.

The values of maximal and minimum torque during the processing of different materials are given in Figure 10. According to the presented results, rPP is characterized by the lowest values of T_{min} and T_{max}. The presence of 5 wt% PLA in the rPP matrix leads to an enhancement in both torques relative to rPP, which reflects the limited compatibility of the polymers. The filling of the rPP/PLA matrix with the alkali-treated BMS microparticles increases the T_{max} by 34% and the T_{min} by 17% compared to the same torques for the composite filled with the untreated BMS. The high values of the torques are associated with the increase in the melt viscosity of the composite due to the improved compatibility between the polymer matrix and the treated MBS microparticles, which have an enhanced specific surface due to the added content of the functional groups.
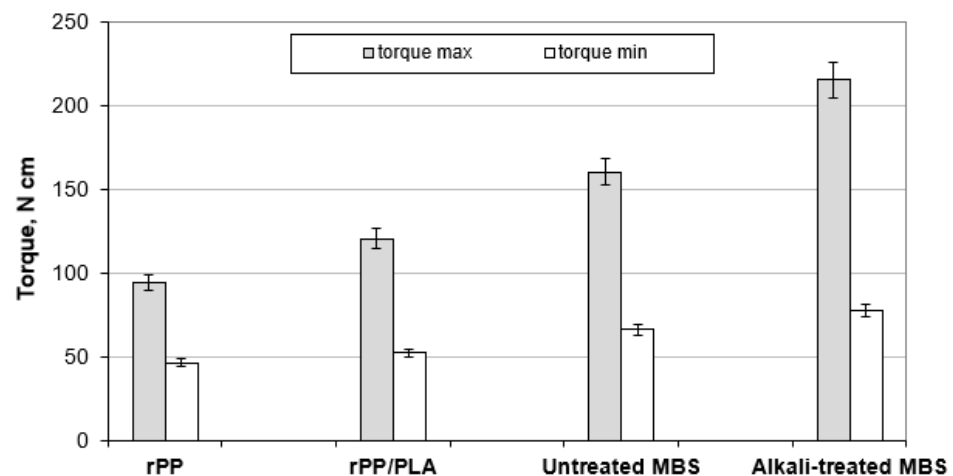

Figure 10. Maximal and minimum torque for the polymer matrixes and the composite samples.

In order to improve the processability of the composite, filled with the alkali-treated MBS, and reduce the energy consumption for its making, SAs were incorporated into the composite system. The T_{min} values of the composite samples without and with SAs, depending on their content at different rotor speeds, are presented in Figure 11.
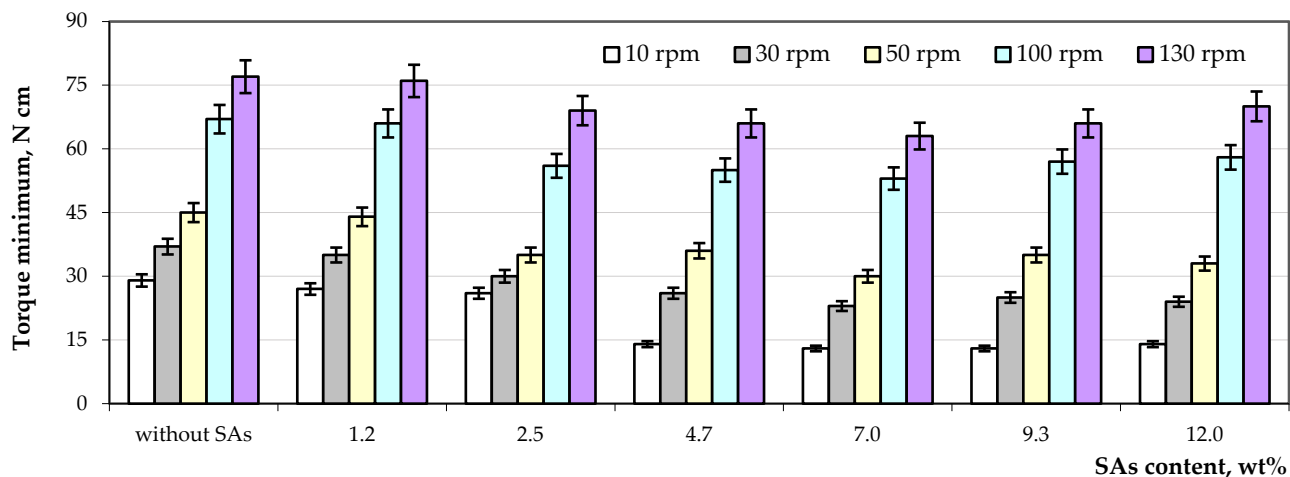
Figure 11. Effect of SAs content on minimum torque for the rPP/PLA composite at different rotor speeds.

It can be seen that with the growth of the rotation speed, the T_{min} increases several times, which reflects the non-Newtonian character of the melt flow of the composite, whose melting behavior is similar to that of pseudoplastic polymer liquid. According to Figure 11, the presence of SAs in the composite samples decreases the T_{min} values compared with the T_{min} values for the sample without SAs in its formulation. The dependence of the minimum torque on the content of SAs in the composite samples has a non-linear character. The lubrication effect increases with the growth of the content of SAs in the composite to a certain threshold value. The lowest value of the T_{min} of 63 N·cm at a rotor speed of 130 rpm corresponds to the content of SAs equal to 7.0 wt%, and this value is almost 23% lower than the value of the T_{min} found for processing the composite without SAs. At the same time, the content of SAs in the sample of more than 9.3 wt% causes an increase in the values of the minimum torque. This testifies that the lubrication effect of SAs in the developed composite is possible up to a certain content. Thus, the obtained results show that, due to the presence of fatty acids, SAs can perform the function of an internal lubricant in the developed composite, improving its melt flowability duringprocessing. With a decrease in the minimum torque, the injection molding pressure for fabricating the composite samples reduces (Table 3).

Table 3. Comparison of WPC sample processing parameters.

Lubricant	Minimal Torque, N cm	Injection Pressure, MPa
Without	72 ± 3	690 ± 20
2 wt% ZnSt	66 ± 4	550 ± 30
7 wt% SAs	63 ± 4	520 ± 25

In Table 3, the values of the minimum torque and the injection pressure for the processing of the WPC formulations filled with the alkali-treated BMS microparticles, without and with SAs, and a commercial lubricant—ZnSt are given. It can be seen that the presence of ZnSt and SAs in the WPC formulation leads to a decrease in the T_{min} value by 10% and 14% and the injection pressure by 25% and 32%, respectively, in comparison with the same indicators for the WPC sample without a lubricant. The comparison of the obtained results (Table 3) shows that SAs are a more effective lubricant than ZnSt at the optimal content in the WPC sample.

The optical images of the extrudates obtained without and with SAs at the optimal content in the biocomposite are illustrated in Figure 12. According to the images, the

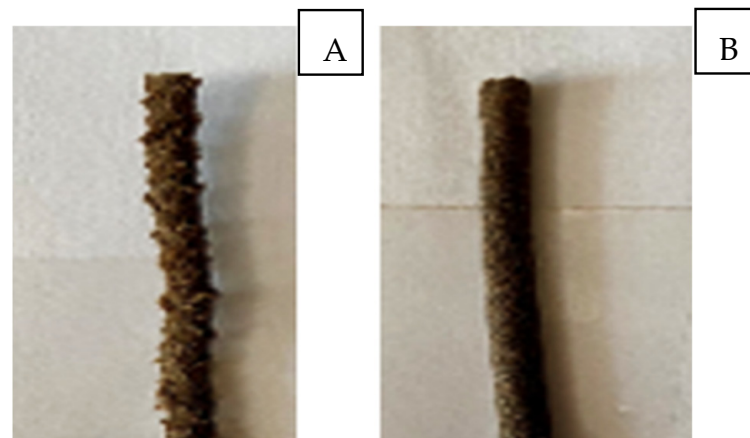extrudate containing SAs (B) has a more even and smoother surface than the sample without the bioadditive (A).

Figure 12. Extrudates of the biocomposite obtained without (**A**) and with SAs (**B**).

3.3. WPC Properties

Table 4 shows the values of the mechanical strength of the samples with different contents of SAs as well as ZnSt in an amount of 2 wt%. It can be seen that the effect of SAs on the mechanical properties of the composite is ambiguous. The increase of the SAs content to 7 wt% leads to an increase in the values of mechanical strength at break, both in tension and bending, in comparison with the composite sample filled with the alkali-treated BMS without SAs. The tensile and bending strengths increase by 11 and 19%, the corresponding mechanical moduli increase by 41 and 14%, and the tensile and bending deformability of the composite drop by 30 and 38%, respectively. With a further increase in the SAs content, a noticeable drop in the mechanical properties of the composite occurs. It is known that the excess of a lubricant in woodplastic composites favors the formation of a lubrication layer on a lignocellulosic surface, decreasing the interfacial interaction between the matrix and the filler [26,49].

Table 4. Mechanical properties of the composite samples with SAs and ZnSt.

Lubricant Content, wt%	Tensile Strength, MPa	Tensile Modulus, MPa	Deformation, %	Bending Strength, MPa	Bending Modulus, MPa	Deformation, mm
0	17.5 (2.2) *	686 (15)	3.0 (0.3)	18.7 (2.3)	2990 (20)	2.6 (0.3)
SAs						
2.3	17.8 (±2.1)	732 (±12)	2.6 (±0.2)	20.6 (±2.3)	3241 (±17)	2.3 (±0.1)
4.9	18.3 (±2.3)	956 (±14)	2.2 (±0.3)	21.2 (±2.2)	3358 (±18)	1.9 (±0.2)
7.0	19.5 (±2.0)	988 (±12)	2.1 (±0.2)	22.3 (±2.2)	3364 (±16)	1.6 (±0.2)
9.3	17.3 (±2.5)	644 (±15)	3.7 (±0.4)	20.8 (±2.5)	3139 (±23)	2.2 (±0.3)
12.0	15.2 (±2.4)	458 (±17)	4.6 (±0.4)	18.5 (±2.8)	3016 (±23)	2.5 (±0.4)
ZnSt						
2.0	17.9 (±2.4)	755 (±17)	2.4 (±0.4)	21.0 (±2.2)	3175 (±16)	1.8 (±0.2)

* The numbers in parentheses are standard deviation values.

The obtained results show that the SAs content of 7 wt% in the composite can be considered optimal since it has a maximal positive effect on its mechanical properties. Because the action of plasticizing and coupling in the composite is opposite, it can be assumed that, due to the presence of aromatic structures covalently bonded with SAs, which are capable of interacting with polylactide from the polymer matrix, SAs at the defined content in the composite can simultaneously exhibit the property of an adhesion

enhancer. Table 4 also shows the mechanical strength values for the composite containing 2 wt% ZnSt, which is a widely used commercial lubricant. A comparison of the mechanical properties of the composite samples containing different lubricants at their optimal content indicates that ZnSt, unlike the SAs, does not remarkably improve the mechanical properties of the composite due to the dominance of its plasticizing effect in this composite system.

Wettability is one of the crucial characteristics of WPCs for their exploitation, determining their end-use applications. It fully depends on the interfacial adhesion strength between a polymer matrix and a lignocellulosic filler. As a rule, the smaller the interfacial adhesion is between the components, the greater the wettability of a woodplastic composite is observed. The obtained results showed that both lubricants positively affected the hydrophobicity of the composite samples. The wettability of the composite samples was evaluated by measuring their contact angles and water sorption/swelling (Figure 13). As can be seen, the value of a contact angle for the composite sample filled with the alkali-treated BMS microparticles in the absence of a lubricant is 87.5°, but for the composite sample containing 7 wt% SAs, its value is 97.2°, which is 9.7° and 4.9° higher than in the case of the samples without any lubricant and in the presence of 2 wt% ZnSt, respectively. This can indicate that SAs can decrease the wettability of the composite, performing the function of an adhesion enhancer.
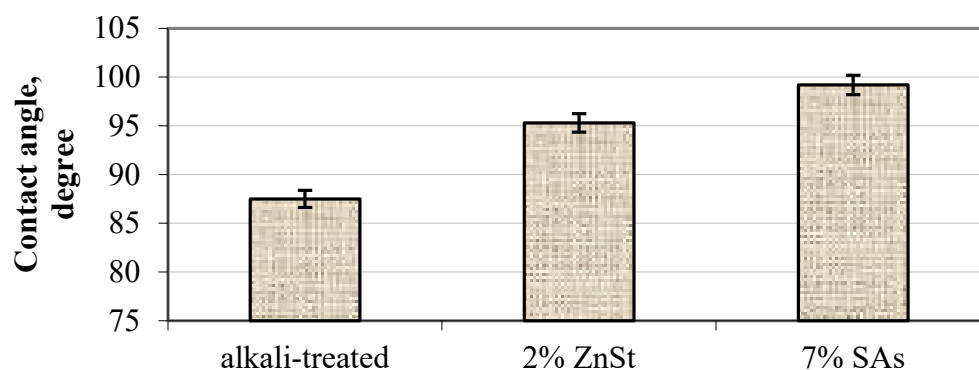

Figure 13. Contact angles of composite samples containing different lubricants.

The water sorption results for the composite samples are consistent with the obtained contact angle values. The water uptake and swelling of the samples were measured for 24 days. According to Figure 14, the highest water sorption and swelling values belong to the sample without a lubricant. The incorporation of the lubricants in the composite formulation leads to a decrease in the water absorption and swelling of the samples. With an increase in the SAs content in the samples up to 7 wt%, water sorption decreases by 15% and swelling by almost 30% relative to the same indicators for the composite without a lubricant. A further increase in the content of the SAs to 9 wt% provokes growth in both the water uptake and the thickness of the sample. It should be noted that, for composite samples containing SAs in amounts of 4.9 wt% and 7.0 wt%, the swelling values of the samples exceed the values of water sorption, which may be a sequence of the pronounced plasticizing effect of SAs. As seen in Figure 14, ZnSt also has a positive effect on the hydrophobicity of the composite. However, the decrease in water uptake and swelling relative to the sample without a lubricant is not so significant in comparison with SAs.
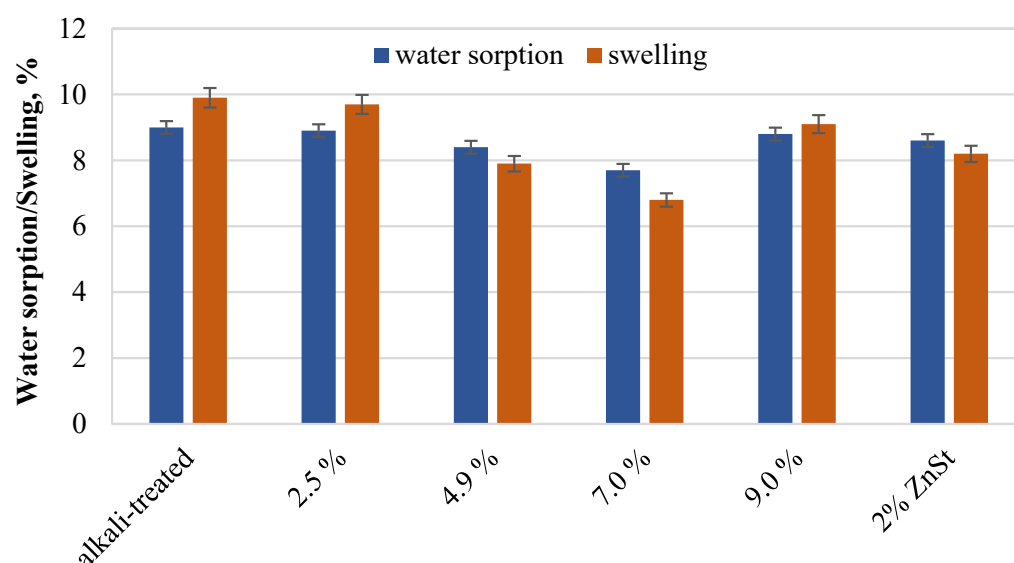
Figure 14. Water sorption and swelling of composite samples with different contents of SAs and ZnSt.

4. Conclusions

The alkali treatment of birch shaving microparticles improves their compatibility with the rPP/PLA polymer matrix in the composite, creating difficulties in the processing process, expressed in an increase in the extruder rotor torque and injection pressure. The incorporation of suberinic acids as a lubricant in the formulation of the composite, due to the presence of fatty acids in their composition, improves the processing of the composite by reducing the rotor's minimum torque and injection pressure. The dependence of the torque reduction on the suberinic acid content bears an extremal character. The greatest torque reduction occurs at a biolubricant content of 7 wt% of the weight of the developed composite. Due to the chemical composition of the suberinic acids, including the covalently bound aromatic structures, they can exhibit the property of a coupling agent at the optimal content, increasing the mechanical properties of the composite and reducing its wettability. Thus, the results show that the suberinic acids can be used as an internal lubricant, which can positively affect the properties of the woodplastic composite.

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