Lignin-containing Adhesion Enhancer for Wood-plastic Composites

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A lignin-containing adhesion enhancer, a water-soluble polyelectrolyte complex (LPEC) composed of soda hardwood lignin (HASL) and polyethylenimine (PEI), and the effect of the treatment of hydrolyzed and ammoxidized aspen sawdust with the LPEC nanoparticles were studied relative to the properties of wood-plastic composites (WPCs) based on recycled polypropylene (rPP). The presence of the excess of free amine groups and salt bonds between PEI and soda lignin, forming hydrophobic sites in the LPEC structure, caused the enhanced surface activity of the LPEC. The treatment with the LPEC nanoparticles increased the content of the fixed nitrogen in the modified sawdust samples and was accompanied by decreasing their water sorption and increasing contact angles that favored the decrease in the polar part of their surface free energy. The decreasing wetting ability enhanced the mechanical and water sorption properties of the obtained WPC samples. The improvement of the interfacial adhesion between the nitrogen-containing groups of the treated sawdust and the oxygen-containing groups of rPP was explained by the formation of both covalent and physicochemical bonds.

INTRODUCTION

The principles of the Circular Economy (Korhonen *et al.* 2018) dictate the sustainable, rational, and efficient management of wastes and by-products because their annual volume remarkably increases and negatively affects the environment. In contrast, waste recovery can provide a huge secondary resource for producing new materials and reducing their costs. Great attention must be drawn to the rational and effective utilization of both wood and polymer wastes.

The use of wood fibers as a filler for obtaining wood-plastic composites (WPCs), due to their renewability, easy availability, low cost, biodegradability, light mass, enhanced filling degree, *etc.*, is widely known (Faruka *et al.* 2012; Pickering *et al.* 2016). They are mainly used for building and construction applications, in the automobile industry, for production materials for domestic and technical needs, *etc.* According to the NOVA-Institute's statistical data, the demand for WPCs is growing globally (Carus *et al.* 2014).

Recycled polyolefins are among the major components of global municipal solid waste, and they present a promising raw material source for producing WPCs due to their large volume and low cost. The use of recycled synthetic polymers as a polymer matrix in

WPCs is a promising practice for rational recovering of these wastes and reducing their load on the environment (Najafi 2013; Turku *et al.* 2018)**.**

The high-performance properties of WPCs suffer from the problem of low compatibility between the hydrophobic polymer matrix and the hydrophilic wood filler. The improvement of the adhesion affinity between polyolefins and wood fibers in WPCs can be achieved by the modification of the fiber surface and/or the application of specific functional additives such as compatibilizers, coupling agents, or adhesion enhancers (Farsi 2012; Kabir *et al.* 2012). The functional additives can improve the properties of the filler particles, thus preventing their agglomeration and improving the adhesion interaction between a wood filler and a polymer matrix at the interface. They are applied in a small amount of 3 to 5 wt% by dry mass of the composite (De La Orden *et al.* 2010). The treatment of the wood surface with the functional additive can be done various ways, for example, by its addition as a solid ingredient in the raw blend of a polymer with a wood filler before their processing, by immersion or dipping of wood fibers in a solution, containing the functional additive, or by spraying this solution on the wood particle's surface before processing. The treatment of wood fibers by their immersion in the adhesion enhancer solution is an effective and inexpensive method for improving the properties of WPCs, allowing even distribution and adsorption of the enhancer over the wood surface before mixing with a polymer matrix. The choice of the adhesion enhancer is determined by its chemical composition, structure, molecular mass, reactivity, and depends on the origin of lignocellulosic fibers (wood species), fiber properties (specific surface area, porosity, surface charge density, *etc.*), filling degree, type of processing (extrusion, injection molding, pressing, *etc.*), and the required end-use properties of the WPCs (Lu *et al.* 2000; Kabir *et al.* 2012).

In the last decades, silanes, isocyanates, maleic anhydride-grafted polypropylene (PP-g-MAH), and polyethylene (PE-g-MAH) have been applied as interface adhesion modifiers for formulation of WPCs (La Mantia and Morreale 2011). The application of polyethylenimine (PEI) as a coupling agent for increasing the compatibility between a lignocellulosic filler and a polymer matrix is also known (De La Orden *et al.* 2007, 2010). Unfortunately, the most used functional additives for improving interfacial adhesion at the filler/polymer interface, such as maleated polyolefins, are synthetic, high-priced, and not biodegradable. In addition, maleated polyolefins can react with humidity during storage, with the release of free acid that can decrease their functional effectiveness (Taib *et al.* 2006). Many attempts have been made to use biodegradable polymers and their modified derivatives for obtaining the interface adhesion modifiers for application in WPCs, including lignin (La Mantia and Morreale 2011).

Lignin, a wood polymer, is the second most available polymer next to cellulose and comprises 25 to 30% of the non-fossil organic molecules on earth (Sarkanen and Ludwig 1971). The vast majority of technical lignins are co-products of pulp mills, where they are combusted in the form of lignin-rich black liquor streams to recycle process chemicals and produce steam for electrical energy generation. Lignin's great economic and industrial potential constitutes the real challenge of any study dedicated to valorization of lignins for their rational and effective utilization for obtaining value-added products (Karunarathna and Smith 2020).

Due to the peculiarities of the chemical structure, lignin can be included in blends with thermoplastic polymers, performing the function of a compatabilizer. Attempts have been made for the development of methods for lignin modification by its complexation with metal ions, hydroxyalkylation, esterification, alkylation, grafting with synthetic polymers and oligomers, mixing with reactive synthetic compatibilizers, *etc.* (Hu *et al.* 2014). Each of these methods had drawbacks, such as the enhanced product cost, complicated technique, use of organic solvents, and high applied temperatures and pressures. Only a few lignin valorization products, mainly the etherified lignin products, met the requirements of an interfacial adhesion enhancer for WPCs (Mariotti *et al.* 2014; Kun and Pukanszky 2017).

Polyelectrolyte complexes (PECs) are polyelectrolytes self-assemblies that are formed because of the interaction of oppositely charged polyelectrolytes (Tsuchida 2008). The driving force of their formation is the gain in entropy caused by the release of low-molecular-mass counter ions due to electrostatic interactions. Other types of interactions, such as hydrogen bonding and hydrophobic interactions, can additionally contribute to the complexation process. Due to the manifested adhesive and sorption properties, PECs have great potential and multiple practical applications in various practical fields, namely, in medicine as drug deliverers (Lankalapalli and Kolapali 2009; Verma and Verma 2013), for obtaining binders (Yuan *et al.* 2014), soil improving agents (Shulga *et al.* 2001, 2007), macrosurfactants (Shulga *et al.* 2009), *etc*. One of the prominent applications of PECs is the improvement properties of cellulose fibers and inter-fiber bonding (Gärdlund *et al.* 2003; Maximova *et al.* 2005; Hubbe 2006; Gärdlund *et al.* 2007; Hubbe *et al.* 2008; Ankerfors *et al.* 2009) in the papermaking process.

The polyanionic nature of soluble lignins enables it to interact with cationic polymers in aqueous media with the formation of lignin-containing polyelectrolyte complexes (LPECs) (Ström and Stenius 1981; Shulga *et al.* 1984; Li and Pelton 1992; Lappan *et al.* 1997). The LPECs can be fully soluble in water, form stable colloidal systems, or precipitate. The behavior depends on many factors, including the base strength of the cationic polymer, the interacting polyelectrolytes molecular masses, their charge densities, the lignin/polycation charge ratio, the medium's pH, and the ionic strength. Water-soluble polyelectrolyte complexes at the low concentrations in dilute aqueous solutions may be regarded as specific block-copolymers, consisting of hydrophilic and hydrophobic blocks, forming "core-shell" nanoparticles (Kabanov 2005; Pergushov *et al.* 2010). The charge-compensated structural fragments of a polyelectrolyte complex contain charged polyelectrolytes that relate to each other by salt bonds and form a hydrophobic "core", while the disconnected regions of polyelectrolyte chains are in the "shell" of the nanoparticles. In contrast, the water-soluble LPECs may be regarded as polyampholytes, present in the polymer chains' positive and negative ionic groups. It is known that the polyampholyte structural features are the reason for their pronounced ability to be adsorbed on cellulosic surfaces, adapting to the changing external conditions at the interface (Hubbe 2006). The change in the charge ratio of the interacting polyelectrolytes, pH values, and ionic strength can dramatically affect their adsorption on the interfaces (Shulga *et al.* 2002; Maximova *et al.* 2005; Hubbe 2006).

The aim of this study was to obtain an enhancer of interfacial adhesion in the form of a water-soluble polyelectrolyte complex, composed of soda lignin synthetic cationic polymer, and to study its effect on the properties of a wood-plastic composite based on recycled polypropylene.

EXPERIMENTAL

Materials

Aspen sawdust, representative of a waste of the mechanical processing of aspen wood (*Populus tremula*), was supplied by a Latvian company (4 PLUS Ltd., Aizkraukle, Latvia). The sawdust was characterized by elemental analysis (Elementar Analysensysteme, Langenselbold, Germany) and wood polymers' composition according to the procedures of Klason and Kürschner for lignin as per the TAPPI T222 om-11 standard (2011) and for cellulose as per the TAPPI T203 cm-99 standard (1999), respectively. The hemicellulose content was determined according to the TAPPI T264 om-97 (1997) standard. The elemental composition of the aspen wood sawdust was the following: 48.77% C, 6.25% H, 44.77% O, 0.11% N, and 0.10% S. The contents of cellulose, lignin, hemicellulose, extractives, and ash in the aspen wood were 50.6%, 18.5%, 28.7%, 4.51%, and 0.4%, respectively. The extractives and ash content were determined according to Zakis (1994).

Soda lignin, as a component of the LPEC, was obtained by the delignification of the acid hydrolyzed aspen sawdust in a laboratory reactor under the following laboratory conditions: hydromodulus – 1/7, NaOH concentration – 4.0%, temperature – 165 °C, and duration – 1.5 h. The hydrolyzed aspen soda lignin (HASL) was separated from the cooking solution of aspen sawdust by precipitation with 20% sulfuric acid, with the following: filtration, washing with hot distilled water, and subsequent drying. The content of Klason lignin in the sample was 90.8% as per the TAPPI T222 om-02 standard (2002). The chemical composition of the lignin was determined by elemental analysis (Elementar Analysensysteme GmbH, Langenselbold, Germany). Functional group analysis was performed using the Fibok-Shvappakh method for methoxyl groups, the acetylation method for aliphatic hydroxyl groups, the interaction with hydroxylamine hydrochloride for carbonyl groups, and potentiometric and conductometric titration for phenolic hydroxyl and carboxyl groups, according to Zakis (1994). The purified lignin had the following chemical composition: 62.3% C, 6.5% H, 0.15% N, 0.25% S, 30.8% O, OCH3 – 19.3%, total OH – 5.6%, phenolic OH – 3.5%, aliphatic OH – 2.1%, COOH – 2.1%, and CO – 3.9%. The average molecular weights of the lignin (M_w, M_n), determined with a SEC-MALS20 (Malvern Panalytical, Malvern, United Kingdom) in dimethyl sulfoxide (DMSO) with lithium bromide as an eluent at 60°C, were close to 10.5 kDa and 5.7 kDa, respectively.

High molecular branched polyethylenimine (PEI, M_w = 750 kDa, M_n = 60 kDa) in a 50% water solution, supplied by Acrōs Organics (ThermoFisherScientific, Fair Lawn, NJ, USA), was used as a component of the LPEC.

The used reagents were purchased from Sigma-Aldrich Chemie (Taufkirchen, Germany).

Activation of aspen sawdust

The hydrolyzed sawdust was obtained by low temperature hydrolysis with the dilute solution of hydrochloric acid under mild conditions (60 °C, 5 h, and weight ratio of wood particles to water 1:20) according to Shulga *et al.* (2016b). The ammoxidation of the hydrolyzed sawdust particles was completed by adding aspen microparticles to a NH4OH solution in the presence of persulfate ammonium as an oxidizing agent according to Shulga *et al.* (2016c). The content of the fixed organic nitrogen in the ammoxidized sawdust was equal to 1.09. Both the hydrolyzed and ammoxidized sawdust particles were washed with

double-distilled water using a Büchner funnel and a Bunsen flask, then dried to a neutral medium, dried, and milled with a planetary ball mill (Retsch, Haan, Germany) for 15 min at 300 rpm. After sieving, a fraction of the particles less than 100 μm was used for the treatment with the LPEC. The sieving was performed with a Vibratory micromill "Pulverisette 0" (Frisch GmbH, Idar-Oberstein, Germany).

Obtaining the LPEC

An adhesion enhancer in the form of LPEC was obtained by adding 0.2% aqueous solutions of PEI to 0.2% alkaline aqueous solutions of HASL (1:1 on dry matter) at pH 10.5 and room temperature by stirring the reaction mixture at 200 rpm using a magnetic stirrer (IKA RCT basic IKAMAG, IKA-Werke GmbH, Staufen, Germany) for 15 min. The soda lignin/PEI reaction mixture was prepared immediately before its application. Double-distilled water was used for preparation of the solutions of HASL, PEI, and their reaction mixture.

Treatment of the sawdust microparticles with the LPEC

The treatment of the hydrolyzed and ammoxidized aspen particles, < 100 μm, was performed by immersion of 7.5 g of the modified aspen particles in 1 L of the prepared HASL/PEI reaction mixture for 24 h under constant slow stirring at room temperature. After the treatment, both the hydrolyzed and ammoxidized particles were washed to neutral pH and dried at 60 °C for 48 h and 2 h at 105 °C, respectively. The moisture content in the treated sawdust particles was less than 1.0%. The content of nitrogen (N) in the treated hydrolyzed sawdust was equal to 1.12%, but in the treated ammoxidized particles it was 2.38%.

Preparation of WPC samples

Recycled polypropylene (rPP) (0.9 t/m^3, 5.2 g/10 min at 230 °C, and 2.16 kg) was used as a thermoplastic polymer matrix and supplied from a Latvian polymer recycling plant (Nordic Plast Ltd., Olaine, Latvia).

Before obtaining the WPC samples, the powdered rPP and aspen sawdust microparticles were mixed for 5 min at room temperature with a vibratory micromill PULVERISETTE 0 (Frisch GmbH, Idar-Oberstein, Germany). The samples for tensile and bending tests were prepared by the extrusion and moulding method using HAAKE MiniLab II and MiniJet II (Thermo Fisher Scientific, Karlsruhe, Germany) at a temperature of 175 °C, a circulation time in the two-screw extruder of 5 min, and a molding pressure of 60 MPa at a temperature of 120 °C. The content of the hydrolysed and ammoxidized sawdust microparticles in the WPC samples was 50 wt%.

Methods

Surface tension

The surface tension (γ) at the water-air interface for HASL and PEI aqueous solutions, as well as their reaction mixture, was measured by a Wilhelmy plate (Della Volpe and Siboni 2018), using a tensiometer K100M (KRUSS, Hamburg, Germany) at 25 °C with a circulation thermostat. The preparation of the samples and the measuring procedure were similar to those described by Shulga *et al.* (2006). Three replicates were made for each sample.

Zeta potential and size

Zeta potential (ζ) for the sawdust microparticles was measured with a dynamic light scattering device Zetasizer Nano SZ (Malvern Panalytical, Malvern, UK) at 25 °C, using 0.1% suspensions of the particles in bi-distilled water. For circulation of the suspension, an autotitrator MPT-2 (Malvern Panalytical, Malvern, UK) was used. Three replicates were made for each modified sawdust.

Viscometry

Specific viscosity of soda lignin, PEI, and LPEC was determined using a capillary viscometer Ubbelohde (Schortt Instruments, Mainz, Germany) with the flow time of bi-distilled water at 300 ± 0.01 s at 25.0 ± 0.1 °C, as described previously (Shulga *et al.* 2006). Three replicates were made for each sample.

Potentiometric and conductometric titration

The titration curves of HASL and PEI aqueous solutions were obtained using an InoLab Level 3 Multiparameter Meter (Wissenschaftlich-Technische Werkstätten, Weilheim, Germany) at constant stirring at 25 °C. For the adjustment of pH values, 0.1 M NaOH and 0.1 M HCl solution were used.

UV spectroscopy

The UV-spectra were recorded with a Genesys 10UVUV/VIS spectrophotometer (Termo Fisher Scientific, San Jose, CA, USA).

Wetting properties of WPC samples

To study the surface properties, WPC samples with dimensions of $60 \times 10 \times 1$ mm^3 were prepared. Before testing, the samples were conditioned at 60 °C in a drying cabinet for 24 h and then stored for 1 h at room temperature in a desiccator with phosphorus pentoxide.

The advancing contact angles of the modified aspen particles and the WPC samples were measured with a tensiometer Kruss K100M (Kruss, Hamburg, Germany) using the Washburn (Washburn 1921) and Wilhelmy (Della Volpe and Siboni 2018) methods, respectively. The work of adhesion was calculated using the Young-Dupre equation (Eq. 1),

$$W = \gamma(1 + \cos\theta) \tag{1}$$

where W (mN/m) is the work of adhesion, γ is the liquid surface tension (mN/m), and θ (°) is the contact angle.

The total surface free energy (SFE) and its dispersive (Lifshitz – Van der Waals interactions) and polar (Lewis acid-base interactions) components were calculated using the Owens-Wendt-Rabel-Kaelble method (Adamson and Gast 1997), for which the contact angle values with different liquids: water, DMSO, and diiodomethane were measured. For the calculation of SFE, a special software program (Advance Software Assurance, version 3.2, Kruss, Hamburg, Germany) provided in the tensiometer system was applied. Three replicates were tested for each sample and their arithmetic mean value was calculated.

The water vapor sorption of the composite samples was determined using the desiccator's method at a relative humidity of 98% and room temperature. Three replicates were made for each modified sawdust and WPC sample.

Mechanical tests

Mechanical properties were determined using a universal machine "Zwick" (Zwick/Roell, Ulm, Germany) with a load capacity of 0.5 kN at a rate of 50 mm/min and 2 mm/min for tensile and bending tests according to ASTM D638 (2007) and ISO 178 (2010) with the help of the software program (TestXpert I, Zwick/Roell, Ulm, Germany). Before testing, the samples were conditioned at 60 °C for 24 h and then placed in a desiccator with phosphorus pentoxide. Five replicates were made for each mechanical testing, and the standard deviation for each index was found.

Scanning electron microscopy (SEM)

The morphology of the obtained WPC samples was examined using a scanning electron microscope (Tesla, Brno, Czech Republic).

Milling

The milling of wood sawdust was carried out with a planetary ball mill (Retsch, Haan, Germany) and sieved using a mill "Pulverisette 0" (Frisch GmbH, Idar-Oberstein, Germany).

RESULTS AND DISCUSSION

Adhesion Enhancer

The working hypothesis of the study was the following: a water-soluble non-stoichiometric polyelectrolyte complex lignin/polyethyleneimine could ensure optimal physicochemical interaction with both a weakly negative surface of the rPP matrix and a negatively charged activated wood surface that would positively affect the compatibility between the wood filler and recycled polypropylene. A water-soluble, non-stoichiometric polyelectrolyte complex was obtained by the interaction of HASL and PEI in the reaction mixture with their mass ratio close to 1. The content of amine groups in the cationic polymer was more than 3-fold higher than the content of phenolic hydroxyl and carboxyl groups in the soda lignin in the reaction mixture. The excess of the amine groups of PEI in the LPEC was motivated by their expenditure on the formation of covalent bonds with both the surface's carbonyl and carboxyl groups of sawdust, and the oxidized groups of the rPP during the processing.

The needed functional groups ratio in the reaction mixture HASL/PEI was chosen based on the results of potentiometric and conductometric titration of amine groups of the PEI (Fig. 1A) and phenolic hydroxyl and carboxyl groups of soda lignin (Fig. 1B). The initial pH value of the LPEC HASL/PEI water solution was alkaline (pH 10.5). The alkaline medium of the LPEC HASL/PEI water solution was conditioned by the nucleophilic mechanism of the interaction between primary and secondary amine groups of the PEI and carbonyl and carboxyl groups of the modified sawdust and rPP during the processing, leading to the formation of the covalent bonds, namely, amide and imine (De La Orden *et al.* 2007, 2010), with both the wood filler and the recycled polymer matrix.

Table 1 shows the values of surface tension and specific viscosity of alkaline aqueous solutions of the LPEC HASL/PEI and its initial components – HASL and PEI, with the same concentrations, as well as the sizes and Zeta potential values of the LPEC, HASL, and PEI.
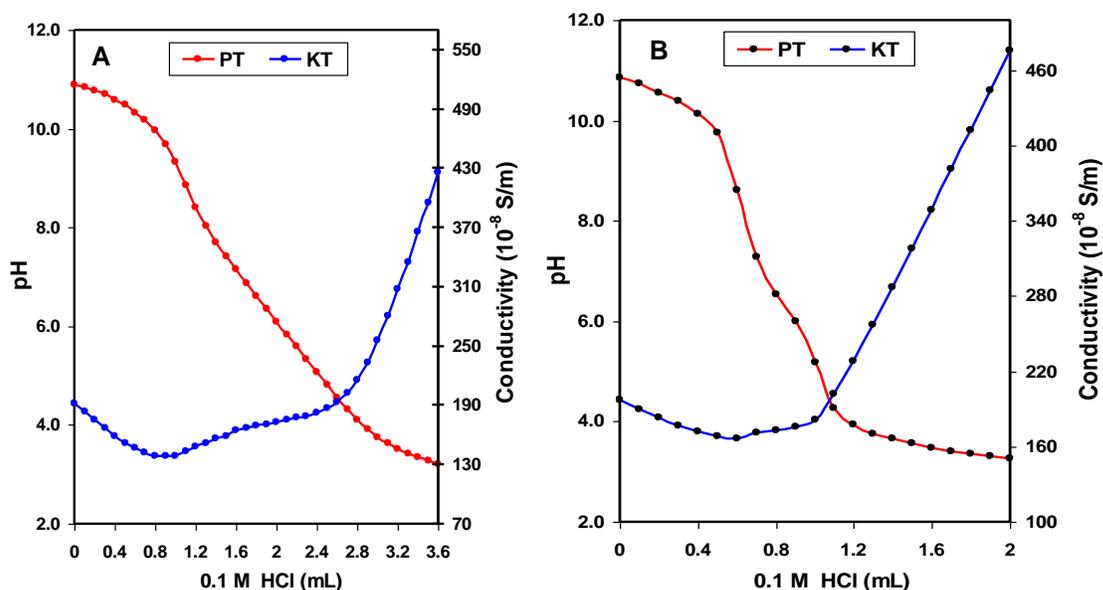
Fig. 1. Potentiometric (PT) and conductometric (KT) titration curves of (A) 0.01% PEI and (B) 0.01% HASL aqueous solutions

Table 1. Characteristics of 0.1% HASL, PEI, and Aqueous Solutions of Polyelectrolyte Complex HASL/PEI (1:1) at pH 10.5

Index	HASL	PEI	HASL/PEI
Surface tension (mN/m)	60.6	69.8	50.6
Zeta potential (mV)	-23.1	-7.5	-19.0
Size (nm)	**134**	**95**	**98**
Specific viscosity	0.019	0.045	0.056

According to the data obtained, the LPEC was characterized by better surface-active properties than the initial components. Thus, the LPEC expressed lower surface tension at the air-water interface compared to the initial components. Simultaneously, the value of its specific viscosity in the alkaline solution was less than the additive value of specific viscosity of the initial components, which may indicate a compact structure of the formed LPEC nanoparticles. The sizes of the nanoparticles of HASL, PEI, and the LPEC were in the range of 108 to 134 nm. The diameter of the formed LPEC nanoparticles was smaller than the size of the lignin nanoparticles, and close to that of the PEI nanoparticles. Taking into account the fact that the amino groups of PEI at this pH were practically not protonated, it can be assumed that, under these conditions, the LPEC nanoparticles can be only formed by H-bonding between the non-protonated amino groups of PEI, carbonyl (α- and β-ketogroups, aldehyde groups, quinone groups), and hydroxyl groups of soda lignin. At the same time, the visible increase in the intensity of the absorption curve of the UV spectrum of the alkaline solution of the LPEC HASL/PEI relative to the lignin solution (PEI does not absorb in the UV region) (Fig. 2) most pronounced in the range of 260 to 340 nm, testified the presence of the electrostatic interaction in the LPEC between the induced protonated amine groups of PEI and phenylpropane chains of soda lignin, containing non-conjugated phenol hydroxyl groups (absorption in the range of 280 to 300 nm), phenol hydroxyl groups conjugated with α-carbonyl groups (absorption at 310 nm), and carbonyl and carboxyl groups (absorption at 328 and 345 nm) (Faix 1992).
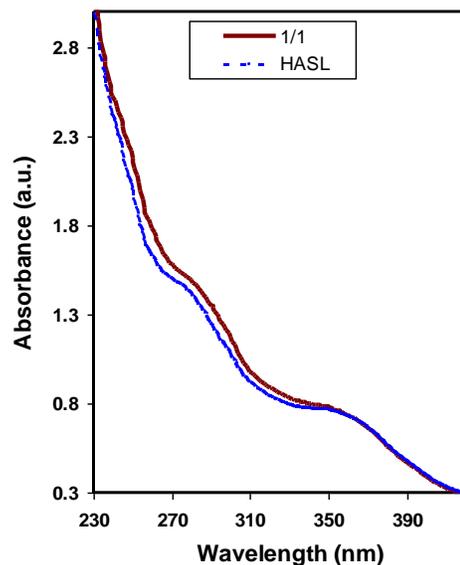
Fig. 2. UV spectra of dilute alkaline solutions of HASL and LPEC (1:1)

The change in the absolute value of ζ potential of the LPEC nanoparticles by 4.1 mV relative to the ζ potential of the negatively charged soda lignin (Table 1) could also confirm the presence of the electrostatic interaction between HASL and PEI at the alkaline pH value. The salt bonds between the positively charged amine groups of PEI and negatively charged functional groups of soda lignin are electrically neutral and can form hydrophobic sites in the resulting LPEC structure. Thus, the formation of the water-soluble LPEC in an alkaline medium may be regarded as a result of hydrogen and electrostatic interactions between the functional groups of soda lignin and PEI. It is obvious that hydrophobic, π-cationic and weak Van der Waal's interactions can also contribute to the formation of the LPEC nanoparticles. The presence of the excess of the free non-protonated amine groups, capable of forming imine and amide bonds with carbonyl and carboxyl groups, as well as the presence of salt bonds, forming hydrophobic sites in the LPEC, suggested an enhanced reactivity of the obtained LPEC HASL/PEI nanoparticles relative to the wood microparticles and the oxidized surface of the rPP.

Sawdust Filler

Table 2 shows that both the mild acid hydrolysis and ammoxidation affected the chemical composition of the aspen sawdust. The cleavage of ester and ether linkages in the lignocellulosic matrix of the wood during both modifications was accompanied by decreasing the content of hemicelluloses and lignin, but by increasing the relative content of cellulose. This chemical change led to the chemical activation of the lignocellulosic matrix surface and facilitated its accessibility for the following treatment with the adhesion enhancer.

Table 2. Aspen Sawdust Chemical Composition Depending on the Modification

Treatment	Cellulose (%)	Lignin (%)	Hemicellulose (%)	N (%)	O/C
Initial	50.6	18.5	28.7	0.11	0.26
Hydrolysis	52.6	18.2	24.5	0.17	0.24
Ammoxidation	54.8	17.5	22.4	1.09	0.25

The treatment of the modified samples – hydrolyzed and ammoxidized microparticles – with the LPEC was performed *via* their immersion in an alkaline aqueous solution at a room temperature. As a result, the content of the fixed nitrogen in the hydrolyzed and ammoxidized sawdust after drying increased from 0.17 to 1.15% and from 1.09 to 2.38%, respectively (Table 3). Because the sawdust particles modified with the hydrolysis and ammoxidation had a negative charge in the alkaline medium, due to the dissociation of the surface phenolic hydroxyl and carboxyl groups, it can be supposed that the adsorption of the LPEC nanoparticles on the negatively charged wood surface proceeded due to physicochemical interactions including Van der Waals' forces, hydrophobic interactions, and the formation of acceptor-donor complexes between the functional groups. Such type of the interaction of the LPEC nanoparticles with the modified wood surface may resemble the adsorption of the negatively charged lignin particles onto the negatively charged pulp fibers (Wågberg and Annergren 1997).

The main drawback of wood particles as a WPC filler was their pronounced hydrophilicity, which was expressed in the enhanced wetting ability. According to Table 3, the more pronounced ability to take up water vapor belonged to the initial milled sawdust. The content of water in these particles during 25 d reached almost 18% (on dry matter). This was caused by the presence of the hydroxyl and carboxyl groups emerging because of the mechanical treatment of the sawdust. This was evidenced by the highest negative value of the ζ potential for the milled particles, which correlates with the amount of the charged groups present at the sawdust surface.

Table 3. Characteristics of Initial, Modified, and Treated Modified Aspen Sawdust Microparticles (< 100 μm)

Sample	(-)ζ (mV)	Contact Angle (°)	Adhesion Work (mN/m)	Water Sorption (%)	Fixed Nitrogen (%)
Initial	18.2	79.70	85.82	17.9	0.11
Hydrolysed	16.5	85.10	79.02	15.8	0.17
Hydrolysed + LPEC	15.8	87.20	75.30	14.9	1.13
Amooxidised	16.3	84.30	80.03	16.4	1.09
Amooxidised + LPEC	15.3	88.00	74.90	14.5	2.38

The modified sawdust microparticles, namely hydrolyzed and ammoxidized ones, adsorbed water to a lesser extent, 15.8% and 16.4%, respectively, and had lower negative values of the ζ potential (Table 3). Evidently, the lower ability to uptake water may be conditioned by the reduction of the content of hemicelluloses by 4 to 6% (Table 1) in both samples, as well as the formation of covalent amide bonds in the ammoxidized sample. The treatment of the modified sawdust particles with the LPEC led to a further increase in

their surface hydrophobicity, which was reflected in a decrease in the amount of adsorbed water by 6 to 12% relative to the untreated modified samples and 20 to 23% relative to the initial sawdust. Evidently, the decreasing ability to be wetted by water was a result of the formation of imine and amide bonds between the free amino groups of the LPEC and the carbonyl and carboxyl groups of the lignocellulosic matrix of the modified sawdust (Shulga *et al.* 1982; De La Orden *et al.* 2007).

According to Table 3, with decreasing of the absolute values of the ζ potential, the contact angles of the treated sawdust particles were increased. Partial removal of hemicelluloses in the hydrolyzed sawdust sample and the formation of amide bonds in the ammoxidized sawdust sample increased their contact angles from 79.7° (for the initial particles) to 85.1° (for the ammoxidized sample) and 84.3° (for the hydrolyzed d sample). The lower contact angle of the ammoxidized sawdust particles, in comparison with the case of the hydrolyzed sawdust sample, may be caused by both the insufficient amount of the formed amide bonds due to the low content of the fixed nitrogen, and the presence of the hydrophilic carboxylic groups formed during the ammoxidation (Shulga *et al.* 2016c). The increase in the content of nitrogen in the ammoxidized particles treated with the LPEC nanoparticles allowed for an increase in their contact angle compared with the contact angle of the treated hydrolyzed sawdust particles. According to the values of the calculated adhesion energy (Table 3), the treated modified sawdust particles had lower affinity to water relative to the initial and untreated modified sawdust samples.
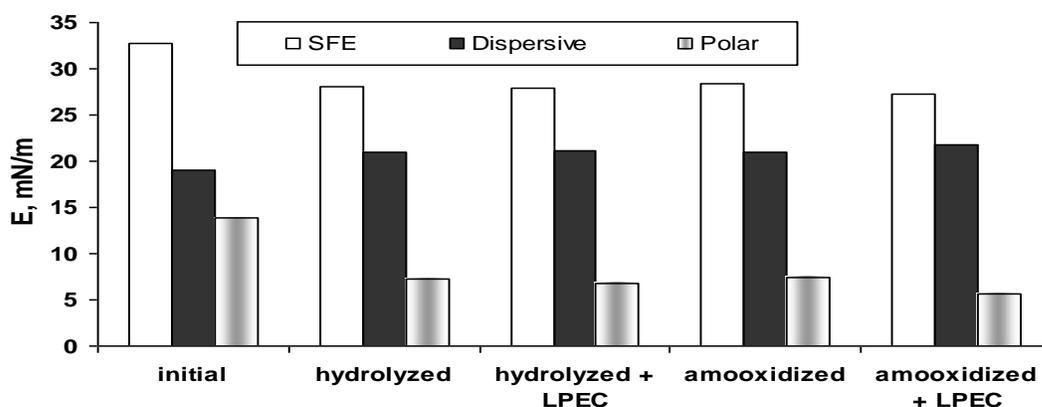

Fig. 3. Surface free energy, its polar and dispersive parts of the sawdust samples

The SFE, as well as its polar and dispersive parts for sawdust samples, was calculated using different organic liquids (Fig. 3). It was found that the SFE of the initial sawdust was higher than that of all the modified sawdust samples. At the same time, the treatment with the LPEC nanoparticles, to a greater extent, affected the polar part of the free energy of the sawdust samples.

The treatment with the LPEC reduced the polar part of the free energy of the ammoxidized sample by almost 57%, while the decrease in the polar part of the SFE of the treated hydrolyzed sawdust reached 52% relative to the untreated sawdust. The observed drop of the polar part of the SFE of the treated modified samples, compared with the untreated modified ones, could be explained by the formation of new amide and imine bonds between carboxyl and carbonyl groups, being on the surface of the modified sawdust

samples, and the free amine groups of PEI contained in the LPEC nanoparticles. The dispersion force component of the treated modified sawdust samples also increased, compared with the initial and untreated modified sawdust, although these changes were less pronounced.

Wood-plastic Composites

The composite samples were prepared from rPP powder and the aspen sawdust microparticles according to the following scheme (Fig. 4).
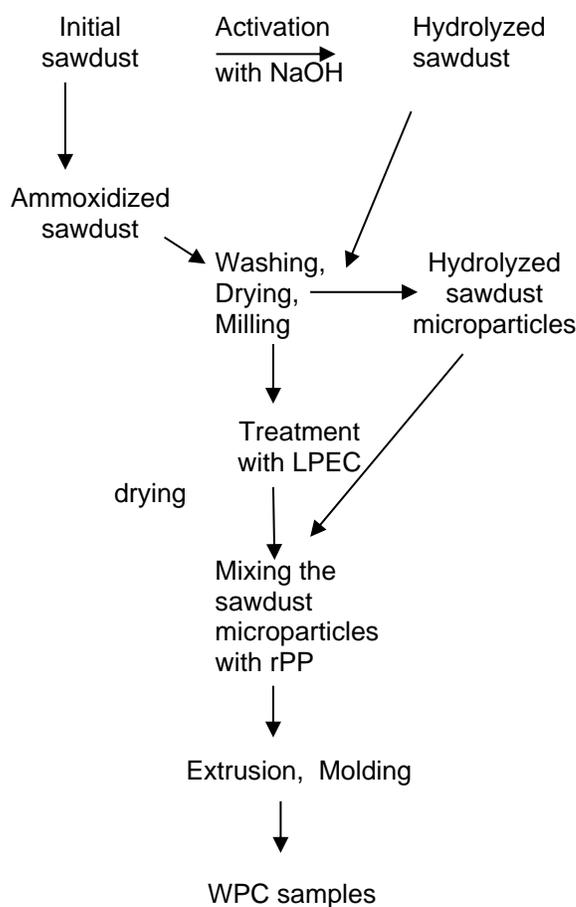

Fig. 4. Scheme of preparing the WPC samples

The values of contact angles, adhesion energy, and water sorption after 25 d for the obtained wood-polymer composites are shown in Table 4.

Table 4. Characteristics of Wetting Properties of the WPC Samples

WPC Sample	CA (°)	Adhesion Work (mN/m)	Water Sorption (wt%)
Initial/milled	90.6	70.8	3.4
Hydrolyzed + LPEC	96.3	64.4	2.5
Ammooxidized + LPEC	97.8	62.7	2.3

The comparison of the values given in Tables 3 and 4 shows that the composite samples had larger contact angles, lower adhesion energy, and remarkably lower water sorption compared with the modified sawdust particles, which was gained by the hydrophobicity of the polymer matrix in the WPC samples.

According to Table 4, the WPC samples filled with the treated hydrolyzed and ammoxidized microparticles were characterized by an increase in the contact angle values from 90.6° to 96.3° and 97.8°, a decrease in the adhesion energy from 70.8 to 63.4 mN/m and 62.7 mN/m, and a reduction in the water sorption during 25 days from 3.4% to 2.5% and 2.3%, respectively, compared with the WPC sample containing the initial milled sawdust. These results indicated that the improvement of the compatibility between the filler and the recycled polymer matrix during the processing could be explained by their physicochemical interaction at the interface due to both the ion-pairing within a polyelectrolyte complex system, the formation of covalent bonds (amide, imine) between the oxidized groups (carbonyl, carboxyl) of rPP, and the free uncharged amino groups of the LPEC nanoparticles located on the treated modified wood surfaces, and H-bonding between the nitrogen-containing groups of the filler and the oxygen-containing groups of rPP.
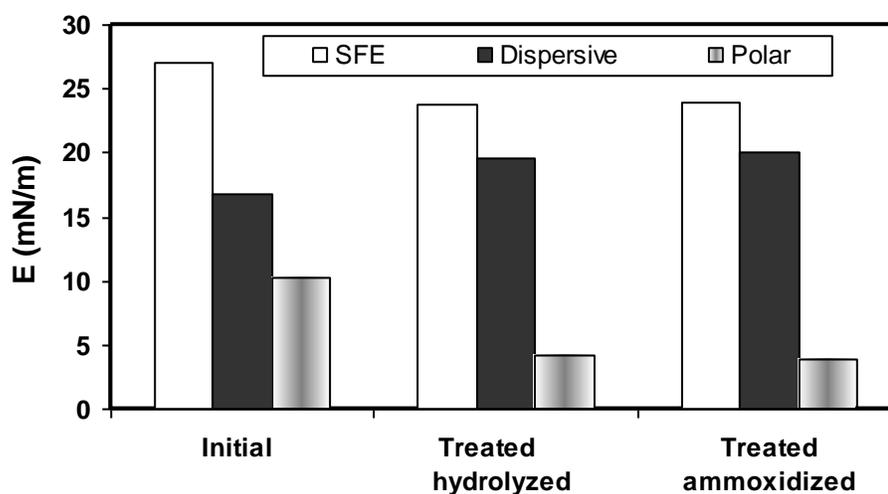

Fig. 5. Surface free energy, its polar and dispersive parts of the WPC samples

The negligible difference in the values of the indices (Table 4) for the WPC samples filled with the treated hydrolyzed and ammoxidized sawdust particles may be caused by the insufficient difference in their hydrophobicity.

According to Fig. 5, the SFE of the WPC samples filled with the initial sawdust was 12.9 to 13.3% higher than the same values for the WPC samples, containing the treated modified sawdust microparticles. The decrease in the SFE values for the WPC samples, containing the treated hydrolyzed and ammoxidized particles, was gained by an essential drop in their SFE polar part by almost 2.4 and 2.6 times, respectively, compared to the WPC sample filled with the initial sawdust. This could be explained by the decrease in the hydrophilicity of the modified sawdust particles treated with the LPEC. Simultaneously, there was a decrease in the dispersion force component of the WPC samples, which was less pronounced than the drop in their SFE polar part. The remarkable decrease in the polar part of SFE and the increase in the dispersion force component of SFE for the WPC

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samples, containing the modified particles treated with the LPEC, testified to the effectiveness of the application of the LPEC nanoparticles as an adhesion enhancer, which was able to improve the interfacial adhesion by forming physicochemical bonds with both the modified sawdust particles and the recycled polymer matrix. The insignificant difference in the values of free energy and its polar and dispersion parts for the WPC samples filled with the hydrolyzed and ammoxidized sawdust microparticles, treated with LPEC, was reflected in the insignificant difference in their hydrophobicity (Table 3), and can be explained by the minor difference in the hydrophobicity of the used modified sawdust particles.

The formation of covalent and hydrogen bonds between the filler and recycled polypropylene led to the structuring of the interfacial layers and the reinforcement of the interfacial adhesion in the composites. These factors are reflected in the improvement of the mechanical properties of the obtained wood-polymer composite samples (Table 5).

Table 5. Mechanical Properties of the WPC Samples

Filler	Tensile Strength (MPa)	Tensile Modulus (MPa)	ε_T^* (%)	Bending Strength (MPa)	Bending Modulus (MPa)	ε_B^{**}(mm)
Initial/Milled	26.2 ± 0.2	725 ±12	11.5 ± 0.5	29.1 ±0.2	1635 ±31	5.9 ±0.2
Hydrolyzed + LPEC	38.5 ±0.3	1028 ±15	5.1 ±0.6	41.5 ±0.4	3455 ±23	1.8 ±0.3
Ammoxidized + LPEC	39.8 ±0.4	1120 ±17	4.9 ±0.8	42.7 ±0.4	3510 ±25	1.6 ±0.2

$^*\varepsilon_T$: Elongation at break; $^{**}\varepsilon_B$: deflection

According to the data, the composite samples containing the treated modified sawdust particles were characterized by an increase in the mechanical strength and stiffness, compared with the recycled polypropylene composites reinforced with the milled initial aspen sawdust. The maximum tensile strength and the tensile modulus of rupture of the composite samples filled with the treated hydrolyzed and treated ammoxidized particles increased an average of 46% and 52%, respectively, relative to the same indexes of the composite samples filled with the initial sawdust. The maximum bending strength and the bending modulus of the composites incorporating the treated hydrolyzed and treated ammoxidized particles grew 1.4 to 1.5 and 2.1 to 2.2-fold, respectively. Simultaneously, the deformability of these composites essentially decreased, namely the elongation at break (ε_T) dropped more than 2.3 to 2.4 times, but deflection ability (ε_B) diminished more than 3.2 to 3.6 times, compared with the composite filled with the initial sawdust. A relatively minor improvement in the mechanical properties of the WPC sample containing the treated ammoxidized sawdust in comparison with the sample filled with the treated hydrolyzed sawdust may have been caused by the minor difference in their water wettability.

Scanning electron microscope images of the rPP-based wood-plastic composites are shown in Fig. 6. The SEM surface image of the WPC sample filled with the initial sawdust (A, C) shows the non-uniform surface with the presence of microcracks and other surface defects. On its cross-section, pullouts of the microparticles, debonding, and the presence of internal voids can be observed. This may provide evidence of weak adhesion between the unmodified sawdust microparticles and rPP. At the same time, the surface of the composite sample containing the treated ammoxidized microparticles was

characterized by homogeneity (B); the particles pullout and debonding as well as the formation of voids (D) on its cross-section are minimal, which may confirm the good interfacial adhesion between the treated modified sawdust microparticles and rPP in the presence of the new adhesion enhancer.
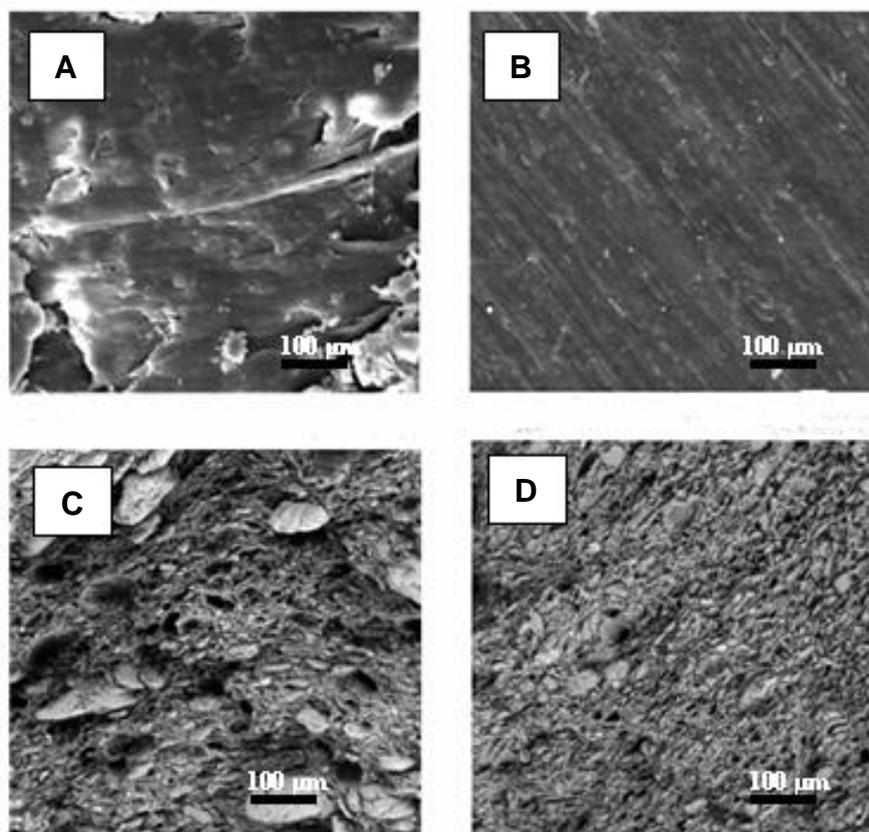

Fig. 6. Images of surface and cross-section of the composite samples (x 500) containing the (A, C) initial and (B, D) treated ammoxidized sawdust microparticles

CONCLUSIONS

1. The water-soluble, non-stoichiometric polyelectrolyte complex—hydrolyzed aspen soda lignin (HASL)/polyethylenimine (PEI)—formed the nanoparticles in alkaline water solution. Their average diameter was smaller than the size of the lignin nanoparticles, and close in size to the PEI ones. The lignin-containing polyelectrolyte complexes (LPEC) nanoparticles had a lower surface tension at the air-water interface in comparison with the initial components, as well as a lower specific viscosity than the additive value of specific viscosities of the lignin and PEI. The formation of the LPEC nanoparticles was regarded as a result of hydrogen and electrostatic interactions between the components.

2. The treatment with the LPEC nanoparticles led to an increase of the fixed nitrogen content in the modified (hydrolyzed and ammoxidized) aspen sawdust microparticles. This caused a decrease in the amount of adsorbed water, an increase in the contact

angles values, and a reduction in the polar part of the total surface free energy (SFE) of the modified wood. The decreasing ability to be wetted by water may be a result of the formation of imine and amide bonds between the free amino groups of the adsorbed LPEC nanoparticles and the carbonyl and carboxyl groups of the lignocellulosic matrix of the modified sawdust. The lower contact angle of the ammoxidized sawdust particles, in comparison with the hydrolyzed sawdust ones, may be caused by both the insufficient amount of the formed amide bonds onto the ammoxidized wood surface, due to the low content of the fixed nitrogen, and the presence of the hydrophilic carboxylic groups formed during the ammoxidation.

3. The composite samples containing the modified aspen sawdust, treated with the LPEC nanoparticles, were characterized by the improved mechanical properties and the decreased water's wettability in comparison with the samples filled with the initial sawdust. The enhanced interfacial adhesion was explained by the formation of covalent and physicochemical bonds between the nitrogen-containing groups of the treated sawdust particles and the oxygen-containing groups of rPP during the processing. A relatively minor improvement in the mechanical properties for the wood-plastic composites (WPC) sample filled with the treated ammoxidized sawdust, compared to the composite sample containing the treated hydrolyzed sawdust, was explained by the negligible difference in their hydrophobicity.

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