

# Valorized Soda Lignin and Its Possible Application

**Galia Shulga**

Latvian State Institute of Wood  
Chemistry,  
27 Dzerbenes St., Riga, Latvia

**Jevgenijs Jaunslavietis**

Latvian State Institute of Wood  
Chemistry,  
27 Dzerbenes St., Riga, Latvia

**Sandra Livcha**

Latvian State Institute of Wood  
Chemistry,  
27 Dzerbenes St., Riga, Latvia

**Sanita Vitolina**

Latvian State Institute of Wood  
Chemistry,  
27 Dzerbenes St., Riga, Latvia

**Anrijs Verovkins**

Latvian State Institute of Wood  
Chemistry,  
27 Dzerbenes St., Riga, Latvia

**Talrits Betkers**

Latvian State Institute of Wood  
Chemistry,  
27 Dzerbenes St., Riga, Latvia

**Brigita Neiberte**

Latvian State Institute of Wood  
Chemistry,  
27 Dzerbenes St., Riga, Latvia

**Jurijs Ozolins**

Riga Technical University,  
3 Paula Valdena St., Riga, Latvia

**Abstract** – The aim was to obtain a valorized soda lignin and to study its properties for the followed treatment of hardwood sawdust as a filler for obtaining a wood-polymer composite. It was shown that the treatment of aspen sawdust microparticles by their immersion into a water solution of the valorized soda lignin, that is a water-soluble soda lignin/polyethylenimine polyelectrolyte complex, leads to hydrophobisation of the sawdust particles, which in turn positively affects the mechanical performance of the obtained wood-polymer composite.

**Keywords** – soda lignin, valorization, wood polymer composite

## I. INTRODUCTION

Lignin is a biopolymer being one of the main constituents of all plants, where it performs the role of adhesive of cellulose fibres. The peculiarities of the macromolecular structure of lignin, combined with their renewability, low cost, biocompatibility, and biodegradability, make the design of new lignin-based polymer products a challenge for fundamental and applied researches. Technical lignins as by-products are formed during wood chemical processing, namely, in the paper and bioethanol industry, and their production estimated almost 50 mln tons annually [1]. Unfortunately, 98% of this amount is burnt for energy regeneration at the plants. The rest of the total amount of produced technical lignins have found widespread application as a renewable resource at a competing price level for obtaining various value-added products such as adhesives, surfactants, stiffness enhancers, soil improvers, lignin carbon fibres, chemical, as well as functional additives in polymer blends and polymer composite materials. Due to the fact that technical lignins are available in large amounts and have a relatively low price, the valorization of lignin regardless of application will be beneficial and would result in considerable economical gain.

The major limiting factor for incorporation of technical

lignin in polymer blends and composite materials is its limited compatibility with a polymer matrix [2, 3]. The compatibility between lignin and synthetic polymers can be achieved, for instance, via purposeful chemical valorization of lignin. There are many methods for valorization of lignin by complexation with metal ion, hydroxyalkylation, esterification, alkylation, grafting, mixing with reactive polymers, etc. [4, 5].

One of the perspective ways of lignin valorization may be the formation of polyelectrolyte complexes on lignin basis [6, 7]. The polyanionic nature of water-soluble lignin gains spontaneous interaction with polymeric cations in water solutions with the formation of polyelectrolyte complexes that may be regarded as one of the advanced added value lignin products due to the simplicity of their preparation technology and a wide range of their possible applications [8, 9]. Owing to the features of the structure of lignin-based polyelectrolyte complexes formed, their macromolecules can be easily adsorbed at the different surfaces due to the formation of physicochemical and covalent bonds.

The aim of the work was to obtain a valorized soda lignin and to study its effect on the mechanical properties of a wood polymer composite

## II. MATERIALS AND METHODS

### Materials

*Soda lignin.* Soda lignin was extracted from hydrolysed aspen sawdust in a laboratory reactor under the following laboratory conditions: hydromodulus – 1/7, NaOH concentration – 4.0 mass %, temperature – 165 °C and duration – 1.5 h. The hydrolysed aspen soda lignin (HASL) was separated from the cooking solution by precipitation with 20% sulphuric acid. The chemical composition of lignin was studied by elements (Elementar Analysensysteme GmbH, Germany) and functional groups analysis, according to [10]. The purified lignin had the following chemical composition: 62.3% C, 6.5% H, 0.15% N, 0.25% S, 30.8% O; OCH<sub>3</sub> - 19.3%, total

Print ISSN 1691-5402

Online ISSN 2256-070X

<http://dx.doi.org/10.17770/etr2019vol3.4122>

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OH - 5.6%, phenolic OH - 3.5%, aliphatic OH - 2.1%, COOH - 2.1%, CO - 3.9%. The average molecular of the lignin ( $M_w$ ,  $M_n$ ) were found by SEC-MALS20 (Malvern, United Kingdom) in DMSO with lithium bromide as an eluent at 60°C and closed to 10.5 kDa and 5.7 kDa, respectively.

**Polyethylenimine.** High molecular branched polyethylenimine (PEI,  $M_w = 750$  kDa,  $M_n = 60$  kDa, 50% water solution) contains primary, secondary tertiary amine groups was used for obtaining the functional additive. It was supplied from Sigma Aldrich.

**Obtaining of the valorized soda lignin.** The valorized soda lignin as a water-soluble polyelectrolyte complex (LPEC) was obtained in a reaction mixture by mixing equal volumes of dilute alkaline water solutions of hydrolysed soda lignin and polyethylenimine at a room temperature. The pH value of the obtained lignin/PEI reaction mixture was about 10.5. The mixture was used after 2 hours after its obtaining.

**Treatment of sawdust particles with the LPEC.** The treatment was performed by immersion of the hydrolysed aspen particles < 100  $\mu\text{m}$  in a HASL/PEI reaction mixture during 24 h at a constant stirring and a room temperature.

**Sawdust.** The aspen sawdust, representing a waste of the mechanical processing of aspen wood (*Populus tremula*), was supplied by a Latvian company. The sawdust was characterised by elemental analysis (Elementar Analysensysteme GmbH, Germany) and wood polymers composition according to chemical procedures for lignin, hemicelluloses, cellulose and extractives [11]. The content of cellulose, lignin, hemicelluloses, extractives and ash in the aspen wood was 50.6%, 18.5%, 28.7%, 4.51% and 0.4%, respectively. The hydrolysis of the sawdust was performed at a low temperature with a hydrochloric acid under mild conditions (60°C, 5 h, mass ratio of wood particles to water of 1/20) with a purpose to decrease the content of hemicelluloses in the sawdust. After the hydrolysis, the sawdust particles were washed to a neutral medium, dried and milled with a planetary ball mill (Retsch, Germany) during 15 min at 300 rpm.

**Polymer matrix.** Recycled polypropylene (rPP) (0.9 t  $\text{m}^{-3}$ , 5.2/10 min at 230°C, 2.16 kg) was used as a thermoplastic polymer matrix and supplied from a Latvian polymer recycling plant.

**Wood-polymer composite samples.** The composite samples were prepared from rPP and the modified aspen microparticles, treated with the LPEC, with a moisture content < 1.0%, using a twin screw extruder and a moulding machine (HAAKE MiniLab II with MiniJet II, Thermo Scientific "HAKKE") at temperatures of 175°C. The extruder screw rotational speed was 130 rpm, while the injection moulding pressure was 600-700 bar. The microparticles content in the composites was 50 %.

#### Experimental Procedure

**Surface tension.** The surface tension ( $\sigma$ ) of HASL, PEI and LPEC water solutions at the water-air interface was measured by a Wilhelmy plate, using a tensiometer K100M (KRUSS, Germany) at 25°C with a circulation thermostat, according to [12]. Three replicates were

made for each sample.

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

**Viscometry.** Specific viscosity was determined using a capillary viscometer Ubbelohde with a flow time of pure water closed to  $300 \pm 0.01$  sec at  $25.0 \pm 0.1^\circ\text{C}$ , according to [12]. Three replicates were made for each sample.

**Potentiometric and conductometric titration.** The titration curves were obtained using InoLab level 3 Multiparameter Meter (WTW, Germany) at the constant stirring. 0.1 M NaOH and 0.1 M HCl were used for adjustment of pH values of the water solutions of polyelectrolytes. Three replicates were made for each sample.

**UV-VIS spectroscopy.** The UV-spectra were recorded with a Genesys 10UV UV/VIS spectrophotometer (Termo Fisher Scientific).

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

**Milling.** The milling of wood sawdust was carried out with a planetary ball mill (Retsch, Germany) with the followed sieving, using a mill "Pulverisette" (Fritsch, Germany).

### III. RESULTS AND DISCUSSION

#### Valorized soda lignin

The polyelectrolyte complex with a mass ratio of HASL/PEI equal to 1 was obtained in the reaction mixture by blending dilute alkaline solutions of the soda lignin and PEI. A content of amine groups of PEI in the obtained LPEC was more than 3-folds higher than the content of phenolic hydroxyl and carboxyl groups in the soda lignin. The pH value of the reaction mixture was about 10.5. The alkaline medium of the reaction mixture was chosen, taking into account a nucleophilic character of interaction of amine groups of PEI with carbonyl and carboxyl groups that were contained in both the soda lignin, milled hydrolysed sawdust and recycled polypropylene. The charged ratio between HASL and PEI were chosen basing on the results of potentiometric and conductometric titration of ionogenic groups of the soda lignin (phenolic hydroxyl and carboxyl groups) (Fig. 1) and amine groups of PEI (Fig. 2). The excess of amine groups was dictated by both the need to compensate for the negative surface charge of the modified lignocellulosic particles in order to increase their hydrophobicity and to form chemical bonds with the lignin and recycled polymer matrix, containing

carbonyl and carboxyl groups [13, 14], the concentration of which are increased during obtaining

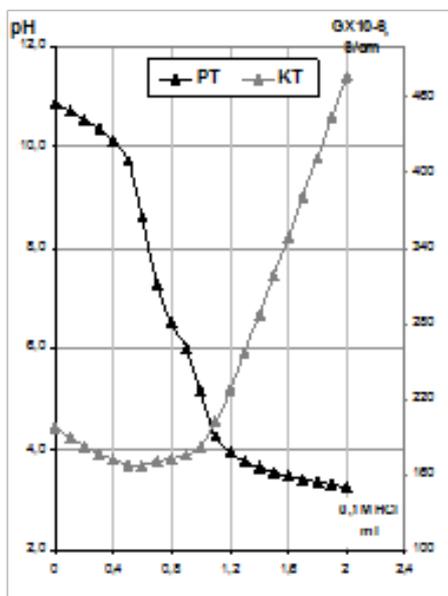


Fig. 1. Curves of potentiometric and conductometric titration of a 0.01% HASL water solution

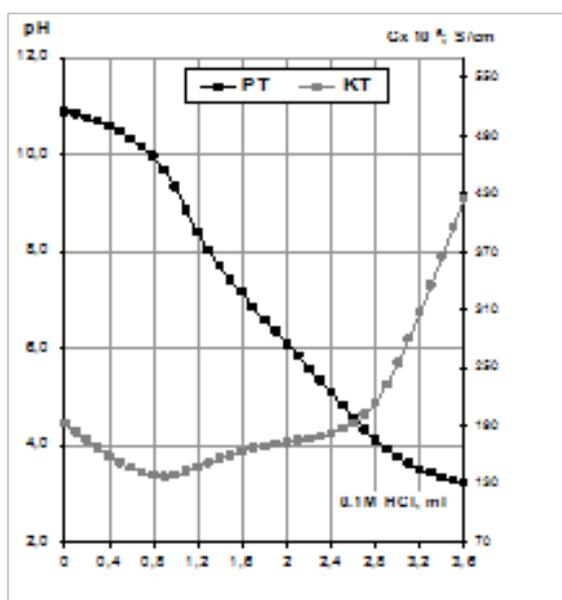


Fig. 2. Curves of potentiometric and conductometric titration of a 0.01% PEI water solution

wood polymer samples. Taking into account the fact that the amino groups of PEI are practically not protonated in a strong alkaline medium, it can be assumed that the LPEC can be formed by H-binding of non-protonated amino groups of PEI with carbonyl ( $\alpha$ - and  $\beta$ -ketogroups, aldehyde groups) and hydroxyl groups of the soda lignin. At the same time, a visible increase in the intensity of the absorption curve of the UV spectrum of the alkaline solution of the reaction mixture relative to that of the lignin solution (PEI does not absorb in the UV region) (Fig. 3), pronounced in the range of 260-340 nm, may indicate the presence of electrostatic interaction between the induced protonated amine groups of PEI and lignin's fragments, containing non-conjugated phenol hydroxyl groups (absorption at 280-300 nm), phenol hydroxyl groups conjugated with  $\alpha$ -carbonyl groups (absorption

at 310 nm), carbonyl and carboxylic groups (absorption at 328 and 345 nm). The presence of the electrostatic interaction in the alkaline medium between the negatively charged groups of the soda lignin and partially positively charged amine groups of PEI, leading to the formation of salt bonds, is also confirmed by a decrease in the zeta potential value of the resulting polyelectrolyte complex relative to the zeta potential of the soda lignin (Table 1).

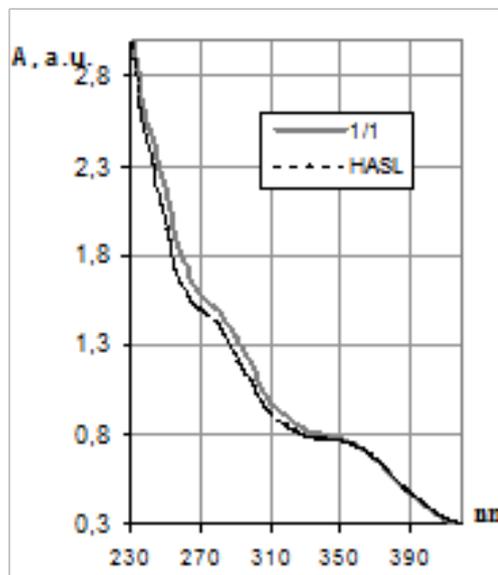


Fig. 3. UV spectra of dilute water solutions of HASL and LPEC

TABLE 1. Characteristics of HASL, PEI and their polycomplex HASL/PEI (1:1), pH 10.5

INDEX	HASL, 0,1%	PEI, 0,1%	HASL /PEI complex
Surface tension, mN/m	60,6	69,8	50,6
Zeta potential, mv	-23,1	-7,5	-19,0
Size, nm	134 100%*	95 100%*	98 91%*
Specific viscosity	0.019	0.045	0.056

\* relative intensity

Table 1 shows the values of sizes and zeta potential for the LPEC, HASL and PEI, as well as a surface tension and a specific viscosity of aqueous solutions of the water-soluble LPEC and its initial components, having the same concentrations as in the reaction mixture. Lower values of a surface tension of the LPEC at the water-air interface compared with the soda lignin and PEI, and the value of a specific viscosity of the LPEC, which is less than the additive value of the specific viscosities of the soda lignin and PEI, testify the formation of a new polymeric product in the alkaline water solution and indicate its enhanced surface activity in comparison with the lignin and the polycation. According to Table 1, the particles of HASL, PEI and the obtained water-soluble LPEC are characterized by sizes of 108-134 nm. According to Fig. 4, the diameter of the LPEC particles are smaller than the sizes of the soda lignin ones and closed to the size of the PEI particles.

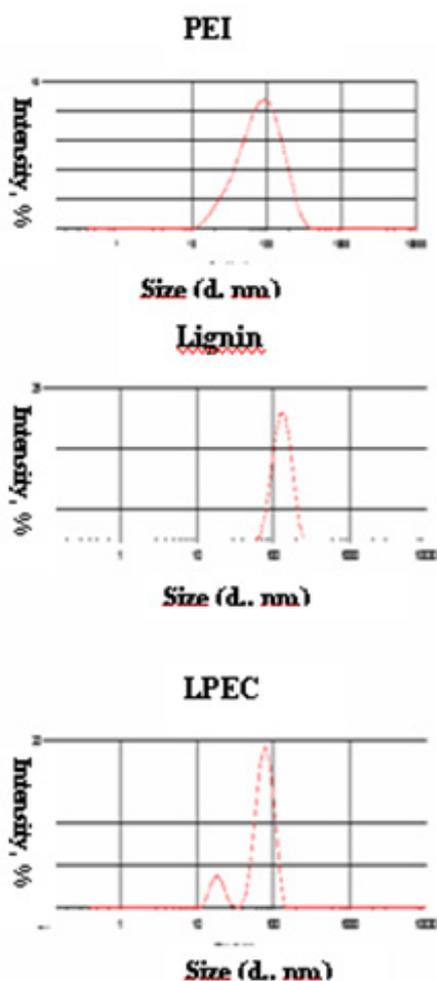


Fig. 4. Particle-size distribution pattern of PEI, HASL and HASL/PEI particles in alkaline solutions with pH 10.5.

Thus, the obtained valorized soda lignin is a water soluble polyelectrolyte complex formed in an alkaline medium as a result of hydrogen and electrostatic interactions between the functional groups of the soda lignin and PEI. The presence of the excess of the amine groups, capable of forming covalent bonds with carbonyl and carboxyl groups, as well as the presence of the salt bonds, forming the hydrophobic sites in the LPEC, indicate the increased surface activity of the valorized soda lignin obtained.

*Wood polymer composite*

The treatment was performed by immersion of the sawdust particles in an alkaline water solution of the HASL/PEI polyelectrolyte complex. The treated particles were separated from the suspension by a filtration using a Buchner funnel in order to remove the excess of the cationic polymer, and then they were dried. The content of a fixed nitrogen in the treated hydrolysed sawdust was equal to 1.12 %. The wood polymer composite samples with a filling degree 50 % were prepared from a recycled polypropylene powder and the hydrolysed aspen sawdust microparticles treated with the HASL/PEI polyelectrolyte complex. The obtained composite samples are shown in Fig. 5.



Fig. 5. Wood polymer composite samples obtained for testing

As follows from the Table 2 and Table 3, the presence of nitrogen-containing groups in the hydrolysed sawdust microparticles, treated with the valorized soda lignin, positively affects the mechanical properties of the obtained wood polymer samples.

TABLE 2. Tensile properties of wood polymer composites filled (50%) with the treated sawdust

Filler	Maximal tensile strength, MPa	Tensile modulus, MPa	$\epsilon_T$ , %
Initial	26.2±0.2	725±12	11.5±0.5
Hydrolysed + LPEC	38.5± 0.3	1028±15	5.1±0.6

TABLE 3. Bending properties of wood polymer composites filled (50%) with the treated sawdust

Filler	Maximal bending strength, MPa	Bending modulus, MPa	$\epsilon_B$ , mm
Initial	29.1±0.2	1635±31	5.9±0.2
Hydrolysed + LPEC	41.5±0.4	3455±23	1.8±0.3

According to the presented data, the composite samples are characterised by an essential increase in the mechanical strength and stiffness in comparison with the recycled polypropylene composites reinforced with the untreated sawdust. The maximal tensile strength and the tensile modulus of rupture of the composites incorporating the treated hydrolysed sawdust particles increases 1.46 and 1.42 folds, respectively. The maximal bending strength and the bending modulus of the composites filled with the treated sawdust grows 1.43 and 2.1 folds, respectively. Simultaneously, the deformability of these composites essentially decreases, namely, elongation at break drops more than 2.3 times, but deflection ability diminishes more than 3.2 folds in comparison with the case of the composite filled with the initial sawdust. Evidently, the formation the covalent bonds between the treated sawdust microparticles and the recycled polypropylene leads to the structuring of the interfacial layers and contribute to the increase in interfacial adhesion in the composite. It also may be supposed that the possible formation of a hydrogen bonds network between the functional groups of the treated sawdust and recycled polypropylene can also contribute

to the decreasing of the interfacial free energy. Thus, the treatment of the hydrolysed sawdust microparticles with the valorized soda lignin has a favourable effect on their compatibility with the recycled polymer matrix in the wood polymer composite.

#### IV. CONCLUSION

The valorized soda lignin was obtained in the form of a water soluble polyelectrolyte complex formed as a result of hydrogen and electrostatic interactions between the oppositely charged groups of the soda lignin and PEI in an alkaline medium. The presence of the excess of free amine groups as well as the presence of salt bonds, forming hydrophobic sites in the polyelectrolyte complex, indicate an increased surface activity of the valorized soda lignin.

The composite samples, filled with the hydrolysed sawdust microparticles, which are treated with a water solution of the valorized soda lignin, are characterised by better mechanical properties compared with the composite, contained the untreated sawdust. This testifies the enhancement of the interfacial adhesion between the aspen sawdust particles and recycled polypropylene in the wood-polymer composite.

#### V. ACKNOWLEDGMENTS

The authors would like to thank the Ministry of Education and Science of the Republic of Latvia for the financial support of the National Research Programme (ResProd) and the institute's grant "AtkritBiomassKM".

#### VI. REFERENCES

- [1] Zion Research, Lignin Market (Lignosulfonates, Kraft Lignin and Others) for Concrete Additive, Animal Feed, Dye Stuff, and Other Applications: Global Industry Perspective, Comprehensive Analysis and Forecast 2014 – 2020, Market Research Store, Deerfield Beach, 2015.
- [2] J.F. Kadla, S. Kubo, Lignin-Based Polymer Blends: Analysis of Intermolecular Interactions in Lignin-Synthetic Polymer Blends, *Composites Part A*, 35, 2004, pp. 395–400.
- [3] B. Košíková, E. Sláviková, Use of Lignin Products Derived From Wood Pulping as Environmentally Desirable Additives of Polypropylene Films, *Wood Research*, 55, 2010, pp. 87–92.
- [4] V.K. Thakur, M.K. Thakur, P.Raghavan, M.R. Kessler, Progress in Green Polymer Composites from Lignin for Multifunctional Applications: A Review, *ACS Sustainable Chem. Eng.* 2, 2014, pp.1072–1092.
- [5] F. Lu, Lignin: structural analysis, applications in biomaterials and ecological significance. Nova Science Publishers, New York, 2014.
- [6] G. Ström, P. Stenius, Formation of complexes, colloids and precipitates in aqueous mixtures of lignin sulphionate and some cationic polymers, *Colloids and Surfaces*, 2(4), 1981, pp. 357-371.
- [7] G. M. Shulga, R. I. Kalyuzhnaya, L. N. Mozheyko, F.V. Rekner, A.B. Zevin, V.A. Kabanov, Features of the reactions between lignosulphonates and polymeric bases in aqueous solutions, *Polymer Science*, 26(2),1984, pp. 319-324.
- [8] L. Gärlund, L. Wägberg, R. Gernandt, Polyelectrolyte complex for surface modification of wood fibres. II. Influence of complexes on wet and dry strength of paper, *Colloids and Surfaces: A Physicochemical and Engineering Aspects*, 218(1): 2003, pp. 137-149.
- [9] G. Shulga, F. Reknerns, J. Varlavans. Lignin-based Interpolymer complexes as a novel adhesive for protection against erosion of sand soil, *Journal of Agricultural Research Engineering*, 78 (3), 2001, pp. 309-316.
- [10] G. F. Zakis Functional analysis of lignins and their derivatives. Atlanta: TAPPI Press, GA, 1994.
- [11] A.V. Obolenskaya, Z.P. Elnitskaya, A.A. Leonovich, Laboratory Manual on Wood and Cellulose Chemistry, Ecologia, Moscow, 1991.
- [12] G. Shulga, V. Shakels, O. Aniskevicha, T. Bikova, A. Treimanis, Effect of alkaline modification on viscometric and surface-active properties of soluble lignin. *Cell. Chem. Techn.*, 40, 2006, pp. 383-392.
- [13] G. M. Shulga, L. N. Mozeyko, F.V. Rekner, R.I. Kalyuzhmajya, A.B. Zevin, V.A. Kabanov, Chemical conversions in polyelectrolyte complexes based on lignosulfonates. *Khim. Drev.*, 1, 1982, pp. 87-93.
- [14] De La Orden, M.U., Gonzalez Sanchez, C., Gonzalez Quesada, M., Martinez Urreaga, J. Effect of different coupling agent on the browning of cellulose-polypropylene composites during melt processing, *Polymer Degradation and Stability*, 95(2), 2010. pp. 201-206.