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Polyelectrolyte Complex Nanoparticles of Soluble Lignin and Chitosan as Interfacial Modifier

Galia Shulga
Latvian State Institute of Wood Chemistry
Riga, Latvia
galshulga@inbox.lv

Vadims Shakels
Latvian State Institute of Wood Chemistry
Riga, Latvia
vadim@saint-tech.lv

Sanita Vitolina
Latvian State Institute of Wood Chemistry
Riga, Latvia
sanita.vitolina@kki.lv

Brigita Neiberte
Latvian State Institute of Wood Chemistry
Riga, Latvia
bricis46@inbox.lv

Anrijs Verovkins
Latvian State Institute of Wood Chemistry
Riga, Latvia
anrivero@inbox.lv

Abstract. **A water-soluble non-stoichiometric polyelectrolyte complex (LCP) was obtained as a result of the interaction of oppositely charged kraft lignin and high molecular chitosan by mixing their dilute water solutions. The sizes of the LCP nanoparticles were characterized by a bimodal distribution at pH 6, and their values were essentially smaller than the sizes of the chitosan particles. It was found that the LCP nanoparticles were characterized by remarkably lower values of surface tension at the air-water and the water-organic liquid interface in comparison with the initial biopolymers. With decreasing pH and increasing concentration of the LCP nanoparticles in the water solution, their adsorption ability at the interfaces was enhanced. The interface tension at the water-heptane interface changed non-linearly with increasing the polyelectrolyte complex concentration that was associated with the "saturation" effect. The dependence of the ability of the LPC nanoparticles to stabilize oil-in-water emulsion on pH values of the water phase was found.**

Keywords: kraft lignin, chitosan, polyelectrolyte complex, interfacial modifier, oil-in-water emulsion.

I. INTRODUCTION

The strategy of the EU based on the Bioeconomy and the Circular economy principles focuses on the rational and effective utilization of polymeric by-products and wastes. Lignin could play more than a catalytic role in the deployment of bioeconomy in the EU, due to its huge multiple and flexible utilization opportunities and vital links to a great spectrum of biobased industries.

Technical lignins, by-products of the industrial pulping process, have found widespread application as a renewable resource at a competing price level for obtaining surface active agents that are used both as an emulsifier, an emulsion stabilizer and a dispersant, used in asphalt, bitumen, latex and soaps, herbicides, insecticides, clay suspensions, etc. Lignin-based surface-active agents can stabilize emulsions and suspensions due to various mechanisms such as an electrostatic repulsion, a formation of condensed interfacial films and space interactions at the interface. This application is conditioned by an amphiphilic nature of water-soluble lignin macromolecules [1] – [3] due to the presence of hydrophobic aromatic rings and ionogenic functional groups in phenyl-propane chains that give them the properties of weak polyelectrolyte. To increase surface activity, technical lignins must be modified chemically to obtain favourable surface-active properties. The known methods for modification have several drawbacks, such as high energy demand, complexity, and the necessity of a step-by-step modification by utilization of organic solvents, etc. The polyanionic nature of soluble lignins due to the presence of ionogenic functional groups allows to interact them with opposite-charged polyelectrolytes in aqueous solutions with the formation of polyelectrolyte complexes [4] – [7].

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Chitosan (Ch) is a co-polyaminosaccahride containing amine and amide groups in its glucose units. Over 100 billion tons of chitosan have been obtained annually via the deacetylation process of chitin, a by-product of a marine industry including shellfish and fish processing. The structural and composition features of chitosan make it an attractive material for chemical modification with the aim to improve its properties (ionogenic, amphiphilic, hydrophobic). The presence of amino groups is conditioned by its property as a weak polycationic electrolyte with pK_b of 6.2-7.0 [8].

Polyelectrolyte complexes are self-assemblies that are formed as a result of the electrostatic interaction of oppositely charged polyelectrolytes [9], [10]. Much attention is paid to the study of reactions between oppositely charged polyelectrolytes since their study is of interest both from the fundamental and practical point of view. The polyelectrolyte complexes can be regarded as advanced products due to the simplicity of their preparation technology and a wide range of possible applications, for example, in papermaking [11], production of binders [12], improvement of soil structure [13], medicine [10], etc. The driving force of the formation of polyelectrolyte complexes is the gain in entropy caused by the release of low-molecular ions due to the interpolyelectrolyte reaction. The formed polyelectrolyte complexes can be fully soluble in water, and form stable colloidal systems or precipitates that depend on many factors such as the chemical structure of polyelectrolytes, the ratio of interacted charged groups, their molecular mass, concentration, medium pH, etc.

Although there are many works on the preparation and study of lignin/chitosan products [14] – [16], there is limited literature devoted to the research of the behaviour of water-soluble lignin-chitosan polyelectrolyte complexes at different interfaces.

The aim of the work was to study the behaviour of a non-stoichiometric polyelectrolyte complex (LPC) formed between kraft lignin and chitosan in a water medium as an interface modifier.

II. MATERIALS AND METHODS

A. Materials

Commercial softwood kraft lignin (KL) was used for obtaining a water soluble, non-stoichiometric polyelectrolyte complex. The content of Klason lignin in the sample was 92,5%. The chemical composition of the lignin was studied by elements (Elementar Analysensysteme GmbH, Germany) and functional groups (methoxyl, aliphatic hydroxyl, carbonyl, phenolic hydroxyl and carboxyl groups) analysis using the Fibok-Shvappakh method, acetylation, interaction with hydroxylamine hydrochloride, and potentiometric and conductometric titration, according to [17]. The purified lignin had the following chemical composition: 63.9 % C, 5.5 % H, 2.7 % S, 27.9 % O; OCH_3 – 12.2 %, total OH – 9.7 %, phenolic OH – 5.1 %, aliphatic OH – 4.6 %, COOH – 5.4 %, CO – 3.5 %. The average molecular weights of the lignin (Mw, Mn), determined with SEC-MALS20 (Malvern, United Kingdom) in DMSO with lithium bromide as an eluent at 60ºC, were close to 15.7 kDa and 5.7 kDa, respectively. KL was dissolved in 0.01 M NaOH for obtaining 0.1 g dl^{-1} water solution. Viscometric and surface-active properties of water solutions of the biopolymers and LPC were measured after 24 h of their obtaining. Bi-distilled water was used as a solvent.

Chitosan (Ch) with a deacetylation degree of 85 % was purchased from Sigma-Aldrich. Its average molecular mass (Mw) was 400 kDa calculated from the viscometry results. It was dissolved in 0.1 M HCl for obtaining a 0.1 g dl^{-1} water solution.

Lignin-chitosan polyelectrolyte complex (LCP) with a composition (n-/n+) = 3/1 (KL /Ch charge ratio) was obtained by mixing equal volumes of the prepared water solutions of the biopolymers for obtaining LPC with a concentration of 0.01-0.1 g dl^{-1} in the reaction mixture at room temperature. A charge density of KL and Ch macromolecules was determined from the conductometric curves of their water solutions in the presence of $1 \cdot 10^{-3}$ M NaCl. The solution pH values were changed by using concentrated NaOH and HCl solutions.

B. Methods

The size and zeta-potential (Z) of the LCP particles were determined in the reaction mixtures, using a ZS Zetasizer Nano ZS (Malvern Instruments, United Kingdom). The surface tension (σ) at the air-water and the n-heptane-water interface was measured by the Wilhelmy and Du Nouy methods, respectively, using a tensiometer K 100M (KRUSS, Germany), at 25ºC. Reduced viscosity for LPC, KL and Ch solutions was determined with a capillary Ubbelohde viscometer at 25°C with a flow time of the bi-distilled water close to 170 sec. The stabilizing effect of LPC in terms of the volume and time of water separation was studied in heptane oil-in-water emulsions (O/W) at a volume ratio of 40/60, obtained with a rotor homogenizer Ultra-Turrax T10 basic (IKA Labortechnik, Germany) for 1 min at 9500 rpm. Surface pressure-area isotherms for water solutions were obtained at 25°C using a KSV NIMA Langmuir through the double-barrier device (KSV Chemicals, Finland) with a barrier speed of 10 mm/min. Three replicates were done for each test.

III. RESULTS AND DISCUSSION

The interpolyelectrolyte reaction between KL and Ch macromolecules has electrostatic nature and in the acidic medium can be represented by the following scheme:

$$\text{KL-COO}^{-}\text{Na}^{+} + \text{Ch-NH}^{+}{}_{3}\,\text{Cl}^{-} \longrightarrow$$

$$\text{KL-COO}^{-+}\,\text{NH}_3\,\text{-Ch} + \text{nNa}^{+} + \text{nCl}^{-}$$

where: $\text{KL-COO}^{-+}\,\text{NH}_3\,\text{-Ch}$ is a stoichiometric LPC.

As rule, stoichiometric polyelectrolyte complexes are fully hydrophobic products and precipitate from reaction mixtures [9], [10]. Water-soluble complexes are prepared at a non-stoichiometric mixing ratio of oppositely charged polyelectrolytes, as in our case. It is known [18] that the formed products may be regarded as specific block-copolymers consisting of hydrophilic and hydrophobic blocks. In our case, the chains of lignin and chitosan, forming ionic bonds, may be considered as hydrophobic blocks, while the disconnected fragments of the polymer chains with free phenolic hydroxyl and carboxyl groups of KL and amino groups of Ch as hydrophilic blocks. The amphiphilic structure of soluble technical lignins determines their surface-active properties [1], [2], [19].

Fig. 1 shows a dependence of surface tension at the air-water interface for the LCP reaction mixture and the biopolymers water solutions depending on pH values. The values of the surface tension of the studied solutions at the air-water interface are aligned as follows: σCh > σKL > σLCP. The LPC is characterized by lower values of the surface tension in comparison with the case of KL and Ch solutions with the same concentration. This indicates a synergetic effect governed by the peculiarities of the polymer structure of the formed complex particles; more precisely: hydrophilic-hydrophobic balance within the particles is decisive.

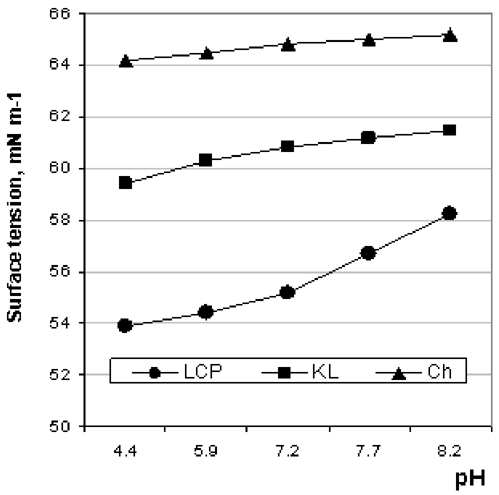

Fig. 1. Surface tension of KL, Ch and LPC water solutions at the air-water interface vs pH.

With increasing the LCP concentration in water solution from 0.01 g dl^{-1} to 0.1 g dl^{-1} and decreasing pH values from 8.2 to 4.4 (Fig. 2), the surface tension at the air-water interface remarkably drops from 59.6 mN m^{-1} to 50.4 mN m^{-1}, reflecting the enhancement of hydrophobicity of the formed LCP structure with increasing the concentration of the biopolymers and the grow of the conversion degree in the polylectrolyte complex [7]. The essential decrease in the surface tension occurs in a pH range of 4.4 – 5.9, in which the soluble LCP particles are characterized by the maximal content of the hydrophobic structural fragments, due to the high degree of dissociation of both Ch amino groups (pKb 6.5) and KL carboxyl groups (pKa 5.1).

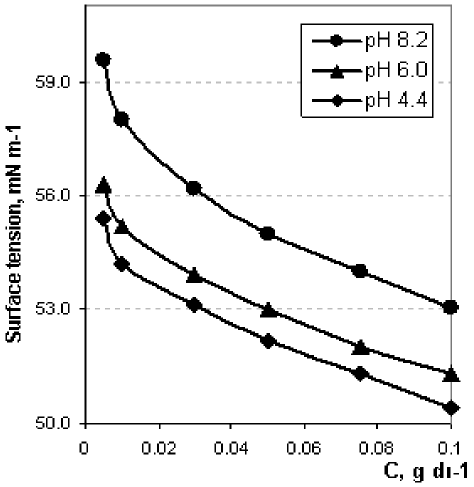

Fig. 2. Surface tension vs LCP concentration at various pH values.

It is found that water-soluble LCP is nanoparticles that are correlated with the findings in other work [20]. The sizes of the LCP particles are characterized by a bimodal distribution at pH 6 with an average hydrodynamic radius of 61 nm, corresponding to the formed LCP nanoparticles, and 12 nm, being caused by the presence of low molecular lignin molecules (Fig. 3). The Ch particles in water solution at the same pH were characterized by a monomodal size distribution with an average particle size more than 100 nm. The average size of the Ch particles was higher than those of KL and LCP nanoparticles.

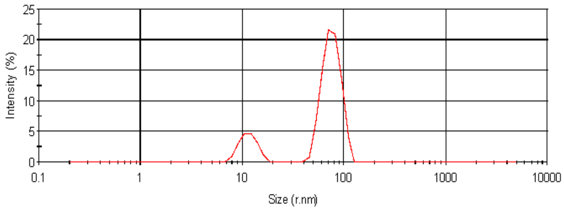

Fig. 3. Particle-size distribution pattern of the LCP particles at pH 6.0.

This finding is in accordance with the results of the viscometric study of the LCP and the biopolymers (Fig. 4). It can be seen that, in the pH range of 4.4 – 8.2, the values of reduced viscosity of the LCP reaction mixture change from 0.69 g dl^{-1} to 0.85 g dl^{-1}, which are significantly lower than those of the Ch water solution, whose values are close to 0.76 – 1.04 g dl^{-1}. These results testify to the formation of compact polymeric structures in the water-soluble LCP nanoparticles.

Due to the partial compensation of the KL negative charge with the positively charged chitosan macromolecules at pH 6.0, the obtained LCP nanoparticles had a smaller value (in an absolute sense) of average negative zeta potential (- 17 mv) in comparison with the zeta potential value for the KL particles (- 31 mv).

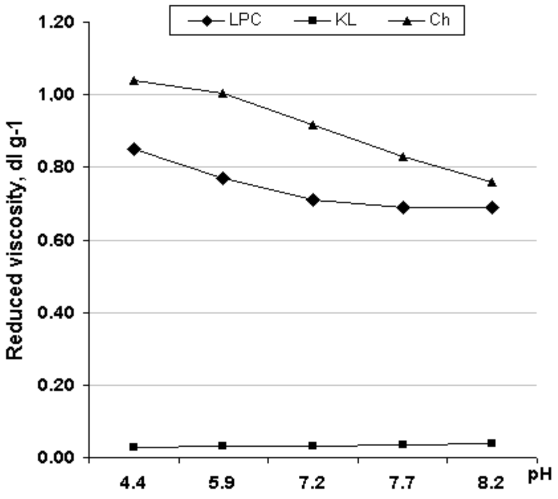

Fig. 4. Reduced viscosity of water solutions of 0.01 g dl^{-1} KL, 0.001 g dl^{-1} Ch and LCP with the same concentration of KL and Ch.

Surface pressure–area (π-A) isotherms of the biopolymers and the LCP at the air-water interface were studied with a KSV NIMA Langmuir through the double-barrier device (Fig. 5). The presence of the hydrophobic structures in the LCP nanoparticles and their more compact form in comparison with Ch nanoparticles, as evidenced by the obtained viscometric results (Fig. 4), favour the LCP nanoparticles orientation and packaging at the interface via interparticle interaction due to hydrogen and hydrophobic bonding that leads to the formation of a surface mono- and then, multilayers with increasing of the compression values. As a result, the initial and final pressure of the surface film, formed by the LCP nanoparticles, have higher values in comparison with those for the films formed by the individual biopolymers (Fig. 5). The high start surface pressure for the LCP nanoparticles testifies that the interaction between the LCP nanoparticles at the interface exists yet at the initial stage, and the formed LCP film is stronger than the films formed by KL and Ch.

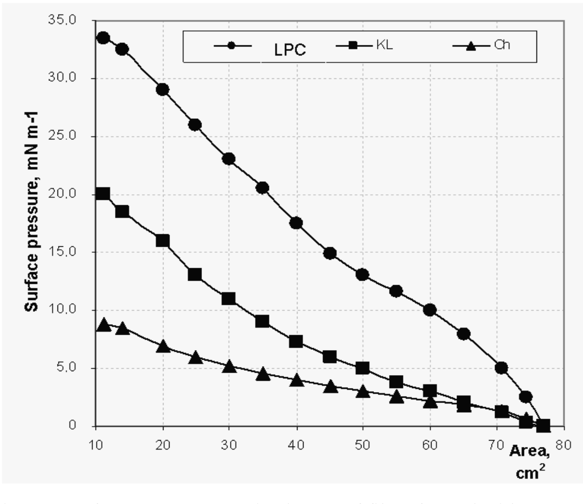

Fig. 5. Surface pressure–area isotherms of films formed with KL, Ch and LCP water solutions.

The concentration dependences of surface tension curves at the heptane-water interface for water solutions containing KL, Ch and LCP, as well as for water without any additive are given in Fig. 6. It can be seen that, at all the used concentrations, the LPC nanoparticles are able to more extent adsorb at the heptane-water interface than the biopolymers. This can reflect a synergetic effect, governed by the peculiarities of the “core-shell” structure of the formed complex nanoparticles, promoting their adsorption at the interface. At the same time, the surface tension values at the heptane-water interface change non-linearly with increasing the concentration of the LPC nanoparticles in the water solution and achieve the minimal value of 36.9 mN m^{-1} at the LPC concentration of 0.05 g dl^{-1}. It can be supposed that the character of the found correlation σ-C is associated with the “saturation” effect of the LCP nanoparticles at the interface.

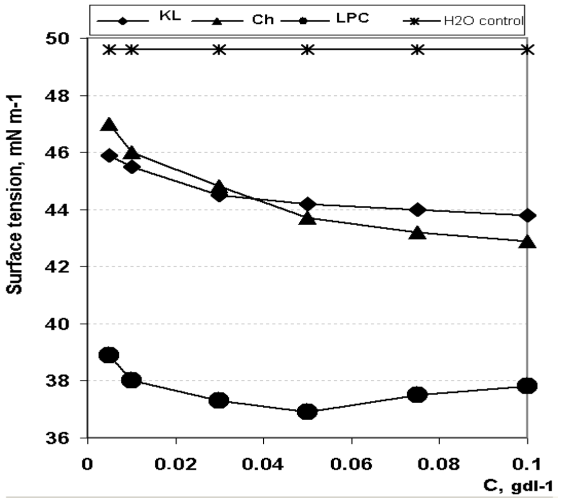

Fig. 6. Surface tension of KL, Ch and LCP water solutions at the heptane-water interface.

The study of the LCP nanoparticles as a stabiliser of O/W emulsion was carried out using the rapeseed oil-water emulsion. The ability of the LCP nanoparticles to stabilize the rapeseed oil-water emulsion was examined depending on the pH value at the defined concentration of the applied polyelectrolyte solutions. The separation process of the emulsion over time resulted in the appearance of a distinct interface between the water and oil phase volumes. Fig. 7 shows the values of the separation volume of the rapeseed oil-water emulsion containing the LCP nanoparticles with a concentration of 0.1 g dl^{-1}, depending on the pH water solution. It can be seen that the emulsion prepared with the water solution of the LCP nanoparticles in an acidic medium at pH 4.4 is characterized by lower separation water volumes, consequently, by higher stability compared with the emulsion stabilized with the alkali LPC solution at pH 8.2.

The different behaviour of the nanoparticles at the interface can be conditioned by a higher degree of conversion in the LCP polyelectrolyte complex in the acidic medium due to the maximal protonation of chitosan macromolecules, enhancing the LCP hydrophobicity. The growth of the hydrophobicity of the LPC nanoparticles gains the formation of more organized structured interfacial layers and more effective spatial stabilization of the emulsion droplets.

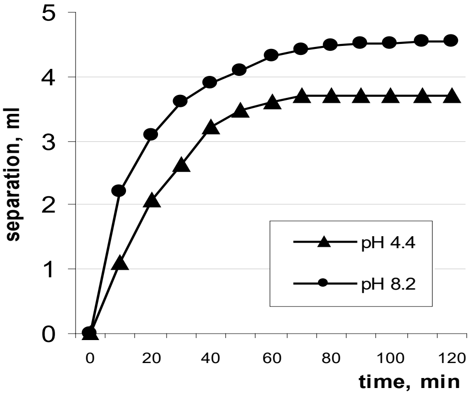

Fig. 7. Water phase separation in the rapeseed oil-water emulsion vs time, depending on pH value of 0.1 g dl^{-1} LCP water solution.

IV. CONCLUSIONS

A water-soluble non-stoichiometric polyelectrolyte complex consisting of kraft lignin and high molecular chitosan macromolecules was obtained. The formed particles of the polyelectrolyte complex were nanosized and characterized by remarkably lower values of surface tension at the air-water and the heptane-water interface in comparison with the initial biopolymers. With decreasing pH and increasing concentration of the nanoparticles, their adsorption ability at the interfaces was grown. The ability of the formed nanoparticles to stabilize the O/W emulsion increased in the acidic medium as a result of the enhancement of the conversion degree in the polyelectrolyte complex due to the maximal protonation of chitosan macromolecules.

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