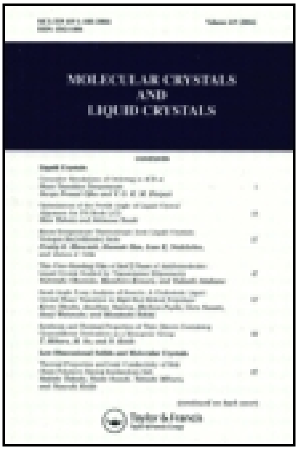

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New Lignin-Based Polymers for Ecological Rehabilitation

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New Lignin-Based Polymers for Ecological Rehabilitation

Galia Shulga[1], Talrits Betkers[1], Julia Brovkina[1], Brigita Neiberte[1], Anrijs Verovkins[1], Olga Belous[2], Dalia Ambrazaitene[2], and Audrone Žukauskaite[2]
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It has been shown that the found regularities of the interaction between lignosulfonate and polymeric cations in aqueous media can serve as a scientific basis for chemical modification of lignin by way of the formation of the interpolyelectrolyte complexes. This energy-saving and non-complicated method of modification was applied for obtaining new lignin-based soil improving agents. Water-soluble polymeric products of the interaction of lignosulfonate with three synthetic polymeric cations have been used in order to study the effect of their adsorption at the clay soil surface on the water stability of the artificially soil aggregates formed by the treatment of soil with lignin-based polyelectrolyte complexes (LPECs). The obtained results are explained from the viewpoint of the complex mechanism of soil structure formation, combining simultaneously the flocculation of soil particles and stabilization of the formed aggregates. The conducted field tests have shown that the application of the lignin-based polyelectrolyte complex as a soil conditioner at a deep loosening of heavy clay soil allows the improvement of the hydrophysical properties and the filtration ability of the soil sublayers and, thereby, to enhance the barley yield.

Keywords: adsorption; deep loosening; interpolyelectrolyte complex; lignosulfonate; modification; soil conditioner

INTRODUCTION

Recently, due to the petroleum cost, the interest for the commercial use of wood components such as lignin for the production of new

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products, chemicals and fuels has been remarkably increased [1]. Lignin, a space biopolymer with cross-linked phenyl-propane structural units, is one of the most renewable natural polymers after cellulose. In plant cell wall, it acts as a glue-like matrix for cellulose fibers [2]. Technical lignin–lignosulfonate (LS) is produced during industrial delignification of wood in sulfite pulp mills. The annual production of solid LS is estimated to be close to 1 million tons [3]. Due to the introduction of sulfonic groups, lignin macromolecules become water-soluble and bear a negative charge. The biodegradability, cheapness and availability of lignosulfonate as well as the peculiarities of its aromatic structure allow its use in a wide range of applications as a dispersant, emulsifier, a rheoregulator, a dust suppressant, an improving additive for concrete and cement, etc.

There are a lot of literature data regarding the possibilities of chemical modification of LS for obtaining lignin-based polymers with defined adhesive properties [4,5]. Many of the known methods for its modification have a whole range of drawbacks, including the complicacy of the modification process and its power intensity.

The dualistic essence of LS, combining the properties of a polymer and an electrolyte, allows them to interact with synthetic and natural polyelectrolytes (opposite charged, same sign charged, amphiphilic, etc.) in water solutions with the formation of lignin-based interpolyelectrolyte complexes (LPECs) representing interpolymer assemblies [6–8]. Such polymeric products may be formed as a result of the interpolymer electrostatic or donor-acceptor interaction. The considerable difference in the behavior of the initial polymer components and the formed products in aqueous media indicated that LPECs are individual high-molecular polymers and may be considered as a novel class of polymeric compounds.

The current and future field of the application of modified LS with high production potentialities may be its use as soil improving agents with pronounced adhesive properties, and, in particular, in the form of soil conditioners, structures and stabilizers [9]. The application of technical lignins for this purpose under the following trademarks such as Sandstop, Dustex, Lima, Lia, Copolima, Copoliba, RoadBond, RP Ultra Plus^{TM} etc., is well known. Soil conditioners based on technical lignins have a pronounced advantage over synthetic polymeric ones, since they are biodecomposed and form humus-like substances during biotransformation in soils.

Environmentally friendly and non-expensive LPECs with pronounced adhesive capacity and structure-forming properties for improvement of various kinds of soil have been developed by the Latvian State Institute of Wood Chemistry. The compositions of the developed

LPCs have been synthesized by modification of LS with polymeric cations in the presence of salts of multivalent metals. Thereby, the lignin-based conditioners have been approximated, to some extent, the structure and properties of soil organo-mineral formations. The results of the study of these modified lignins for protection of sandy soil from water and wind erosion have been shown [10–12].

One of the most serious clay soil problems is its compaction at depth, which significantly decreases water infiltration and root growth that leads to diminishing agricultural crops. Soil deformation and compaction are also enhanced when large tractors and heavy equipment are used. The negative factors could be minimized, if proper tillage of clay soil is applied [13].

This article generalizes some our publications [14–18] on the creation and study of lignin-based interpolyelectrolyte complexes and their application for clay soil improvement.

MATERIALS AND METHODS

Objects

To study the interpolyelectrolyte interactions, fractionated LS obtained as a result of commercial and laboratory delignification of the wood of different species (Table 1) were used for creation of LPECs. The obtained samples were carefully purified from non-lignin admixtures by methods traditionally accepted in lignin chemistry [19]. Based on the data of elementary, functional and spectral analysis, an empirical formula was calculated for each LS, and the results of liquid chromatography made it possible to assess its weight-average molecular weight (M_w) and MMD. Poly-N,N′dimethylaminoethylmethacrylate ($M_w = 5 \cdot 10^5$) synthesized in laboratory conditions was used as a polymer cation.

To investigate the adsorption ability as well as structuring properties of LPECs, commercial non-fractionated LS with the structural formula $C_9H_{8.17}O_{4.54}(OCH_3)_{0.73}S_{0.38}$ ($M_w = 2.8 \cdot 10^4$) as well as three

TABLE 1 Characteristics of the Applied Lignosulfonate

No.	Delignification	Wood	Type of lignin	M_w	M_w/M_n
1.	commercial	softwood	lignosulfonate	fractions from $8 \cdot 10^3$–$1.3 \cdot 10^5$	—
2.	laboratory	spruce, pine	lignosulfonate	$4.8 \cdot 10^4$–$5.4 \cdot 10^4$,	2.2–2.4
3.	laboratory	birch, alder	lignosulfonate	$2.2 \cdot 10^4$–$2.7 \cdot 10^4$	2.5–2.7

synthetic commercial polyelectrolytes (PE) differed from each other by the type of amino groups, molecular weight and charge density were used as components for the formation of lignin-based interpolyelectrolyte complexes. They were as follows: co-polymer of dimethylaminoethylmethacrylate and methacrylamide, containing amide and tertiary amino groups (PE-1) ($M_w = 1.0 \cdot 10^6$), polydimethyldiallylamonium chloride, containing quaternary amino groups (PE-2) ($M_w = 1.7 \cdot 10^5$) and branched polyethylenimine, containing primary, secondary and tertiary amino groups ($M_w = 6 \cdot 10^4$) (PE-3).

LPEC Synthesis

The reaction between the polyelectrolytes was carried out by mixing aqueous solutions of a polymeric cation and sodium LS at room temperature. The composition of the reaction mixture was expressed by the ratio $Z = [\text{polyelectrolyte}]/[\text{LS}]$, in which the concentrations of the components were expressed in base-mole/L.

Methodological Approach

The interaction between LS and polymer cations is regarded in the context of chemical equilibriums. This makes it possible to gain qualitative and quantitative information relevant to interpolyelectrolyte reactions from the viewpoint of the basic idea of the polyelectrolyte-polyelectrolyte interaction in aqueous media [20].

Methods for Investigation

The interpolyelectrolyte reactions and the LIPCs structure were investigated with the help of the methods of functional analysis, potentiometry and conductometry, turbidimetry, viscosimetry, liquid chromatography, speed sedimentation, laser light scattering, UV- and IR-spectoscopy.

A quantitative description of the interpolyelectrolyte reactions was made in terms of the dependence of the extent of conversion (θ) on pH for the reaction mixtures of equimolar composition ($Z = 1$). θ for the interpolymer reaction was determined as a ratio of the number of the formed intermolecular bonds (x) to the maximum possible number (y):$\theta = x/y$.

Adsorption Test

For the adsorption test, the molar ratio of LS to PE in LPECs was less than 1. In terms of molecular weight, IPECs were arranged in the following series: LPEC-1 > LPEC-2 > LPEC-3, which was established by the viscometric measuring of the dilute reaction mixtures of LS and PE at a low value of Θ. In terms of the charge density, evaluated by potentiometric titration for the same LPECs, the sequence of the series was opposite in direction.

The adsorption test was carried out in dilute aqueous solutions of LPECs with the known fixed concentration in the presence of $1 \cdot 10^{-3}$ mol l^{-1} NaCl at the pH 5.5 and the temperature 20°C. Kaolin particles with the size equal to and less than $2\ 10^{-6}$ m and with the surface area 12.5 m^2g^{-1} were applied. An amount of the dried kaolin (from 25 to 500 mg) was mixed with 50 ml of a water solution of LPEC for 3 hours and left for 24 hours to reach the adsorption equilibrium. The adsorption ability of LPEC at the liquid-solid interface was studied by determination of the adsorption isotherms at 20°C. The amount of LPEC, remaining in the solution, was determined in a supernatant after centrifugation spectrophotometrically at 280 nm and by potentiometric titration of the supernatant at room temperature.

To study of LPEC structuring ability, heavy clay soil from the depth 20–40 cm with the pH 5.8 and the content of particles with the size <0.01 mm about 70 wt. % was used. The clay soil was used in a powdered dusty state with the particle size <0.25 mm. The structuring was performed by means of simultaneous spraying of 0.5–3.0 g dl^{-1} of PE solutions and 5–30 g dl^{-1} of LS solutions into a dusty soil with mixing of the soil at the optimum moisture content. A soil sample modified with the LS solution served as the control.

The amount of the artificial soil aggregates with the size >0.25 mm was determined by way of fractional screening of the structured soil sample in the air-dry state on sieves. Water stability was determined by fractional screening of the formed artificial soil structure in the wetting state on sieves according to the Savvinov method, and expressed as the mass ratio of water-resistant aggregates with the size >0.25 mm to all the artificial aggregates.

Field Test

Deep loosening with simultaneous application of a LPEC solution was carried out on a clay derno-gley soil with a content of 70 wt % of clay particles and the filtration coefficient equal to 0.02 m/day. It was performed using specially developed original equipment consisting of a tractor, a device for applying an aqueous solution of the soil conditioner and a ripper developed at the Latvian Research Institute for Water Management and Land [21]. The application rate of the LPEC solution varied from 3600 to 4500 l ha^{-1}, which was chosen based on the results of laboratory tests.

To study the physical properties, soil samples were taken several times per year in different subsoil layers (20–40 cm and 40–60 cm). The bulk density, total and capillary porosity as well as moisture content were determined by traditional methods [22]. Penetration resistance was determined using a Revyakin penetrometer. The water stability of the soil structural species was assessed by the Savvinov method. The filtration coefficient was determined using a Boldyrev-Nesterov infiltrometer.

RESULTS AND DISCUSSION

Interpolyelectrolyte Reactions as a Method for Development of Soil Improving Agents

Lignosulfonate interacts with polymer cations – weak and strong polymer bases in aqueous media with the formation of interpolyelectrolyte complexes. The reaction between water-soluble lignin and polymeric bases can be represented schematically in the following manner:

$$\text{a)}\mathrm{LS} \vdash \mathrm{A}^- \quad + \quad \mathrm{B} \dashv \mathrm{PC} \quad \xrightarrow{\mathrm{H_2O}} \quad \mathrm{LS} \vdash \mathrm{A}^- \ {}^+\mathrm{HB} \dashv \mathrm{PC} \quad + \quad \mathrm{n(OH^-)};$$

$$\text{b)}\mathrm{LS} \vdash \mathrm{A}^- + \quad \mathrm{Hal}^- \ {}^+\mathrm{B} \dashv \mathrm{PC} \quad \xrightarrow{\mathrm{H_2O}} \quad \mathrm{LS} \vdash \mathrm{A}^- \ {}^+\mathrm{B} \dashv \mathrm{PC} \quad + \quad \mathrm{n(Hal^-)},$$

where: A^-—$\mathrm{SO_3^-}$, $\mathrm{COO^-}$; B—$\mathrm{NH_2^-}$, NH=, N≡ or $^+$NH≡; Hal^-—Cl^-, Br^-.

Such a type of the interactions has an electrostatic nature. From the thermodynamic point of view, such interpolyelectrolyte reactions are analogous to the reactions between complementary biopolymers responsible for the self-assembly of most biological structures.

The found pH dependences of the extent of conversion θ (Fig. 1) have shown that the interpolyelectrolyte reactions, irrespective of the LS molecular weight, proceed in a narrow range of the variation of pH, which testifies a co-operative nature of the LS/polycation interaction. On the other hand, the reaction between the polycation and LS ($M_w = 8$ kg/mole) with a lower value of molecular weight is characterized by a more gentle θ-pH profile and its noticeable shift towards the region of lower values of pH. Such a behavior indicates a less pronounced cooperativeness of the interaction between lignin and PDMAEMA.

The less pronounced co-operative nature of the interaction between PDMAEMA and LS of deciduous wood species is governed by the

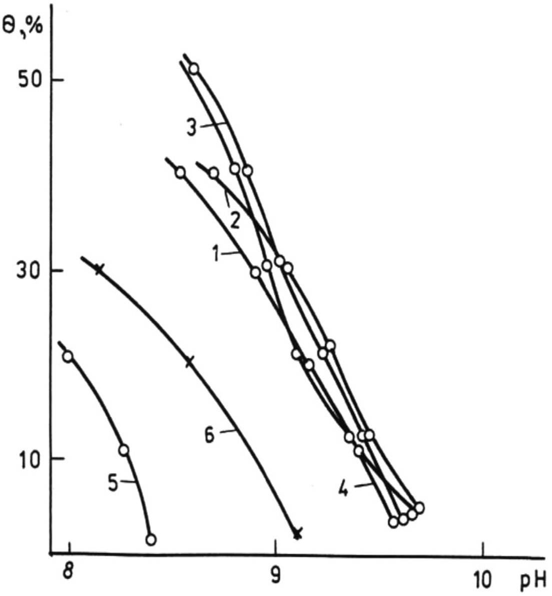
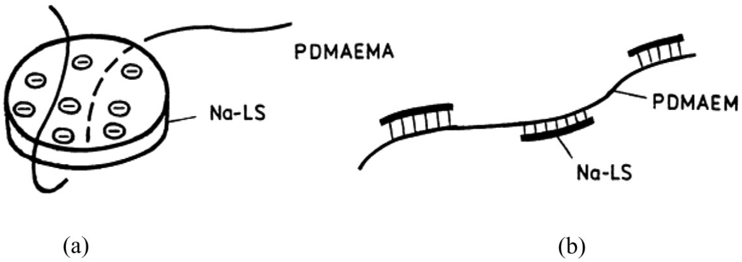


FIGURE 1 θ-pH-dependence for reactions of poly- N,N′-dimethylaminoethylmethacrylate with Na-LS with different molecular weight: $1.3{\cdot}10^5$(1), $9.9{\cdot}10^4$(2), $7.5{\cdot}10^4$(3), $4.0{\cdot}10^4$(4), $8.0{\cdot}10^3$(5), non-fractionated Na-LS (6); Z = 1.

dominating content in deciduous lignins of phenyl propane units with methoxyl substituents in 3- and 5-positions of the aromatic ring, spatially hampering the Coulomb attraction between the components of LPECs.

A study of the chemical equilibriums in the interpolyelectrolyte reaction shown significant effect of the LS molecular weight on the degree of the interpolymer association. The association with the polymeric cation increases with an increase in the LS molecular weight. The composition of the formed associates depends on the extent of conversion in the interpolyelectrolyte reaction. When the reaction proceeds to a deeper conversion, the number of LS macromolecules incorporated within the formed particles of the interpolymer complex significantly is increased. It has been found that the equilibrium in the interpolyelectrolyte reactions can be shifted to the polymer products formation as the pH of the reaction mixtures decreases, while, on introducing of low-molecular electrolytes such as lithium, sodium and potassium chlorides, the equilibrium is shifted to the opposite side.

The formed products in dilute reaction mixtures may be regarded as specific block-copolymers composed of hydrophilic and hydrophobic



(a) (b)

FIGURE 2 Schematic structure of LPEC products formed with high- (a) and low-molecular (b) sodium lignosulfonate.

blocks (Fig. 2). The blocks formed by sequences of the pairs of the chains of LS and polycation, connected with each other by salt bonds, are assigned to hydrophobic blocks, while the dislinked regions of polymeric chains, incorporating the charged groups of both the polyelectrolytes, are assigned to hydrophilic ones.

The possibility to form both soluble (non-stoichiometric), and insoluble (stoichiometric) LPECs depends on the mixture composition, pH, ionic strength, solvent thermodynamic quality, reaction temperature as well as the molecular weight of lignin. With increasing LS molecular weight, decreasing pH value and ionic strength of the mixture, and lowering the solubility of the polymer products formed testifies the growth in the number of hydrophobic blocks and their extension.

The features of the LPECs structure such as the presence of hydrophilic and hydrophobic sequences, as well as LPICs high molecular weights impair them pronounced adhesive properties and the affinity for different surfaces. These properties can be regulated by changing the hydrophilic-hydrophobic balance of their structure, which can be achieved by choosing the proper polymer cation, the LS/polycation weight ratio and the extent of conversion in the interpolyelectrolyte reaction. The polymeric nature and amphiphilic character of the lignin-based interpolyelectrolyte complexes determine their structuring and stabilizing properties with respect to various soils.

Laboratory Tests on Modifying Clay Soil

Figure 3 illustrates a Langmuir type of the LS adsorption isotherm. Earlier, it has been found [23] that LS is adsorbed in a monomolecular layer upon the positive edge surface of the kaolin particles. The LS adsorption leads to an increase in the specific surface of kaolin and its hydrophilicity, which is confirmed by the absence of the water stability of the formed soil aggregates (Fig. 4). At the same time, the

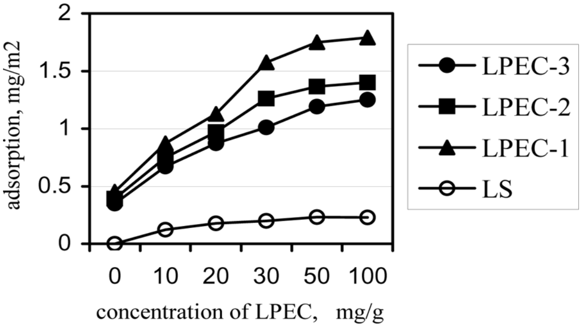


FIGURE 3 Adsorption of LS and LPECs on kaolin.

adsorption of LPECs on kaolin particles demonstrates high affinity type isotherms at low concentrations and is characterized by the formation of multilayers. The maximum values of LPECs adsorption are 4–6 times higher than those in the case of LS. The high adsorption ability of LPEC molecules on the clay surface testified a chemisorption mechanism conditioned by the formation of clay-LPEC bonds. The energy for the chemisorption of LPECs at the kaolin surface could be derived from both Coulomb and donor-acceptor interactions, including specific π-interactions between the aromatic ring of LS and the kaolin surfaces. Such a type of the interactions has been revealed in the study devoted to the interaction of LS with sodium alumomethylsiliconates in aqueous media [24].

It is supposed that the formation of two waves in the adsorption isotherms is evidently due to the multilayer adsorption of LPECs. Using neutron reflectometry [25], it has been found that the surface multilayers formed by adsorbed polyelectrolyte complexes represent

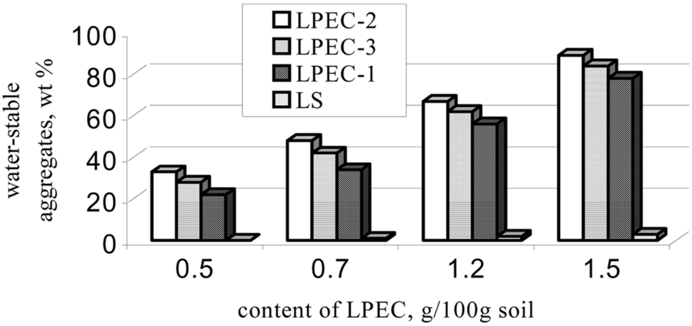


FIGURE 4 Dependence of the quantity of water-stable clay aggregates on the content of LPECs.

stratified structures. The main reason for the progressively larger number of the adsorption sites for consecutive generations of macromolecules of the adsorbed polyelectrolyte complex may be the roughening of successively deposited layers.

In terms of the maximum value of saturated adsorption, LPECs have shown the following sequence: LPEC-1 > LPEC-2 > LPEC-3 (Fig. 3). The obtained results testify a crucial role of the molecular mass of LPEC on its adsorption on the kaolin surface, which is analogous to the influence of the molecular weight of a polymer on its flocculation ability. At the same time, the higher the molecular weight of LPECs, the lower its charge density and the higher hydrophobicity. The strengthening of the hydrophobic interactions between the LPEC and the kaolin particles with increasing molecular weight of LPEC may be of a considerable general importance in the understanding of the adsorption peculiarities of these polymeric conditioners at the soil surface.

The water stability of the artificial aggregates formed by applying LPECs to fully dusty clay soil at the application rate from 5 to 15 mg g $^{-1}$, depending on the application rate and polycomplex composition, varied from 0.21 to 0.82. The content of the water-stable aggregates formed by LS was equal to zero. In terms of the efficiency of the structuring action, LPECs were arranged in such a sequence: LPEC-2 > LPEC-1 > LPEC-3. The obtained results are explained from the viewpoint of the complex mechanism of the structural formations in the soil, combining simultaneously the flocculation of soil particles and the stabilization of the formed soil aggregates. Thus, the molecular weight of the polymer is a crucial factor for flocculation, hence, the density of its charge plays a decisive role for stabilization in disperse systems. The established values of the maximal adsorption of LPECs on kaolin and the application rate of LPECs, which are necessary for achieving the maximum water stability of the soil structure, make it possible to agree with the notions of La Mer [26] on the sufficiency of the "half-filling" of the particles' surface with a polymer for achieving the maximum effect.

Field Tests on Clay Soil Amelioration

It is known that the loosening of heavy clay soil to the depth up to 0.8–1.0 m makes it possible to increase the drainage and water ensuring in subsoil layers. At the same time, the clay soil aggregates created thereby are water-unstable, which, at the same time, impairs the effect of loosening in time. To enhance the water stability of the soil clay structure, deep loosening and the simultaneous application of the lignin-based soil conditioner by spraying its solution into subsoil layers of clay soil have been performed. In this part of the article, the results of the comparative investigation of the physical properties of the subsoil layers formed at deep loosening of clay soil without and with the application of LPEC-1 during the first year under study are represented. The ratio of the components in IPEC-1, their concentration in a water solution and the application rate of the conditioner for deep loosening were chosen based on the results of laboratory studies. To enhance the aggregative stability of IPEC-1, aqueous ammonia was introduced to its working solution.

Deep loosening was carried out in autumn (October) on a clay derno-gley soil with a content of 70 wt % of clay particles and the filtration coefficient equal to 0.02 m/day. Deep loosening was performed using specially developed original equipment. The application rate of the LPEC solution varied from 3600 to 4500 l ha^{-1}, which were chosen based on the results of laboratory tests.

Table 2 lists the hydrophysical properties of subsoil layers (20–40 cm) after deep loosening, determined during the vegetation period. The results obtained have shown that, in one year, in the plots of deep loosening with the application of IPC, the volume weight at a depth of 20–40 cm decreased by 7.1–12.0%, total porosity grew by 2.6–4.1%, while capillary porosity increased by 0.7–3.2% in comparison with the plot, where deep loosening was carried out without applying the conditioner. One of the main indicators of the efficiency

TABLE 2 Physical Properties of Clay Soil in Subsoil Layers in the Vegetation Period

Time of determination	Volume weight, g · cm^{-3}	Total porosity, %	Total moisture capacity, %	Capillary moisture capacity, %
Plot without deep loosening				
May	1.52	43.8	28.8	28.5
September	1.52	43.7	28.7	28.6
Plot with deep loosening only				
May	1.38	46.0	33.1	32.9
September	1.42	45.2	31.9	30.2
Plot with deep loosening + LPEC				
Application rate – 3600 l ha^{-1}				
May	1.37	46.5	33.9	33.0
September	1.39	45.7	32.7	32.3
Application rate – 4500 l ha^{-1}				
May	1.36	46.6	34.1	33.2
September	1.38	45.9	33.0	32.5

of the deep loosening of heavy soils is the alteration of the filtration ability. In the plots of deep loosening with the application of LPEC, the improvement of the soil hydraulic properties was more pronounced than in the plot with loosening alone: the water drainage was enhanced, and the level of ground water standing decreased. The value of the coefficient of filtration above the loosening slot in the plots with the application of LPEC increased from 0.02–0.06 m/day to 0.27–0.31 m/day. The characteristic features of the water filtration process as a result of deep loosening of soil should be noted, governed by the formation of artificial large pores. As a rule, the stage of water penetration into subsoil layers initially occurs, mainly through the formation of large pores, then the stage of absorbing the water by the formed soil structure proceeds, and further, as the soil reaches the full water saturation, the water sorption stage changes to the filtration stage. The intensive discharge of the gravitation water and the increase of the moisture capacity of the 0–60 cm layers ensured the regulation of the water regime in the arable and subsoil layers of clay soil in the vegetation period. In the droughty period (June), the moisture content of the subsoil layers in the plots of deep loosening with the application of the LPEC was by 3.4–6.3% higher than in the control plot. In the rainy period (September), the moisture content of the subsoil layers in the control plot was by 3.7–6.7% lower than that of the arable layer, while, in the plots with the application of the LPEC, the moisture content of subsoil layers exceeded that in the arable layer.

Table 3 shows the values of the penetration resistance and moisture content in subsoil layers in the untreated plot and the plots treated by loosening with and without the application of IPC. A study of the penetration resistance of subsoil layers at a depth of 35–45 cm has shown a decrease in the hardness of the layers by 35–40% and 25–30% in comparison with the untreated plot and the plot with deep

TABLE 3 Penetration Resistance and Moisture Content in Subsoil Layers

	Depth of the layer, m			
	0.35		0.45	
Variant	P, MPa	W, %	P, MPa	W, %
Untreated plot	2.44	25.8	3.12	31.9
Plot with deep loosening	2.21	27.9	3.04	31.9
Plot with deep loosening + IPC:				
3600 $\mathrm{l\,m^{-3}}$	1.80	32.2	2.42	34.7
4500 $\mathrm{l\,m^{-3}}$	1.72	34.1	2.27	35.6

loosening alone, respectively. This fact has testified a partial destruction of the soil structure in the plot with deep loosening alone, already in a year.

The essence of the application of soil conditioners implies the creation of a water-stable soil structure in subsoil layers, which would favor the formation of the developed root system of the plants and would ensure the required intensity of the drying action of the drainage, without the repeated loosening within 6–8 years. The observed improvement of the physical properties of clay soil was governed mainly by an increase in the water stability of the soil structural species formed owing to their stabilizing and structuring with the lignin-based soil conditioner. The results of wet screening have shown (Table 4) an increase in the content of water-resistant aggregates in the 20–40 cm subsoil layers treated with LPEC, on the average, by 30–35% in comparison with the plot where loosening was performed without the application of the soil conditioner. In the macroaggregate composition of clay soil, the content of large water-resistant aggregates (>5 mm) increased, and the dust content decreased (<0.001 mm). The particles 0.5–0.25 mm in size made up the bulk of the water-resistant aggregates in subsoil layers treated with LPEC.

The improvement of the water regime of soil within the vegetation period (May-September) resulted in an increase in the barley yield. Table 5 shows barley yield values in terms of grain and straw, collected in plots without loosening, those with simultaneous loosening, and loosening with applying soil conditioner solutions. The depth of the installation of drain-pipes in all plots was 1.2 m, and the distance between them was equal to 14 m. The gains in the barley yield (in terms

TABLE 4 Content of Water-Resistant Soil Aggregates in Subsoil Layers (20–40 cm)

	Macro-structural composition of soil, wt%					
Variant	>5 mm	5–3 mm	3–1 mm	1–0.5 mm	0.5–0.25 mm	Total content of water-resistant aggregates >0.25 mm
Plot with deep loosening	–	–	1.9	17.2	30.4	49.5
Plot with deep loosening + IPC:						
3600 $\mathrm{l\,m^{-3}}$	–	2.8	8.6	18.9	33.5	63.8
4500 $\mathrm{l\,m^{-3}}$	0.6	3.5	9.2	20.8	35.2	67.3

TABLE 5 Yield of barley after the first year under study

	Yield, centner ha^{-1}	
Variant	grain	straw
Untreated plot	32.9	40.6
Plot with deep loosening	39.8	82.2
Plot with deep loosening + LPEC:		
3600 l m^{-3}	47.8	86.9
4500 l m^{-3}	50.5	90.6

of grain) in the plots of deep loosening with the application of LPEC were 45–55% and 20–30% as compared with the untreated plot and the plot with deep loosening alone, respectively. Within a year, it is not possible to offer a comprehensive estimation of the efficiency of the action of LPEC as a soil conditioner, therefore, the highest effect of the structuring and stabilizing action of LPEC should be expected in the subsequent years of the maintenance of the drainage system.

CONCLUSIONS

Thus, it has been shown that LS forms with polymeric cations LPECs in aqueous media. The possibility to form soluble or insoluble LPECs depends on the mixture composition and the reaction conditions as well as the molecular weight of lignin and its wood species. Water-soluble LPECs may be regarded as specific block-copolymers composed of hydrophilic and hydrophobic blocks that feature pronounced structuring and stabilizing properties with respect to clay soil. The maximum adsorption of LPECs on kaolin and the application rate, which is necessary for achieving the maximum water stability of the artificial clay soil structure formed, agree with the La Mer concept of the sufficiency of the “half-filling” of the particles’ surface with a polymer for achieving the maximum modifying effect. The conducted field tests have shown that the application of LPEC as a soil conditioner at a deep loosening of heavy clay soil makes it possible to improve the hydrophysical properties of the clay soil sublayers and increase the barley yield.

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