EFFECT OF THE MODIFICATION OF LIGNOCELLULOSIC MATERIALS WITH A LIGNIN-POLYMER COMPLEX ON THEIR MULCHING PROPERTIES

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The lignosulphonate/polymer complex, in which the macromolecules of both components are linked together by physico-chemical bonds, has been applied as a new effective lignin-based soil conditioner (LSC). It has an adhesive affinity both for mineral soil particles and the organic surface of lignocellulosic mulch. The modification of the mulch particles with aqueous solutions of the developed conditioner by means of impregnation makes it possible not only to anchor mulch to sandy soil and, thereby, to diminish significantly the evaporation from the soil surface, but also, due to mulch biodegradation, to enrich soil with the main nutrient elements and to create favourable conditions for plant growth. The effect of the mulch modification is determined by the complex composition and depends on its content in the aqueous solution and the application rate.

Keywords: Lignocellulosic mulch, Lignin-polymer complex, Soil conditioner, Modification, Impregnation, Hydrolysis lignin, Sawdust, C/N ratio

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INTRODUCTION

Biomass in the form of lignocellulosic waste represents an abundant renewable feedstock for the production of both energy and new organic materials for mankind's needs. The purposeful application of lignocellulosic waste in agriculture and forestry may be regarded as an innovative avenue for its utilization.

A known management practice for controlling soil erosion combines the application of grass seedings and mulch as a soil surface covering. Possibilities of different types of lignocellulosic mulch for protection of the soil surface have been demonstrated (Barkley et al. 1965; Bristow 1988). For the Baltic countries, having well-developed wood processing, the application of lignocellulosic waste such as sawdust, bark, and hydrolysis lignin as a soil mulch is economically grounded and promising. Hydrolysis lignin is formed during the treatment of wood with sulphuric acid at high temperature and pressure. In the hydrolysis industry, this treatment of wood is carried out mainly within Eastern Europe for manufacture of poly- and monosaccharides, followed by further processing to ethanol and fodder yeast (Sarkanen 1971). However, the use of unanchored dispersed mulch leads to its washout, blowing off, and, as a result, to the destruction of the mulch layer under the action of unfavourable weather conditions. One of the attractive solutions to this problem may be the simultaneous application of organic mulch, grass seeds, and a soil polymer conditioner, which acts as an adhesive. A polymer conditioner attaches the mulch and grass seeds to the sandy surface, thus preventing their washout, leaching and blowing off, as well as reinforcing the sandy surface, forming an upper stabilised layer that resists the water runoff and soil loss (Kay 1978; Shulga et al. 1998).

The application of commercial technical lignins, a low-cost polymeric feedstock for the production of lignin-based soil stabilisation agents, is well-known. Commercial products include the following: Sandstop, Dustex, Lima, Lia, Copolima, Copoliba, RoadBond, RP Ultra Plus^{TM}, etc.

Environmentally friendly, inexpensive, lignin-based soil conditioners (LSCs) with a pro-nounced adhesive and gluing ability have been developed by the Latvian State Institute of Wood Chemistry (Shulga et al. 1998; Shulga et al. 2001). They were synthesised by modification of both sodium- and ammonium lignosulphonate with various complementary eco-friendly water-soluble polymers or oligomers (Shulga et al. 2000, 2002). Chemically, LSCs represent interpolyelectrolyte complexes, in which the macromolecules of both components are linked together *via* physico-chemical bonds. The developed interpolymer complexes may be used as an effective conditioner and amendment for improving hydrophysical properties of sandy and clay soils. Some of them have been already applied as ameliorants under field conditions in Latvia (Smilga et al. 1982, Shulga et al. 1984).

A new effective lignin-based soil conditioner (LSC) has been specially developed for protecttion of erodable sandy soil in the sea coastal zone, with the application of mulch and plant seeds. It differs by having a higher aggregation stability in aqueous solutions and the ability to change viscosity within a wide range, depending on its composition.

The objective of this work is to study the effect of the modification of lignocellulosic waste materials with the developed LSC on the mechanical properties of the composite coverings formed from mulch and soil particles, as well as the moisture evaporation and chemical transformations in sandy soil.

EXPERIMENTAL

Materials

Commercial sodium lignosulphonate (LS) by-products of softwood delignification, were used for obtaining the new soil conditioner. The LS elementary and functional analysis performed according to (Zakis 1994) gave the following formula:

$$C_9\ H_{8.35}O_{4.54}(OCH3)_{0.82}\ S_{0.41}$$

Its average molecular weight was 30 kg mol^{-1}. The new lignin-based soil conditioner (LSC), representing a lignin-polymer complex, has been obtained as a result of the interpolyelectrolyte interaction of LS with an environmentally friendly acrylic polyelectrolyte by mixing their concentrated solutions under well-defined synthesis conditions. The LSC composition of Z = polymer/lignin in the solutions was varied from 0.02 to 0.2. For the obtained polycomplex solutions, the dynamic viscosity in the indicated range of Z varied from 30 mPa·s to 1.25 10^4 mPa·s, and their pH values did not exceed 5.0.

The air-dried fractionated sawdust of different wood species such as aspen, birch, spruce, and pine, representing a heavy-tonnage waste of Latvia's woodworking enterprises, and fractionated hydrolysis lignin after the manufacture of fodder yeast, representing the remaining wide-scale waste of the former Lithuanian hydrolysis industry, were used as mulches. The fractions of particles with the size between 1.0 and 2.0 mm and less than 0.5 mm dominated the mechanical composition in both mulch types after grinding.

The chemical composition of the applied sawdust (content of cellulose, lignin and extractives) is represented in Table 1. The chemical composition of hydrolysis lignin is listed in Table 2. Besides lignin substances, this organic waste also contained non-hydrolysed polysaccharides, sugars, organic acids, as well as small quantities of cations of polyvalent metals.

Table 1. Chemical Composition of Sawdust

Wood species	*Moisture, %*	*Ash, %*	*OCH_3, %*	*Cellulose, %*	*Lignin, %*	*Extractives, %, soluble in*	
						hot water	*organic mixture*[*]
Pine	4.8	0.21	5.1	58.2	28.4	1.8	3.2
Spruce	5.1	0.18	4.9	57.6	28.1	1.5	2.1
Birch	4.9	0.23	5.6	51.7	20.2	1.4	1.6
Aspen	5.0	0.33	5.2	52.1	21.4	1.1	1.5

[*] ethyl alcohol : benzene is close to 1:2

Table 2. Chemical Composition of Hydrolysis Lignin

pH	*Moisture, %*	*P_2O_5, mg kg^{-1}*	*K_2O_5, mg kg^{-1}*	*Organic carbon, wt %*	*Total nitrogen, wt %*
5.1	7.1	404	831	30.91	0.34

The soil under study was a sandy dune soil (humus content 0.08 wt% and pH 5.9). It contained 3.1% of particles ranging from 1.0 to 0.25 mm, 93.9% of particles ranging from 0.25 to 0.05 mm, and 3.0% of particles less than 0.01 mm in size.

Methods

The modification of the 2-cm sawdust and hydrolysis lignin mulched soil surface was carried out by spraying of 5-20 wt % water solutions of LSC at the rate 1.5-6.0 l m^{-2}. After applying an aqueous solution of the developed LSC onto the mulched soil, the impregnation of the mulch and soil with the solution occurred, and a two-layer sandwich-type composite covering was formed upon drying. It consisted of an upper glued thicker layer of mulch and a lower reinforced thinner layer of sandy soil.

To study the ability of the soil conditioner to bind sandy soil particles, the soil was treated by spraying aqueous solutions of LSC on its surface at different application rates, and then the soil was dried at room temperature. The penetration resistance and thickness of the reinforced upper sandy layers was measured, using a manual laboratory coner penetrometer (angle 30) and a calliper square. The number of replicates was equal to three, and the presented results were average arithmetic values.

To study the ability of the soil conditioner to bind mulch particles, raw composite blends were made by mixing the mulch with LSC at different weight ratios with their subsequent compacting in the form of cylinders at the pressure 0.1 MPa and duration 3 min. The ability of the air-dried cylinders to withstand the crushing force was determined in 7 days after their preparation and was characterised by the value of compressive strength according to ASTM D695 using a universal testing machine. Three replicates tests were carried out, and average arithmetic values are presented.

The water evaporation from the mulched soil was evaluated from the weight loss upon its standing in the open air. For this purpose, at first, the 2-cm mulch surface was treated with an aqueous solution of LSC with a concentration of 50-200 g l^{-1} at an application rate of 1.5-6.0 l m^{-2}. The obtained soil samples were brought to an air-dry state. Then equal amounts of water were applied to the surface of each sample so that the total content of moisture in all samples was equal and made up 12.5-12.8 wt %. The water evaporation from the soil surface was evaluated from the weight loss of the bath using an electron balance upon its standing in the open air at the temperature 293 ± 2K and an air humidity of 60 ± 2% in every 24 hours. The soil sample was considered air-dry, if the weight of the bath stopped varying with increasing storage time in the given experimental conditions. Again, the number of replicates was three, and the presented results were average arithmetic values.

The biochemical transformation process in the upper soil layers was investigated, using 10 litre buckets. A mulch layer of different thickness was placed on the soil top and treated with LSC water solutions. The effect of LSC alone and with mulch on the chemical composition of soil was estimated based on the alteration in the content of carbon and nitrogen in one and three months, and a year after the beginning of the experiments. The mulched soil samples were taken with a special soil perforator at the full depth of the buckets (height 32 ± 1cm including the mulch layer). Taking into account the density of sandy soil and wood sawdust, as well as the relative heights of the mulch layer and soil one in the bucket, the obtained results reflected mainly the changes on the content of C and N in soil. Phosphorus in the form of P_2O_5 was determined by the photoelectric colorimeter method with molybdate; K_2O using a flame photometer by the A-L method; carbon by the burning method (ISO 10694, 1995) using a "Heraeus" devise; and total N by the Kjeldahl method (ISO 11261, 1995). The presented results are average arithmetic values, as the number of replicates of each experiment was equal to three.

RESULTS AND DISCUSSION

Properties of Sand- and Mulch Composite Materials

The reinforced upper soil layers, representing soil-based composite coverings, were obtained by spraying the water solutions of LSC on the soil surface. The penetration resistance and thickness of the reinforced sandy layers depend both on the concentration of the applied water solutions at the specified application rate, as well as on the lignin/polymer complex composition (Fig. 1). The observed increase in the strength of the reinforced soil layers can be governed by the enhancement of the soil conditioner's adhesion to the soil particles as a result of an increase in the molecular weight of the interpolymer complex with increasing Z. The latter was demonstrated by the growth in the dynamic viscosity of the LSC solutions with the growth of Z. At the same time, the thickness of the reinforced layers decreased with the growth in the composition of the soil conditioner. In this case, the higher was the concentration of the applied conditioner solution, the lower was the thickness of the reinforced soil layers. Evidently, the high viscosity of the LSC solutions limited the depth of their infiltration into the soil. The higher values of thickness for the reinforced layers were typical for the sandy soil of the solutions of LSC with the composition Z = 0.02-0.05, having lower values of dynamic viscosity.

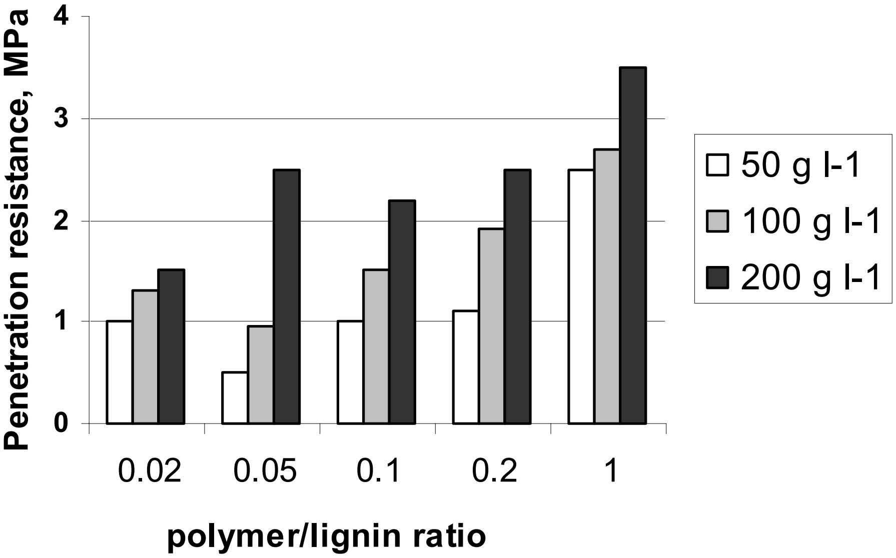

Fig. 1. Penetration resistance of reinforced soil layers *versus* LSC composition at different concentrations of the applied solutions; application rate - 1.5 l m^{-2}.

The application of LSC water solutions to the top of the mulch led to the formation of mulch-based composite coverings. To investigate the binding properties of the soil conditioner with respect to the mulch, several series of composition materials in the form of cylinders were prepared, in which sawdust and hydrolysis lignin were used as a filler and LSC as a binder. With increasing LSC content from 5 wt % to 25 wt % in the values range of the composition Z = 0.02-0.2, the compressive strength of the composites from the mulch increased 2.1- 4.5 times, which was determined by the adhesion affinity of the soil conditioner to the mulch particles. The effect of the LSC composition on the compressive strength of the composites from sawdust of different tree species and hydrolysis lignin at a mulch content of 75 wt % is demonstrated in Fig. 2. The compressive strength of the obtained composites increased with increasing the lignin/polymer complex composition and was characterised by maximum values at Z = 0.2.

The composites filled with the sawdust of deciduous wood species had higher values of compressive strength than the composites filled with the sawdust of coniferous wood species. The different binding ability of the soil conditioner relative to the sawdust of different wood species is obviously governed by the peculiar features of their chemical composition and different content of resinous substances in them.

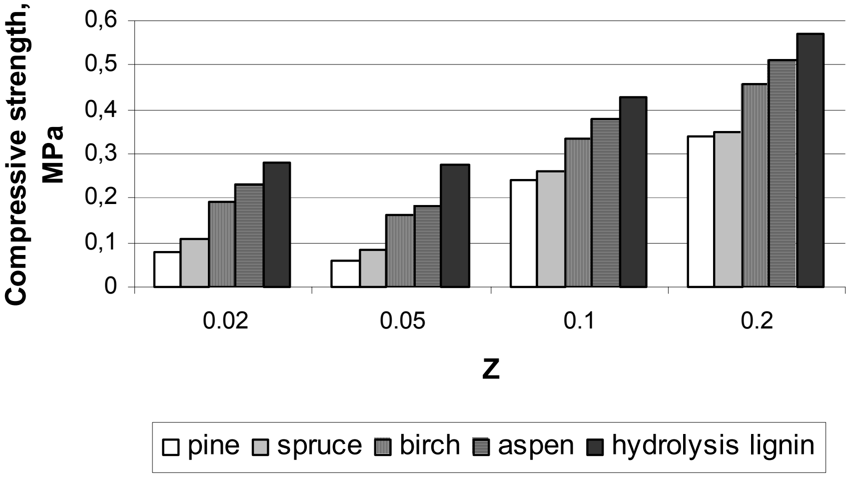

Fig. 2. Compressive strength for the composites made from different mulch *versus* the composition of LSC; content of LCS – 25 wt % (on the dry matter).

This is clearly demonstrated by the data of extraction with the organic solvents of the sawdust of deciduous and coniferous wood species (Table 1). It is known that the presence of a great amount of the resin in conifers weakens the adhesion interaction between glues and the wood filler (Hse et al. 1988). At the same time, the composites from hydrolysis lignin were characterised by the highest values of mechanical strength at the given composition.

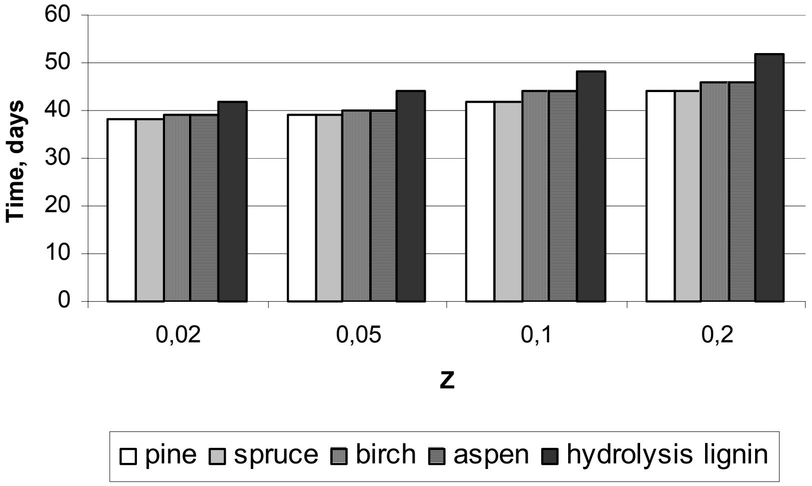

Fig. 3. Time of the achievement of moisture evaporation from the soil surface covered with the composite formed from different mulch *versus* the composition of LSC; concentration – 100 g l^{-1}, application rate – 4.0 l m^{-2}.

Formation of composites having relatively high strength may be favoured by the presence of the active reaction centres on the surface of hydrolysis lignin particles in the form of hydroxyl and carboxyl groups as well as ions of polyvalent metals, enhancing the adhesion interaction at the LSC/filler interface, which is in accordance with literature data (Matte et al. 1988).

Effect of Mulch Modification on Soil Evaporation

The time required for moisture evaporation from the samples covered with the soil conditioner-modified mulch was up 38-52 days and depended on the composition of LSC, the concentration of its solution and the application rate, as well as the type of the mulch. These parameters exceeded the values of the time of moisture evaporation from the non-mulched soil and that covered with untreated mulch. With increasing composition Z, at the same concentration and application rate of the soil conditioner solution, the mulching effect tended to grow. Figure 3 shows the values of the time of moisture evaporation (in days) from the soil samples covered with treated mulch, depending on the composition of the soil conditioner. The increase of the composition of LSC resulted in the increase of the time of moisture evaporation from the soil. In this case, this tendency manifested itself most distinctly with increasing Z in the range 0.05-0.2. The greatest suppression of moisture evaporation from the soil was reached in the case of treating the sawdust of deciduous wood species and hydrolysis lignin with the soil conditioner of the composition Z = 0.1-0.2. In the average, the time of moisture evaporation from the soil samples covered with the LSC-treated mulch exceeded by 16-57% the time of moisture evaporation from the samples covered with untreated mulch.

Effect of Mulch Modification on Soil Chemical Transformations

Hydrolysis lignin, characterised by the most attractive mulching properties, was used for the further study of the influence of the mulch particles modified with the lignin/polymer complex solutions on the chemical composition of sandy soil and its microbiological activity. The concentration of the LSC solutions and their application rate were chosen based on the results of the investigation of the effect of the treated mulch on the duration of the soil moisture evaporation. The changes in the chemical composition of sandy soil without and covered with mulch were defined in one and three months, and one year after the beginning of our experiment.

The quantity of mobile P_2O_5 and K_2O forms in the mulched soil was enhanced, depending on its thickness and the composition of LSC. With increasing thickness of the mulch to 5 cm, the content of mobile forms of phosphorus in the mulched soil increased by 13.6% relative to the uncovered soil and practically did not differ from the content of P_2O_5 in the soil treated only with solutions of the soil conditioner. The impregnation of a 5-cm layer of hydrolysis lignin with the LSC solution with Z = 0.2 increased the content of the potassium form in the soil almost 1.7 times relative to the unmodified mulched soil and 4.2 times relative to the uncovered sandy soil.

It is known that, during biotransformation, organic molecules of wood are able to decompose, mineralise, or be applied as building units for humic substances (Kogel-Knabner 2002). The direction of these transformations is fully determined by the chemical substances participating in the process and the process conditions. The C/N ratio may serve as a "key" indicator showing a dominant process direction. In the uncovered soil, the initial value of the C/N ratio was equal to 6/1, which indicates that the mineralisation process in soil proceeds passively.

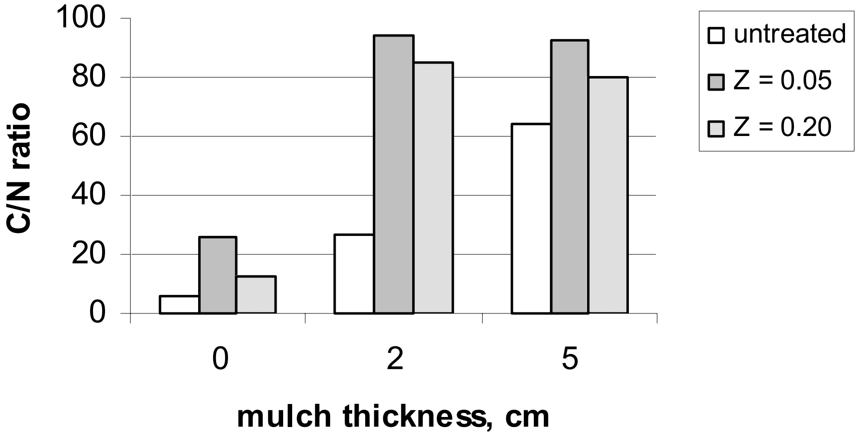

Fig. 4. Effect of the mulch thickness on the C/N ratio at the beginning of the experiment.

In one month after starting the test, the treatment of the soil surface with LSC solutions only led to increasing the C/N ratio from 2.1 to 4.3 times (Fig. 4), depending on the composition Z, in comparison with the case of the unmulched soil. Mulching led to a 4.4- and 10.5-fold increase in the C/N ratio for the soil covered with 2 cm and 5 cm of untreated mulch, respectively. When the mulch was modified with LSC solutions, the C/N ratio in the soil increased 11.4-15.5 times relative to the unmulched soil, and 1.5-3.5 times relative to the soil covered with the untreated mulch. This indicates more favourable conditions for immobilisation of nitrogen in the sandy soil covered with the modified mulch in comparison with the application of LCC solutions and the mulch alone.

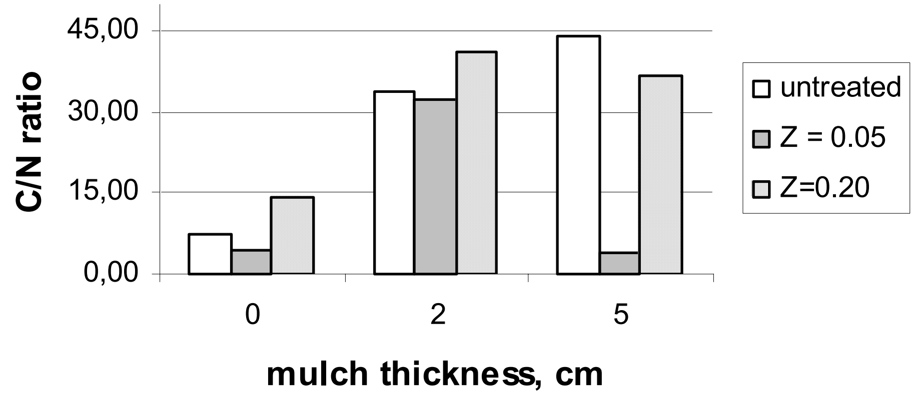

Fig. 5. Effect of the mulch thickness on the C/N ratio in a year after the biginning of the experiment.

In one year after starting the test, according to Fig. 5, the C/N ratio in the unmulched and 5-cm mulched soil samples treated with LSC solutions having Z = 0.05 remarkably decreased, equalling 4.2/1 and 3.6/1, respectively. This indicates an intensive biodegradation and mineralisation of organic matter, with the formation of nutrients in these variants. On the other hand, it may be assumed that the modification of hydrolysis lignin particles within the solutions of LSC, having a lower value of the composition, is more efficient for the acceleration of mineralisation processes in sandy soil. For other mulched soil samples, the C/N ratio also essentially decreased, however, its values changed in the range 30/1 – 40/1. This may testify that the biochemical transformations in hydrolysis lignin mulch modified with the lignin/polymer complex in these variants were still going on (Tuomela et al. 2000, Sjöberg 2003). This suggestion has been confirmed with the analysis of the drainage water determined after 2 years from the beginning of the study. The content of nitrate ions in the drainage water determined for these variants with the modified mulched soil was very high and sometimes exceeded their permissible available concentration.

Our experiments have revealed that the observed compositional transformations of the mulch modified with the lignin/polymer complex during the immobilisation and mineralisation of nitrogen were accompanied by an essential enhancement in the biocenosis activity of bacteria and micromycetes in the soil samples (Ambrazaitiene et al. 2006). Earlier, our vegetation test has also shown that the developed LSC has a beneficial action on the germination and development of seeds of plants typical for the Baltic coastal dune zone (Belous et al. 2006).

CONCLUSIONS

1. The modification of sawdust and hydrolysis lignin used as mulch by impregnation with water solutions of the developed lignosulphonate/polymer complex leads to the formation of a layered composite covering consisting of an upper modified layer of mulch and a lower reinforced layer of sandy soil.
2. With increasing composition of the lignosulphonate/polymer complex, at the same concentration and application rate of its water solutions, the mechanical properties of the composite layers and the time of moisture evaporation from the mulched soil increase, which indicates the enhancement of the adhesion affinity of the polycomplex structure for the mulch and soil surface particles as a result of its molecular weight growth with increasing Z.
3. The modified mulch-based composites, containing the bark of deciduous wood species, have higher values of compressive strength than composites containing the bark of coniferous wood species. However, the modification of hydrolysis lignin mulch gives the highest values of this indicator at the same composition and application rate of the polycomplex.
4. The changes in the soil chemical composition (P, K, C, N) have shown their dependence on the thickness of the modified mulch layer and the lignosulphonate/polymer complex's composition at the same application rate.
5. The increase in the C/N ratio for the soil covered with modified hydrolysis lignin relative to the soil covered with the unmodified one at the beginning of the experiment

indicates more favourable conditions for immobilisation of nitrogen. The remarkable decrease in C/N ratio values in one year indicates an intensive biodegradation and mineralisation of hydrolysis lignin for soil, where the solution of the polycomplex having a lower value of the composition was applied.

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