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Application of a Triple Interpolymer Complex Based on a Wood Polymer in Manufacture of Lignocellulosic Composites

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The present work shows the results of the development of an environmentally compatible hybrid binder that is a triple polymer complex formed as a result of the interaction of modified lignosulphonate and UF-oligomers in aqueous medium. The dependence of the adhesive and rheological properties of the developed binder on the composition of the modified lignosulphonate, as well as the type and content of the filler, has been shown. Using the developed binder, new environmentally sound lignocellulosic composites filled with papermaking and wood hydrolyzed processing wastes have been developed. The complex of the found properties of the composites allows recommending them as a thermo-insulating material in building engineering.

Keywords: composites, lignin-containing binder, lignocellulosic wastes.

1. INTRODUCTION

Recently, much attention has been paid to the problems of the effective utilization of biomass. As a result of the introduction of rational technologies of lignocellulosic waste application, the utilization of biomass may reach more than half a billion tons in national economies annually [1].

In the context of this problem, many efforts are made to combine wastes and by-products of wood origin with synthetic resins into composites. The primary benefit for developing such composites is a result of: decreasing the material costs by combining a more expensive material with a lower-cost one, developing products that can utilize recycled materials and be recyclable themselves, making composites with specific properties that are superior to those of the constituents, and preventing environmental pollution due to using little applied wastes.

The application of technical lignin, a cheap by-product of pulp and paper mills, for partial substitution of synthetic thermosetting resins (UF, PF) in the manufacture of building composite materials such as fibreboard, particleboard and plywood is well known [2]. However, the content of unmodified lignin in resins more than 10 – 15 wt % is limited due to a significant worsening of the properties of the composite materials and the necessity of additional power consumption for their manufacture. The chemical modification of lignin makes enables to increase the content of this by-product in the UF-resin binder without worsening the properties of the composites.

One of the promising modes of the modification of lignin is the development of interpolyelectrolyte complexes on its basis [3]. Such a type of polymer products consists of lignin and a water-soluble synthetic polymer, coupled together due to the chemical affinity and complimentariness of the polymer structures.

This work is devoted to investigating the properties of a combined binder consisting of a lignin-based interpolyelectrolyte complex and UF-oligomers, and obtaining purposeful composites from lignocellulosic wastes with the application of the developed binder.

2. EXPERIMENTAL

2.1. Materials

Technical ammonium lignosulphonate (LS), a commercial by-product of pulp and paper mills, was applied for obtaining a lignin-containing combined binder. LS was characterized by the following parameters: 45 wt % of dry matter, 4.6 wt % of ash, pH of 20 wt % solution 4.4.

Synthetic water-soluble polymers (SP) with high molecular mass and pronounced proton-accepting properties were used as a modifier of LS for forming a lignin-based interpolyelectrolyte complex (IPC).

IPC was prepared by blending concentrated water solutions of LS and SP for 30 min at 293K. The composition of IPC was designated as Z = [SP]/[LS] that varied from 0.02 to 1.00.

UF-oligomers, which were a product of polycondensation of urea, formaldehyde and polyethylenpolyamine, had a 60 wt % concentration in aqueous solution with pH 7.5. The content of free formaldehyde made up less than 1 wt %.

The combined binder was obtained by blending solutions of UF-oligomers with the modified lignosulphonate in the mass ratio of IPC/UF-oligomers 0.5 – 1.5 for 30 min at room temperature. The stoichiometric ratio between the IPC and UF-oligomers in the combined binder was calculated from the content of acidic groups in the IPC and amine groups in the UF-oligomers.

A papermaking lignocellulosic waste containing more than 50 % of short cellulose fibres with a minor addition of sawdust was granulated to aggregates with a size of 5 – 20 mm and applied as a coarse filler. Hydrolyzed lignin, a waste of the chemical processing of wood,

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represents polydispersed aggregates with the size from 0.1 to 15.0 mm. Fractionated milled sand, coal ash, cement dust, leather dust and wood flour with a particle size of less than 1 mm were used as a fine dispersed filler. The moisture content in the filler did not exceed 10 – 15 wt %.

Composites were made by blending a binder and a filler in a laboratory mixer. The specimens with a width of 35 mm, length of 155 mm and height of 35 mm were prepared by pressing of raw blends at 20 – 110 °C and a pressure of 0.11 – 0.12 MPa for 30 min. The drying process of the specimens obtained was carried out at 60 – 120 °C to a state close to an air-dry one.

2.2. Methods

The properties of the binder and the composites were determined using the following methods:

- the potentiometric titration of polymer solutions was performed using a "Radiometer" pH-meter at 293 K;
- UV-spectra of polymer solutions were determined using a UV-VIS Specord;
- IR-spectra of solid polymers were determined using a Specord IR in pellets with KBr;
- the dynamic viscosity of the binder was determined on a Hoppler rheoviscometer;
- the adhesion strength (A) of the binder was determined according to EN 301: 1992 “Klebstoffe fur tragene Holzbauteile Phenoplastic und Aminoplaste” at 293K;
- the bulk density of the composite material was determined according to the Russian State Standard GOST 17177.3-81;
- the static bending strength (R_d) at a dry state was determined according to ASTM-D790;
- the static bending strength (R_s) at a wetting state was determined after soaking for 24 h in cold water;
- the water resistance of the composite materials was characterized by the value represented as a ratio of R_s to R_d;
- the coefficient of heat conductivity was measured according to the Russian State Standard GOST 7076-78;
- the content of free formaldehyde was determined by the exsiccator method according to [4].

The number of the samples per one type of tests varied from 3 to 7. The results of the experiments were processed by the method of least squares.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Formation of the triple polymer complex

Our study has shown that lignin-based IPC and UF-oligomers interact in the aqueous solution, with the formation of a triple polymer complex, which includes all the three polymer components of the reaction system, namely, LS, SP and UF-oligomers.

Fig. 1 shows UV-spectra of the components of the system and the polymer product of their interaction in the region 230 – 400 nm. The higher intensity of the absorption band with a maximum in the region 280 nm on the UV-curves of the IPC (curve 3) and the formed product (curve 4) relative the absorption curve of the initial LS (curve 2) indicates the participation of guajacyl propane structures of lignin, containing phenolic hydroxyl groups, with the amine and methylol groups of UF-oligomers in this interpolymer interaction.

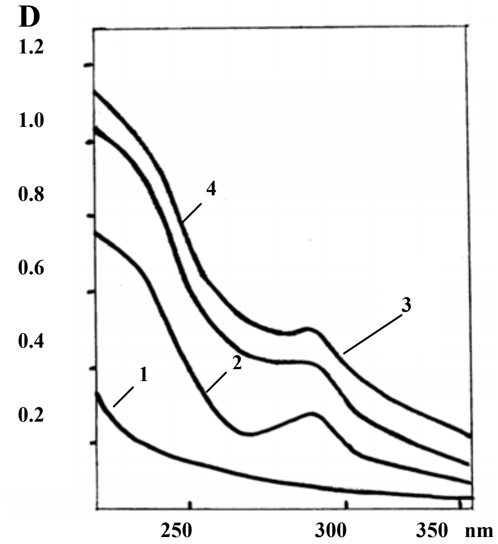

Fig. 1. UV absorption spectra of dilute polymer solutions with the concentration $1.35 \cdot 10^{-4}$ N: 1 – UF-oligomers, 2 – LS, 3 – IPC, 4 – triple polycomplex with the stoichiometric ratio of IPC to UF-oligomers; D – optical density

Such an interaction is, probably, the reason for the hypsochromic shift of the B-band in the spectrum of the triple product relative the absorption band of LS. Carbonyl groups, conjugated with phenolic groups, owing to the electron-donor function, can also participate in the formation of the polymer product with resin oligomers. This is testified by an increase in the intensity of the absorption band in the region 300 – 360 nm in the UV-spectrum of the triple product (curve 4) relative the UV-spectra of LS (curves 2) and IPC (curve 3). As can be seen from Fig. 1, the found values of the absorption maximum at 280 nm *versus* the absorption minima at 260 nm and 310 nm for the IPC (curve 3) and the triple system (curve 4), respectively, appeared to be lower than the same for the UV-spectrum of LS. According to the data [5], it means that the triple product and IPC have a higher molecular mass than the initial LS.

Fig. 2 shows IR-spectra of the triple polymer system (curve 4) and its initial components (curves 1 – 3). It is known that the absorption band in the region 3200 – 3500 cm^{-1} in the IR-spectra of polymers is the absorption band of the alcohol and phenolic hydroxyl groups included into intermolecular hydrogen bonds [5]. It can be seen that this band for the product of the interaction of IPC and UF-oligomers (curve 4) is characterized by a higher intensity, than the same absorption bands in the IR-spectra of IPC (curve 3) and the initial components (curves 1, 2), while the location of its maximum is shifted relative the maxima of the absorption bands of the initial components and IPC by 20 – 50 cm^{-1} to the low-frequency region. The observed increase in the intensity of the band, the shift of its maximum to the low-frequency region, as well as its noticeable broadening, indicate the formation of an interpolymer network of hydrogen bonds between IPC and UF-oligomers in the triple system.

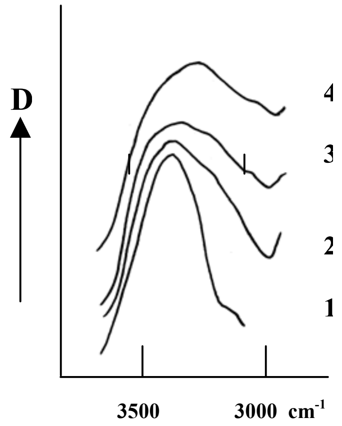

Fig. 2. IR absorption spectra of the solid polymer products: 1 – UF-oligomers, 2 – LS, 3 – IPC, 4 – triple polycomplex with the stoichiometric ratio of IPC to UF-oligomers; D – optical density

The presence of amino groups in the composition of UF-oligomers makes it possible to stabilize the formed polymer product owing to the ion-ion interactions. Fig. 3 shows the curves of the potentiometric titration of IPC (curve 1), UF-oligomers (curve 2) and the product of their interaction (curve 3). It can be seen that the interaction between IPC and UF-oligomers results in the shift of the acid-base equilibrium in the triple system. The titration curve for the reaction product is located much higher than the titration curves for UF-oligomers and IPC. This may testify the electrostatic nature of the interaction of UF-oligomers and IPC in the triple product, whose formation mechanism can be schematically represented in the following way:

$$\text{IPC–A}^- + \text{=N–UF} + \text{H}_2\text{O} \rightarrow \text{IPC–A}^-\text{H}^+\text{N≡UF} + \text{OH}^-,$$

where A^- is an acid group.

3.2. Properties of the triple polymer complex as a binder

The interaction of IPC with UF-oligomers in concentrated aqueous solutions, taken in the UPC/UF mass ratio 0.5 – 1.5, resulted in the formation of new submolecular polymer structures that were testified by the comparative investigation of the rheological properties of the initial components and the products of their interaction. According to the flow curves, taken in the wide range of shear strength values (σ = 0.1 – 1.2 Pa), the triple systems, similarly to IPC, demonstrated a pronounced non-Newtonian flow already in 30 min, while the UF-oligomers were a typical Newtonian fluid. The initial values of the efficient viscosity of the triple system depended greatly on the composition of IPC. Thus, with an increase in the composition Z from 0.02 to 0.2, the efficient viscosity of the triple system, containing IPC and UF-oligomers in the mass ratio 1 : 1, grew from $1.10 \cdot 10^2$ to $1.98 \cdot 10^6$ mPa·s^{-1}, while the viscosity of the IPC of the same values of the composition Z varied only in the range $0.93 \cdot 10^2 – 9.73 \cdot 10^3$ mPa·s^{-1}, and the viscosity of UF-oligomers did not exceed $0.35 \cdot 10^2$ mPa·s^{-1} at minor values of shear strength (σ = 0.1 – 0.2 Pa). As the interaction time increased, the structurization process in the triple system grew dramatically and resulted in the formation of a hard water-insoluble polymer product, while the initial components retained their fluidity and water-solubility during the setting. The setting time and mechanical hardness of the product formed was determined by the composition of the IPC at a constant mass ratio of the IPC to the UF-oligomers.

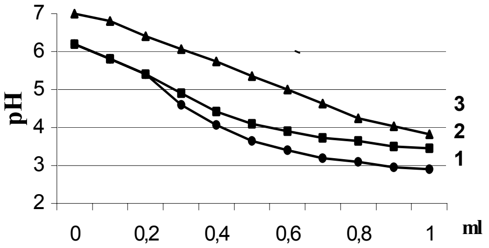

Fig. 3. Curves of potentiometric titration of dilute polymer solutions: 1 – $1.35 \cdot 10^{-3}$ N IPC, 2 – $1.35 \cdot 10^{-3}$ N UF-oligomers, 3 – $1.35 \cdot 10^{-3}$ N triple polycomplex with the stoichiometric ratio of IPC to UF-oligomers; $2.5 \cdot 10^{-2}$ N HCl

It may be assumed that the pronounced structurization in the concentrated solutions of the triple complex was governed by both the formation of a spatial fluctuation network of entanglements between the components of the system, strengthened in the sites of the mechanical contacts by their physico-chemical interaction, and the processes of the polycondensation of UF-oligomers in the presence of the IPC matrix. The manifested tendency to structurization and the presence of various reactive functional groups in the triple complex determined its adhesive function and affinity to different solid surfaces.

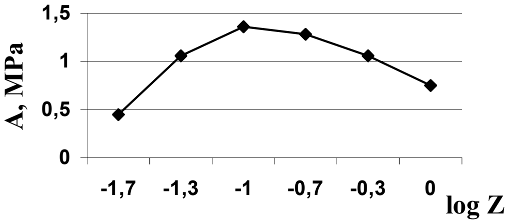

Fig. 4. Dependence of the adhesion strength of birch/birch joints glued with the triple polycomplex on the composition (Z) of IPC; mass ratio of LS to UF-oligomers in the triple polycomplex is equal to 1.5

Fig. 4 shows the dependence of the adhesion strength of a birch-birch joint glued with the triple polymer system on the composition of IPC. It can be seen that this dependence has an extreme nature. The maximum value of the adhesion strength of the compound is reached in the region of minor values of the IPC composition Z = 0.1. The further decrease in the adhesion strength with the growth in Z may be determined by the noticeable increase in the viscosity of the triple system, with the IPC composition Z > 0.1, which limits the diffusion of the binder inside the wood surface.

It is possible to improve the adhesive properties of a binder by creating optimal conditions for its structurization. One of the promising methods for development of such conditions may be the application of a fine dispersed filler in a binder composition. Moreover, the presence of the filler can promote the reduction of the formaldehyde emission and decrease the shrinkage of the composites obtained. Fig. 5 shows the dependence of the adhesion strength of the combined binder (Z = 0.1; IPC/UF = 1), containing different fine dispersed fillers, on the content of a filler. Irrespective of their nature (organic or inorganic), the inclusion of fillers implies an increase in the binder adhesion strength. According to the maximum values of adhesion strength, milled sand is the best reinforcing agent (curve 5).

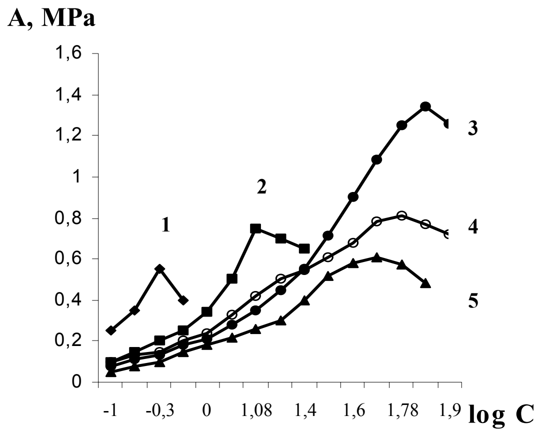

Fig. 5. Dependence of the adhesion strength of birch/birch joints glued with the triple polycomplex (Z = 0.1 and LS/UF–resin = 1.5) on the filler content and type: 1 – leather dust, 2 – wood flour, 3 – milled sand, 4 – ash, 5 – cement dust

It doubles the adhesion strength of the triple polycomplex in comparison with the polycomplex containing no filler. Cement dust, in fact, is the worst reinforcing agent (curve 3). Evidently, in this case, the lowest values of the adhesion strength of the filled binder are caused by the dust alkali value (pH > 7) that significantly inhibits the structure forming processes in the triple system. Leather dust, wood flour and coal ash, as reinforcing agents, occupy an intermediate position between sand and cement dust (curves 1, 2, 4).

It can be seen from Fig. 5 that the maximum value of adhesion strength is reached by the addition of wood flour to the binder in amounts of 4, 5 and 6 times lower than in the case of cement dust, coal ash and milled sand, respectively. It is obvious that the high specific surface of a lignocellulosic material such as wood flour as well as a considerable number of reactive hydroxyl and carbonyl groups on its particle surface causes a sufficient intensification of the structure formation process in the binder. The surface functional groups are capable of forming a multitude of hydrogen bonds with binder macromolecules at the interface. As a result of such an interaction, the adhesion strength of the binder is remarkably increased. However, after reaching the crucial concentration of wood flour in the binder (which is up to 12 mass %), it falls noticeably owing to the thinning of the binder interlayer between the filler particles. It is supposed that the increase in the speed of the structure forming processes in the binder can be promoted also by the high hygroscopicity of the lignocellulosic filler. For the non-reactive fillers such as milled sand and coal ash, the values of the crucial concentration are much higher and vary from 60 to 70 mass %.

Since the spatial structure of the triple polycomplex is formed by two non-covalently bonded network polymers (lignin and UF-resin are network polymers), and taking into account the peculiarities of its rheological and adhesion behaviour, the triple polycomplex formed may be classified as a hybrid binder, i.e. the type of the interpenetrating polymer network (IPN).

3.3. Lignocellulosic composites obtained with the triple polycomplex

The new representatives of building composites have been developed applying the lignin-containing triple polymer complex and lignocellulosic wastes. Table 1 shows the compositions of the raw material mixtures of the composites, in which granules are used, made from a papermaking waste containing waste short cellulose fibres mixed with a low addition of sawdust as well as hydrolyzed lignin and their mixture taken in the mass ratio 1 : 1. It should be noted that the significance of hydrolysis lignin as an industrial raw material tends to increase owing to the growth in the bioethanol production in the world's practice [6]. For comparison of the properties of the binders, a triple polymer complex with the IPC Z = 0.1 and a polymer mixture consisting of unmodified LS and UF-oligomers was used. The content of the lignin-containing component in the tested binders made up 50 wt %.

The different mechanisms of the structurization of the binders, i.e. the polymer mixture and the triple polymer complex caused the distinctions in the technological conditions of obtaining lignocellulosic composites. The obtaining of composites using the polymer mixture required high temperatures of moulding and drying (110 – 120 °C), as well as the presence of a low-molecular hardener. The application of the triple polymer complex made it possible to decrease the moulding and drying temperature to 20 °C and 60 °C, respectively, and to discard the hardener.

Table 2 shows that, at the same degree of filling, the composites, irrespective of the type of the binder, have relatively equal bulk density, but differ considerably in terms of their properties. Thus, the bending strength values and water resistance of the lignocellulosic composites obtained using the triple polymer complex exceed the same parameters of the composites obtained by binding the filler with a polymer mixture 3.0 – 3.5 and 1.7 – 2.5 times, respectively. According to Table 2, the composites containing a mixture of cellulose granules and hydrolysis lignin as a filler, as in the case of both the triple polymer complex and the polymer mixture, are characterized by better strength and water resistance properties. The high polydispersity, high specific surface and high acidity of the mixed filler (pH of the hydrolysis lignin aqueous extract

Table 1. Compositions of new materials

Components	Composition number / filler content, wt %					
	1	2	3	4	5	6
LS + UF + low-molecular acid	79	80	79	–	–	–
Triple polycomplex	–	–	–	67	80	79
Hydrolysis lignin	–	20	–	–	20	–
Cellulose granules	21	–	–	33	–	–
Lignin + granules	–	–	21	–	–	21

Table 2. Physico-mechanical properties of the composites

Properties	Composition number					
	1	2	3	4	5	6
Density, kg m^{-3}	482	640	558	479	613	540
Bending strength at dried state (R_d), MPa	0.38	0.32	0.40	1.29	0.96	1.42
Bending strength at soaked state (R_s), MPa	0.15	0.12	0.16	0.98	0.60	1,12
Water resistance, $R_s / R_d \cdot 100$	39	37	40	76	63	79
Heat conductivity coefficient, W/mK	0.095	0.113	0.105	0.085	0.108	0.097

was < 3) may be supposed to have a synergistic effect in improving the structurization conditions of the lignin-containing binders and their interaction with the interface.

The test determining the concentration of free formaldehyde [4] has shown that the new composites obtained using the triple polymer complex have a very low formaldehyde emission, close to zero both during their obtaining and maintenance.

The moderate values of bulk density, sufficient mechanical strength and water resistance, as well as the low values of the thermal conductivity coefficient, make it possible to recommend the obtained composites consisted of the triple polymer complex and lignocellulosic wastes for thermal insulation of walls, floorings, attic spans, etc. in living spaces and production areas.

4. CONCLUSIONS

1. The formation of a new polymer binder by mixing concentrated aqueous solutions of the modified lignosulphonate and UF-oiligomers under the certain conditions has been found. The obtained binder is a triple polymer complex and can be classified as a hybrid binder.
2. The dependence of the adhesion and rheological properties of the triple polycomplex on the composition of the modified lignosulphonate has been shown.
3. It has been found that the application of fine fillers implies an increase in the adhesion strength of the new binder. The optimum content of the filler in the binder is determined by both the nature of the filler surface and its pH.
4. The values of the bending strength and water stability of the lignocellulosic composites obtained using the triple polymer complex containing 50 wt % of modified lignosulphonate exceed 3.0 – 3.5 and 1.7 – 2.5 times, respectively, the same parameters for the composites obtained by way of binding the filler with the polymer mixture, containing unmodified lignosulphonate.
5. Using the developed binder, the new environmentally sound lignocellulosic composites filled with papermaking and wood hydrolyzed processing wastes have been developed. The complex of the found properties of the composites allows recommending them as a thermo-insulating material in building engineering.

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