Transformations of Wood Structure under Mechanochemical Treatment

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Abstract

The structure transformations of the wood under mechanochemical treatment in vibratory centrifugal, planetary, and ball mills are investigated by means of electron microscopy, X-ray diffraction, thermomechanical spectroscopy. Specific surface of the samples is estimated. Features of the changes in wood properties under grinding in these types of mills are established. Under wood treatment in vibratory centrifugal and planetary mills, no complete amorphization of the structure of wood matrix occurs; quite contrary, some ordering is observed.

INTRODUCTION

Search for the rational ecologically safe processing means of plant raw material is very urgent because resources of nonrenewable natural resources exhaust. In our opinion, the required methods should involve solvent-free procedures taking minimal time; mechanochemical activation meets these requirements.

The data on chemical transformations of polymer macromolecules under mechanical action had been obtained for the first time by Staudinger who subjected polystyrene, cotton, wood to grinding in ball mills [1]. An increase in the accessibility of wood components for chemical modifying after fine grinding was reported by the authors of [2].

The application of one or another kind of mechanochemical treatment is determined by a kind of polymer. For instance, highly elastic polymers undergo intensive destruction during forge-rolling while vitreous polymers do so under grinding [3]. As a rule, preliminary treatment of plant raw material in dispersing devices described in the above-mentioned works takes much time.

Taking into account the above considerations, and starting from the fact that the plant and especially lignified tissue is a rigid-chain cellulose reinforcement immersed into an amorphous lignocarbohydrate matrix which is in vitreous state, we were the first to apply the mills designed and manufactured at the Institute of Solid State Chemistry and Mechanochemistry, SB RAS, to perform preliminary mechanochemical treatment of the plant material before chemical modification, and directly for solid-phase syntheses. These mills are distinguished by high energy strain (up to 60 *g*) and intensity of the load input into the system, and corresponding possibility to decrease the time of treatment.

Features of structural and chemical transformations of metals, minerals and other substances under treatment in these mills have been thoroughly investigated [4]; one cannot say the same about plant materials and especially wood.

The goal of the present investigation is to study some structural transformations which occur in wood under mechanical treatment in vibratory centrifugal (VCM), planetary (PM), ball (BM) and ball rotary (BRM) mills.

EXPERIMENTAL

Mechanochemical treatment of sawdust of air-dry aspen wood was performed in the mills of above-indicated types. The volume of the ceramic drum of VM-type ball mill was 1800 ml; steel balls 20 mm in diameter were used as milling tools (MT); ball mass was 2.4 kg; total mass of the material loaded into the mill was 50 g.

A VTsM-10type vibratory centrifugal mill was adjusted to the periodic action mode; efficient volume of the milling chamber was 800 ml; milling tools were either balls 10 or 5 mm in diameter (their total mass was 1.1 kg) or a steel cylinder 30 mm in diameter (with a mass of 1.1 kg). Efficient load of the material under treatment was 40 g.

The drum volume of the AGO-2 planetary mill was 30 ml; the load of balls 5 mm in diameter was 75 g; the load of material was 2 g.

A rotor was introduced into the foundation of the ball rotary mill 250 ml in volume. Mechanical treatment of the material was performed due to collisions with metal balls with a mass of 5.5 g each, accelerated by the rotor with the rotation frequency of 2000 rpm. The number of balls was 12; the fraction of total filling of the milling chamber was 0.2; the material under treatment accounted for 4.5 % of this volume.

The design and performance parameters of the vibratory centrifugal mill were described in [5], planetary mill in [4], ball mill in [6] and ball rotary mill in [7].

The molecular-topological structure of the initial and modified wood was examined according to the procedure described in [8]. Ther-momechanical curves were recorded with UIP-70M instrument by means of penetration of the quartz semi-spherical probe (4 mm in diameter) into the sample cooled to the temperature of $20-30$ °C below the vitrifying point under the load of 200 mg, thus providing dilatometry mode. The temperature scanning rate was 2.5 °C/min.

Molecular mass of the fraction in the region of transition from vitrifying to flowing or from melting to flowing was calculated using equations [8–15].

The X-ray diffraction patterns were recorded with the DRON-2 X-ray diffractometer within the 2θ region from 3 to 60°. The plate for measurements was prepared by pressing the powder sample at the pressure of 100 kg/cm^2. A tube with CuK_α radiation and nickel filter were used (voltage: 40 kV, current: 10 A, slit width: $1-0.5-0.5$). The procedure allowed measuring diffraction angle with an accuracy of 6′.

The crystallinity degree was calculated in per cent as a ratio of the area of crystalline peaks to the total area beneath the scattering curve within the angle range $4-60$° in the diffraction pattern.

The structure of the surface of the initial and modified wood was investigated with Tesla BS-242E scanning microscope.

Specific surface was determined using the comparative method based on thermal desorption of argon [16, 17] by comparing the area of desorption peaks for the materials with known and unknown specific surface. Relative error of a single determination did not exceed 4 %.

RESULTS AND DISCUSSION

In order to perform efficient chemical processing of wood, it is necessary to change the system of submicroscopic capillaries, to increase specific surface, to achieve microlayering and to change phase state of the matrix; destruction of the lignocarbohydrate net and globular network of lignin is also necessary. These factors provide an access of reagents to the functional groups of the components of the matrix (lignin, hemicellulose) and cellulose microfibrils.

The disposition of reinforcing or plasticizing components in wood macrostructure is of importance for wood grinding. Lignin reinforces the morphological structure of wood and thus hinders grinding and separation into fibres; glucomannan simplifies garneting and decelerates mechanical destruction of cellulose due to intrafibrillar plasticizing; xylan acts as a plasticizer being amassed on the fibril surface. In the case of the structure with the net of cross links (in the case under consideration, this is lignocarbohydrate matrix into which cellulose fibrils are immersed), grinding products lose their fibrous structure at the early stages of grinding.

When wood sawdust (the 0.4−0.75 mm fraction) is treated in a mill of any type: BRM, VCM, PM, BM − the ground products are fine powders. The loss of fibrous structure occurs within different grinding time in different kinds of mills. The fibrous structure is most slowly destroyed during grinding in BM, then come BRM and VCM. In PM, the fibrous structure is destroyed most rapidly. For the grinding of cotton linters and cellulose under the same conditions as those for wood, partial grinding and conservation of the fibrous structure of samples were observed.

In traditional mills under mechanical action for a long time (several hours), cellulose preparations lose their fibrous structure and turn into fine powder [18]. The particle size of cellulose and changes in its other properties depend mainly on the character [19] and intensity of mechanical action [20]. Particle diameter reaches several micrometers.

We estimated the size of particles obtained after treatment of aspen wood sawdust in VCM with balls of 10 or 5 mm in diameter as milling bodies. It was established that under all grinding modes the particle size changes within the range 2.9−15.9 μm. With an increase in treatment time from 20 to 60 min (with the balls of 10 mm in diameter), the mass ratio of larger to smaller particles changes. For example, after activation for 20 min, mass fraction of particles with a size up to 2.9 μm was 11.5 %; after 60 min, it was 15.5 %. With an increase in the duration of grinding, particle size gets leveled within the range 2.9−15.9 μm.

The structure of wood particles after mechanical treatment in the planetary mill for 30 s was estimated according to the electron microscopic data (Fig. 1). With a 74-fold magnification, one can see that the wood mass still contains intact fibres and bundles (see Fig. 1, a). A 510-fold magnification allows determining their fibrillar structure (see Fig. 1, b). In Fig. 1, c, d one can clearly see damage of separate fibres such as cracks; the outer layer of the secondary shell of the fibrous cell S_1 is almost completely taken off [21]; a small amount of the particles of fine fraction is present. With an increase in grinding time to 2 min, uniform grinding of the wood occurs; fibrous structure is completely destroyed.

Grinding in VCM with balls as MT for 15 min occurs non-uniformly: fragments of separate fibres and a substantial number of fine particles can be observed. Grinding proceeds along fibres; fragments of the fibrous structure still can be seen. The residual fibres are strongly destroyed thus some layers are taken off and as the scales are covering their surface.

One of the most important consequences of grinding for chemical processing of wood is an increase in its specific surface [22].

Specific surface characterizes the quantity of submicroscopic capillaries and pores between the layers of wood components, as well as changes in pore size and their quantity during mechanical treatment. Specific surface and crystallinity degree (CD) were determined for wood samples ground in AGO-2, BM and VCM (with balls or cylinders as milling bodies). Crystallinity degree was estimated using the X-ray diffraction data and the results of thermomechanical spectroscopic investigation (Table 1).

Maximal specific surface develops during the treatment of samples in BM for 315 min. For the treatment of aspen wood sawdust in PM and VCM with balls as MT, close S_{sp} values are achieved; however, time of mechanical treatment of samples differs substantially. The smallest increase in specific surface is observed for the sample ground in VCM with cylinder as MT. So, the shape of MT affects the formation of specific surface and porous structure of wood during grinding.
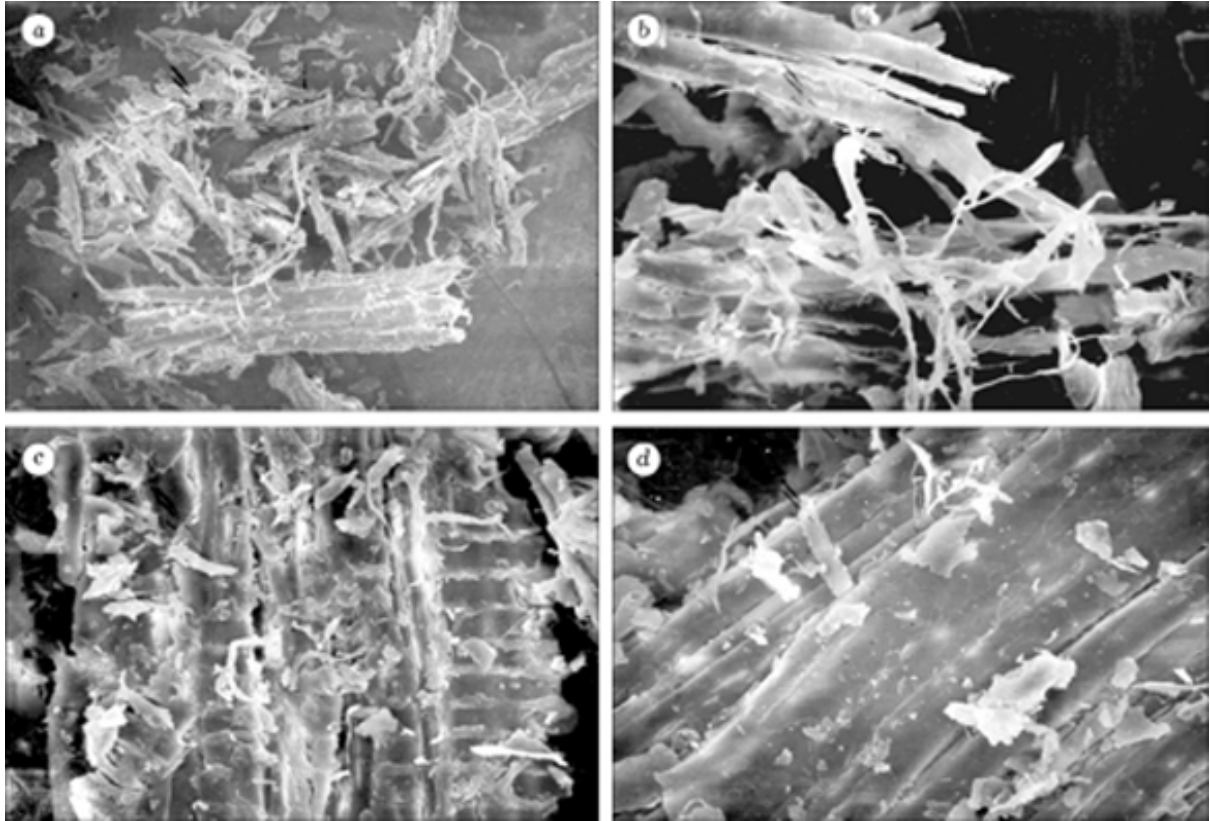
Fig. 1. Aspen wood ground in planetary mill for 30 s. Magnification: 74 (*a*), 510 (*b, c*), and 740 (*d*).

Intensive mechanical action on polymers, able to cause destruction of macromolecular chains, leads to mutual displacement of separate structural elements. Displacement of structural elements of polymeric chains is first of all accompanied by distortion of initial packing of the chains and loss of ordering [23]. Under vibratory grinding of different preparations of cotton and wood cellulose, as well as hydrate cellulose fibers, identical X-ray diffraction patterns characteristic of the amorphous product are obtained. In addition,

TABLE 1

Effect of mechanical treatment on wood properties

Mill	τ, min	S_{sp}, m^2/g	Crystallinity degree, %
Ball	315	3.0	–
Planetary	2	2.2	100
VCM (balls)	15	2.5	100
VCM (cylinders)	15	1.1	63
Initial wood	0	0.6	81

heat capacity of ground cellulose decreases [24–26].

The X-ray phase analysis of aspen wood structure after treatment in BRM and VCM helped us obtaining unexpected results differing from those obtained for cellulose.

The X-ray diffraction pattern of the initial aspen wood sample is similar to the pattern of wood cellulose. It contains three crystal maxima (reflections 002, 101, 10$\bar{1}$ with angles 2θ = 21, 18.5 and 17.5°). The amorphous halo has a maximum at 2θ = 19°. The X-Ray diffraction pattern of aspen wood samples grounded in BRM is similar to that obtained in the VCM with cyliner but the angles of reflection scattering are shifted to larger angles 2θ = 18 and 26°, the maximum of scattering at 2θ = 17.5° is absent; amorphous halo has a maximum at 2θ = 22°. The X-ray diffraction pattern of wood sample grounded for 15 min in VCM but with balls as milling tools, are substantially different from the patterns of the initial wood and two former samples. For instance, there are four crystal maxima with angles 2θ = 7, 24,

TABLE

Characterization of the structure of ground aspen wood

Sample	Characterization
Initial in the form of sawdust subjected to pressing	Amorphous-crystalline polymer with the amorphous to crystal fraction ratio 0.19 : 0.81
Ground in planetary mill	Crystal polymer containing crystal structures of 2 types with $T'_{melt} = 54$ °C and $T''_{melt} = 198$ °C
Ground with vibratory centrifugal mill with balls	Amorphous-crystalline polymer (fraction ratio 0.18 : 0.82) containing crystal structures of two types with $T'_{melt} = 37$ °C and $T''_{melt} = 197$ °C
Ground with vibratory centrifugal mill with cylinders	Amorphous-crystalline polymer with the amorphous to crystalline fraction ratio 0.37 : 0.63

Note. Sample preparation was identical in all cases.

37, 53° on the diffraction curve within the scattering angle range 4−60°. The first two maxima are similar with those in the diffraction pattern of cellulose but are more diffuse and have lower intensity. The presence of narrow intensive reflections at $2\theta = 37$ and 53° is the evidence of the formation of a new crystal structure during wood grinding in VCM with balls as MT. Thus, the formation of a new crystal structure takes place along with the development of specific surface of a sample.

When investigating heterogeneous destruction of wood polysaccharides under mechanical treatment of the samples wetted with sulphuric acid one can stress that complete amorphization of the samples does not take place; recrystallization of the amorphous phase is observed during grinding [19]. Grinding in VCM with balls is accompanied by the rise of process temperature to 80−90 °C. This is likely to promote recrystallization of lignocarbohydrate matrix, which was amorphized during the initial stages of grinding, after the sample is cooled in the air.

Loosening and change in the initial packing of polymer macromolecules help increasing their reactivity [27]. This regularity is conserved also for etherification of wood subjected preliminarily to grinding in the presence of catalysts [28, 29].

Wood grinding leads to a substantial change in its molecular topological structure. The relations between crystalline and amorphous fractions in the initial and ground wood and melting points of crystal modifications formed after grinding were investigated by the thermo-mechanical spectroscopy (Table 2). Grinding in VCM with balls as milling tools and in PM is accompanied by the appearance of new crystal modifications in the structure of wood matrix. This occurs because of high mobility of the destruction fragments with small molecular mass. The breakage of H-bonds between OH groups of the adjacent polysaccharide molecules and the formation of new ones lead to various crystal modifications.

The statement that displacement of structural elements of polymer chains should first of all cause destruction of the initial packing of chains is quite evident but the loss of ordering during this process [30] is ambiguous. This is evidenced by the characteristics of molecular topological structure of wood samples after mechanochemical treatment, as obtained by us.

Molecular topological structure of wood undergoes substantial changes depending on grinding time. Thermomechanical curve of aspen wood treated in VCM for 20 min with balls as milling tools is shown in Fig. 2. This structure is amorphous-crystalline monoblock for each type. In the investigated sample at the temperature about 140 °C at the stage of molecular flow the thermal destruction starts; the branching or even cross-linking which suspends flowing appears. The flowing resumes again at the temperature of 224 °C.

Segmental relaxation of the chains of amorphous block starts at $T_s = 0$ °C.

Expansion of the amorphous fraction of the polymer in vitreous and highly elastic states
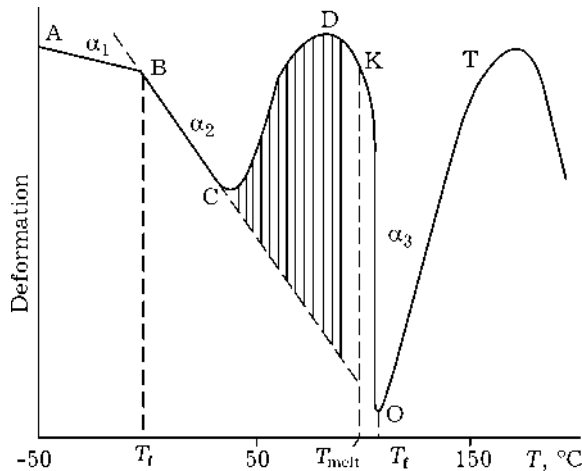
Fig. 2. Thermomechanical curve of the aspen wood sample ground in vibratory centrifugal mill for 20 min.

occurs at the rate equal to $\alpha_1 = 4.20\ 10^{-5}\ \mathrm{deg}^{-1}$ and $\alpha_2 = 12.50\ 10^{-5}\ \mathrm{deg}^{-1}$, respectively, which is preconditioned by the geometric free volume $V_\mathrm{f} = 0.068$. This value is typical for tightly packed structure approaching crystal state.

The crystallized fragments of polymer macromolecules start melting at 61 °C and pass into molecular flow state at $T_\mathrm{f} = 81$ °C. The mass ratio between crystalline and amorphous fractions is 0.83 : 0.17. The functions of molecular mass distribution (MMD) of chains in both fractions are shown in Fig. 3. The averaged molecular characteristics of chains in crystal and amorphous blocks are correspondingly equal to

$$M'_{cn} = 3.85 \cdot 10^3,\ M_{cn} = 2.24 \cdot 10^3;$$

$$M'_{cw} = 16.3 \cdot 10^3,\ M_{cw} = 2.92 \cdot 10^3;$$

$$K' = 4.2,\ K = 1.3.$$

Wood sample ground under the same conditions but for 10 min has also amorphous-
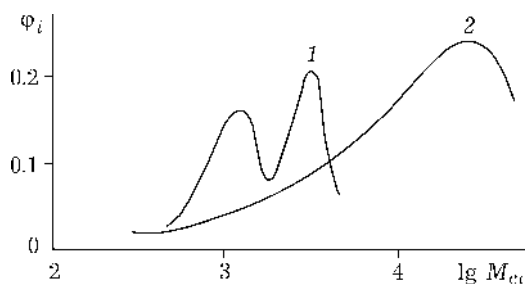
crystalline structure with two crystal modifications; their melting points are $T'_\mathrm{melt} = 37$ °C and $T''_\mathrm{melt} = 197$ °C. Molecular flow starts at $T_\mathrm{f} = 233$ °C. Low-melting crystal modification has molecular mass about $723.0\ 10^3$ ($\Delta T = 39$ °C), while high-meling one has $716\ 10^3$ ($\Delta T = 36$ °C).

Segmental relaxation of the chains of amorphous block starts at $T_\mathrm{s} = -43$ °C. Thermal expansion rate in vitreous and highly elastic states is $\alpha_1 = 3.64\ 10^{-5}\ \mathrm{deg}^{-1}$ and $\alpha_2 = 22.64\ 10^{-5}\ \mathrm{deg}^{-1}$, respectively. Free geometric volume is equal to 0.131, which is characteristic of rigid-chain polymer with hindered orientation of macromolecules.

Mass content of high- and low-melting crystal modifications and amorphous block form the ratio of 0.25 : 0.57 : 0.18. Molecular characteristics of internodal chains in the pseudo-net of the amorphous block are follows: $M_{cn} = 13.55\ 10^3$, $M_{cw} = 18.93\ 10^3$ and $K = 1.40$. The MMD function is unimodal and symmetrical (Fig. 4).

Thermomechanical curve of the wood sample ground in planetary mill is shown in Fig. 5. It is characteristic of a crystal polymer, which is evidenced by the obtained ratio of the rate of expansion deformation accumulation in the crystallized (α_1) and highly elastic states (α_2). In this case, $\alpha_2/\alpha_1 > 10$. The unfreezing state of the amorphous polymer and melting of the crystal one can equally be related to the high-elastic state. For example, the rate of linear thermal expansion of this sample ($\alpha_1 = 5.95\ 10^{-5}\ \mathrm{deg}^{-1}$) is of the same order of magnitude as the similar parameter in the amorphous block of the initial aspen wood.

At the temperature of 49 °C, intensive accumulation of expansion deformation starts; it proceeds at the rate of $\alpha_2 = 80\ 10^{-5}\ \mathrm{deg}^{-1}$; this

Fig. 3. MMD function for chains in low- (*1*) and high-temperature (*2*) amorphous block of aspen wood sample ground in vibratory centrifugal mill for 20 min.
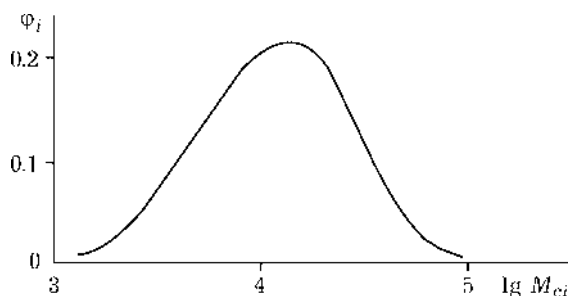

Fig. 4. MMD function for chains of the amorphous block of aspen wood sample ground in VCM for 10 min.
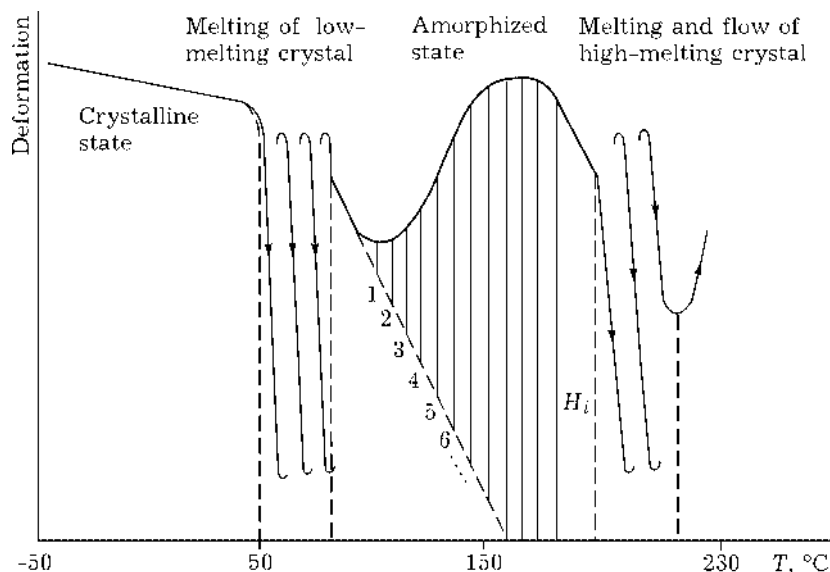
Fig. 5. Thermomechanical curve of the aspen wood sample ground in planetary mill for 2 min.

is melting of polymeric crystals. This process is completed at the temperature of 85 °C by amorphization of the melted polymer followed by (at temperature rise) transition into the high-elastic deformation state, which is typical for this fraction, and exit into the plateau of high elasticity.

Similar to the initial wood [31], amorphized polymeric fraction has a pseudo-net structure; nodes of this net are crystal fragments with higher melting point (198 °C). Above this point, we again observe an increase in the rate of expansion deformation accumulation rate; this is melting of polymeric crystals, which is completed at the temperature of 240 °C by passing into the molecular flow mode.

Molecular mass characteristics of the fragments of macromolecules in both crystal blocks are correspondingly equal to:

$$M'_{cn} = 2.14 \ 10^5, \ M'_{cw} = 3.0 \ 10^5 \ \text{и} \ K' = 1.40;$$

$$M''_{cn} = 1.1 \ 10^6, \ M''_{cw} = 1.4 \ 10^6 \ \text{и} \ K'' = 1.27.$$

The mass ratio of blocks is 0.64 : 0.36.

If we compare molecular topological structure of the aspen wood polymeric matrix after grinding in the mills involved with the corresponding parameters of its structure after treatment till sawdust, the following conclusions can be made. Both types of grinding change the structure of natural aspen wood from completely amorphous pseudo-net structure to amorphous-crystalline under soft grinding till sawdust and to almost fully crystal state under treatment in planetary mill. After wood grinding by both methods, crystal formations of two types with different energy of inter-chain interaction and density of packing are discovered in the polymeric matrix. In the case of grinding in planetary mill, total degree of the crystallinity of matrix increases, mass ratio between crystal structures and molecular parameters of the fragments of chains comprising them changes.

CONCLUSIONS

The experimental data, obtained by us for the first time, on structural transformations of wood subjected to mechanical treatment in energy-strain mills make a definite contribution into the development of fundamental and applied research in the area of chemistry of wood and in the area of mechanochemical treatment of natural plant high-molecular compounds.

Electron microscopic investigation of the structure of wood ground in vibratory centrifugal, planetary, ball mills showed that the loss of fibrous structure occurs in samples within a very short time. Treatment of wood in the mills of these types is accompanied by an in-

crease in specific surface. So, changes in the structure of wood during grinding obey some general laws which were previously revealed in the studies of grinding of synthetic high-molecular compounds and other natural polymers [32].

Thermomechanical spectroscopy, used to estimate changes in wood structure, allowed us to reveal some features that have not been described earlier, because they take place as a result of the unique action of the treatment of plant tissue in the indicated types of mills.

It is stated by means of X-ray diffraction and thermomechanical spectroscopy that grinding for a short time (2−60 min for mills of different types) is accompanied by a decrease in the molecular mass of high-molecular composition and some ordering of the structure of wood matrix, which leads to an increase in the crystallinity of samples. The largest ordering and formation of new crystal phase is observed for wood sample ground in planetary mill.

The data on transformations of the molecular topological structure of wood during mechanochemical treatment, obtained by us for the first time, can be used for choosing the conditions of pretreatment and methods of synthesis of chemically modified wood with the required properties. The application of mills designed at the Institute of Solid State Chemistry and Mechanochemistry, SB RAS, for these purposes has a series of advantages, which allows us to recommend these mills for wide application.

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