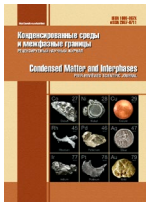


ISSN 1606-867X (Print)
ISSN 2687-0711 (Online)
Condensed Matter and Interphases
Kondensirovannye Sredy i Mezhfaznye Granitsy
https://journals.vsu.ru/kcmf/

Original articles

Research article
https://doi.org/10.17308/kcmf.2025.27/12490

The role of nanofillers of various nature in the morphological changes of the polymer binder for plywood production

E. V. Yushchenko[1]✉, L. I. Belchinskaya[1], A. V. Kostyuchenko[2], D. A. Zhukalin[3]

[1]Voronezh State University of Forestry and Technologies named after G. F. Morozov, 8 ul. Timiryazeva, Voronezh 394087, Russian Federation

[2]Voronezh State Technical University, 84 ul. 20 let Oktyabrya, Voronezh 394006, Russian Federation

[3]Voronezh State University, 1 Universitetskaya pl., Voronezh 394018, Russian Federation

Abstract

Nanomodification of the adhesive composition is one of the promising methods for improving the quality of wood laminated materials. Morphological changes in nanostructures make it possible to control the functional characteristics of the resulting nanocomposites. The shape and distribution of nanomodifiers of nanocellulose and multi-walled carbon nanotubes of urea-formaldehyde resin used to produce plywood have been studied by atomic force microscopy. The phase composition and crystal structure of biological and carbon nanofillers of the binder are investigated. Data on the qualitative and quantitative composition, structural state of nanocrystalline cellulose and multi-walled carbon nanotubes, as well as cured resin in pure and modified form, were obtained by X-ray diffractometry. The microrelief of the surface of the cured binder in the presence of multi–walled carbon nanotubes is characterized by uniformly distributed nanoclusions of 50 nm – 1 μm; and nanoclusions of 70 nm - 2 μm in the case of resin modification with nanocrystalline cellulose. Unmodified urea-formaldehyde resin is characterized by a low degree of crystallinity: the crystallite size is 10 nm. When modifying the resin with multi–walled carbon nanotubes, the crystal size increases to 18 nm, and when modified with nanocrystalline cellulose - up to 15 nm. The most probable type of lattice of the resin under study is a primitive cubic one with a parameter a = 0.840 nm. An increase in the volume of the unit cell of resin modified with multi-walled carbon nanotubes (a = 0.844 nm) and nanocrystalline cellulose (a = 0.842 nm) is observed. An increase in the size of the crystalline regions in the resin, as well as an increase in the volume of the resin unit cell as a result of the use of nanomodifiers, can help improve the performance of plywood.

Keywords: Crystal lattice, Urea-formaldehyde resin, Multi-walled carbon nanotubes, Nanocrystalline cellulose, Modification

Acknowledgments: Authors thank the reviewers for their contribution to the peer review.

For citation: Yushchenko E. V., Belchinskaya L. I., Kostyuchenko A. V., Zhukalin D. A. The role of nanofillers of various nature in the morphological changes of the polymer binder for plywood production. *Condensed Matter and Interphases*. 2025;27(1): 139–145. https://doi.org/10.17308/kcmf.2025.27/12719

Для цитирования: Ющенко Е. В., Бельчинская Л. И., Костюченко А. В., Жукалин Д. А. Роль нанонаполнителей различной природы в морфологических изменениях полимерного связующего для производства фанеры. *Конденсированные среды и межфазные границы*. 2025;27(1): 139–145. https://doi.org/10.17308/kcmf.2025.27/12719

✉ Ekaterina V. Yushchenko, e-mail: katerina.vgltu@yandex.ru

1. Introduction

Russia is one of the leaders among plywood producing and exporting countries [1]. The need for plywood production is due to its wide range of applications in various fields of production [2]. A relevant direction in plywood production is the use of nanotechnology to improve the quality of laminated materials [3, 4]. Unlike other thermosetting resins, urea-formaldehyde resin has a crystalline structure, which makes it possible to strengthen the structure of the polymer matrix and improve its mechanical characteristics [5]. The crystalline regions are favorable for the hydrolytic stability of plywood [6]. Urea-formaldehyde (UF) resin nanomodification is able to influence the size and dispersion of crystalline regions in the resin and comprehensively improve the performance characteristics of the material [5]. It is known that the composition of CF resin affects the degree of crystallinity and crystal morphology in the binder structure [6]. The crystallinity of the resin is preserved during the curing of the CFS in contact with the wood veneer, but the order of the crystal lattice is disrupted [7]. Bio- and carbon nanomodifiers of carbamide-formaldehyde binder for plywood production were selected for the study: nanocellulose and multi-walled carbon nanotubes. Morphological changes of nanostructures allow controlling their functional characteristics.

Thus, the purpose of this work is to analyze by atomic-force microscopy (AFM) and X-ray diffractometry (XRD) the morphology of the nanostructure of urea-formaldehyde (UF) resin when nanocellulose (NCC) and multi-walled carbon nanotubes (MWCN) are introduced into it.

2. Objects and methods

The object of the study is a binder based on KF-Zh-F grade UF resin, modified with multi-walled carbon nanotubes and nanocrystalline cellulose.

For the experiment, carbamide-formaldehyde resin of the KF-Zh-F brand (Uralximplast PJSC, N. Tagil, Russia) was used as a polymer matrix. The nanofillers were MWCN with an average diameter of 9.5 nm and a length of 1.5 μm (Nanocyl Technology, Sambreville, Belgium) and NCC with an average particle size (width x length): 10–20 × 300–900 nm (Nanografi Nano Technology, Ankara, Turkey). The active substrate was peeled birch veneer (*Betula pendula* L.), produced by GalichLes LLC (Galich, Russia), and the passive substrate was glass. Ammonium chloride was used as a resin hardener (Komponent-Reagent LLC, Moscow, Russia).

A suspension of MWCN in an aqueous solution of lauryl sulfate, a surfactant, was obtained by ultrasonic dispersion under constant cooling for 30 minutes on an ultrasonic dispersant UZD-0.1/22 with a power of 100 W and a frequency of 22 kHz. The concentration of the dispersed phase in the suspension was 4.5%.

To obtain the UF resin/MWCN adhesive composition, the components were mechanically mixed for 10 minutes with the addition of MWCN at a concentration of 1.25 wt. %. Ultrasonic dispersion of the adhesive composition in the resin–filler system was carried out under constant cooling for 3 minutes on an ultrasonic dispersant UZK-1.3 with a power of 80 W and a frequency of 24 kHz. Cooling was carried out in a water bath to a temperature of 20 °C in order to avoid polymerization of the adhesive composition. The hardener was added in an amount of 1 wt. %. The adhesive composition of UF resin /NCC was obtained similarly by adding NCC with a concentration of 2 wt. %.

Then the samples of the modified and unmodified resin were cured in a drying cabinet chamber on an inert glass substrate and an active veneer substrate at a temperature of 115 °C, after which they were kept for 24 hours at room temperature and humidity of 65 ± 5% to complete the polymerization process.

The shape and distribution of nanofillers in the resin were studied using an NT-MDT scanning probe microscope in topology and phase contrast modes. Images of the surface of an unmodified binder cured on an active substrate (veneer), as well as a binder modified with MWCN or NCC, were obtained.

The phase composition and crystal structure of the initial MWCN and NCC powders were studied by electron diffraction in the "lumen" mode on an E'G-100M electronograph. Sample preparation was carried out by ultrasonic dispersion of the test material in surfactants, followed by application to a mesh and drying at a temperature of 20 °C until complete drying.

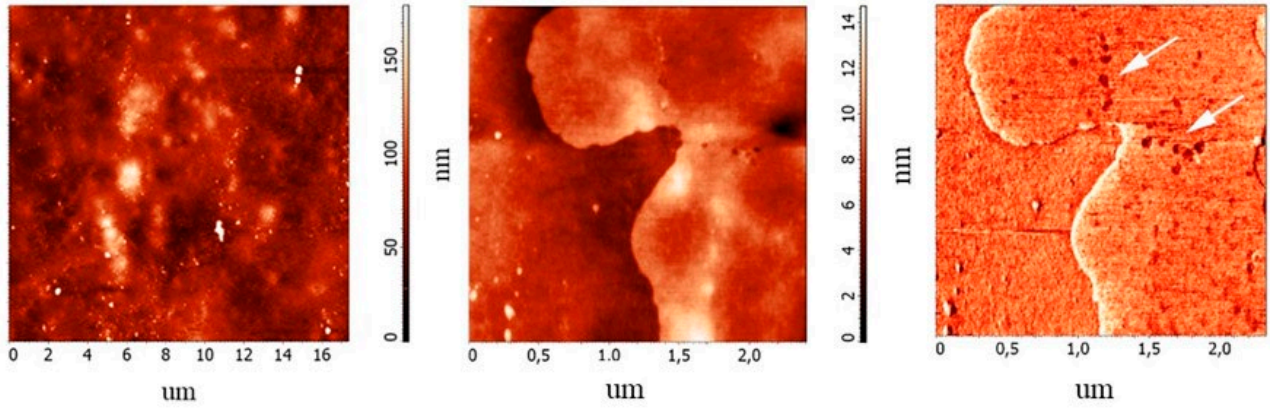
The phase (qualitative and quantitative) composition and structural state of the nanofillers and the cured resin in its pure and modified form were determined by X-ray diffractometry using a Burken D2-Phaser X-ray diffractometer (Germany). X-ray images of the samples were obtained using CuKa radiation (λ =1.5406 Å) in the angle range 2θ from 7 to 70°. During the survey, the samples were placed on a silicon wafer with a "zero" background. To determine the lattice parameters of the crystalline phases and estimate the average size of the crystallites, the profiles of X-ray diffractograms were analyzed using the Rietveld method in the HighScore Plus program.

3. Results and discussions

Atomic-force microscopy in the topology and phase contrast modes has been used to obtain images of the surface of a binder cured on an active substrate (veneer), modified with MWCN (Fig. 1) or NCC (Fig. 2).

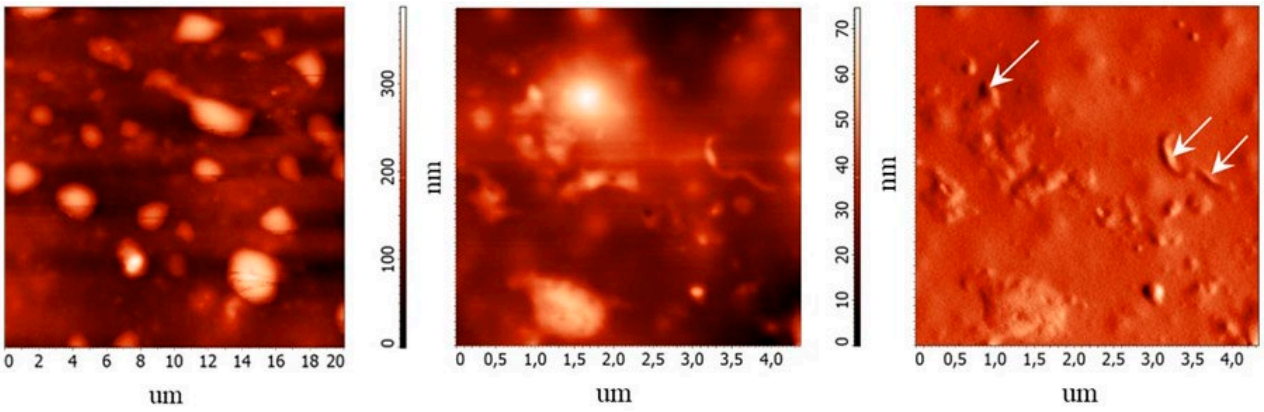
The microrelief of the surface of the resin modified with MWCN is represented by inhomogeneities about 1 μm in size (Fig. 1a). The AFM scan obtained in the topology mode (Fig. 1b) shows nanoscale inhomogeneities in the form of protrusions with a lateral size of about 50 nm. The image obtained in phase contrast mode (Fig. 1c) shows rounded irregularities up to 70 nm in size, darker than the background (indicated by arrows in Fig. 1c). The absence of corresponding inhomogeneities in the image obtained in the surface topology mode indicates that the dark inhomogeneities are nanoinclusions with different mechanical properties compared to the polymer matrix. The nanoscale inhomogeneities very likely correspond to the location of the MWCN.

The microrelief of the resin surface modified by NCC (Fig. 2a) is represented by large,



a b c

Fig. 1. Images of the surface of a binder modified by MWCN cured on an active substrate (veneer)



a b c

Fig. 2. Images of the surface of a binder modified by NCC cured on an active substrate (veneer)

evenly distributed inhomogeneities with a lateral size of 0.5-2 μm and a height of up to 0.5 μm. The microrelief is poorly developed between the inhomogeneities. The relief of the second level in the areas between large inhomogeneities is represented by irregularly shaped inhomogeneities measuring 70–300 nm (indicated by arrows in Fig. 2c), obviously corresponding to inclusions in the form of fibers (Fig. 2b, c). There is no pronounced phase contrast from the inclusions, which can be explained by the similar elastic-plastic characteristics of NCC and resin.

Figure 3 shows the electronograms of the initial components: powders of MWCN (a) and NCC (b).

The electronogram (Fig. 3a) shows a complete set of reflections corresponding to the MWCN [8]. In the electron diagram (Fig. 3b), all the observed reflections correspond to the crystal lattice of cellulose [9].

Figure 4 shows X-ray diffractograms (XRD) of NCC powder (Fig. 4, curve *1*); MWCN powder after dispersion in surfactants (sodium lauryl sulfate (SLS)) and subsequent drying (Fig. 4, curve *2*); mixtures of NCC and MWCN after dispersion in surfactants and subsequent drying (Fig. 4, curve *3*).

On the XRD of the NCC powder (Fig. 4, Curve *1*), very blurred maxima are observed, the position of which coincides with the reflection spectrum from the cellulose crystal lattice. The width of the maxima indicates the nanocrystalline structure of the cellulose.

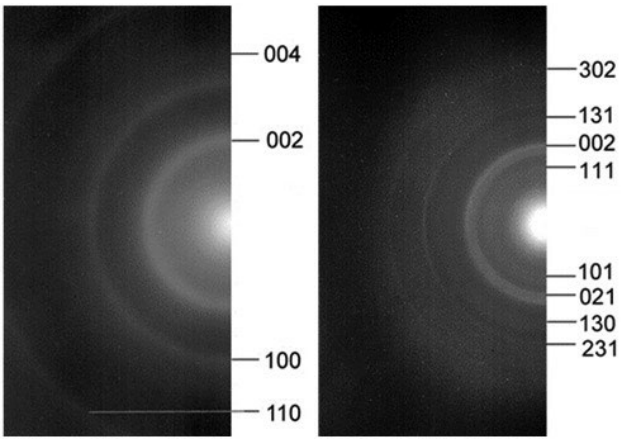


Fig. 3. Electronograms of MWCN (a) and NCC (b) powders

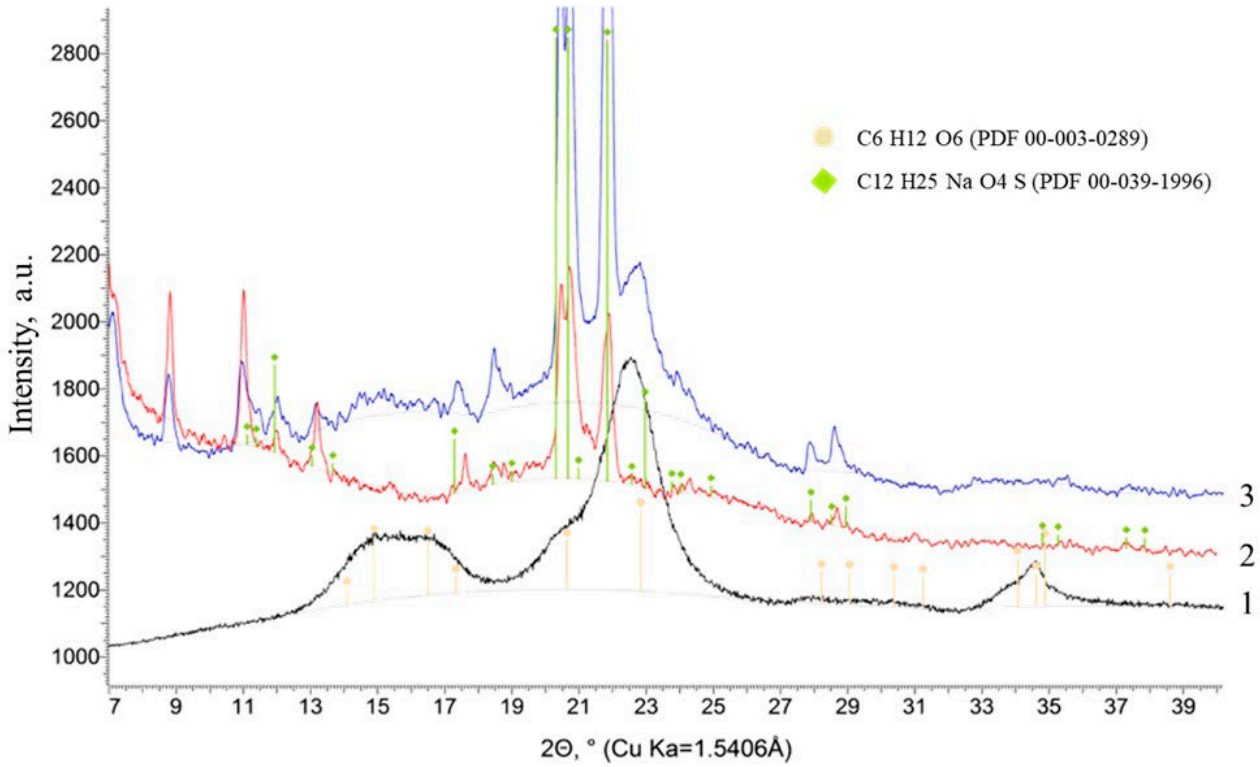


Fig. 4. X-ray diffractograms of NCC powder (*1*); MWCN powder dispersed in surfactants with subsequent drying (*2*); mixtures of NCC and MWCN dispersed in surfactants with subsequent drying (*3*)

All reflections corresponding to the crystalline SLS are observed on the MWCN + SLS XRD (Fig. 4, Curve *2*). The absence of reflections corresponding to MWCN is due to both the low-dimensional nature of the nanotubes and their relatively small number.

All the reflections present in the first two diffractograms are observed on the XRD from MWCN +NCC+ SLS (Fig. 4, Curve *3*). Reflections associated with phases other than NCC and LSN are not observed, which indicates the absence of crystalline products of the reaction of MNT with NCC in the sample.

Figure 5 shows X-ray diffractograms (XRD) of an unmodified binder (Fig. 5, curve *1*) and a binder modified by NCC (Fig. 5, curve *2*) and MWCN (Fig. 5, curve *3*).

The XRD of unmodified resin (Fig. 5, Curve *1*) is represented by wide maxima in the form of halos, the most intense of which is in the angle range 2θ = 18–28 °. A low-intensity peak with a peak of 2θ = 21.11° is observed against the background of this halo. The character of the maxima observed on the diffractogram indicates a low degree of crystallinity of the resin.

In the composite binder containing MWCN (Fig. 5, curve *3*), in addition to the halo, there are 2 pronounced maxima with a peak of 2θ = 21.03° and 23.6°. The higher intensity of the first maximum compared to the XRD of the resin without filler and the appearance of the second maximum indicate an increase in the degree of crystallinity of the resin with filler from MWCN (an increase in the size and proportion of crystallites). The reflections characteristic of MWCN are not observed on XRD, probably due to their small volume fraction in the binder.

Diffraction patterns similar to those of unmodified and modified CNTs of urea-formaldehyde resin are described in the work for formaldehyde resin with different molar ratios. [10]. The authors explain the appearance of pronounced peaks on the resin diffractograms by increasing the degree of polymer crystallinity due to the formation of hydrogen bonds between linear molecules [10].

A halo similar to the unmodified resin is observed on the RD of the resin modified by the NCC (Fig. 5, Curve *2*). There are also peaks with peaks of 2θ = 21.08° and 34.8°. According to [11], these maxima correspond to reflections from the cellulose crystal lattice.

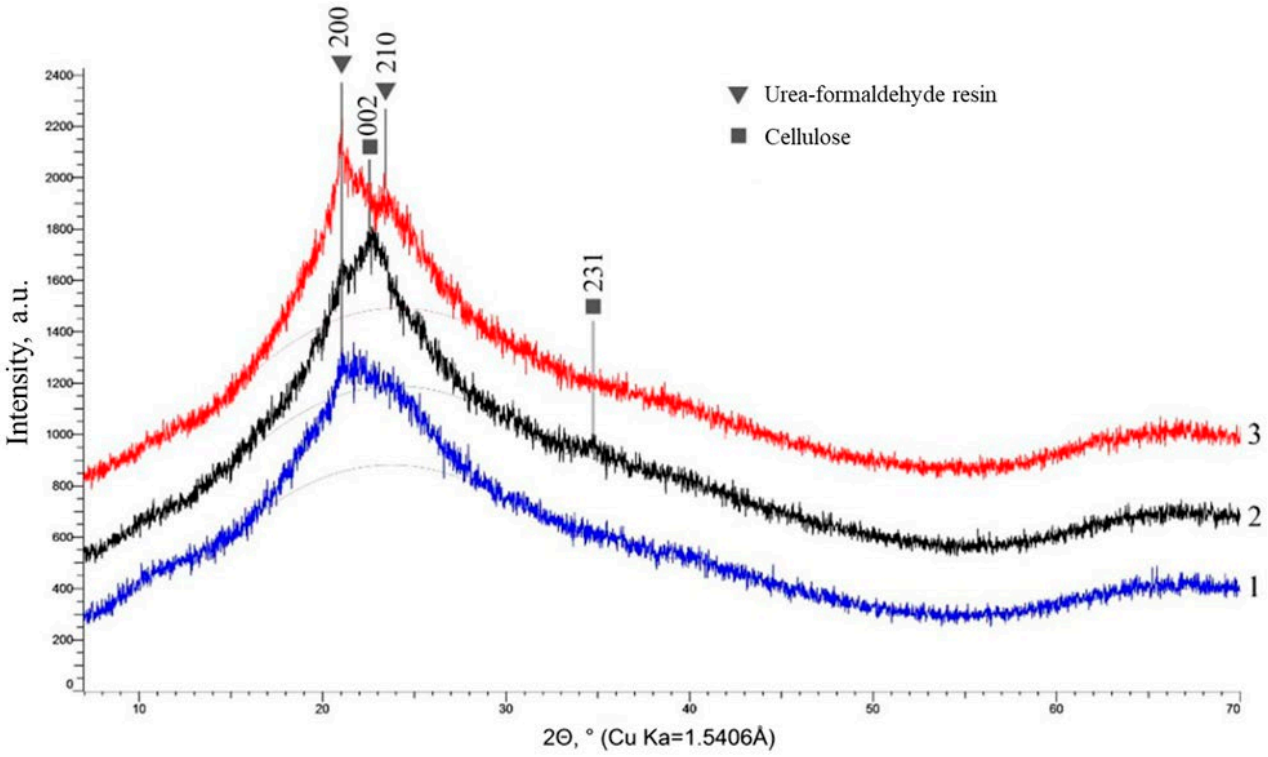


Fig. 5. X-ray diffractograms of unmodified binder (*1*) and binder modified by NCC (*2*) and MWCN (*3*)

The size of the crystallites (coherent scattering regions), calculated as a result of profile analysis of X-ray diffractograms in the region of the maximum with a peak of 21.1°, was about 10 nm for resin without filler, 15 nm for resin with nanocellulose, 18 nm for resin with MWCN. The effect of increasing the size of crystallites on the strength characteristics of the resulting nanocomposite plywood is confirmed by experimental data. Thus, the tensile strength when chipping through the adhesive layer of plywood modified with MWCN increases by 76% (from 0.68 MPa to 1.2 MPa), modified with NCC – by 194% (from 0.68 MPa to 2 MPa) compared with unmodified plywood [12].

Thus, based on comparative diffraction analysis of unmodified and modified resin samples, the following can be noted: a resin containing ultrasound-activated MWCN [12], after curing, has a higher degree of crystallinity compared with unmodified resin. Modification of the NCC resin activated by ultrasound [13] leads to a less pronounced increase in the degree of its crystallinity.

The most likely type of resin lattice is a primitive cubic one. The cubic lattice constant a was 0.840, 0.844, and 0.842 nm for pure resin, UF resin/ MWCN, and UF resin /NCC, respectively. There is a weak tendency to increase the volume of the unit cell when using MWCN as a nanomodifier of KF–Zh-F resin. For NCC resin, the indices of the observed reflections are 200 and 210. Such a set of reflections may indicate a virtually one-dimensional arrangement of polymer fibers parallel to each other with a relatively arbitrary radial rotation. The reflection indices 002 and 231 are characteristic of NCC powder, which is confirmed by the electronogram data (Fig. 3b).

4. Conclusion

The microrelief of the surface of the modified UF resin/MWCN binder cured on an active substrate is characterized by the presence of uniformly distributed MWCN nanoclusions measuring 50 nm – 1 μm. The microrelief of the resin surface modified by NCC shows the presence of evenly distributed nanocellulose inclusions measuring 70 nm – 2 μm. The sets of reflections observed on the electronograms of the nanomodifiers correspond to the MWCN and NCC.

The data of X-ray diffractometry of unmodified resin indicate a low degree of its crystallinity. The modification of the binder of both MWCN and NCC is accompanied by an increase in the degree of crystallinity of the polymer. The crystallite size of the resin without filler is 10 nm; the resin modified with nanocellulose is 15 nm; the resin nanomodified with MWCN is 18 nm. An increase in the size of the crystallites in the resin can lead to an increase in its density, strength, hardness of the material and chemical resistance.

The most probable type of UF resin lattice is a primitive cubic one with parameter a = 0.840 nm. The cubic lattice constant of the resin with MWCN and NCC is 0.844 and 0.842 nm, respectively, i.e. there is a weakly pronounced increase in the volume of the unit cell of the UF resin modified with MWCN.

Thus, the atomic force microscopy data allow us to conclude that the reinforcing components (MWCN, NCC) are evenly distributed in the polymer matrix. The AFM data on the morphology of the surface of composites with NCC obviously correlate with the XRD data: according to the first method, morphological signs of the presence of fibers are observed, according to the second, signs of the NCC crystal lattice. For MWCN, AFM morphology data correlate with electronography data. Electronography confirms that the reinforcing material has a crystalline structure of MWCN. And AFM reveals the presence of inclusions with other elastic-plastic properties in the polymer. Taken together, both methods indicate that the inclusions in the matrix are precisely the MWCN. X-ray diffractometry proved to be insensitive in the case of MWCN.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

References

1. Nazarenko I. N., Nazarenko M. V. The state and prospects of development of plywood production. *Management Accounting*. 2022;1-2: 299–310. https://doi.org/10.25806/uu1-22022299-310 (In Russ., abstract in Eng.)

2. Churkina A.V. Analysis of the use of plywood as raw material. *Forum molodykh uchenykh*. 2019;2(30): 1645–1648. Available at: https://www.elibrary.ru/item.asp?id=38693672 (In Russ., abstract in Eng.)

3. Dorieh A., Selakjani P. P., Shahavi M. H., ... Aghaei R. Recent developments in the performance of micro/nanoparticle-modified urea-formaldehyde resins used as wood-based composite binders: a review. *International Journal of Adhesion and Adhesives*. 2022;114: 103106. https://doi.org/10.1016/j.ijadhadh.2022.103106

4. Kantieva E. V., Ponomarenko L. V., Tomina E. V., Tomenko D. K. The effect of nanoscale silicon oxide on the operational characteristics of plywood. *Systems. Methods. Technologies*. 2022;3(55): 129–134. https://doi.org/10.18324/2077-5415-2022-3-129-134

5. Liu M., Rooban Venkatesh K. G. Thirumalai, Wu Y., Wan H. Characterization of the crystalline regions of cured urea formaldehyde resin. *RSC Advances*. 2017;7: 49536–49541. https://doi.org/10.1039/C7RA08082D

6. Singh A. P., Causin V., Nuryawan A., Park B-D. Morphological, chemical and crystalline features of urea–formaldehyde resin cured in contact with wood. *European Polymer Journal*. 2014;56: 185–193. https://doi.org/10.1016/j.eurpolymj.2014.04.014

7. Ferra J. M. M., Mendes A. M., Costa M. R. N., Carvalho L. H., Magalhães F. D. A study on the colloidal nature of urea-formaldehyde resins and its relation with adhesive performance. *Journal of Applied Polymer Science*. 2010;118 (4): 1956–1968. https://doi.org/10.1002/app.31112

8. Farbod M., Khajehpour Tadavani S., Kiasat A. Surface oxidation and effect of electric field on dispersion and colloids stability of multiwalled carbon nanotubes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2011;384: 685–690. https://doi.org/10.1016/j.colsurfa.2011.05.041

9. Database: JCPDS, Powder Diffraction File Alphabetical Index Inorganic Compounds, Publication SMA - 27, Published by the JCPDS International Center for Diffraction Date

10. Li J., Zhang Y. Morphology and crystallinity of urea-formaldehyde resin adhesives with different molar ratios. *Polymers*. 2021;13: 673. https://doi.org/10.3390/polym13050673

11. Yudhanto F., Yudha V., Ridzuan M., ... Sudarisman. Morphology, crystallinity and thermal properties of nanocrystalline cellulose isolated of sisal fiber by acid hydrolysis-ultrasonication. *International Journal of Nanoelectronics and Materials (IJNeaM)*. 2024;2(17): 180–188. https://doi.org/10.58915/ijneam.v17i2.657

12. Yushchenko E. V., Belchinskaya L. I., Zhuzhukin K. V., Zhukalin D. A. Multi-walled carbon nanotubes and ultrasound modified urea-formaldehyde resins: advantages of using for the production of magnetically processed composite plywood. *Lesotekhnicheskii Zhurnal*. 2024;14(3): 238–259. https://doi.org/10.34220/issn.2222-7962/2024.3/14 (In Russ., abstract in Eng.)

13. Yushchenko E. V., Belchinskaya L. I., Zhuzhukin K. V. Nanocomposite eco-plywood: morphological, ecological, IR spectroscopic substantiation of obtaining. *Lesotekhnicheskii zhurnal*. 2024;14(3): 260–283. https://doi.org/10.34220/issn.2222-7962/2024.3/15 (In Russ., abstract in Eng.)

Information about the authors

Ekaterina V. Yushchenko, postgraduate student of the Department of Wood Science, Voronezh State University of Forestry and Technologies named after G. F. Morozov (Voronezh, Russian Federation).

http://orcid.org/0000-0002-4827-2756

katerina.vgltu@yandex.ru

Larisa I. Belchinskaya, Dr. Sci. (Tech.), Professor, Chief Researcher of the Research Department, Voronezh State University of Forestry and Technologies named after G. F. Morozov (Voronezh, Russian Federation).

http://orcid.org/0000-0003-3921-8018

belbom@mail.ru

Aleksandr V. Kostyuchenko, Cand. Sci. (Phys.–Math.), Associate Professor, Department of Solid State Electronics, Voronezh State Technical University (Voronezh, Russian Federation).

http://orcid.org/0000-0002-0049-3664

av-kostuchenko@mail.ru

Dmitrii A. Zhukalin, Cand. Sci. (Phys.–Math.), Associate Professor, Department of Physics of Semiconductors and Microelectronics, Voronezh State University (Voronezh, Russian Federation).

http://orcid.org/0000-0002-0754-4989

d.zhukalin@mail.ru

Received 17.10.2024; approved after reviewing 13.12.2024; accepted for publication 16.12.2024; published online 25.03.2024.

Translated by the author