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CHARACTERISTICS OF AGING OF WOOD-FIBERBOARD FROM THE POSITION OF IR SPECTROSCOPY

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Fiber boards, like other wood-polymer composites, are widely used in construction. However, their service life is often less than that declared by the manufacturer, which is due to insufficient knowledge of the processes of degradation of polymer components of resin and wood filler under the influence of aggressive environmental factors. In this regard, the task is to reveal, using reflective IR spectroscopy, structural changes in the molecular structure of polymeric substances included in a wood fiber composite after heat aging, artificial UV radiation and exposure to direct sunlight. The results of the study showed that the IR spectra of all samples are identical, but differ in the intensity of individual absorption bands. This suggests that under the influence of aging factors, a free-radical rupture of hydrogen, hydrocarbon and ether bonds occurs in various functional groups of cellulose, hemicellulose, lignin and resin. At the same time, heat aging causes structural changes throughout the entire volume of the slab, and artificial UV irradiation destroys the surface layer about one millimeter thick. Sunlight during the summer season destroys the surface layer less than 0.5 mm thick and contributes to additional structuring of the polymer components of the resin and wood of the inner layers as a result of heating the board.

Key words: fibreboards, heat aging, UV irradiation, IR spectroscopy

INTRODUCTION

Currently, in low-rise construction, there is an increase in the consumption of wood-based panels based on polymer binders. Their relatively low cost, light weight and manufacturability can significantly reduce material and time costs in the construction of such buildings. Unfortunately, the service life of wood composites declared by manufacturers is often overestimated, which leads to a premature loss of performance of structures [1] to [3]. This is due to the fact that when assessing their service life, the susceptibility of the polymer binder to aging under the influence of external non-mechanical factors, which lead to irreversible structural changes, is not fully taken into account [4] to [6].

IR spectroscopy is a unique method for establishing the characteristics of the structure and properties of molecular compounds, determined by the nature and system of intra- and intermolecular interactions. The method is informative for the study of wood and materials based on it [7] to [9], therefore, the goal is to assess the effect of aging factors on the structural changes of an aged wood fiber composite using IR spectroscopy.

MATERIALS AND METHODS

As an object of research, we chose hard fiber boards (Fibreboard) with a thickness of 3.2 mm and a density of 950 kg/m³, made by hot pressing in accordance with GOST 4598-86.

The experimental material accumulated to date and its analysis made it possible to identify the most aggressive types of action for polymer composite materials: temperature and solar radiation, especially its UV part [10], [11]. In this regard, in the work as the main factors of accelerated aging, UV irradiation created by a DRT1000 lamp with a radiant flux of 128 W in the wavelength range of 240-320 nm and an increased temperature of 80 ºС created in a thermal aging installation are taken. The duration of the factors was 500 hours.

To compare the results of laboratory tests with real operating conditions, a series of fiberboard samples were subjected to natural climatic aging in a temperate climate (under direct sunlight) during the months of June and August.

IR spectra were recorded using the ATR (disturbed total internal reflection) method on a JascoFT/IR-6200 type A FT-IR spectrometer with a spectral resolution of 4 cm⁻¹ and a reflection angle of 45 degrees.

To assess the depth of development of degradation processes along the thickness of the slabs, the samples were removed layer by layer. The thickness of the layers was taken to be about 0.4 mm.

RESULTS

Today, most of the fibreboard is produced by hot pressing, in which stable chemical nodes (methylene and dimethylether bonds) and unstable physical nodes (hydrogen bonds between oxygen-containing groups - phenolic...
hydroxyls, methylol hydroxide groups and dimethylene ether bonds) are formed in the composite [12] to [14].

Wood fibers are characterized by an unfolded surface and have a significant amount of hydroxyl, carbonyl and aldehyde groups, which during hot pressing are combined with the same groups of neighboring wood fibers [15] to [17]. Thus, the interaction of wood fibers is carried out not only due to physical interweaving, but also at the chemical level [12].

At the same time, the phenol-formaldehyde binder interacts with the functional groups of wood fibers and hardens, forming hydrogen, simple and complex ether bonds [12].

Under the influence of elevated temperature and the UV part of sunlight, irreversible physicochemical transformations take place in the wood composite, which affects its operational properties.

Thermal and photooxidation leads to disruption of the continuity of the surface layers of the material, increasing its roughness and porosity. The latter is also large enough in the internal volume of wood composites as a result of evaporation of moisture and volatile organic compounds when using the hot pressing method [10].

Air oxygen penetrates through the outer pores into the inner ones, thereby oxidizing the components of the wood composite from the inside. At the same time, atmospheric moisture contributes to the intensification of oxidation processes, increasing the mobility of macromolecular chains. In addition, an uneven distribution of stresses over the volume of the material is created, which leads to a violation of adhesion between wood fibers and a polymer binder [10].

Thermal and photooxidation occurs by a free radical mechanism. Under the influence of elevated temperature or high energy of the UV part of sunlight, a chain of chemical bond ruptures in the polymer composite is initiated. As a rule, ruptures begin near free hydrocarbon radicals, since the strength of the C–H bond is 7 times less than the strength of the skeletal C–C bonds in the polymer [10].

It should be noted that the short-wavelength limit of sunlight on the earth’s surface ranges from 290 to 300 nm and has sufficient energy to destroy most chemical bonds (Table 1) [11].

Further, the formed free hydrocarbon radical is oxidized by atmospheric oxygen, turning into an unstable peroxide radical, which immediately abstracts a hydrogen atom from a neighboring polymer molecule by a radical mechanism [10], [11].

Thus, a hydroperoxide radical and a new hydrocarbon free radical are formed, which is again oxidized by oxygen and detaches a hydrogen atom from a neighboring polymer molecule, thereby continuing the chain of breaking bonds. At this time, the hydroperoxide radical also decomposes into two new free radicals [10], [11].

All reactions leading to the formation of free radicals are reversible, and many primary macroalkyl radicals are reunited intra- or intermolecularly, leading to branching and crosslinking. Sometimes this leads to a short-term improvement in the properties of the composite, but as a result, there is a decrease in molecular weight and complete destruction of polymer macromolecules [10], [11].

For example, the destruction of lignin always occurs through its condensation. First, new carbon is formed – carbon bonds with a sparse spatial network. Then, due to hydrogen bonds and peripheral groups of macromolecules, a three-dimensional structure is formed, which is subsequently destroyed by oxidized free radicals of neighboring molecular chains [10], [18].

Let us trace with the help of IR spectroscopy what changes in the structure occur in fibreboard under the influence of aging factors.

In the work of I. Kotlyarova described the IR spectrum characteristic of wood, in which several regions can be distinguished: the region of 3700–3100 cm⁻¹ characterizes the stretching vibrations of various types of hydroxyl groups involved in hydrogen bonds; area 3100-2750 cm⁻¹ – the region of symmetric and asymmetric stretching vibrations of CH groups of methyl, methylene, methine groups of wood composite components; area 1800-1000 cm⁻¹ (area of "fin

| Communication | Communication energy, kJ/mol | Photon energy, kJ/mol | Wavelength, nm |
|---------------|-----------------------------|-----------------------|----------------|
| C–C           | 955                         | 1197                  | 100            |
| C=O           | 730,8                       | 798                   | 150            |
| C=C           | 609                         | 798                   | 150            |
| C=C (aromatic)| 520,8                       | 598,5                 | 200            |
| O–H           | 462                         | 478                   | 250            |
| C–H (CH4)     | 411,8                       | 478                   | 250            |
| C–O           | 365,4                       | 478                   | 250            |
| C–O (ether)   | 331,8                       | 399                   | 300            |

Table 1: The relationship between the wavelength of UV radiation from the Sun, photon energy and binding energy [11]
Figure 1: IR spectra of the surface of fiberboard samples, initial and exposed to UV irradiation and thermal aging for 500 hours

As a rule, after hot pressing in the surface layer of the boards, the content of free OH groups is insignificant in comparison with the inner layers, since wood particles are coated with resin [15]. This is evidenced by the absence of a pronounced band at 3750 cm⁻¹ for the initial composite. The action of aging factors leads to the destruction of the surface resin film, exposure of wood particles and the release of hydrogen-bonded OH-groups of cellulose, as a result of which a whole series of rather intense bands is observed in the wavenumber region of 3750 cm⁻¹. In this case, a decrease in the intensity of the band at 3330 cm⁻¹ (Figure 1).

In the interval 3000-2600 cm⁻¹ two bands of medium intensity are observed with maxima at 2920 cm⁻¹ and 2850 cm⁻¹, corresponding to stretching vibrations of methine and methylene –CH₂ and –CH groups of cellulose, lignin and phenol-formaldehyde resin [30] to [32].

Under the influence of aging factors, the maximums of these bands do not shift, but their intensity decreases as a result of the breaking of hydrocarbon CH bonds (Figure 1). In this case, photooxidation has a more negative effect.

In the range of 1800-1580 cm⁻¹ For the initial material, bands are observed that are characteristic of stretching vibrations of C=O bonds in carbonyl and C-O bonds in the carboxyl groups of the ligno-carbohydrate complex of the wood filler (Figure 1). There is also a 1595 cm⁻¹ strip, corresponding to stretching vibrations of double C=C benzene and aromatic bonds of lignin [18], [28], [30].
an increase in the number of carbonyl groups occurs, which leads to the appearance of a series of bands of low intensity (Figure 1). Decrease in the intensity of the 1727 cm\(^{-1}\) band indicates the degradation of chemical C-O-C bonds in the molecular structure of cellulose and hemicellulose. At the same time, the band 1595 cm\(^{-1}\), indicates the degradation of chemical C-O-C bonds in the molecular structure of cellulose and hemicellulose. At the same time, the band 1595 cm\(^{-1}\) for all samples. This is the interval of deformation vibrations of groups C-H\(_3\), C-H\(_2\) and O-H and aromatic skeletal vibrations of lignin (1509 cm\(^{-1}\)) [28], [31], [32]. It is worth paying attention to the stripe 1267 cm\(^{-1}\), the intensity of which under the influence of UV irradiation decreases more strongly than after heat aging. This band characterizes the skeletal vibrations of the guaiacyl ring of lignin, which is part of wood fibers [23]. The decrease in the intensity of the band is apparently associated with the rupture of the C-O bonds in the ring as a result of oxidation.

In the range 1200-1000 cm\(^{-1}\) for all samples can be see “fingerprinted”; i.e the most typical for cellulosic materials four intense bands with maxima at 1160, 1105, 1053 and 1025 cm\(^{-1}\). These bands are due to the presence of acetal C-O-C and C-O bonds in alcohols, ethers, and polysaccharides [19], [21], [32].

Decrease in the intensity of the defining band 1025 cm\(^{-1}\) under the influence of aging factors is associated with the weakening of carbon bonds in the C-C and C-H groups as a result of the oxidation of lignin and hemicellulose, which are more reactive than cellulose and therefore more susceptible to degradation [10], [20], [28].

To assess the depth of development of degradation processes along the thickness of the slabs, the samples were removed layer by layer. The thickness of the layers turned out to be about 0.4 mm. The IR spectra of individual layers of boards subject to aging are shown in Figure 2.

Figure 2: IR spectra of the surface and inner layers of fiberboard, initial and subject to thermal aging (a) and UV irradiation with a DRT1000 lamp (b)
It is important to note that UV irradiation and thermal aging do not cause the absorption bands of the inner layers of the composite to shift either to the region of low or high vibration frequencies. The difference is that heat aging initiates destructive processes in the composite at a depth of more than 1 mm (Figure 2a), and it can be safely assumed that the destruction of bonds by a free radical mechanism occurs throughout the entire volume of the slab.

UV irradiation from an artificial light source affects the composite layer with a thickness of less than 0.8 mm, since the behavior of the IR spectra for layers 3 and 4 completely coincides with the behavior of the spectrum of the composite that is not subject to aging (Figure 2b).

Aging in direct sunlight causes similar changes in the structure of the composite (Figure 3). The IR spectrum of the irradiated surface generally coincides with the rest of the spectra, but differs in the degree of change in the intensity of the bands.

It can be seen that the UV part of sunlight promotes the release of hydroxyl groups as a result of breaking hydrogen bonds, which leads to the appearance of a band at 3750 cm\(^{-1}\) and a decrease in the intensity of the band 3330 cm\(^{-1}\).

As in the case of an artificial source of UV radiation for the surface layer of fiberboard, a significant decrease in the intensity of two bands at 2920 cm\(^{-1}\) and 2850 cm\(^{-1}\) as a result of the destruction of CH bonds connection.

The destruction of chemical bonds in the hydrocarbon part of wood fibers under the action of solar radiation is confirmed by a decrease in the intensity of the characteristic band at 1025 cm\(^{-1}\).

An increase in the number of carboxyl groups as a result of photooxidation of polymer resin, lignin and hemicellulose leads to a decrease in the intensity of bands in the range 1800-1580 cm\(^{-1}\). However, in contrast to an artificial radiation source, in this case, the appearance of an additional large number of low-intensity bands is not observed, which is possibly associated with the occurrence of condensation processes from heating the composite under mild conditions under sunlight.

If the composite is irradiated by sunlight, the thickness of the layer damaged by photooxidative processes is less than 0.4 mm. The observed increase in the intensity of the bands under consideration for layer 2, i.e. at a depth of more than 0.4 mm, apparently, is associated with additional structuring of polymer macromolecules of the resin and components of wood fibers as a result of heating the composite.

**CONCLUSIONS**

The study shows that IR spectroscopy is an informative method that allows you to identify changes in the molecular structure of fiberboards caused by thermal and photooxidation processes. Prolonged action of elevated temperature and UV irradiation initiates free-radical reactions of breaking hydrogen and hydrocarbon bonds in...
various functional groups of macromolecules, which is confirmed by a change in the intensity of the corresponding absorption bands.

Artificial UV irradiation degrades the material at a depth of about one millimeter. Under the influence of sunlight, not only the destruction of the surface layer less than 0.5mm thick occurs, but also the heating of the material, which contributes to the additional structuring of the polymer components of the inner layers. In the case of heat aging, destructive changes are observed throughout the entire volume of the composite.

REFERENCES

1. Yemelyanov, S.G., Pakhomova, E.G., Dubrakova, K.O., Dubrakov, S.V. (2019). Stability of statically indefinite physically nonlinear timber structural systems. *Journal of Applied Engineering Science*, vol. 17, br. 3, str. 404-407, DOI:10.5937/jaes17-21686.

2. Yezhov, V.S., Semicheva, N.E., Pakhomova, E.G., Bredikhina, N.V., Emmanuel, S. (2019). To the question of improving energy-saving and environmental characteristics of urban buildings. *Journal of Applied Engineering Science*, vol. 17, br. 4, str. 550-554, DOI:10.5937/jaes17-23629.

3. Mamontov, S., Yartsve, V., Monastyrev, P. (2017). Artificial and natural aging of wood fiber composite. News of higher educational institutions. Textile industry technology, no. 1 (367), 95-101.

4. Erofeev, A., Yartsev, V., Monastyrev, P. (2017). Decorative and protective plates for facade finishing of buildings. Izvestiya vysshikh educational institutions. Textile industry technology, no. 1 (367), 101-104.

5. Shipina, O., Garaeva, M., Aleksandrov, A. (2009). IR-spectroscopic studies of cellulose from herbaceous plants. Bulletin of Kazan Technological University, no. 6, pp. 148-152.

6. Khvivuzov, S., Bogolitsyn, K., Gusakova, M., Zubov, I. (2015). Estimation of the lignin content in wood by FTIR spectroscopy. Fundamental research, no. 9, 87-90

7. Zhbankov, R., Kozlov, P. (1983). Physics of cellulose and its derivatives. Minsk, Science and technology, 296 p.

8. Khabarov, Yu., Pesyakova, L. (2008). Analytical chemistry of lignin. Arkhangelsk, AGTU, 172 p.

9. Lin, S., Dence, C.W. (1992). Methods in Lignin Chemistry. Berlin, Springer-Verlag, 578 p., DOI:10.1007/978-3-642-74065-7.

10. Klyosov, A. (2010). Wood-polymer composites. SPb, Scientific bases and technologies, 736 p.

11. Pavlov, N. (1982). Aging of plastics in natural and artificial conditions. M., Chemistry, 220 p.

12. Trishin, S. (2007). Wood-based panel technology: a tutorial. -3rd ed. M., GOU VPO MGUL, 188 p.

13. Theng, D., Arbat, G., Delgado-Aguilar, M., Ngo, B., Labonne, L., Mutje, P., Evon, Ph. (2019). Production of fiberboard from rice straw thermomechanical extrudates by thermopressing: influence of fiber morphology, water and lignin content. European Journal of Wood and Wood Products, vol. 77, 15–32, DOI: 10.1007/s00107-018-1358-0

14. Dominguez-Robles, J., Tarres, Q., Delgado-Aguilar, M., Rodriguez, A., Espinach, F.X., Mutje, P. (2018). Approaching a new generation of fiberboards taking advantage of self lignin as green adhesive. International Journal of Biological Macromolecules, vol. 108, 927-935, DOI: 10.1016/j.ijbiomac.2017.11.005.

15. Pan, W., Ituralde, K., Bock, T., Martinez, R.G., Juez, O.M., Finocchiaro, P. (2020). A Conceptual Design of an Integrated Facade System to Reduce Embodied Energy in Residential Buildings. Sustainability, vol. 12, no. 4, 5730, DOI: 10.3390/su12145730

16. Boian, I., Tuns, I. (2020). Reducing heat losses - First step toward nZEB. IOP. Conference Series: Materials Science and Engineering, vol. 789(1), 012005 DOI: 10.1088/1757-899X/789/1/012005

17. Chen, H., Zhang, Y., Zhong, T., Wu, Z., Zhan, X., Ye, J. (2020). Thermal insulation and hydrophobization of wood impregnated with silica aerogel powder. Journal of Wood Science, vol. 66, 81, DOI: 10.1186/s10086-020-01927-7.

18. Kotlyarov, I. (2019). IR spectroscopy of pine, birch and oak wood modified with monoethanolamine (n → b) trihydroxyborate. Chemistry of plant raw materials, no. 2, 43-49, DOI:10.14258/jcprm.2019024609

19. Bazarnova, N., Karpova, E., Katrakov, I. and other (2002). Methods for the study of wood and its derivatives. Barnaul, Publishing house Alt. state University, 160 p.

20. Panov, V. (1983). Medium density fiberboard production technology based on phenol-formaldehyde binders. Diss ... for the degree of candidate of technical sciences, Moscow, 191 p.

21. Nicole, M. Stark, Laurent, M. Matuana, (2007). Characterization of weathered wood-plastic composite surfaces using FTIR spectroscopy, contact angle, and XPSˆ. Polymer Degradation and Stability, no. 92(2007), 1883-1890, DOI: 10.1016/j.polymdegradstab.2007.06.017.

22. Dong Fang Li, Li Li, Jin Chi Zhou. (2010). Applications of Infrared Spectroscopy in the Study of Wood Plastic Composites. Advanced Materials Research, no. 113-116, 2003-2006, DOI:10.4028/www.scientific.net/AMR.113-116.2003.

23. Wenbo Chen, Hui He, Hongxiang Zhu, Meixiao Cheng, Yunhua Li, Shuangfei Wang. (2018). Thermo-Responsive Cellulose-Based Material with Switchable Wettability for Controllable Oil. Water Separation. Polymers, no. 10(6), 592, DOI:10.3390/polym10060592.
24. Hui Zhang, Yaoguang Xu, Yuqi Li, Zexiang Lu, Shilin Cao, Mizi Fan, Liulian Huang, Lihui Chen. (2017). Facile Cellulose Dissolution and Characterization in the Newly Synthesized 1,3-Diallyl-2-ethylimidazolium Acetate Ionic Liquid. Polymers, no. 9(10), 526, DOI:10.3390/polym9100526.

25. Voronych, O., Starchevskyy, S., Fedorchenko, Sofia, V. (2016). Technology of Recycling, Properties and Use of Polyvinylchloride-Coated Paper Waste. Chemistry and Chemical Technology, vol. 10, no. 2, 219-226, DOI:10.23939/chcht10.02.219.

26. Ghavidel, A. Scheglov, A. Karius, V. Mai, C. Tarmian, A. Viol, W. Vasilache, V. Sandu, Ion. (2020). In-depth studies on the modifying effects of natural aging on the chemical structure of European spruce (Picea abies) and silver fir (Abies alba) woods. Journal of Wood Science, no. 66, 77(2020).

27. Gu, Y.; Bian, H.; Wei, L.; Wang, R. (2019). Enhancement of Hydrotropic Fractionation of Poplar Wood Using Autohydrolysis and Disk Refining Pretreatment: Morphology and Overall Chemical Characterization. Polymers, no. 11, 685, DOI: 10.3390/polym11040685.

28. Azarov, V., Burov, A., Obolenskaya, A. (1999). Chemistry of wood and synthetic polymers. Textbook for universities. SPb, SPbLTA, 1999.- 628.

29. Chukhchin, D., Mayer, L., Kazakov, J., Ladesov, A. (2017). Application of IR spectroscopy to study the stress state of cellulosic materials. Problems of the mechanics of pulp and paper materials: materials of the IV Intern. scientific and technical conf., dedicated in memory of professor V. Komarova (Arkhangelsk, September 14-16, 2017). Arkhangelsk, North. (Arctic) Feder. un-t them. M.V. Lomonosov, 86-91.

30. Osetrov, A. (2016). Formation of chipboards based on modified phenol-formaldehyde resin. Diss ... for the degree of Ph.D. Kostroma, 147 p.

31. Zhbankov, R. (1972). Infrared spectra and structure of carbohydrates. Minsk, Science and Technology, 456 p.

32. Dekhanta, I. Infrared Spectroscopy of Polymers. M., 472 p.