Digital differential spectrometry in the assessment of the structural characteristics of wood and wooden composite materials

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Abstract. The results of the application of digital differential spectrometry in the processing of the results of the study of the structure of wood and wood materials by dynamic mechanical analysis (DMA) are shown. The experimental temperature dependences of the dynamic shear modulus $G'$ are smoothed using cubic splines. Smooth curves $G'(t)$ are obtained that are suitable for automated processing, including for finding the temperature derivatives of $G'$. The analysis of the temperature dependences of the first and second derivatives of the dynamic shear modulus allows us to determine the position, range, and intensity of temperature transitions in the components of the material under study. The results of the practical application of the DMA method and digital data processing are presented on the example of studying the dynamic mechanical characteristics of birch wood, apple wood, composite material made of hydrolyzed wood, particle board. It is shown that the use of digital processing of experimental data provides more accurate results, simplifies their interpretation, and expands the understanding of the processes occurring in wood materials at the level of intermolecular interaction.

1. Introduction

Digital technologies are involved in all spheres of modern human activity. First, they are used to store and transmit various types of data. However, digital technologies also allow data processing. Including the data that was obtained because of the experiment. Digital processing methods can be used directly during the experiment and in the analysis of the results obtained. Digital processing can significantly reduce random errors, detect new, previously invisible effects, and make it easier to interpret the results obtained. The processing of experimental data, the construction of their dependencies directly during the experiment allows you to evaluate the characteristic features of the experiment in real time. The researcher can adjust the conditions of the experiment, justify the need to perform intermediate measurements.

An urgent task in the areas of woodworking and/or pulp and paper production is to predict the physical, mechanical and strength characteristics of the resulting materials. When creating new materials, it is important to analyze the structural changes that occur in their components at different stages of the technological process. One of the methods that allows you to identify structural changes
in materials of different nature is dynamic mechanical analysis (DMA). Traditionally, the DMA method is used to study the structure and properties of synthetic polymer and composite materials [1-4]. It is used to study the features of relaxation processes in the high-molecular components forming them, and to determine the position of phase transitions. Based on the results obtained by the DMA method, the influence of technological modes, processing methods, additives of chemically active and/or inert components on the structure and properties of materials, on the relative displacement of temperature transitions can be studied [2].

Wood is a natural composite material [5]. The use of the DMA method in study allows us to expand our understanding of the processes occurring in the structure of its components under the conditions of technological and natural factors. A special feature of the DMA method is to obtain a series of discrete experimental points corresponding to the values of the dynamic shear modulus of the material in a wide temperature range [2]. To obtain the results from them (for example, to determine the position of temperature transitions), it is necessary to use special processing techniques, which often give significant errors. The use of the digital processing method makes it possible to significantly simplify the data processing process. At the same time, the DMA method becomes more informative, its results are more reliable and accurate, and its interpretation is simpler.

The aim of the work is to demonstrate the possibility of digital processing of experimental data of DMA of wood and wood composite materials in a wide temperature range by differential spectrometry to improve the interpretation of the results. The results obtained can contribute to a wider application of the DMA method and digital data processing methods in the study of the structure and properties of plant-based materials and secondary materials obtained on their basis.

2. Experimental part

The choice of dynamic mechanical analysis for studying the structural features of wood and materials obtained on its basis is due to the possibility of measuring the dynamic shear modulus \(G'\) and the tangent of the angle of mechanical losses \(\tan \delta\) in a wide temperature range [2]. In the studied range, there are transition regions corresponding to the processes of a sharp change in the molecular mobility in the components, their transition from a glassy to a highly elastic state, as well as phase processes and processes of interfacial interaction [1, 6-8]. A special feature of each of the transition regions is the corresponding sharp increase in mechanical losses, at which the values of \(G'\) and \(\tan \delta\) within a not wide temperature range can vary by several orders of magnitude [1, 6-8]. Wood and other lignocellulose materials are a complex multicomponent complex formed not only by the main components (lignin, cellulose, and hemicelluloses), but also by other components that are often present in such materials. The advantage of using DMA for the study of materials of this kind is the high sensitivity of the method. It allows you to isolate not only the transients in the components, but also the influence of impurities (water, binders, plasticizers, etc.). In addition, measurements by the DMA method are performed with small deformations of the sample [2, 9], which eliminates the influence of the method on the structure of the material under study during the measurement process.

The studied samples are made in the form of plates with a size of ~ 60..80 × 6..10 × 1 mm. After fixing in the installation, the samples are subjected to longitudinal flexural-torsional vibrations on the reverse torsional pendulum [4]. The operation of the device is automated and allows you to perform periodic calculation of the period and decrement of mechanical damping index in real time. The values of the parameters depend on the features of the molecular structure of the substance at the appropriate temperature. In the process of heating the sample, they can change significantly. Based on the parameters, the value of the dynamic shift modulus is calculated, which is placed in a digital database for subsequent processing.

Traditional methods for determining the boundaries of temperature transitions in the components of composite materials according to DMA data are based on a graphical representation of experimental data. Several methods involve determining the position of the fractures on the temperature dependence of the low-frequency speed of sound in the material [2] or its dynamic modulus of elasticity [10]. The use of these methods is justified by the linear dependence of the speed of sound or the magnitude of
the elastic modulus on temperature. Thawing of any type of molecular mobility leads to a sharp change in them, caused by the phenomenon of structural glass transition [2, 7]. An example of determining the position of temperature transitions along the fractures on the temperature dependence of the low-frequency speed of sound is shown in figure 1.

Another way is to find the temperature of the maxima on the temperature dependence $\operatorname{tg} \delta$ [8, 10, 11], corresponding to the transients in macro-molecular chains (figure 1). The disadvantages of both options are low accuracy and significant subjectivity, due to obvious methodological limitations.

To increase the accuracy and reliability of the results, the presented work uses an analytical method based on the principle of digital differential spectrometry [12]. The temperature dependence of $G'$ was approximated by smoothing cubic splines according to the method proposed in [13]. After the approximation, the dependence was numerically differentiated twice in terms of temperature. The position of each of the minima on the temperature dependence of the first derivative $dG' / dt$ corresponds to the maximum speed of the transition process in any of the components of the material under study (figure 2). In our case, this temperature can be considered an analog of the transition temperature determined by traditional graphical methods.

Using the second temperature derivative $G''$ allows you to determine the boundaries of the transition regions—they correspond to the inflection points on the graph of the temperature dependence $dG'/dt$. 

![Figure 1](image1.png)

**Figure 1.** Determination of the position of temperature transitions by the graphical method based on the temperature dependences of the low-frequency speed of sound and the tangent of the angle of mechanical losses in a sample of a composite material made of flax bonfire.

![Figure 2](image2.png)

**Figure 2.** Determination of the position of temperature transitions by digital differential spectrometry based on the temperature dependences of the dynamic shear modulus $G'$, the first and second temperature derivatives $G'$ of the composite material from the flax bonfire.
The temperatures of the beginning and end of the transition process coincide, respectively, with the minimum and maximum temperatures of the second temperature derivative $G'$ (figure 2), and the transition of the value $d^2G'/dt^2$ through zero occurs at the point of the maximum intensity of the transition process.

Several samples of woody and non-woody materials were selected as the object for the DMA study with data processing by digital differential spectrometry:

- downy birch wood (Bétula pubéscens) with a moisture content of 20%,
- freshly cut apple tree wood of the "Decabrenok" variety (Malus "Decabrenok") after its fast and deep freezing to a temperature of -90 °C,
- composite material obtained from hydrolyzed birch wood without the use of binders by the method described in [14-16],
- the inner layer of a three-layer particle board (chipboard) with a thickness of 16 mm, produced by JSC "Tomsk Plant of Particle Boards". To produce the material, the plant used technological wood chips GOST 15815-83 and carbamide-formaldehyde resin of the KF-MT-15 brand (TU-6-06-12-88).

3. Results and Discussion

Examples of the results of digital processing of experimental data are shown in figures 2-6. Birch wood is characterized by the presence of three pronounced regions of temperature transitions with intensity maxima at 35, 209 and 265 °C (figure 3). The transition region in the range of 19..49 °C should be associated with the processes of devitrification of the amorphous part of cellulose, hemicellulose and lignin plasticized with water [17, 18]. Based on the works [16-19], the process is in the range of 194..224 °C can be associated with the de-vitrification of the non-plasticized part of hemicelluloses and lignin. The participation of the crystal component in the formation of this temperature transition is unlikely, since there are no transients in this range, for example, in sulfate cellulose [16]. The second transition region is located in the range 253..277 °C. The most pronounced temperature transition in sulfate cellulose is in a similar range [16]. Based on the results presented in [20], it can be argued that in this range there is a process of transition of cellulose from the crystalline to the amorphous phase.

![Figure 3. Temperature dependences of the dynamic shear modulus $G'$, the first and second temperature derivatives $G'$ of downy birch wood.](image_url)
reference point for assessing the effect of processing native wood by various methods on the nature of the molecular mobility of components in its crystalline and amorphous regions.

An example of the result of applying the DMA method in the region of negative temperatures is shown in figure 4. Sharp and deep freezing of freshly cut wood provides almost instantaneous fixation of the state of the wood substance at the time of the start of the G' measurements. Thus, the probability of adaptation of plant tissue to the conditions of the surrounding space with the accompanying changes in the molecular structure and the nature of intermolecular interaction decreases. The most intense temperature transition is observed in the range from -21 to -5°C with a maximum intensity at -16°C. In accordance with the material presented in [21, 22], this range should be considered as a region of the transition process caused by the presence of water in the wood cells and in its intercellular space. The sharp change in G' is caused by the peculiarities of the interaction of water with macromolecules of wood tissue and correlates with the threshold of frost resistance of plant tissue, traditionally determined by other methods [21]. Thus, the measurement of freshly cut plant shoots by the DMA method at negative temperatures and under conditions of preliminary shock freezing, in conjunction with the proposed data processing method, allows us to evaluate the threshold value of frost resistance of living plant tissue.

![Figure 4](image1.png)

**Figure 4.** Temperature dependences of the dynamic shear modulus G', the first and second temperature derivatives G' of the "Decabrenok" apple tree wood.

![Figure 5](image2.png)

**Figure 5.** Temperature dependences of the dynamic shear modulus G', the first and second temperature derivatives G' of a composite material made of hydrolyzed birch wood.

Figure 5 shows the temperature dependences of G' and the temperature derivatives of G' of a composite material obtained from hydrolyzed birch wood without the addition of binders [14, 15].
There is a significant change in the nature of the transition process in complex amorphous material components compared to the original wood (figure 3). The offset into the region of lower temperatures is to begin the process 76°C, to the point of its highest intensity 67°C, and the completion point 64°C. The width of the transition area increases from 30 to 42°C. This indicates a significant decrease in the structural uniformity of the amorphous component of the composite material compared to the original wood. The reason for such significant changes should be considered the phenomenon of structural plasticization of the composite material by low-molecular fragments of hemicelluloses and lignin formed during barothermal wood processing [16]. The speed of the transition process in a composite material, determined by the value of the first derivative $G'$, is twice the speed of a similar process in wood. Significant differences in speed are due to the almost twofold excess of the value of the $G'$ value of the composite material over the same indicator of wood at the beginning of the transition process.

Figure 6 shows an example of the temperature dependences of $G'$ and the temperature derivatives of $G'$ for the inner layer of a particle board. According to the presented data, four ranges of temperature transitions can be distinguished. The position of the three temperature transitions approximately coincides with the temperature transitions in wood (figure 3). The process in the range of 32..50°C with a maximum intensity at 42°C is associated with the decomposition of the amorphous part of cellulose, hemicellulose and lignin, plasticized with water. The process is in the range of 237..260°C with a maximum intensity at 247°C is caused by the melting of the crystalline regions of cellulose. The difference between the parameters of the marked transients – their position, width, and intensity-and the parameters of similar processes in birch wood (figure 3) is due to the use of particles from a mixture of different wood species to obtain this variant of chipboard. In the range of 188..208°C the form of the temperature dependences of the first and second temperature derivatives $G'$ differs from similar dependences in wood. It is not symmetric. Two closely spaced relaxation processes overlap here. One of them, as well as in wood, is caused by the non-plasticized part of the lignin and hemicelluloses. The second process is slightly shifted to a higher temperature region. It is associated with the de-vitrification of the chipboard binder, which was completely cured during the production of the plate. This transition is located at a temperature that is close to the pressing temperature of the material [23]. Thus, differential spectrometry made it possible to determine the presence of a double temperature transition. Identifying the duplicity of a process without the use of digital processing would be difficult or impossible.

In the context of the chipboard structure and its production technology, the transition process in the range of 95..150°C is of particular interest. Any polymer and composite materials, as well as wood, are characterized by a gradual decrease in the value of the elastic modulus (shear modulus) with an
increase in temperature [7,9]. Therefore, a short-term sharp increase in \( G' \) at a temperature of 137°C is abnormal and may be associated with the formation of cross-links or hardening of polymer chains [1]. This indicates that a chemical process occurs inside the material directly when performing measurements using the DMA method. It is most likely that this is the process of curing the part of the binder that remained under-cured after the manufacture of chipboard [24]. Additional curing leads to an increase in the stiffness of the material and the \( G' \) value.

4. Conclusion

The analysis of the temperature dependences of the dynamic shear modulus of wood and wood composite materials using the method of digital differential spectrometry allows us to obtain information about the nature of the molecular mobility of the components forming them. Regardless of the type of material under study and the selected temperature range, the use of digital data processing reduces the subjective factor, increases the resolution of the DMA method and the accuracy of the results obtained, and allows us to evaluate the comparative intensity of transients. In particular, three temperature transitions with the boundaries 19..49, 194 were found in birch wood in the range 16..289°C..224 and 253..277°C. In the freshly cut apple tree wood, a temperature transition in the range of -21..-5°C was revealed, which determines the threshold value of frost resistance of living plant tissue. In the composite material obtained based on wood without binders, a decrease in the structural uniformity of the amorphous component was found in comparison with the material of the original wood. The changes are caused by the plasticization of the material by the decomposition products of hemicelluloses and lignin. In addition, the speed of the transition process in the amorphous part of the composite material is twice the speed of a similar process in the original wood. In the material of the inner layer of the particle board at a temperature of 137°C, the binder – resin KF-MT-15 is re-cured.

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