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UTILIZATION OF MODIFIER FOR ENHANCING THE MECHANICAL PROPERTIES OF CELLULOSE FIBERS

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Abstract
The utilization of a modifier with active centers allows obtaining new biodegradable cellulose polymers with improved mechanical characteristics. A mixture of epichlorohydrin and triethanolamine was used as the modifier at different consumption rates for treating sulfite bleached softwood fibers. The influence of the modifier consumption on the strength indicators of cellulose was demonstrated. A full factorial experiment was applied as a mathematical processing method to determine the optimal conditions for cellulose fiber modification.

Key words: *cellulose, epichlorohydrin, triethanolamine, modifier, full factorial experiment, mechanical indicators.*

The utilisation of biopolymers as alternatives to synthetic materials represents a pivotal strategy in the context of the concept of sustainable development. Consequently, the investigation of novel chemical agents (modifiers) for the treatment of cellulose fibres with the objective of enhancing their properties represents a significant area of scientific inquiry [1-3].

Cellulose is regarded as one of the most prevalent renewable natural biopolymers. It is distinguished by low toxicity and favourable conditions for biological degradation, as well as being readily amenable to modification processes. In its purest form, cellulose fibres are insoluble in both water and organic solvents, however, their mechanical characteristics do not reach the level of synthetic materials. The utilisation of such a natural polymer to supplant synthetic materials with enhanced mechanical properties enables the reduction of the detrimental impact on the environment and the establishment of an efficacious waste management system [2].

The modification of cellulose fibres was achieved by the use of a modifier, obtained by mixing triethanolamine and epichlorohydrin. The triethanolamine served as the donor of ammonium groups, while the epichlorohydrin acted as a crosslinking agent. The utilisation of such a modifier enables the enhancement of the mechanical characteristics of cellulose fibres and the expansion of their range of applications [4].

The objective of this study is to examine the impact of modifier consumption rates on cellulose fiber properties.

The preparation method of the modifier involved the mixing of epichlorohydrin and triethanolamine in an equimolar ratio of 1:1 in the presence of 1 N hydrochloric acid, followed by an exposure time at 40 °C for varying durations. The chemical reagents interact in a manner illustrated in Fig. 1.

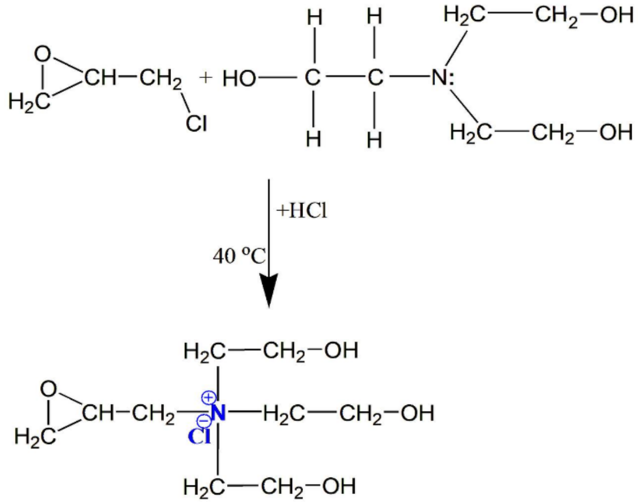

Figure 1 – The mechanism of interaction between epichlorohydrin and triethanolamine

In order to ascertain the active groups that have been formed as a consequence of the interaction between epichlorohydrin and triethanolamine, the IR spectrum of the obtained modifier was subjected to investigation (Fig. 2).

In the IR spectrum of the modifier, absorption bands at 1361 cm^{-1} and 1446 cm^{-1} are attributed to the vibrations of the -CH_2- groups, respectively, which are present in the fragment of 2-hydroxypropyltriethylammonium chloride formed as a result of the interaction between triethanolamine and epichlorohydrin. The band at 1045 cm^{-1} is attributed to the -CH_2-N group. The bands at 2885 cm^{-1} are indicative of the stretching vibrations of -OH groups, while the band at 3261 cm^{-1} is attributed to the stretching of C-N bonds.

The investigated sample exhibits bands in the intensity range from 1250 to 1020 cm^{-1}, which indicates the presence of aliphatic amines C-N. The sample exhibits intensity in the vibration range from 840 to 870 cm^{-1}, which characterizes the presence of valence vibrations of C-N bonds.

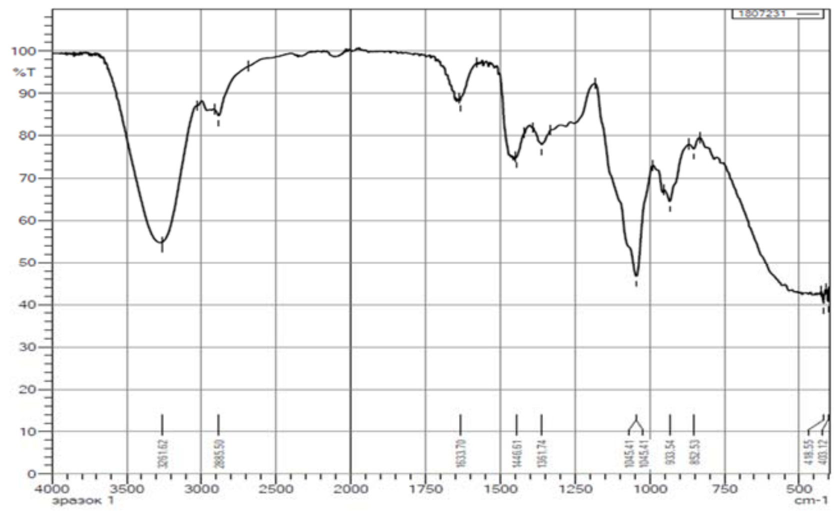

Figure 2 - IR spectrum of the modifier

In order to assess the influence of modifier consumption on the strength indicators of cellulose fibre samples, samples with a mass of 80 g/m² were prepared from sulfate bleached softwood cellulose of grade HB-5. The Schopper-Riegler degree of cellulose beating was found to be 91 ± 2 °SR. The rates of modifier consumption exhibited a range of values between 20 and 50% of the absolute dry fibre mass. The prepared fibrous mass was thoroughly mixed and placed in a thermostat at 40°C for varying durations, ranging from 30 to 120 minutes. The mixing process was conducted at regular intervals of 10 minutes to ensure uniform distribution of the modifier within the cellulose mass.

The strength indicators for the cellulose samples were determined according to the regulatory documents [5-7]: compression resistance, tensile strength, and moisture resistance. The sample testing was conducted in the accredited laboratory of the Institute of Paper LLC. The results of the research are presented in Figure 3.

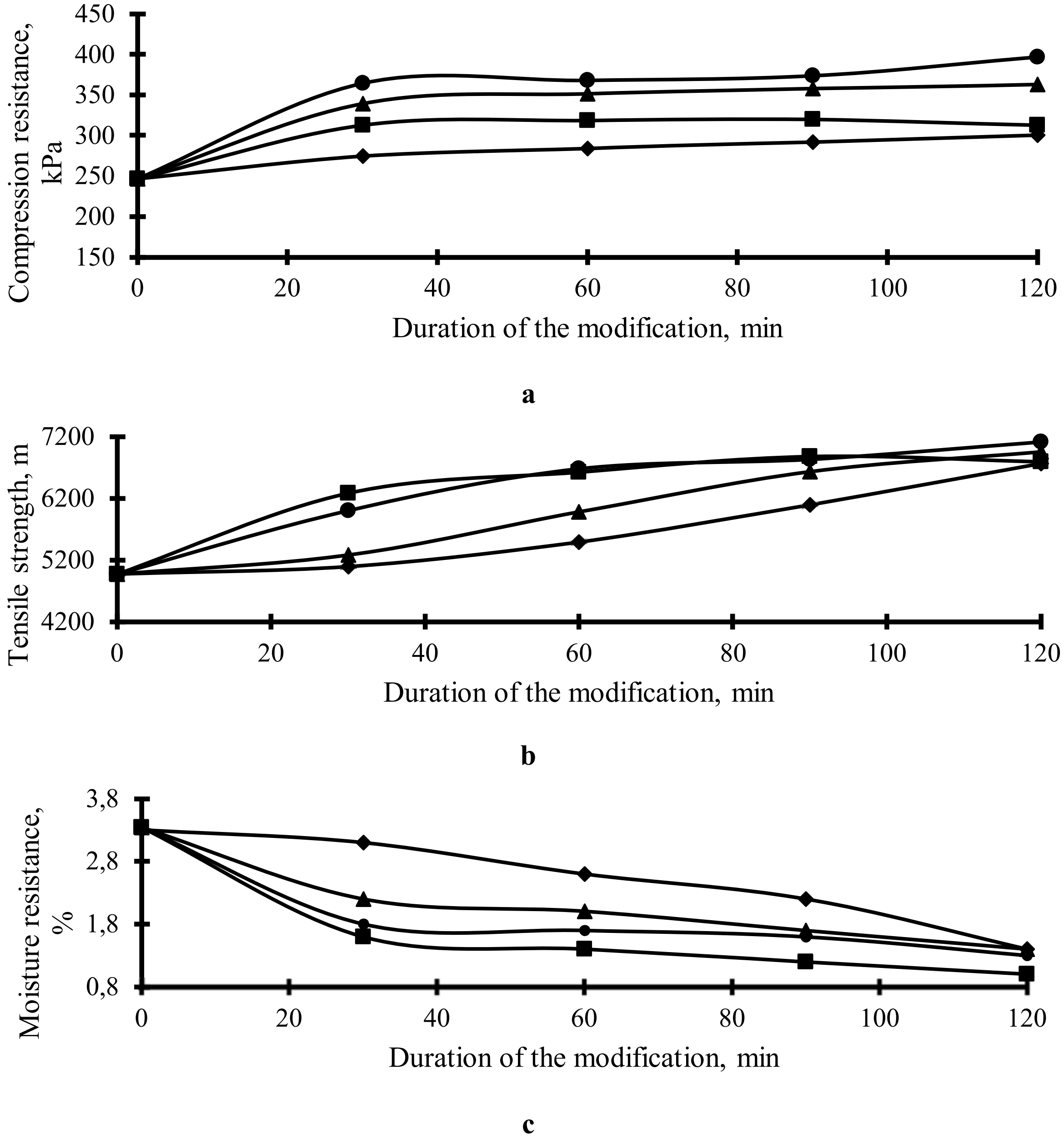

Figure 3 - Dependence of strength indicators (a - compression resistance; b - tensile strength; c - moisture resistance) of cellulose samples on modifier consumption:
♦ - 20 %, ▲ – 30 %, ● – 40 %, ■ – 50 %

The data presented indicates that an increase in modifier consumption and the duration of the cellulose fibre treatment process is associated with a 60 % increase in compression resistance. An increase in modifier consumption has a positive effect on this indicator, due to the active interaction of the OH-groups of cellulose with the active groups of the modifier. Nevertheless, when the modifier consumption reaches 50 % of the absolute dry fiber mass, a reduction in this indicator is observed. At such consumption rates, the OH-groups of cellulose react maximally with the active groups of the modifier, thereby creating obstacles for further cationisation.

With regard to the tensile strength indicator, its alteration is analogous to that observed in compression resistance, thereby substantiating the inefficacy of employing a modifier in excess of 50 % of the absolute dry fibre mass.

In Figure 3(c), the change in the moisture resistance of cellulose samples is demonstrated in relation to modifier consumption. The research has demonstrated that this indicator decreases with increasing modifier consumption. This is due to the reduction of free OH-groups in the cellulose molecule and the disruption of hydrogen bonds between water molecules.

In order to ascertain the optimal conditions for the modification process, a full factorial experiment (FFD) of type 2^n was employed as the mathematical planning method.

The selected quality indicators of the modified cellulose sample are as follows: compression resistance, kPa (Y_1); tensile strength, m (Y_2); moisture resistance, % (Y_3). The initial factors influencing the modification process are chosen as the modifier consumption, % (x_1), and the duration of modification, min (x_2).

The result of the mathematical processing of the modified cellulose fibre production process yielded regression equations that adequately describe the dependencies of the output variables Y_i on the factors x_i:

a) The mathematical model for the physical-mechanical indicator of compression resistance, kPa

$$Y_1 = +372,29 + 16,069x_1 + 10,031x_2 - 5,0468x_1 \bullet x_2 - 70,186x_1^2 - 0,18281x_2^2$$

b) The mathematical model for the physical-mechanical indicator of tensile strength, m

$$Y_2 = +6557,2 + 398,93x_1 + 559,05x_2 - 381,15x_1 \bullet x_2 - 303,75x_1^2 - 156,37x_2^2$$

c) The mathematical model for the physical-mechanical indicator of moisture resistance, %

$$Y_3 = +1,7594 - 0,5175x_1 - 0,45x_2 + 0,2745x_1 \cdot x_2 + 0,14062x_1^2 - 0,1125x_2^2$$

The regression equations indicate that modifier consumption exerts a more pronounced influence on the compression resistance indicator. An increase in consumption results in an increase in the indicator. In contrast, modification duration exerts a more pronounced effect on the tensile strength indicator. Its enhancement is accompanied by a corresponding rise in this indicator.

The modification process parameters exert opposing effects on the moisture resistance indicator. An increase in these parameters results in a reduction in the quality indicator of the cellulose material.

The optimal point is identified when the factor values of x_1 and x_2 assume the following values: modifier consumption x_1 = 40 %, modification duration x_2 = 60 min. The quality indicators of the cellulose material obtained at the optimum point are as follows: compression resistance – 368,1 kPa, tensile strength – 6680 m, moisture resistance – 1,7 %.

The statistical regression equations $Y_1 – Y_3$ were employed in a multi-criteria optimisation process utilising the Gauss-Seidel method. This enabled the determination of the compromise region for the production of modified cellulose material, contingent on the primary technological parameters (x_i), as illustrated in Fig. 4. The region is situated on the plane $x_1 – x_2$.

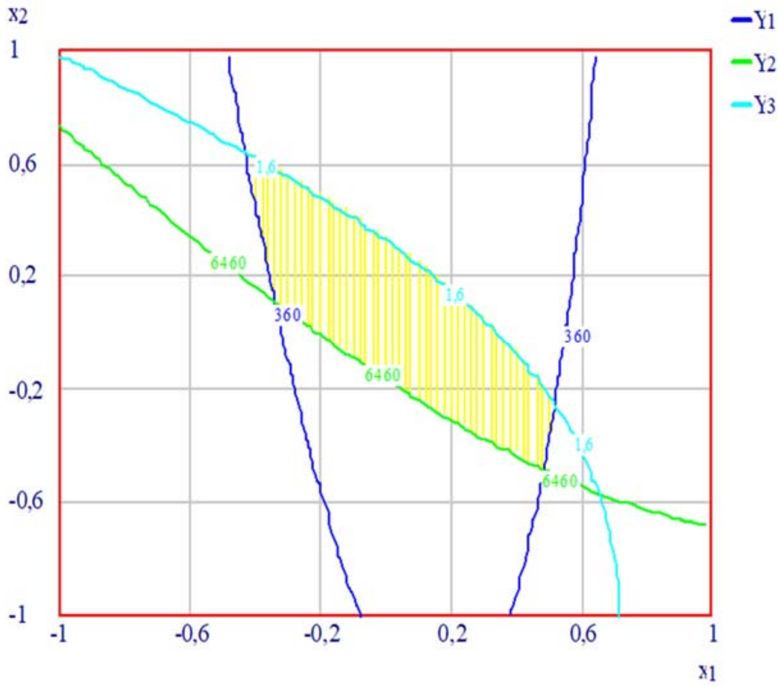

Figure 4 - Compromise region for the modification of sulfate bleached softwood cellulose: Y1 - compression resistance, kPa; Y2 - tensile strength, m; Y3 - moisture resistance, %

Conclusions. The use of a modifier with an ammonium complex allows obtaining cellulose material with improved mechanical properties and expands its application range. Such modified material is more attractive for use as a biodegradable material and can be employed for water purification purposes.

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ВИКОРИСТАННЯ МОДИФІКАТОРА ДЛЯ ПОКРАЩЕННЯ МЕХАНІЧНИХ ВЛАСТИВОСТЕЙ ЦЕЛЮЛОЗНИХ ВОЛОКОН

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Ключові слова: *целюлоза, епіхлоргідрин, триетаноламін, модифікатор, повний факторний експеримент, механічні показники.*

Анотація
Використання модифікатора з активними центрами дозволяє отримати нові біодеградабельні целюлозні полімери з покращеними механічними характеристиками. В якості модифікатора було використано суміш епіхлоргідрину та триетаноламіну за різної її витрати для оброблення сульфатних хвойних вибілених волокон. Показано вплив витрати модифікатора на показники міцності целюлози. Застосовано повний факторний експеримент в якості математичної обробки для визначення оптимальних умов модифікації целюлозного волокна.