Improvement of properties of cellulose dielectrics by their structure modification with nanocellulose produced of wastes of agricultural crops

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Abstract. A comparative study of laboratory castings of insulating paper was fulfilled: the traditional composition made of insulating cellulose of pine and cellulose, modified with the nanocellulose of the agricultural waste (composite). The positive effect of the introduction of this structure-forming modifier on the electrical and mechanical strength of the cellulose dielectric, as well as its heat resistance was revealed. Confirmation of expediency of development of works of this direction for expansion of raw material base for producing of the bio component promoting increase of working capacity of the cellulose dielectrics used in high-voltage insulation of power devices is received.

1. Introduction
Increasing electrical and mechanical strength, as well as resistance to prolonged exposure to elevated temperatures at the conditions of destructive processes in the components of paper-impregnated insulation (PII) is one of the priorities for the production of power transformers [1]. It is the aging of insulation, the resource of which is determined by the state of the cellulose dielectric, in most cases causes the failure of power transformers (PT), often with serious consequences. High quality electrical insulation paper (EIP) in its original state, in particular, good parameters of electrical and mechanical strength that strive to achieve in the production of paper, do not guarantee good heat resistance of the material. The gradual degradation of cellulose during operation of PT leads to a decrease in the degree of polymerisation of its macromolecules and mechanical destruction of paper, which is aggravated by the dynamic effects on the transformer windings at the event of short-circuit modes. Among the many ways to reduce the intensity of EIP degradation, the structural modification of the paper web, which provides strengthening of the cellulose base by introducing components that have an affinity for cellulose [1-3], is of particular practical interest.

One of the ways of such modification is the use of so-called bacterial cellulose (BC). However, the synthesis of bacterial cellulose is not only complex, but also expensive process, in particular, due to the use of food raw materials as a nutrient medium for the used strains of bacteria. Therefore, the creation of technologies that reduce the cost of a valuable product is an urgent and practically significant task. A possible direction for solving this problem is the use of oat hulls [4] for the synthesis of biopolymer from non-food renewable raw materials. The present research is devoted to...
the study of electrophysical and mechanical properties, as well as the heat resistance of prototypes of a composite made of EIC and bacterial cellulose derived from oat waste (BC MG) in accordance with the technology described in the patent [2]. If successful, we can expect to create technologies that provide cost-effective conditions for the production of bacterial cellulose in industrial volumes.

2. The objects of study and technique of the measurements

In the course of comparative tests, laboratory castings of electrical insulating paper of traditional manufacturing from industrial EIP of pine sulphate processing (sample No. 1) and experimental composite material (sample No. 2) at the manufacture of which 7.5% of biopolymer was introduced into the paper mass and was disintegrated with the Valley roll, were studied. This modifier was nanocellulose (NC) derived from the waste of a certain type of agricultural products, in particular, oat hulls. The electrical ($E_b$, kV/mm) and mechanical ($\sigma_b$, MPa) strength of these materials in the initial state were studied; as well as their heat resistance (by assessing the intensity of the reduction of the mechanical tensile strength in the process of thermal aging in an air-dry environment at the temperature of 140°C). Fragments of the samples (15x60 mm) were subjected to thermal aging during which 10 strips of each material has been tested. Preparation of test samples for measurements was carried out in accordance with the existing standard [5].

Morphological features of cellulose materials were investigated by scanning electron microscope (SEM) "Supra 55VP-25-78". Ash content ($A_{sc}$) of the studied paper samples and pH of their aqueous extract (AE) in accordance with the existing standards [6] were also measured. The sorption capacity of the standard EIP and EIP with the modified structure was determined by comparing the relative light transmission coefficients at the wavelength of 458 nm ($K_{rt.458}$, %) of transformer oil samples after its thermal aging with the test paper. Measurements were carried out using the MKMF-1 micro colorimeter in standard measuring cell (10x10 mm). More detailed information about the measurement methods used is given in [7-8].

3. Obtained results

The images of the electrical insulating paper structure obtained using SEM presented in the Fig. 1 and Fig. 2. Figure 2 is illustrating the structure-forming function of the NC in the composite where are shows the finest fibers filling the voids of the web of standard cellulose insulating paper. This modification of the cellulose dielectric web, in our opinion, led to a significant increase in its characteristics compared with the EIP made of 100% EIC. Information about the structure of the standard insulating paper and its parameters are also presented in the works of the authors [3,9-10].

![Figure 1. The obtained image of the structure of the standard electrical insulating paper. Magnification – 54.64 Kx.](image1)

![Figure 2. The obtained image of the structure of the EIP modified with BC MG. (sample No. 2). Magnification – 50.53 Kx.](image2)
It was found that the $E_b$ of the composite (sample №2) in the initial state is 1.5 times higher than the same parameter of traditional EIP. It was also found that at the process of thermal aging (studies were conducted up to 861 hours), the breakdown electric field strength decreased slightly (less than 5% for sample No.1 and less than 1% for sample No. 2).

The measured electrical and mechanical characteristics of the two insulating paper samples at initial state are summarized in Table 1. From Table 1 it follows that the mechanical characteristics of the composite (sample No. 2) exceed the characteristics of EIP of traditional manufacture (sample No. 1) in the value of the mechanical tensile strength 2.5 times, and the resistance to extrusion ($P_p$) – 2 times. It should also be noted that the pH of the aqueous extract of the composite is lower than the maximum permissible value – 9.0 (units pH), but the ash content is slightly higher than the acceptable limit by standard [6] (not more than 0.6 %).

**Table 1.** Electrical and mechanical characteristics of the studied EIP.

| The parameter          | Sample No. 1 | Sample No. 2 |
|------------------------|--------------|--------------|
| $E_b$ (kV/mm)          | 6.4 ± 0.3    | 9.6 ± 0.6    |
| $\sigma_t$ (MPa)       | 15.5         | 41.5         |
| $P_p$ (KPa)            | 2.4          | 4.7          |
| $A_{ac}$ (%)           | 0.55         | 0.8          |
| pH AE (units pH)       | -            | 6.5          |

The results of measuring changes in the mechanical strength of the EIP samples during thermal aging are shown in the Fig. 3. As can be seen from the Fig. 3 at the initial stage of thermal aging, the limit of the mechanical strength of the paper samples increased. This known effect can be explained by the gradual removal of water from the EIP samples and the formation of additional hydrogen bonds between the cellulose macromolecules. This effect is most pronounced for standard EIP samples.

![Figure 3](image_url)  
*Figure 3. The dependence of mechanical strength limit ($\sigma_t$) on thermal aging time ($t$): 1 – for the standard EIP, 2 – for EIP with modified structure (experimental points and spline approximation).*
Throughout the thermal aging process, the mechanical tensile strength limit of the sample No. 2 was more than 1.5 times higher than that of the sample No. 1. At the end of aging, the value of $\sigma_b$ of the composite (s. No. 2) was at least 2 times higher than that for standard (not modified) insulating paper (s. No. 1). It is possible to assume, as at aging time more than 1000 hours the specified regularity to remain.

The results of the coefficient $K_{rt,458}$ measurement are summarized in the Table 2. Tests have shown that at the initial stage of aging, the light transmission coefficient of the oil aging of which was carried out with a copper catalyst and composite EIP (sample No. 2) more than in the case of aging oil with copper catalyst and unmodified EIP (sample No. 1). The data in Table 2 describe the aging of petroleum transformer oil "GK" when heated it in the presence of a copper catalyst. Row 1 of Table 2 corresponds to the presence of standard EIP (s. No. 1) in the oil, line 2 – to EIP with modified structure (s. No. 2) and line 3 (“+Cu”) – for aging oil without EIP. Thus, the measurements confirm the high sorption capacity of the insulating paper with the modified structure, especially in the early stages of aging of transformer oil.

Table 2. Light transmission coefficient measured the aged oil.

| $t$ (h) | 0  | 80 | 130 | 162 | 188 | 208 | 230 | 244 | 283 | 306 | 332 | 354 | 400 |
|--------|----|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| No. 1  | 88.5 | 76.5 | 68.0 | 29.5 | 20.5 | 16.5 | 14.0 | 12.5 | 10.0 | 8.0 | 6.0 | 5.0 | 4.5 |
| No. 2  | 88.5 | 78.0 | 71.0 | 57.0 | 28.5 | 20.5 | 14.0 | 12.0 | 9.0  | 6.5 | 5.0 | 4.0 | 2.5 |
| +Cu    | 88.5 | 23.5 | 13.0 | 11.5 | 9.5  | 6.5  | 5.0  | 4.8  | 1.0  | 1.0 | 0.5 | 0.2 | 0   |

4. Conclusion

The presented results indicate the feasibility of research aimed at the use of renewable non-food raw materials (in particular, oat hulls) in the development of technologies for the synthesis of bacterial cellulose for its use, in particular, as a modifier of cellulose dielectrics, characterized by increased heat resistance and improved electrophysical properties.

References

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