CELLULOSE CHEMISTRY AND TECHNOLOGY

COMPATIBILITY OF MODIFIED *HERACLEUM SOSNOVSKYI* CELLULOSE-BASED MATERIAL WITH SOME POLYMERS

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The aim of the present work was to investigate the compatibility prediction of *Heracleum sosnovskyi* plant material, modified with monoethanolamine (N→B)-trihydroxyborate, with organopolymer binders, such as polyvinyl acetate, polyurethane and casein. To achieve the goal, the following tasks were solved: first, the composition of the modified plant materials was studied and the degree of their antifungal resistance was determined; and then, the compatibility of the modified cellulosic material and organopolymer binders was predicted based on the calculation of the Hildebrand solubility parameter by determining the cohesive energy and the van der Waals volume of elementary bonds of the modified substrate. The investigation showed that the modification of plant raw materials results in the removal of the amorphous part of the lignin-carbohydrate complex of cell walls (lignin and hemicelluloses) from the substrate composition and chemical interaction of the modifier with secondary cellulose hydroxyls. This makes the plant material fully biostable and thus it can be used in the development of composite materials. The method of mutual solubility calculation can be used to predict the compatibility of the modified plant material with organopolymer binders. Based on this method, it was found that the best compatibility is observed when an excess of casein and polyurethane are used as binders for the modified cellulose-based material. Two formulations, namely casein (excess)-modified cellulose-based material and polyurethane (excess)-modified cellulose-based material, can be recommended for developing composites.

Keywords: modified cellulose-based material, polyvinyl acetate, polyurethane, casein, compatibility, cohesion energy

INTRODUCTION

Ecofriendly technologies for the production of composites based on plant raw materials allow the development of effective materials, without harming the environment.[1-4] The nature and structural features of the main component of plant raw materials – cellulose – determine its technological properties and functionality in the creation of polymer composites. The initial raw material is modified to improve the technological properties of the cellulose filler, as well as to ensure the final product's bio- and fire resistance.[5-8] The data on polymer compatibility available in the literature provide evidence that polymers that are close in chemical structure are often not compatible with each other. At the same time, polymers that differ in their chemical nature are compatible.[9]

The thermodynamic condition of spontaneous mixing is a negative value of the Gibbs energy of mixing, which takes into account the enthalpic (H) and entropic (TΔS) factors. However, according to Gee's calculations,[10] which take into account only the combinatorial entropy of mixing due to the number of permutations of dissimilar molecules, the entropy change in polymer mixing does not play a role. However, one cannot ignore the non-combinatorial contribution to the mixing entropy due to the interaction between the components. This was confirmed experimentally for the first time in the work of Tager *et al.*, who found that for many compatible polymer-polymer pairs, negative H and S values were observed.[11] A similar conclusion was reached by Robenson and Robar,[12] who theoretically showed that polymer compatibility is possible if $H < 0$. The authors point out that negative enthalpies of mixing are often accompanied by negative values of mixing entropy, and the competition of these values determines the G sign, *i.e.*, polymer compatibility.

The predictions of thermodynamics have played a major role in understanding the mechanism of polymer compatibility and laid the scientific foundation for the development and production of new compatible compositions. In addition to the thermodynamic aspect, the compatibility of polymers is also considered from the perspective of macromolecule interaction. This is reflected in the monograph of Nesterov *et al.*,[13] who indicate two ways of improving compatibility. The first one is to link macromolecules by chemical bonds, which is achieved as a result of the synthesis of block copolymers, interpenetrating networks and cross-linking reactions of mixture components. Chemical bonding prevents macro-fragmentation of mixtures, even if the components are thermodynamically incompatible. The second way to improve compatibility is to change the chemical structure of the miscible polymers in such a way that the Gibbs energy of mixing is negative. This, in turn, is achieved in two ways: by mixing polymers characterized by the presence of functional groups capable of interacting; and by modifying one of the miscible polymers by changing the chemical structure of the monomer units or by copolymerization.

Belousov *et al.*[14] put forward the concept of "complementary difference", according to which unrestricted mixing of polymers is possible if macromolecules of each of them contain different functional groups capable of interacting with each other. It was found[15-18] that the best compatibility is observed for macromolecules with opposing functional groups. The influence of electronegativity of substituents on polymer compatibility was reviewed in earlier works.[19-22]

There is no doubt that the affinity between macromolecules of different chemical structures is related to the affinity of their monomer units. An example is the high affinity of nitrocellulose and polyvinyl acetate.[23,24] In the absence of affinity between monomer links, polymers certainly do not combine, but also, unrestricted mixing of monomers does not mean that the polymers themselves will be mutually soluble. To predict the compatibility of polymers, the following types of intermolecular interactions between them should be taken into account:[25] binding by formation of hydrogen bonds and intermolecular hydrogen bonding. Specific intermolecular interactions are also of high importance in this connection. Such interactions include dipole-dipole (orientation/Kissom), strain (induction/Debye), and dispersion (London).[26]

In our work, we used the stems of Sosnovsky's hogweed, widely distributed in the European part of the Russian Federation, which is an invasive species, as a source of plant raw material. The fight against the spread of this species across the ecosystems of the Moscow region has reached the governmental level. Since 1 November 2018, administrative liability has been introduced in the Moscow region for failing to carry out measures to remove Sosnovsky's borschievik from land plots (part 5 of Article 6.11 of Law of the Moscow region No 37/2016-OZ "Code of the Moscow region on administrative offences"). This attitude towards this species is caused by the high risk it poses to humans through contact with its foliage during the active vegetation period. Furanocoumarins contained in the green parts cause severe burns and poisoning.[27,28] Thus, we tried to solve two problems at once: to save on raw materials for the production of composites and, by removing the vegetative parts of the hogweed from the composition of plant communities, to clean the ecosystems of the region from its presence.

Due to the porous structure of its stems, the biomass of hogweed can be used for the production of heat-insulating composite materials. The raw material was collected in autumn, after the end of the active vegetation period. Dried stems of hogweed are not dangerous. The collected material was cleaned, ground and modified with boron-nitrogen compounds to make it more biostable. The main achievements in this direction have been published previously.[29,30] In the present work, we attempted to predict the compatibility of modified plant material with some polymers to create thermal insulation composites. This was the aim of the work.

EXPERIMENTAL

The raw material used was the stems of Sosnowsky's hogweed. The stems were cleaned of surface impurities, dried and ground to 5 mm. In the chopped state, the material was air-dried to constant weight. The modification of the chopped stems was carried out with an aqueous solution of monoethanolamine (NB)-trihydroxyborate (MEATHB) at a 30% concentration by weight of the modifier, and the pH of the solution was 8.8. The modification was carried out by the immersion method, with constant stirring for 3 hours, at the temperature of 25 °C. After the modification, the samples were air dried to constant weight. Then, a threefold extraction with distilled water was carried out to remove excess unreacted modifier, and the samples were again air dried to constant weight at room temperature.

The surface layer of the samples was examined by infrared spectroscopy. Measurements were made on a Bruker Vertex 70v FTIR spectrometer, with an NPVO GladyATR attachment from PIKE (USA), with a diamond working element. Spectra were obtained directly from finely ground samples, without additional preparation. The measured spectra by the method of disturbed total internal reflection (DNIR) were converted into absorption spectra by taking into account the wavelength dependence of the infrared radiation penetration depth into the sample, using the OPUS software included in the instrument software.

Tests of modified and control samples for resistance to fungi were carried out in the Laboratory of Tropical Technologies of IPE RAS, according to GOST 9.048-89.

Based on criteria (1) and (2) proposed in earlier works,[31–35] a compatibility analysis of modified monoethanolamine (NB)-trihydroxyborate (MEATHB) hogweed pulp with organopolymer binders was performed.

Compatibility is observed if the condition is fulfilled when the first polymer is introduced into the second polymer:

$$\mu_1 = \frac{\delta_{p,1}^2}{\delta_{p,2}^2} < 1.374\beta_1 \tag{1}$$

and when introducing the second polymer into the first one:

$$\mu_2 = \frac{\delta_{p,2}^2}{\delta_{p,1}^2} < 1.374\beta_2 \tag{2}$$

where δ_1 and δ_2 are parameters of solvability of polymers 1 and 2, respectively.

According to Lesar *et al.*:[35]

$$\beta_1 = F\left(F - \sqrt{F^2 + \frac{\gamma_{p,1}}{\gamma_{p,2}} - 2F\left(\frac{\gamma_{p,1}}{\gamma_{p,2}}\right)^{0,5}}\right) \tag{3}$$

$$\beta_2 = F\left(F - \sqrt{F^2 + \frac{\gamma_{p,2}}{\gamma_{p,1}} - 2F\left(\frac{\gamma_{p,2}}{\gamma_{p,1}}\right)^{0,5}}\right) \tag{4}$$

where $\gamma_{p,1}$ and $\gamma_{p,2}$ are surface energies of polymers 1 and 2, respectively. The value F (5) is calculated via the ratio of polymers' molar volumes:[35]

$$F = \frac{4\left(V_{p,1}V_{p,2}\right)^{1/3}}{\left(V_{p,2}^{1/3}+V_{p,1}^{1/3}\right)^2} \tag{5}$$

where $V_{p,1}$ and $V_{p,2}$ are molar volumes of polymers 1 and 2, respectively.

By means of the computer program "Cascade" (INEOS RAS), the compatibility prediction of widespread polymers can be made by calculating the values of surface tension (γ), solubility parameter (δ) and molar volume (V), required for compatibility analysis. However, since the structure of the modified cellulosic material is not included in the "Cascade" software, the calculations were done manually.

To experimentally confirm the compatibility of the modified substrate with organopolymer binders, they were tested to determine the bond strength of the components by the cylinder tear-off method, in accordance with GOST 32299-2013 (ISO 4624: 2002), using a DYNA Z...E device, with a DYNAMETER electronic display unit.

The composition of the plant material before and after modification was determined as follows. The cellulose content was determined by the method of Kürschner and Hoffer based on nitric acid and alcohol; the lignin content was determined by the Klason method using 72% sulfuric acid; the amount of hemicelluloses was analyzed by treatment with 2% hydrochloric acid, followed by precipitation of the obtained furfural by the bromide-bromate method. In addition, the content of extractive substances soluble in organic solvents was determined.

RESULTS AND DISCUSSION

Infrared spectroscopy data (Fig. 1) show that the lignin-carbohydrate complex of cell walls changes significantly when hogweed stems are treated with monoethanolamine-(N→B)-trihydroxyborate. Most of the changes in the impregnated substrate can be seen in the peaks relating to hemicelluloses (1737, 1268, 1100, 1056 cm^{-1}) and lignin (1601, 1268 cm^{-1}). These changes are the result of depolymerisation of lignin and hemicelluloses caused by the modifier, whereas cellulose has not been depolymerised, which ensures a reliable fixation of the modifier in the composite.[36-39]

After modification, the 1735 cm^{-1} band practically disappears and the intensity of the 1580 cm^{-1} absorption band decreases significantly. This indicates chemical interaction of lignin hydroxyls with the modifier molecules and hydrolysis of the aromatic component of the lignin-carbohydrate complex of hogweed.[36-39] The structure of the broad absorption band in the range of 1200–1500 cm^{-1} is altered. The changes indicate a chemical interaction of the modifier with the substrate. The broad absorption band appearing after modification in the 1315–1470 cm^{-1} region (Fig. 1) indicates the presence of an N→B coordination bond in the modified substrate.[36–39] We also see the appearance of a band around 1630 cm^{-1}, which corresponds to the NH_2 binding effect in the spectra of the samples.[36-39]

The results of the analysis of the composition of the plant materials before and after modification are presented in Table 1. A comparative analysis of the plant materials, before and after modification, shows significant differences in the component composition (Table 1). In particular, it concerns the content of lignin and hemicelluloses.

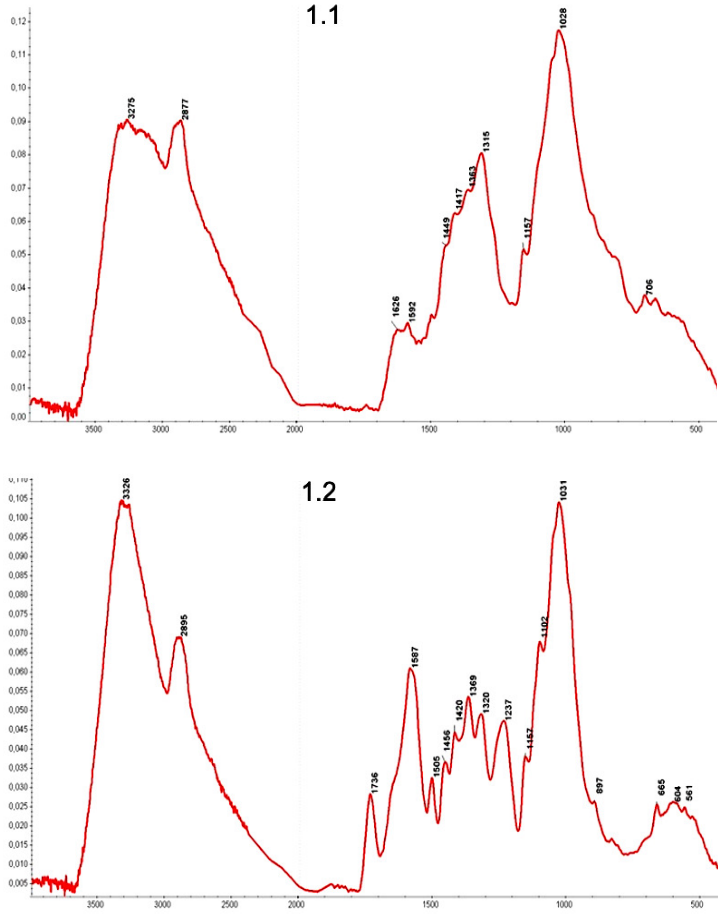


Figure 1: Infrared spectra of modified and control specimens: 1.1 – modified specimen; 1.2 – control (unmodified) specimen

Table 1
Composition of *Heracleum sosnovskyi* plant material in % by mass

Sample	Cellulose, %	Lignin, %	Hemicelluloses, %	Extractives, %
Unmodified sample	60.19	24.00/24.00*	6.80	7.27
Sample modified with monoethanolamine(NB)-trihydroxyborate	61.27	22.00/8.00*	63.60**	8.00

*lignin content after extraction with organic solvents; **inflated value explained in the text

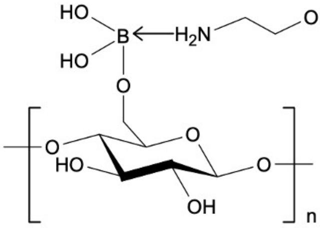


Figure 2: Structure of modified unit cell of cellulose

Here, it is necessary to make some explanations. Lignin was determined before and after extraction with organic solvents. As a result of the experiment, it was found that, after extraction, the lignin content in the modified samples decreased sharply (Table 1). This can be explained by the fact that the alkaline modifier causes destruction of lignin macromolecules, which, when determined before extraction, form resin-like fine unfiltered products, defined as Klason lignin, in the amount of 22.00% by mass. After extraction of the modified samples, most of the degraded lignin fragments are removed from the substrate composition and we detect only 8.00% lignin by weight, which is in good agreement with the infrared spectrometry data presented in Figure 1, in which we detect no aromatic hydroxyls. Taking into account the high reactivity of aromatic hydroxyls in the composition of low-molecular-weight lignin of grassy raw material, it is likely to be assumed that not only the destruction process, but also the formation of low-molecular-weight ethers took place under the action of the modifier.

When determining hemicelluloses in the modified samples, we obtained overestimated results (Table 1). We rechecked several times and each time obtained a confirmation of 63.60% of hemicelluloses by mass, determined after treatment with hydrochloric acid. The following explanation can be given. The alkaline modifier promotes the depolymerization of the cellulose macromolecules. The Küschner method does not pick this up. Fragments of partially depolymerized cellulose are detected as hemicelluloses in subsequent experiments with hydrochloric acid. Thus, the modification of Sosnovsky's hogweed stems by monoethanolamine-(N→B)-trihydroxy-borate changes the component composition and the structure of the lignin-carbohydrate complex of the substrate in the direction of reducing the degree of polymerization and the formation of esters. Considering the changes in the characteristic frequencies in the IR spectra of modified samples after extraction, compared to the IR spectra of unmodified samples, we can speak of a chemical interaction of the modifier with the substrate, which takes place with the most reactive secondary carbon atom of cellulose. Furthermore, because the IR spectroscopy data show nearly complete hydrolysis of hemicelluloses and lignin, the substrate composition is mainly represented by modified cellulose, the elementary bond structure of which is shown in Figure 2.

Table 2 and Figure 3 show the results of the biostability tests on modified and control samples. In accordance with GOST 9.048-89, the samples were placed in open Petri dishes and infected with a suspension of spores of fungi: *Aspergillus niger* van Tieghem, *Aspergillus terreus* Thom, *Aureobasidium pullulans* (de Bary) Arnaud, *Paecilomyces varioti* Bainier, *Penicillium funiculosum* Thom, *Penicillium ochro-chloron* Biourge, *Scopulariopsis brevicaulis* Bainier, *Trichoderma viride* Pers. ex Fr. Inoculated specimens were placed in a desiccator and incubated for 28 days under optimal fungal growth conditions: temperature at 27–28 °C and 98% humidity. At the end of the tests, the stage of fungal development was evaluated in scores, according to a 6-point scale (GOST 9.048-89): 0 points – absolutely clean samples, no germinated conidia and colony development (visually and under the microscope); 1 point – visually clean samples, under the microscope only small foci of mycelium in the form of individual spots are visible, sporosis is absent; 2 points – superficial mycelium development in the form of numerous spots, sporosis is absent; 3 points – mycelium abundantly growing on the surface of the sample, sporoferrulation started; 4 points – visual inspection clearly shows continuous mycelium growth and sporoferrulation; 5 points – mycelium deeply penetrating the whole sample with intensive sporoferrulation.

From the data presented, it is clear that the control samples, not treated with MEATHB, presented fungal growth on 100% of the surface; they showed intensive mycelial development of all types of fungal test cultures. The biostability of these samples was 0%. Samples modified with a 30% solution of MEATHB showed no fungal overgrowth at 100% biostability (Table 2 and Fig. 3). Thus, the modifier as part of the substrate prevents the development of fungi and provides 100% bioresistance.

Table 2
Fungal resistance of *Heracleum sosnowskyi* crushed stems (untreated and treated with MEATHB) after 28 days of fungal exposure

Sample and % MEATHB	Appearance	Point	Biostability, %
Heracleum sosnowskyi crushed stems treated with 50% MEATHB	Visually and through the microscope: the absence of conidium and germinated fungal spores	0	100
Untreated crushed stems of *Heracleum sosnowskyi*	100% of surface is covered by filamentous fungi and germinated fungal spores	5	0


3.1 3.2

Figure 3: Appearance of *Heracleum sosnowskyi* stem specimens after 28 days of antifungal resistance testing; 3.1 – reference (unmodified) specimens; 3.2 – modified specimens

Table 3
Chemical bond lengths and intermolecular radii of atoms

Lengths (d_i)	Value (Å)
d_{H-O}	1.08
d_{B-O}	1.35
d_{B-N}	1.60
d_{N-H}	1.08
d_{N-C}	1.37
d_{C-O}	1.50
d_{C-H}	1.08
d_{C-C}	1.54
Radius (R_i)	**Value (Å)**
R_O	1.36
R_H	1.17
R_B	1.65
R_C	1.80
R_N	1.57

To determine the compatibility of the modified plant material with organopolymer binders, such as polyvinyl acetate (PVA), polyurethane (PU), and casein, the solubility parameters of the elemental link of modified cellulose and the listed binders were calculated.

The van der Waals atomic volumes (ΔVi) were calculated by the following formula:[35]

$$\Delta V_i = \frac{4}{3} * \pi R^3 - \sum_i \pi h_i^2 (3R - h_i) \qquad (6)$$

where R is the intermolecular radius of a given atom, and h_i is the height of the globular segment, which is cut off at a given atom by a chemically bonded atom adjacent to it. The values of h_i were calculated by the formula:[35]

$$h_i = R - \frac{R^2 + d_i^2 - R_i^2}{2d_i} \quad (7)$$

where R_i is the intermolecular radius of the neighbouring chemically bonded atom; d_i is the chemical bond length. The chemical bond lengths are given in Table 3.[35,40,41] The intermolecular radii of the atoms are also given in Table 3.[35,40,41]

Let us plot the modified fragment of the cellulose elementary unit, for which solubility parameters were calculated, separately, in Figure 4, and mark with dashes the recurring atoms of elements in its composition having a similar environment. The calculated values of the heights of the globular segments and the van der Waals volumes of the atoms calculated on this basis are shown in Table 4.

Based on the data in Table 4, we calculated the van der Waals volume of a repeating fragment of cellulose modified with MEATHB:

$$\sum_i \Delta V_i = 2 * \Delta V_{O'} + \Delta V_{O''} + \Delta V_{O'''} + 2 * \Delta V_{C'} + \Delta V_{C''} + \Delta V_B + \Delta V_N + 2 * \Delta V_{H'} + 3 * \Delta V_{H''} + 6 * \Delta V_{H'''}$$

$$\textstyle\sum_i \Delta V_i = 2 * 7.101 + 3.64 + 5.6 + 2 * 16.21 + 14.63 + 10.48 + 5.8 + 2 * 3.5 + 3 * 4.7 + 6 * 2$$

$$\sum_i \Delta V_i = 119.75 \text{ Å}^3$$

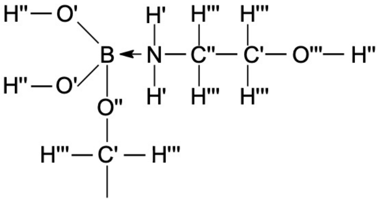


Figure 4: Modified cellulose elementary unit

Table 4
Estimated values of the spherical segment heights and van der Waals volumes of the atoms

Atom	h_i, Å	ΔVi, Å³
O'	$h_{O-H} = 0.597$ $h_{O-B} = 1.008$	7.101
O''	$h_{O-C} = 1.073$ $h_{O-B} = 1.008$	3.637
O'''	$h_{O-C} = 1.074$ $h_{O-H} = 0.598$	5.6
C'	$h_{C-O} = 0.586$ $h_{C-H} = 0.394$ $h_{C-C} = 1.03$	16.21
C''	$h_{C-N} = 0.8321$ $h_{C-H} = 0.394$ $h_{C-C} = 1.03$	14.63
B	$h_{B-O} = 0.652$ $h_{B-N} = 0.770$	10.48
N	$h_{N-B} = 0.851$ $h_{N-H} = 0.523$ $h_{N-C} = 1.168$	5.8
H'	$h_{H-N} = 1.137$	3.5
H''	$h_{H-O} = 0.853$	4.7
H'''	$h_{H-C} = 1.496$	2.0

The cohesive energy was calculated by the following formula (8) :[35]

$$\textstyle\sum_i \Delta E_i^* = 4 * \Delta E_O^* + 11 * \Delta E_H^* + 3\Delta E_C^* + \Delta E_N^* + \Delta E_h^* + x$$

$$\sum_i \Delta E_i^* = 4 * 596 + 11 * 200 + 3 * 2300 + 5040 + 16423 + x$$

$$\sum_i \Delta E_i^* = 32947 + x$$

where x – cohesive energy of boron atom.

The value $\delta_{п}$ was calculated by Equation 9:[35]

$$\delta_{P1}^2 = \frac{\Delta E^*}{N_A * \sum_i \Delta V_i} = \frac{\sum_i E_i^*}{N_A * \sum_i \Delta V_i} \qquad (9)$$

where $\Delta E^* = \mathrm{k}\Delta E_0$ is the cohesive energy of a liquid or repeating polymer link decreasing as many times as the van der Waals volume of the molecule or link is less than the molar volume; k is the liquid or polymer's molecular packing factor; and is the Avogadro number.

The Gildebrand solubility parameter was calculated according to the relation:[35]

$$\delta_{P1} = \sqrt{\frac{\sum_i E_i^*}{N_A * \sum_i \Delta V_i}} \qquad (10)$$

In our case, the value δ depends on the value x:

$$\delta_{P1} = \sqrt{\frac{\sum_i E_i^*}{N_A * \sum_i \Delta V_i}} = \sqrt{\frac{32947 + x}{0.6023 * \sum_i \Delta V_i}} = \sqrt{\frac{32947 + x}{0.6023 * 119.75}} = \sqrt{\frac{32947 + x}{72.125}}$$

Surface tension was estimated by Equation 11:[35]

$$\gamma_{P1} = \frac{A_j * \sum_i E_i^*}{\sum_i \Delta V_i^{\frac{2}{3}}} \qquad (11)$$

where, according to the literature,[35] $A_j = 0.0287$. Then, the surface tension of the repeating fragment of *Heracleum Sosnowskyi* cellulose-based material modified with MEATHB was calculated by the relation (12):

$$\gamma_{P1} = \frac{A_j * \sum_i E_i^*}{\sum_i \Delta V_i^{\frac{2}{3}}} = \frac{0.0287 * (32947 + x)}{(119.75)^{\frac{2}{3}}} = 0.0011813127(26351 + x)$$

The values of δ and γ at different values of x are given in Table 5.

The molar volume was calculated using Equation 13:[35]

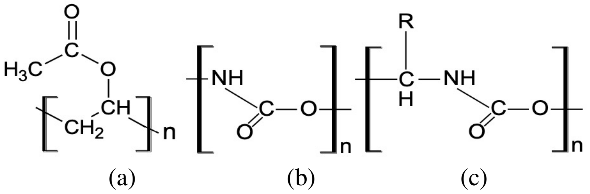
$$V_{P1} = \frac{N_A * \sum_i \Delta V_i}{k} = \frac{0.6023 * 119.75}{0.681} \qquad (13)$$

$$V_{P1} = 105.92\ \text{Å}^3$$

The solubility and surface tension parameters for the organopolymer binders under study, *i.e.* polyvinyl acetate (PVA), polyurethane (PU) and casein, were calculated in a similar way. The structures of the elementary units of these polymers, for which the calculations were carried out, are shown in Figure 5.

Table 5
Solubility parameter δ and surface tension γ for the repeating unit of cellulose modified by MEATHB at different values of x

Value x, J/mol	Solubility parameter δ, $(J/cm^3)^{1/2}$	Surface tension γ, mN/m^2
0	21.37	38.92
1000	21.69	40.10
3000	22.32	42.46
3640	22.52	43.22
5000	22.94	44.83
7500	23.68	47.78
10000	24.40	50.73



(a) (b) (c)

Figure 5: Structures of elementary units for polymer binders: (a) PVA, (b) PU, (c) casein

The obtained values were used to calculate the compatibility criteria of the cellulose-based material with the organopolymer binders. Calculation results are presented in Tables 6, 7 and 8. The data in the tables show that when the modified plant material is mixed with PVA, for almost all but zero values of boron atom cohesive energy, compatibility is observed for an excess of modified cellulose. For an excess of PVA, only at zero boron atom cohesive energy, satisfactory compatibility is likely (Table 6). When polyurethane and casein are used as binders for the modified cellulosic material, satisfactory compatibility is likely with an excess of binders at all boron atom cohesive energy values (Tables 7 and 8).

From Equations 1 and 2, it is clear that the polymer unit-particle compatibility is probable, provided that (1.374β1/μ1) > 1 and (1.374β2/μ2) > 1. It is evident that the greater the absolute value of the quotient, the greater the compatibility of the polymers. Figure 6 shows compatibility curves for various polymer pairs at different values of boron atom cohesive energy (x-value). The figure shows that the modified cellulosic material (excess)-polyurethane pair has the worst compatibility of the polymer pairs studied. The modified cellulosic material (excess)-casein and modified cellulosic material-PVA (excess) pairs have slightly better, but still unsatisfactory compatibility. The above polymer pairs, in the above ratios, cannot be recommended for composites, because of unsatisfactory predicted compatibility.

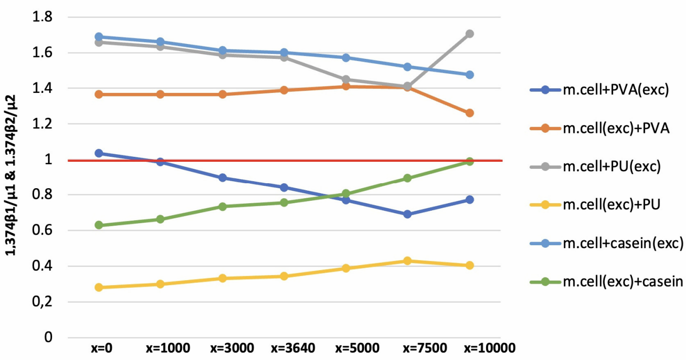


Figure 6: Dependence of modified cellulose-based material compatibility with some polymers on the value of cohesive energy for boron atom (x) and polymer nature

Table 6

Solubility parameters for modified cellulose-based material and polyvinyl acetate

Modified cellulose-based material			Polyvinyl acetate		F	Excess of polyvinyl acetate			Excess of modified cellulose-based material		
Value x, J/mol	δ_{P1}	$\gamma_{P,1}$	$\delta_{P,2}$	$\gamma_{P,2}$		β_1	μ_1	$1.374\beta_1$	β_2	μ_2	$1.374\beta_{21}$
0	21.37	38.92	19.6	32.6	0.995	0.894^{*}	1.188^{*}	1.229^{*}	0.911^{*}	0.917^{*}	1.252^{*}
1000	21.69	40.10				$0.878^{\ddagger}$	$1.224^{\ddagger}$	$1.206^{\ddagger}$	0.898^{*}	0.904^{*}	1.234^{*}
3000	22.32	42.46				$0.846^{\ddagger}$	$1.296^{\ddagger}$	$1.162^{\ddagger}$	0.873^{*}	0.878^{*}	1.199^{*}
3640	22.52	43.22				$0.836^{\ddagger}$	$1.368^{\ddagger}$	$1.149^{\ddagger}$	0.865^{*}	0.855^{*}	1.188^{*}
5000	22.94	44.83				$0.815^{\ddagger}$	$1.458^{\ddagger}$	$1.120^{\ddagger}$	0.849^{*}	0.828^{*}	1.167^{*}
7500	23.68	47.78				$0.777^{\ddagger}$	$1.549^{\ddagger}$	$1.068^{\ddagger}$	0.823^{*}	0.804^{*}	1.130^{*}
10000	24.40	50.73				$0.740^{\ddagger}$	$1.319^{\ddagger}$	$1.017^{\ddagger}$	0.798^{*}	0.871^{*}	1.097^{*}

* - polymers are compatible; ‡ - polymers are incompatible

Table 7

Solubility parameters for modified cellulose-based material and polyurethane*

Modified cellulose-based material			Polyurethane		F	Excess of polyurethane			Excess of modified cellulose-based material		
Value x, J/mol	δ_{P1}	$\gamma_{P,1}$	$\delta_{P,2}$	$\gamma_{P,2}$		β_1	μ_1	$1.374\beta_1$	β_2	μ_2	$1.374\beta_2$
0	21.37	38.92	27.09	63.55	0.959	0.751^{*}	0.622^{*}	1.031^{*}	$0.615^{\ddagger}$	$3.012^{\ddagger}$	$0.845^{\ddagger}$
1000	21.69	40.10				0.762^{*}	0.641^{*}	1.047^{*}	$0.633^{\ddagger}$	$2.923^{\ddagger}$	$0.870^{\ddagger}$
3000	22.32	42.46				0.784^{*}	0.679^{*}	1.077^{*}	$0.667^{\ddagger}$	$2.760^{\ddagger}$	$0.916^{\ddagger}$
3640	22.52	43.22				0.791^{*}	0.691^{*}	1.087^{*}	$0.677^{\ddagger}$	$2.712^{\ddagger}$	$0.931^{\ddagger}$
5000	22.94	44.83				0.806^{*}	0.764^{*}	1.107^{*}	$0.734^{\ddagger}$	$2.615^{\ddagger}$	$1.009^{\ddagger}$
7500	23.68	47.78				0.832^{*}	0.811^{*}	1.143^{*}	$0.767^{\ddagger}$	$2.453^{\ddagger}$	$1.054^{\ddagger}$
10000	24.40	50.73				0.857^{*}	0.691^{*}	1.178^{*}	$0.677^{\ddagger}$	$2.310^{\ddagger}$	$0.931^{\ddagger}$

* - polymers are compatible; ‡ - polymers are incompatible

Table 8
Solubility parameters for modified cellulose-based material and casein*

Modified cellulose-based material			Casein		F	Excess of casein			Excess of modified cellulose-based material		
Value x, J/mol	δ_{P1}	$\gamma_{P,1}$	$\delta_{P,2}$	$\gamma_{P,2}$		β_1	μ_1	$1.374\beta_1$	β_2	μ_2	$1.374\beta_{21}$
0	21.37	38.92	26.5	57.37	0.995	0.798*	0.650*	1.097*	0.701‡	1.537‡	0.964‡
1000	21.69	40.10				0.810*	0.670*	1.113*	0.719‡	1.492‡	0.988‡
3000	22.32	42.46				0.834*	0.710*	1.145*	0.752‡	1.409‡	1.033‡
3640	22.52	43.22				0.841*	0.722*	1.156*	0.762‡	1.384‡	1.046‡
5000	22.94	44.83				0.857*	0.749*	1.177*	0.782‡	1.335‡	1.074‡
7500	23.68	47.78				0.884*	0.799*	1.215*	0.816‡	1.252‡	1.121‡
10000	24.40	50.73				0.911*	0.848*	1.252*	0.848‡	1.179‡	1.165‡

* - polymers are compatible; ‡ - polymers are incompatible

Table 9
Adhesive strength of composites

Composite components	Component ratio	Average adhesive strength, MPa
Modified cellulose-based material and polyurethane	Excess of modified cellulose-based material	0.117
	Excess of polyurethane	0.213
Modified cellulose-based material and polyvinyl acetate	Excess of modified cellulose-based material	0.045
	Excess of polyvinyl acetate	0.104
Modified cellulose-based material and casein	Excess of modified cellulose-based material	0.100
	Excess of casein	0.132

The test results for determining the adhesion strength of the components are shown in Table 9. Regardless of the panel type, there is a definite difference in this mechanical property. The average results range from 0.117 MPa to 0.213 MPa for polyurethane binder panels, which exceeds the minimum value (0.1 MPa) recommended by ANSI A208 for low-density panels (ANSI A208, 1999). Then, for casein bound panels, the average results range from 0.100 MPa to 0.132 MPa, which also exceeds the minimum value (0.1 MPa) recommended by the standard.

Meanwhile, for PVA boards, only boards with PVA concentrations greater than those of the modified cellulosic material mass have a mean value of 0.132 MPa, exceeding the minimum value (0.1 MPa) recommended by ANSI A208 for low-density boards (ANSI A208, 1999), while the boards with mass concentrations less than that of the modified cellulosic material have an average value below the minimum value (0.1 MPa) recommended by ANSI A208 for low-density panels (ANSI A208, 1999).

It should be noted that the data in Table 8 correlate with those in Tables 6 and 7. According to Table 6, the best compatibility of the modified plant material with the polyurethane binder is observed when an excess of the latter is used. In turn, as we can see from the data in Table 8, when using an excess of polyurethane binder, a higher value of adhesion strength to the substrate is observed compared to the composition, in which an excess of modified vegetable material was used. A similar pattern is observed when using casein as a binder (Tables 7 and 8). As for the use of PVA as a binder, unsatisfactory bonding strength is observed when an excess of modified plant material is used. Although according to the calculations in Table 5, the best compatibility is observed in this case. Tables 5 and 8 show the correlation between the calculated compatibility values and the value of adhesion strength of the components when using PVA. This is observed only at a zero value of x.

Modified cellulose-based material-casein (excess) has the best compatibility of all the investigated polymer pairs. The second most compatible is the modified cellulose-based material-polyurethane (excess) pair. The high affinity of casein and polyurethane, consisting of elementary fragments found in living material and natural polymer cellulose, explains the noticeable difference between these polymer pairs and the less compatible modified cellulose-based material (excess)-PVA pair.

CONCLUSION

Thus, the following conclusions can be made on the basis of the conducted research. The modification of plant raw materials by an aqueous solution of monoethanolamine-(N→B) trihydroxyborate results in the removal of the amorphous part of the lignin-carbohydrate complex of cell walls – lignin and hemicelluloses – from the substrate composition and chemical interaction of the modifier with secondary cellulose hydroxyls. This makes the plant material fully biostable and it can be used to develop composite materials based on it. The method of mutual solubility calculation can be used to predict the compatibility of modified plant cellulose with organopolymer binders. Based on this method, it is found that the best compatibility is observed when an excess of casein and polyurethane are used as binders for the modified cellulosic material. Two formulations, namely casein (excess)-modified cellulosic material and polyurethane (excess)-modified cellulosic material, can be recommended for the development of composites.

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