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Chemistry

BAMBOO-CONTAINING COMPOSITES WITH ENVIRONMENTALLY FRIENDLY BINDERS

Omar Mukbaniani[1,2], Tamara Tatrishvili[1,2,✉], Nikoloz Kvnikadze[1,2], Tinatini Bukia[2,4], Nana Pirtskheliani[2,3], Tamar Makharadze[2,4], Gia Petriashvili[4]

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Abstract. The environmentally friendly binder – poly [(trimethoxy)4-vinylphenethyl)] silane was synthesized for the first time via Friedel-Crafts alkylation reaction, which was conducted by the reaction of polystyrene with vinyltrimethoxysilane in the presence of anhydrous $AlCl_3$. The synthesized polymer was identified using ^1H, ^{13}C, ^1H COSY NMR, and FTIR spectroscopy.
Bamboo sawdust-based composites with various dispersion properties have been created using synthetic trimethoxysilylated polystyrene (TMSPSt) and styrene with various degrees of silylation (5-10%).
Composite materials based on bamboo powder with various organic/inorganic additives, flame retardants, and antioxidants, were processed at different temperatures and pressures using the hot pressing method. Obtained composites were studied by Fourier transformation infrared spectroscopy (FTIR), optical and scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS).
Thermal stability of the obtained materials was determined by thermogravimetry and the Vicat method. Also, water absorption and some mechanical properties were studied.

Keywords: Friedel-Crafts reaction, silylated polystyrene, antipirene, bamboo powder, FTIR and NMR spectroscopy, mechanical properties.

[1] Ivane Javakhishvili' Tbilisi State University, Department of Macromolecular Chemistry. I. 1 Chavchavadze Ave. Tbilisi 0179, Georgia
[2] Institute of Macromolecular Chemistry and Polymeric Materials, Ivane Javakhishvili Tbilisi State University, I. Chavchavadze Ave, 13, Tbilisi 0179, Georgia
[3] Sokhumi State University, Faculty of Natural Sciences, Mathematics, Technologies, and Pharmacy. 61 Politkovskaya St., Tbilisi 0186, Georgia
[4] Vladimir Chavchanidze Institute of Cybernetics of the Georgian Technical University. 5 Z. Andjzaparidze St., 0186, Tbilisi Georgia
✉ *tamar.tatrishvili@tsu.ge*

1. Introduction

Currently, the use of petroleum-based plastics in everyday human activities is increasing.[1] Due to the worldwide growing usage of plastics and the depletion of fossil fuel resources, researchers are increasingly looking for alternatives to petroleum-based matrices that can reduce environmental contamination.[2-5] The combination of both polymers and natural fibers is the appropriate response to this issue.

Additionally, natural resources help avoid air pollution caused by open burning by farmers and reduce the amount of generated waste.[6-8]

Natural fiber composites are in high demand in manufacturing industries, such as transmission towers, automotive, construction, aerospace, furniture, and packaging industries.[9-14] One of the natural resources emphasized is bamboo trees.

There are many types of natural fiber-producing sources from plants such as flax, straw, wood, rice husks, wheat, barley, wheat, rye, sugar cane (sugar and bamboo), grass, reeds, kenaf, hemp, oil palm, empty fruit bunches, sisal, coir, water hyacinth, kapok, mulberry paper, raphia, banana fiber, pineapple leaf fiber, and papyrus.[15] Among them, bamboo fiber is one of the most promising substitutes for synthetic fiber. In addition to its strength, stiffness, and low density, it is cheap, readily available, has a short growth cycle, environmentally friendly, highly flexible, easy to develop, and biodegradable.[15-18]

Natural fibers for producing bio composites are an emerging area in polymer science. The rise in ecological anxieties has forced scientists and researchers worldwide to find new environmental materials. Therefore, it is necessary to expand knowledge about the properties of bamboo fiber composites to broaden the range of their application.[19]

Bamboo is a renewable raw material that is universally accepted for building construction. It plays a fundamental role in industrial and domestic economics in many developing countries.[20] The bamboo-based industries have developed into a multi-million dollar industry with the wide range of products. The products are in great demand both locally and abroad.[21,22]

Various researchers indicated the different values of tensile strength for various forms of bamboo fibers and the following cases were used to analyze the tensile behavior of the bamboo in several forms: chemical isolation, bundle fiber examination, examination of the puny bamboo strip and mechanical separation of vascular bundles. Chemical isolation process enhanced the tensile behavior of the bamboo compared with mechanical separation technique.[23,24]

2. Experimental

2.1. Materials

The composites based on dry bamboo powder plus trimethoxysilylated polystyrene and styrene as a binder and reinforcement agent with different degree of silylation have been obtained.[25]

All synthetic manipulations were carried out under an atmosphere of dry nitrogen gas. All solvents were degassed and purified before using according to standard methods: toluene, hexane, and tetrahydrofuran were distilled from sodium/benzophenone ketyl. Polystyrene, vinyltrimethoxysilane, $AlCl_3$, $Al(OH)_3$, and triethylamine were purchased from Aldrich and used as received or distilled before use.

Alkylation reaction of Vinyltriemethoxysilane with Polystyrene.

3 g of polystyrene pallets (molecular weight is 32 000 g/mol) were dissolved in 7 g of anhydrous toluene and left for 1 day. Then the same amount of absolute toluene was added, because the sample was still viscous.

A 250 mL two-necked flask was loaded with 3 g of dissolved polystyrene. 4.02 g (0.03 mol) of $AlCl_3$ were added with a small portion under constant stirring and cold conditions, and a light-red colour appeared on the bottom of the flask. After a while, 4.45 g (0.03 mol) of vinyltrimethoxysilane were added under the same condition. Then heating was started for 3 hours. The solution changed the colour to dark brown and a black precipitate was formed at the bottom. The heating was stopped, the mixture was left to cool down and 4.18 mL (0.03 mol) triethylamine were added. 4.62 g (yield 62%) of a transparent viscous product was obtained.[26,27]

2.2. Analysis

Fourier transform infrared spectroscopy (FTIR) studies were conducted on a Nicolet TM iS50 FTIR Spectrometer-Thermo Fisher Scientific in the infrared region of 4000–400 cm^{-1} (scan 32, resolution 4 cm^{-1}); band intensities were denominated in transmittance.

An analytical sample was finely dispersed powder (1–2 mg). **^{1}H, ^{13}C NMR and COSY NMR** spectra were recorded on a Bruker ARX400 NMR spectrometer at a 400 MHz operating frequency with C_6D_6 as the solvent.

Thermogravimetric investigations were carried out on an Netzsch Instruments analyzer (model TG 209 F1 Taurus). It measures mass change as a function of temperature and has an operating temperature of between 10 and 1100 °C. During testing, the temperature increases at a rate of about 10 deg/min in an open area.

Optical microscopic examinations of composite materials based on bamboo sawdust and trimethoxysilylated polysterene were performed on an OMAX-type polarized microscope equipped with a high-resolution digital camera A35140U3 14 MP.

Scanning electron microscopic (SEM) **and Energy Dispersion Micro X-Ray Analysis** (EDS) observations were performed. A Tescan Vega 3, LMU microscope with a LaB 6 cathode was used. The maximum accelerating voltage was 30 kV, resolution was 2.0 nm. The microscope was also equipped with an energy-dispersive spectrometer for X-ray-induced electron beam specimens (EDS, Oxford Systems). EDS was used to determine the sample compositions.

2.3. Composition Preparation

Bamboo is one of the most widely used types of wood which is used as lumber. The composites were prepared using hot pressing of highly dispersed (20-30 μm) dry bamboo powder with trimethoxysilylated polystyrene (with 1% dicumyl peroxide) as a binder and reinforcement agent. The composites were created under pressures up to 15 MPa in the temperature range of 473–493 K.

Preparation of Samples for Analysis

In order to study the water absorption of samples, two different types of samples were prepared: cylindrical (d=1.5 cm. h=2 cm) and parallelepipedal ones (12 cm in length, 0.7 cm in height, and 1.5 cm in width). The following properties were determined: strength on bending, impact viscosity, and thermal stability.

2.4. Functional Properties

Water absorption was determined by immersion of specimens in a water bath at room temperature. Measurements were performed in 3 h and 24 h of exposition to water.

Water absorption x (in percent) is calculated by the formula:

$$X = \frac{m_1 - m_2}{m_1} 100,$$

where m_1 and m_2 are the weights of the sample before and after water absorption.

Bending test. Bending test (also known as flexural testing is aimed to measure the flexural stiffness and strength properties of polymer matrix composites) was performed on parallelepipeds with a length of 10 cm and a vertical square cross-section of 1 cm^2. Each specimen was placed on two prisms, with a distance of 8.0 cm between the prisms. The indenter was a metal cylinder with a diameter of 10 mm applied from above to the midpoint of the specimen. Bending strength (or flexural strength) is defined as the tension needed to create a breaking point (a crack) on the outer surface of the test specimen.[28]

Impact viscosity test, also called shock viscosity test, is a technique applied to soft solids[29,30] and is essentially a drop impact test. The drop height (h) is the vertical distance between the upper surface of the tested material (h_1) and the bottom surface of the drop hammer at the end of the impact event (h_2). With the sample mass m and the acceleration g, the work performed by the falling hammer is mg ($h_1 - h_2$), normalized with respect to the horizontal cross-section of the specimen FF.[30,31]

Vicat softening depth, also known as Vicat hardness, is the determination of the depth of the indentation relative to the top surface caused by a flat-ended indenter with a cross-section of 1 mm^2. Several loads defined below were applied; the cross-section of the indenter end was circular.

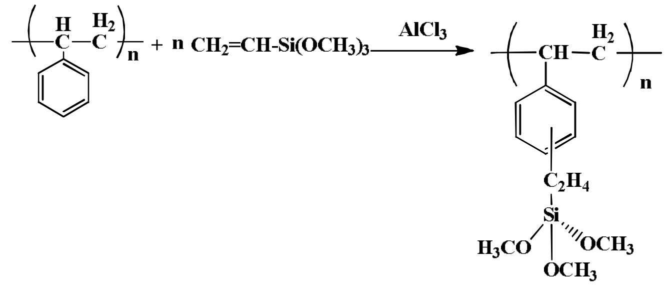
3. Results and Discussion

3.1. Synthesis of poly[trimethoxy(vinylphenethyl]) silane

The aim of the study is the synthesis of poly [trimethoxy(vinylphenethyl]) silane, which will be used as a binder and reinforcing agent for new bamboo-containing composite materials.

Trimethoxysilylated polystyrene was selected because it increases the strengthening of composite materials via the reinforcement of composite. Moreover, trimethoxysilylated groups in polystyrene perform the role of the binding agent. They connect the filler, fire retardant, and organic/inorganic additives with the binding agent, generating the continuous phase in the composite matrix during the chemical reaction of methoxy groups with fillers and additives. The change in the number of methoxy groups in the polystyrene side chain will give the possibility to change and regulate the grid frequency in a wide range according to the properties of composite materials.

The alkylation reaction of vinyltrimethoxysilane with polystyrene in the presence of anhydrous aluminum chloride as the catalyst has been carried out. The reaction proceeds according to the following scheme[26]:



Scheme 1. The Friedel-Crafts alkylation reaction for the silylation of polystyrene

As a result of the reaction, silylated polystyrene, a brown solid, was obtained.

The structure and composition of poly[trimethoxy (vinylphenethyl)] silane was proved via the determination of molecular masses, molecular refraction, FTIR, ^1H, and ^{13}C NMR spectra data.

In the FTIR spectrum of trimethoxysilylated polystyrene (Fig. 1) the absorption bands at 3024, 1600, 1491 and 695 cm^{-1} are characteristic of the stretching and deformation vibrations of antisymmetric and symmetric C–H bonds of the aromatic ring. The stretching and deformation vibrations of aliphatic C–H bonds (–CH–, –CH_2–, –CH_3) are observed at 2920 and 1451 cm^{-1}, respectively. At 1101 and 1001 cm^{-1} the absorption bands characteristic of the Si–O–CH_3 are observed. The absorption bands at 748 cm^{-1} are typical of methylene –$(CH_2)_n$– group.[32]

For the synthesised polymers, NMR investigations have been carried out.

^1H NMR spectra ($CDCl_3$) of the synthesized compound (Fig. 2) show the aliphatic group signals (4H, m, CH_2) as a multiple signals with chemical shifts at δ=1.6–1.8 ppm; CH_2 group signals appear at 1.95 ppm (2H, m - CH_2) as a multiple signal; at the region of 2.62–2.64 ppm (^1H, m, CH) the resonance signal of proton H-7 appears as a singlet signal. The signals of CH_3 group protons appear as a singlet signal at 3.6–3.7 ppm (9H, m, Si- O–C H_3); The signals of an aromatic group can be observed as multiple signals at the region of 7.3–7.6 ppm (4H,m, CH)[33].

In ^{13}C NMR spectra of the synthesized compound (Fig. 3), the carbon atom signals of the aliphatic CH_2 group appear in the 26.5-27.9 and 32.2 ppm region. CH_3-group signals appear at the region of 51.9 ppm, which corresponds to nine carbon atom signals. –CH- carbon atom signal appears at the region of 52.6 ppm and aromatic group signals of phenyl ring - in the 124.4-149 ppm region. ^{13}C NMR spectrum is in agreement with the ^1H NMR spectrum.

According to the ^1H and ^{13}C NMR spectra, it is evident that the alkylation reaction was performed.

However, it is difficult to detect in which direction (para- or ortho-position) the alkylation reaction proceeds, since these signals overlap, which is confirmed by studying the simulated NMR spectra using an online prediction program (ChemBioDraw Ultra 14.0[34] and MestreNova[35]).

But based on the studied quantum-chemical calculations of the alkylation reaction of vinyltrimethoxysilane with styrene (monomer modeling reaction), which were carried out using non-empirical density functional theory (DFT),[36-40] it can be assumed that the alkylation reaction probably took place mainly in the ortho position, that corresponds to the proposed structure.

For the theoretical calculation the online prediction program "Priroda-04: a quantum-chemical program suite" was used.

By the thermogravimetric investigation (Fig. 4), it was established that a 10% mass loss is observed at 423 K. The main destruction process proceeds in the temperature range of 523-623 K. Residual mass is 9.64% at 667.5 K.

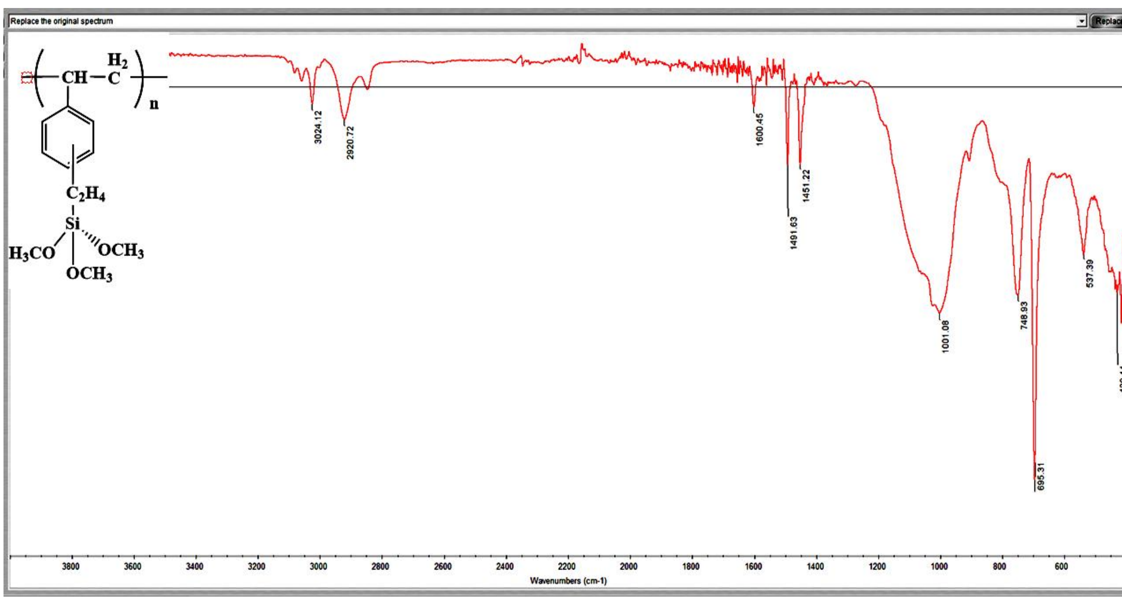


Fig. 1. FTIR spectra of trimethoxysilylated polystyrene

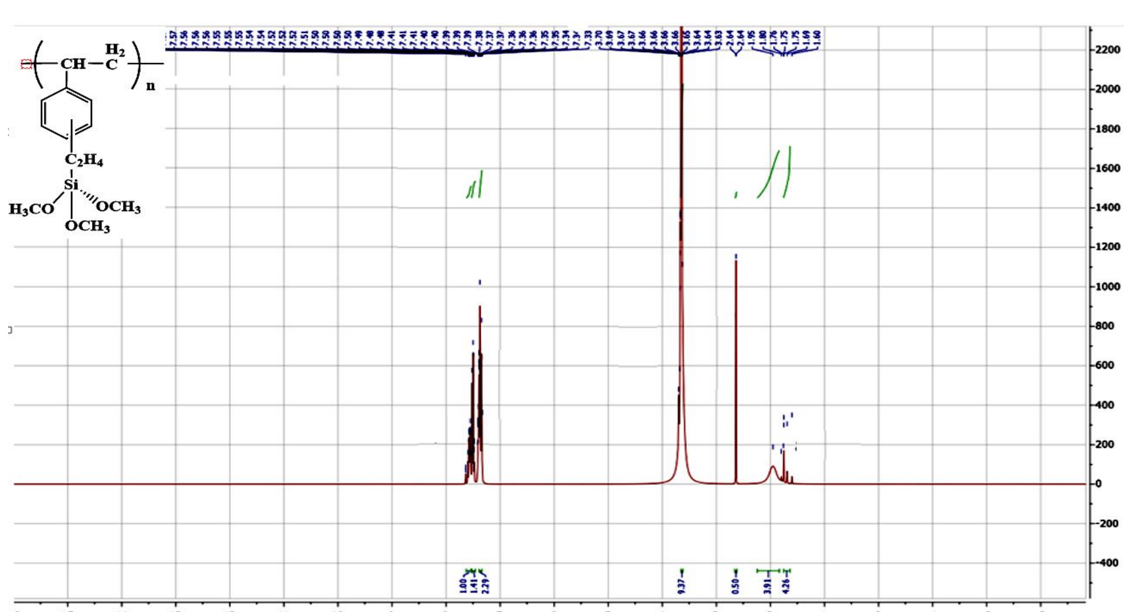


Fig. 2. [1]H NMR spectra of poly[trimethoxy(vinylphenethyl)]silane

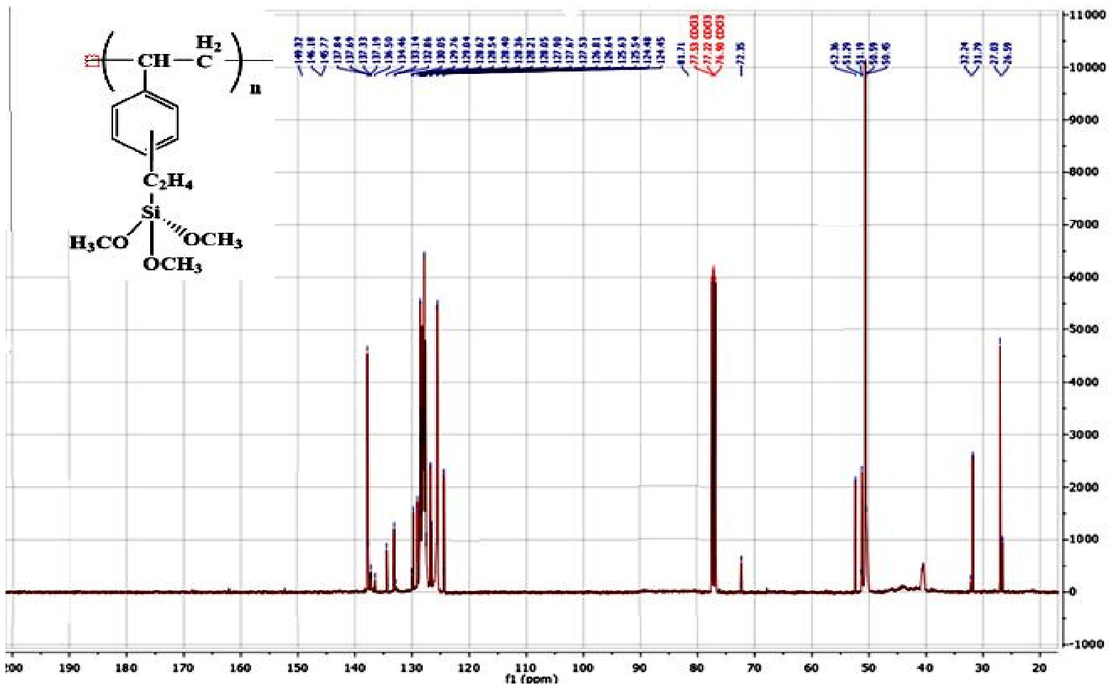


Fig. 3. ^{13}C NMR spectra of poly[trimethoxy(vinylphenethyl)]silane

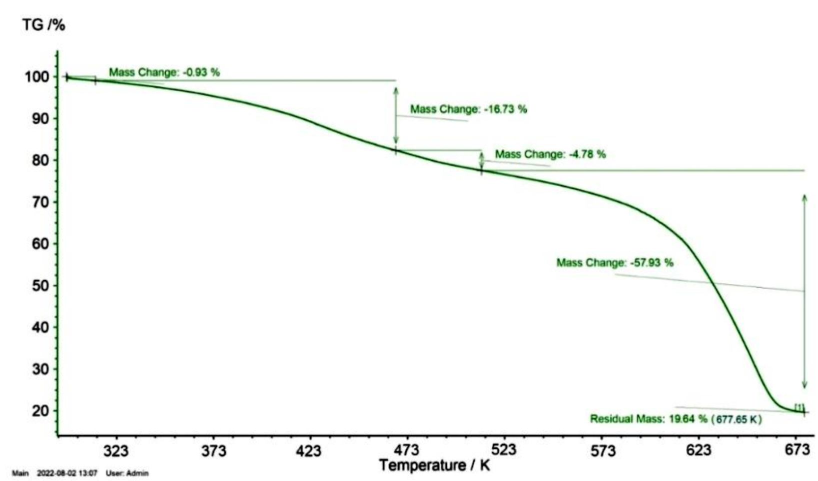


Fig. 4. Thermogravimetric curve of silylated polystyrene

3.2. Obtaining bamboo composites

There are several differences between bamboo and wood. There are no rays or knots in bamboo, which give bamboo a much more evenly distributed stress along its entire length. Bamboo is a hollow tube, sometimes with thin walls, and consequently, it poses some difficulty in joining bamboo pieces than wood.[41]

Bamboo's diameter, thickness, and intermodal length have a macroscopically graded structure while the fiber distribution exhibits a microscopically graded architecture, which leads to favorable properties of bamboo.[42]

3.2.1. Probable chemical reaction:

Binders may react with powdered bamboo, which contains functional groups in cellulose, hemicellulose, pentosanes, lignin, and silicon dioxide with the formation of three-dimensional systems.

So, the following reaction may proceed in powdered bamboo by insertion of binder silylated polystyrene:[43]

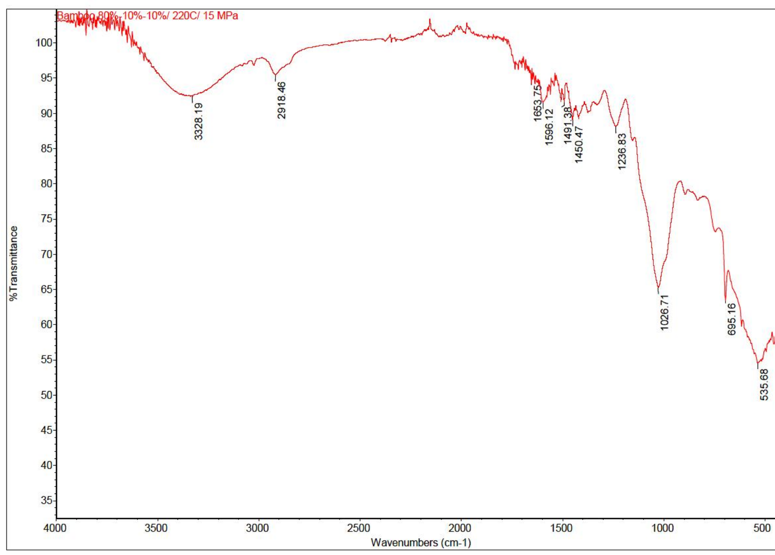
$$-OH + CH_3O\text{-}Si\equiv \rightarrow -O\text{-}Si\equiv + CH_3OH$$

Composites were prepared based on dry bamboo powder with trimethoxysilylated polystyrene as a binder and reinforcing agent. The mass ratio of trimethoxysilylated polystyrene and bamboo were 10:80 (10% $Al(OH)_3$, composite A) and 5:85 (10% $Al(OH)_3$, composite B). The composites were obtained as follows: the initiator, dicumyl peroxide (1 wt.%) and $Al(OH)_3$ were added to trimethoxysilylated polystyrene at room temperature, and then the bamboo powder was added to form a homogeneous mass.

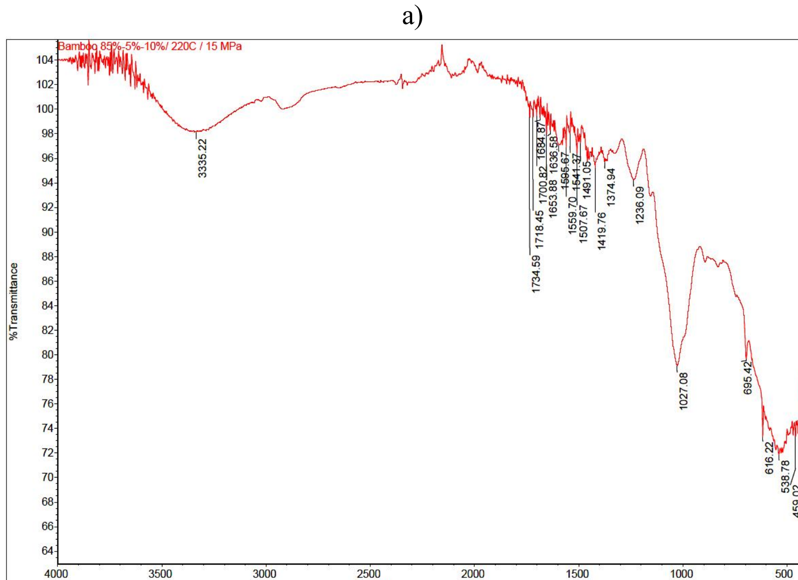
Composites were prepared at 433, 453, and 463 K. During hot pressing at 473 K, the binder in the composites burned and small particles of filler were thrown out from the press mould. Antipirene (flame retardant) $Al(OH)_3$ prevented the combustion of natural raw fillers in the process of pressing, so the composite materials were prepared at 473 K and 493 K and at 10 and 15 MPa. As for obtaining composites under a pressure of 15 MPa, this condition was explored on the basis of studies conducted by our research group.

3.3. Fourier transform infrared spectroscopy (FTIR)

For obtained biocomposites, Fourier transform infrared spectroscopy investigations were carried out (Fig. 5).



a)



b)

Fig. 5. FTIR spectra of bamboo composites at 493 K, 15MPa. (a) for bamboo 80%, (Poly-TMVPES) 10%, $Al(OH)_3$, 10%;(b) bamboo 85%, (Poly-TMVPES) 5%, $Al(OH)_3$ 10%.

Fig. 5 (a&b) represent the infrared spectra of the mixtures with different ratios of bamboo and polystyrene (Fig. 5a is a composite of 80% bamboo, 10% polystyrene, and 10% aluminum oxide, while Fig. 5b is a composite of 85% bamboo, 5% polystyrene, and 10% aluminum oxide). In the infrared spectrum, the absorption peak characteristic of cellulose is clearly visible in the region of 1027-1050 cm^{-1}, which is also typical of asymmetric stretching vibrations of the siloxane Si–O–C, contained in trimethylsilyl polystyrene. But in the composition, the vibrations of the siloxane Si–O–C bonds in trimethylsilyl polystyrene overlap with the absorption bands of cellulose. An asymmetric absorption band appears at 1236 cm^{-1}, corresponding to O–C bonds, which can be attributed to both trimethylsilyl polystyrene and bamboo composites. Absorption of C–OH bending in hemicellulose and lignin is allocated around 3328 and 3336 cm^{-1}.

The stretching and deformation vibrations of aliphatic C–H bonds (–CH–, $–CH_2–$, $–CH_3$), characterizing cellulose and trimethylsilyl polystyrene, are observed at 2918 and 1450 cm^{-1}, respectively. Aromatic bonds are present in both lignin and trimethylsilyl polystyrene. The infrared spectrum clearly shows aromatic bonds with small absorption peaks at 1596 and 1653 cm^{-1}; these absorption peaks correspond to the C=C stretching of unconjugated and conjugated carbonyl of lignin and aromatic bonds in trimethylsilyl polystyrene.

From the mentioned spectra (Figs. 5a and 5b), it can be concluded that the presented spectra are fully suitable for the composite of bamboo and trimethylsilyl polystyrene infrared spectrum.[44,45]

3.4. Study of the microstructure of bamboo-based composite materials

The microstructure of the bamboo composite samples was studied by the optical microscopy. Optical microscopy is typically used in material science. This is often the first step to a successful material analysis, giving a good overview of the material's microstructure and structure-property relationships.

The optical microscopic data of the composite materials under study show two components, which have different colours for different inserts. Inserts do not have a clearly defined border. The scale is indicated in the picture (300 μm).

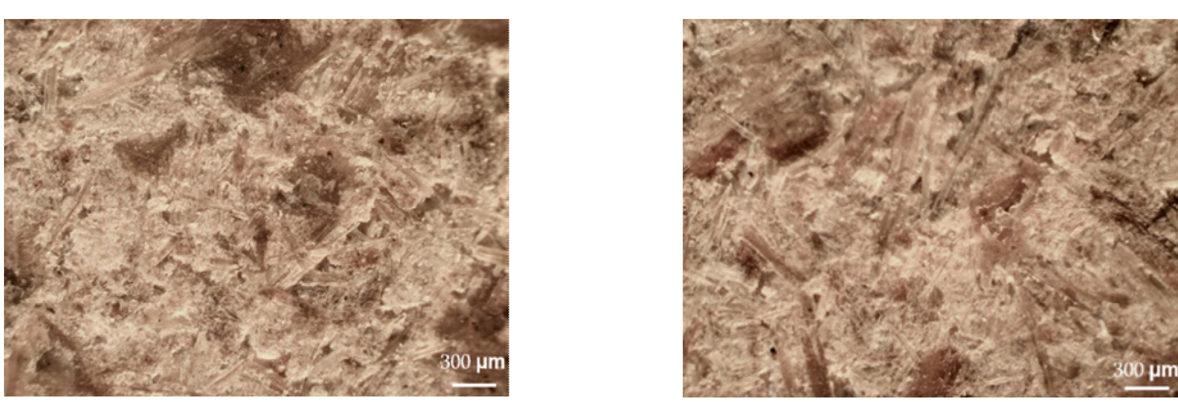
As shown in the micrograms (Fig. 6), the fibrous character of supramolecular structures has been observed.

3.5. Scanning electron microscopic and Energy Dispersion Micro X-Ray Analysis of composites

Scanning electron microscopic (SEM) investigations of new composite materials based on bamboo and silylated polystyrene were performed (Figs. 7 and 8). Energy dispersive X-ray examinations have been conducted in parallel to the micro-spectral (EDS) tests.[45]

SEM micrographs were obtained at different magnification ratios (x100-x1000). A bamboo epidermis (outer layer) with well-organized corrugated structure, including sharp ridge inserts that have a linear profile, is observed. The ridges and grooves in the epidermal cell are the result of the inclusion of fibers.

The outer surface of the hills includes knobs of various sizes. Two significant constituents of bamboo are the rhizomes and the culms. The rhizome is the underground part of the stem and is mostly sympodial (the main stem is terminated, and the growth is continued by one or more lateral stems) or monopodial to a much lesser degree. The culm is the hollow stem in a plant.



a) b)

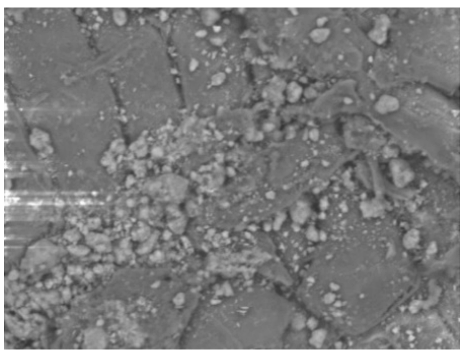
Fig. 6. Optical microscopic data at 493K, 15MPa; (a) for bamboo 80%, (Poly-TMVPES) 10%, Al $(OH)_3$ 10%; (b) bamboo 85%, (Poly-TMVPES) 5%, Al $(OH)_3$ 10%.

Interfacial gaps between fibers and the polymer matrix are clearly seen in Fig. 7, in both (a) and (b) parts. It has been found that the silylated polystyrene and aluminum hydroxide produces different surfaces. The microscopic pattern is established depending on the type and concentration of the ingredients.

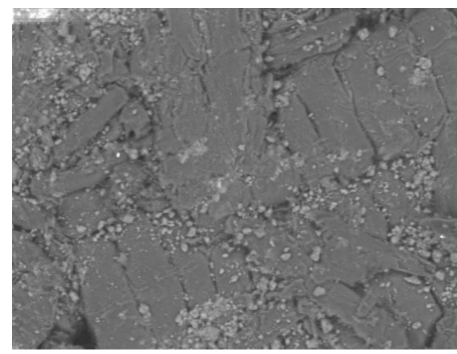
It can be assumed that the lite grey regions of Fig. 7(a, b) correspond to the binder on the background of the bamboo tissue. The picture clearly shows the randomness of the ingredients distribution in the composite.

For bamboo-based composites the energy dispersion micro X-ray analysis has been carried out (Fig. 9), which demonstrates information about elemental composition. These spectra correspond to different regions of the composite sample, allowing us to estimate the degree of homogeneity of microelements distribution in the composite.

Obtained bamboo-based composites contain the following elements: C, O, Si, and Al. The content of elements in samples slightly changes when different binders are used.

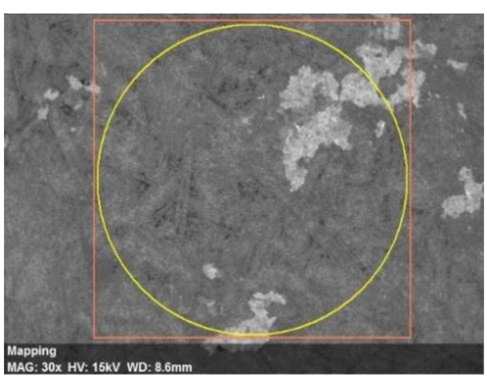


a)

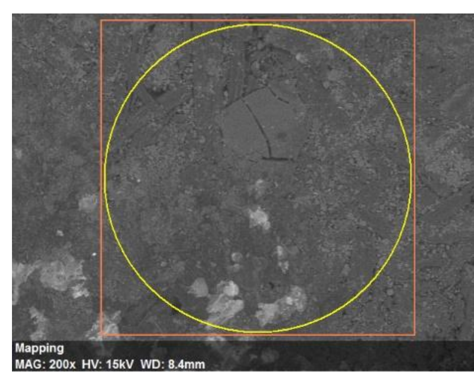


b)

Fig. 7. Scanning Electronic microscopic photo for composite: (a**)** bamboo 85%, (Poly-TMVPES) 5%, $Al(OH)_3$ 10%, 493 K, 15MPa. (b) Bamboo 80%, (Poly-TMVPES) 10%, 10%, $Al(OH)_3$, 493 K,15MPa



a)



b)

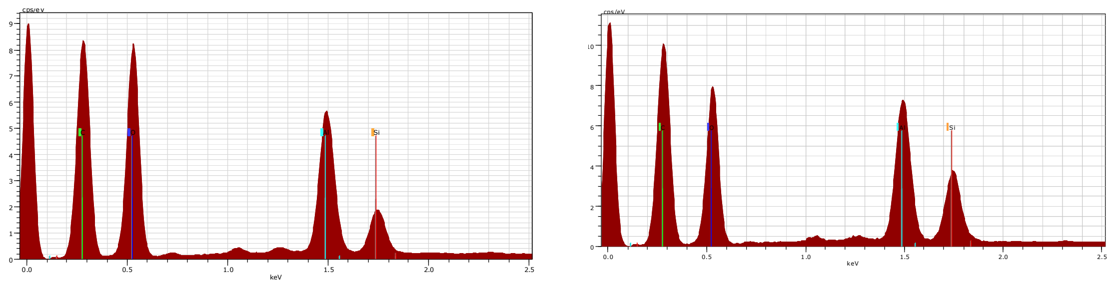
Fig. 8. SEM Micrograph for composites at 493K, 15MPa (a) bamboo 85%, (Poly-TMVPES) 5%, $Al(OH)_3$ 10%, (b) Bamboo 80%, (Poly-TMVPES) 10%, $Al(OH)_3$ 10%

3.6. Thermogravimetric investigation and Vicat softening temperatures

The thermal degradation and thermal oxidation stability of bamboo were investigated. The results showed that in comparison to other wood composites, bamboo composites have greater heat stability. This could be attributed to the higher lignin and cellulose content in the bamboo fibers compared with the studied pine.

Thermogravimetric curves (Fig. 10) show that thermal stability for both composites (a) and (b) is approximately the same. Mass losses of 10% are observed in the temperature range of 450–480 K. Significant thermal degradation for composites begins at approximately near 500 K. Full thermal degradation is seen between 550 K and 700 K, with the ash remaining. Overall, the concentration of the used binder does not affect the thermal stability of the composites.

The thermal stability of the composites on the basis of bamboo has been investigated by the Vicat method.



Spectrum:Point **Bamboo 85%, (Poly-TMVPES) 5%.**

Element	AN	Series	norm. C [wt.%]	Atom. C [at.%]
Oxygen	8	K-series	46.13	41.47
Carbon	6	K-series	44.94	53.82
Aluminium	13	K-series	6.71	3.58
Silicon	14	K-series	2.21	1.13
		Total:	100.00	100.00

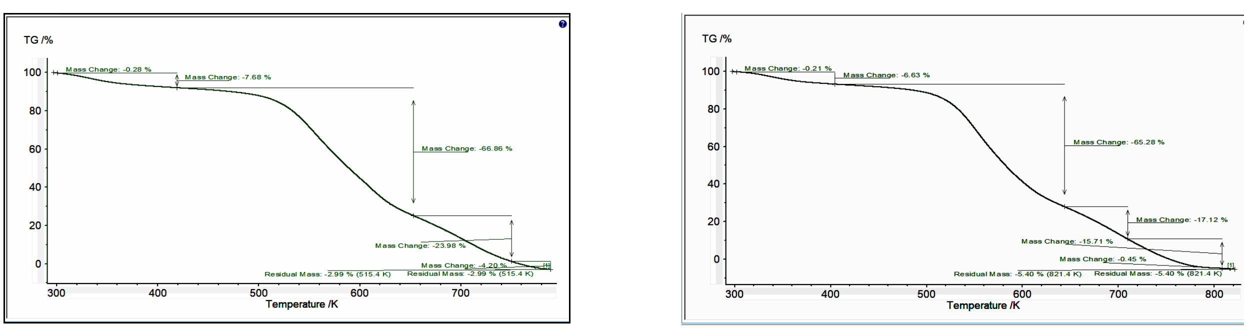
a)

Spectrum:Point **Bamboo 80%(Poly-TMVPES)10%.**

Element	AN	Series	norm. C [wt.%]	Atom. C [at.%]
Carbon	6	K-series	48.59	58.02
Oxygen	8	K-series	40.38	36.20
Aluminium	13	K-series	7.19	3.82
Silicon	14	K-series	3.84	1.96
		Total:	100.00	100.00

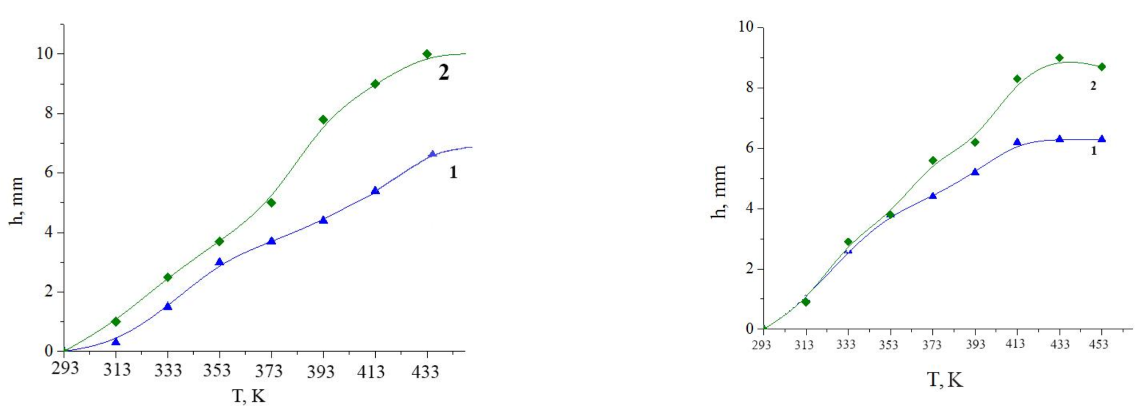
b)

Fig. 9. Energy dispersive X-ray microanalysis of composites prepared at 493 K, 15 MPa; (a) bamboo 85%, (Poly-TMVPES) 5%, $Al(OH)_3$ 10%, (b) Bamboo 80%, (Poly-TMVPES) 10%, $Al(OH)_3$10%



a) b)

Fig. 10. Thermogravimetric investigation for Composites at 15 MPa and 493 K (a) for bamboo 80%, (Poly-TMVPES) 10%, 10%, $Al(OH)_3$,; (b) bamboo 85%, (Poly-TMVPES) 5%, $Al(OH)_3$ 10%



a) b)

Fig. 11. Dependence of the Vicat softening point on the temperature at 15 MPa: (a) Curve 1 for bamboo (85 %) + (Poly-TMVPES) (5 %) at temperature 473 K and curve 2 for bamboo (85 %) + (Poly-TMVPES) (5 %) at 493 K (b) Curve 1 for bamboo (80 %) + (Poly-TMVPES) (10 %) at temperature 473 K and curve 2 for bamboo (80 %)+ (Poly-TMVPES) (10 %) at 493 K

The dependences of the softening point of composites on the temperature are presented in Fig. 11a, b. The curves show that composites' thermal stability essentially depends on a structural factor, on the concentration of the binder. In general, composites with relatively high physical-mechanical properties are characterized by higher thermal stability.

Fig. 11a demonstrates that with increasing temperature the softening point increases and Fig. 11b shows the influence of the percentage of the binders in composites. Softening point of composites with 10% of (Poly-TMVPES) is lower than those with 5%.

3.7. Mechanical characteristics: bending test and impact viscosity

Mechanical properties of bamboo fiber-reinforced polymer composites depend upon the following factors: (i) fiber modulus and strength, (ii) chemical stability, stiffness, and strength of the matrix material, (iii) extent of interfacial bonding between bamboo fiber and its matrix during the transfer of stress from one to the other.[23]

The installation for shredding dry bamboo was designed. It presents the complex of a milling cutter (with a diameter of about 120 mm). This apparatus allows obtaining milled (to some extent) sawdust containing particles of sizes from 50 microns up to 1 mm.

The bending tensile test and impact viscosity of composites were measured at temperatures of 473 and 493 K and at pressures of 10 and 15 MPa. Results of the investigations are shown Table 1.

In accordance with data presented in Table 1, the bending strength of composites increases for all cases. The maximum data was achieved for a composite with bamboo powder 80% + TMSPSt 10% at 493 K and 15 MPa. The results of the impact viscosity measurements showed that the increase in temperature and pressure, as well as the increase the binder concentration, decreases the impact viscosity values. The main reason for such dependences is found in the degree of homogeneity of binder distribution in the composites. At relatively high content of binders, the creation of the own structural phase of the binders as clusters takes place, which in general leads to the weakening of some mechanical properties of the composites.

3.8. Water absorption

Water absorption is important for wood composites since they are often used under high humidity conditions. The numerical data of this parameter are presented in Table 2. First of all, it should be noted that the data on water absorption for obtained composites based on bamboo, in general, are essentially lower in comparison with composites based other natural fillers (sawdust, straw).[46,47] This fact shows that the chemical structure (also microstructure) of bamboo favours the formation of chemical and physical bonds with binders (adhesives). In addition, the structure of bamboo-based composites may contain a variety of micro- and macro-voids, which are not interconnected and create difficulties for the diffusion of water in the composite body. Therefore, the composite matrix for the composites with bamboo is more solid than other analogues. The table data show that the water absorption coefficient depends on the concentration of binders, preparation temperature and pressure.

Table 1. Dependence of bending strength and impact viscosity of composites containing bamboo with trimethoxysilylated polystyrene (TMSPSt) on the preparation conditions (temperature and binder concentration)

#	Composite (wt. %)	Temperature (T), K	Pressure, MPa	R Bending strength (kg/cm^2)	D Impact viscosity, (kJ/m^2)
I	TMSPSt 5% + Bamboo 85% + $Al(OH)_3$ 10%	473	10	8.747	18.880
II	TMSPSt 5% + Bamboo 85% + $Al(OH)_3$ 10%	493	10	7.455	18.862
III	TMSPSt 10% + Bamboo 80% + $Al(OH)_3$ 10%	473	10	17.450	17.857
IV	TMSPSt 10% + Bamboo 80% + $Al(OH)_3$ 10%	493	10	19.251	17.244
V	TMSPSt 5% + Bamboo 85% + $Al(OH)_3$ 10%	473	15	12.931	21.879
VI	TMSPSt 5% + Bamboo 85% + $Al(OH)_3$ 10%	493	15	23.854	19.144
VII	TMSPSt 10% + Bamboo 80% + $Al(OH)_3$ 10%	473	15	36.901	14.660
VIII	TMSPSt 10% + Bamboo 80% + $Al(OH)_3$ 10%	493	15	52.585	13.866

Table 2. Water absorption of bamboo and TMSPSt (trimethoxysilylated polystyrene) composites prepared at different temperatures and pressures

#	Composite, %	Temperature, T, K	Pressure, MPa	Weight, g	Volume, m^3	Density g/cm^3	Weight after 24 h-s of exposure in water (g)	Water absorption after 24h exposition in water (wt.%)
I	TMSPSt 5% + Bamboo sawdust85% + Al(OH)$_3$ 10%	473	10	3.934	2.596	1.518	5.462	38.84
II	TMSPSt 5% + Bamboo sawdust 85% + Al(OH)$_3$ 10%	493	10	3.806	2.522	1.509	4.354	14.40
III	TMSPSt 10% + Bamboo sawdust 80% + Al(OH)$_3$ 10%	473	10	3.702	2.446	1.513	4.034	8.97
IV	TMSPSt 10% + Bamboo sawdust 80% + Al(OH)$_3$ 10%	493	10	3.796	2.529	1.501	4.037	6.35
V	TMSPSt 5% + Bamboo sawdust 85% + Al(OH)3 10%	473	15	3.865	2.540	1.522	5.741	48.54
VI	TMSPSt 5% + Bamboo sawdust 85% + Al(OH)$_3$ 10%	493	15	3.864	2.552	1.514	4.096	6.00
VII	TMSPSt 10% + Bamboo sawdust 80% + Al(OH)3 10%	473	15	3.702	2.469	1.499	4.381	18.34
VIII	TMSPSt 10% + Bamboo sawdust 80% + Al(OH)$_3$ 10%	493	15	3.512	2.312	1.519	3.646	3.82

The increase in pressure, temperature and the percentage of binders results in the decrease of water absorption. This means that the properties of composites improved. The best result was achieved at TMSPSt 10% + Bamboo sawdust 80% + $Al(OH)_3$ 10%, at a temperature of 493 K and 15 MPa.

4. Conclusions

The composites based on bamboo and eco-friendly poly[thimethoxy(vinylphenethyl)]silane binder have been obtained in the presence of $Al(OH)_3$ and dicumil peroxide. The binder's amount in composites was 5 and 10 wt.%. Powders of dry bamboo were blended with binders and the blends were pressed in the spatial press forms at 473 K and 493 K and pressures of 10-15 MPa for 10 min.

Following investigations were provided: 1) structural analysis with the use of Fourier transform infrared spectroscopy (FTIR), optical and scanning electron microscopes (SEM), energy dispersive X-ray microanalysis (EDS); 2) physical-mechanical properties; 3) thermal stability by Vicat method and thermogravimetry; 4) water absorption.

Using FTIR method, the concept of the formation of chemical bonds between the surface active groups of bamboo and binders was proven, due to which the strengthening of composites is enhanced.

Optical and electron microscope investigations data help us to establish the specifical formation of composite microstructure; EDS was used to establish the existence of the microelements in the bamboo.

Physical-mechanical properties such as strengthening on bending and impact viscosity were investigated. It was shown that both strengthening on bending and impact viscosity of composites with the same binder is characterized by extreme dependence on the binder concentration. The composites containing TMSPSt show maximum strengthening values at 10 wt. % concentrations.

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БАМБУКОВМІСНІ КОМПОЗИТИ З ЕКОЛОГІЧНО ЧИСТИМИ В'ЯЖУЧИМИ РЕЧОВИНАМИ

Анотація. *Уперше синтезовано екологічно чисту в'яжучу речовину – полі[(триметокси)4-вінілфенетил)]силан за допомогою реакції алкілування Фріделя-Крафтса, яку проводили взаємодією полістирену з вінілтриметоксисиланом у присутності безводного* $AlCl_3$. *Синтезований полімер було ідентифіковано за допомогою* ^1H, ^{13}C, ^1H *COSY ЯМР і FTIR спектроскопії.*

Композити на основі бамбукової тирси з різними дисперсійними властивостями були створені з використанням синтетичного триметоксисилільованого полістирену (TMSPSt) та стирену з різним ступенем силілювання (5-10%).

Композиційні матеріали на основі бамбукового порошку з різними органічними/неорганічними добавками, антипіренами й антиоксидантами були оброблені за різних температур і тисків методом гарячого пресування. Отримані композити досліджували методами інфрачервоної спектроскопії з перетворенням Фур'є (FTIR), оптичної та растрової електронної мікроскопії (SEM), а також енергодисперсійної рентгенівської спектроскопії (EDS).

Термостабільність отриманих матеріалів визначали за допомогою термогравіметрії та методу Віка. Також досліджено водопоглинання та деякі механічні властивості.

Ключові слова: *реакція Фріделя-Крафтса, силільований полістирен, антипірен, бамбуковий порошок, FTIR і ЯМР спектроскопія, механічні властивості.*