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ECO-FRIENDLY BAMBOO-BASED COMPOSITES

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Abstract. The study focuses on obtaining bamboo-based composite materials and new environmentally friendly binders with different degrees of silylation (15-35%) at different pressures and temperatures. The synthesis was carried out using silylated polystyrene (poly[trimethoxy (4-vinylphenethyl)] silane) and styrene as a binder and reinforcing agent in the presence of organic/inorganic additives, antioxidants and antipirene. Poly[trimethoxy(4-vinylphenethyl)] silane, a solid brown substance, was synthesized via an alkylation reaction of vinyltrimethoxysilane and polystyrene, in the presence of anhydrous $AlCl_3$. This paper presents the development of composites for ecological purposes (eco-composites) using bamboo fibers and their basic mechanical properties. The surface structures of the new composites were studied by several techniques including electron microscopy, energy dispersive X-ray microanalysis, bending test, Charpy impact test, thermogravimetry study, and water absorption determination. The new composites are characterized by good mechanical properties, thermal resistance, ecological purity, and water absorption capacity much smaller than the water absorption of existing particle boards.

Keywords: composites, poly[trimethoxy(4-vinylphenethyl)] silane, antioxidants, bamboo fibers, FTIR, X-ray microanalysis, thermogravimetric investigations.

1. Introduction

Over the past few decades, the successful development and improvement of wood composite panels (with the economic benefits of producing cheap wood materials) have become a major alternative to the use of solid wood.[1] Demand for composite wood products of various types, such as chipboard, plywood, particleboard, oriented strand board, medium density fiberboard, and veneered boards, has grown equally strongly worldwide.[2] In particular, the demand for chipboard is constantly growing due to the construction of housing, interior decoration, furniture, flooring and work surfaces in offices, educational institutions, laboratories and other industrial needs.[3] Bamboo is a good alternative to wooden materials and belongs to the grass family Poaceae, which is a large family of monocotyledonous flowering plants.[4]

Bamboo is one of the most important forest resources in the world. Compared to wood, it grows faster, matures earlier, and produces higher yields. The plantations are characterized by continuous use, which is an inexhaustible green material.[5] The use of bamboo dates back to ancient times, it is considered one of the most efficient materials in nature. Compared to steel and concrete, bamboo has fairly good mechanical properties, thermal insulation performance, good energy saving, and emission reduction effect.[6,7]

Over the past few years, public attention has been focused on natural fibers as a resource because of their rapid growth. Bamboo is an abundant natural resource in Asia and South America because it takes only a few months to grow. It is traditionally used to build various housing structures and tools.[8] Bamboo has a high strength in relation to its weight due to the fibers that are arranged longitudinally in its body.

Therefore, bamboo fibers are often called natural fiberglass. In order to realize the benefits of bamboo fibers, it is necessary to develop a process for manufacturing bamboo composites and to extract the fibers from bamboo trees in a controlled manner.

However, extracting bamboo fibers with their excellent mechanical properties is quite difficult. Bamboo fiber is often brittle compared to other natural fibers because they are coated with lignin. Therefore, a special process must be developed to extract bamboo fibers for reinforcement of composite materials.[9]

There are several differences between bamboo and wood. Bamboo has no rays or knots, so the load on the bamboo is much more evenly distributed along its entire length. Bamboo is a hollow tube, sometimes with thin walls, which means that bamboo is more difficult to join than pieces of wood. Bamboo does not contain chemical extractives like wood and can therefore bond very well.[10] The diameter, thickness, and intermodal length of bamboo

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have a macroscopically graded structure, while the fiber distribution shows a microscopically graded architecture, which leads to the favorable properties of bamboo.[11,12]

It is known from the literature that bamboo mainly contains sufficient amounts of cellulose, semi-cellulose, lignin, extractives, pentosans, ash, and silica.[13,14]

2. Experimental

2.1. Materials

Bamboo composites with different degrees of binder transformation (15-35%) were obtained. All reagents for the binders synthesis (styrene, polystyrene, vinyltrimethoxysilane, $AlCl_3$, $Al(OH)_3$, and triethylamine) purchased from Aldrich were used as received or distilled prior to use. Bamboo sawdust used in the composite materials also was purchased from the internet. All synthetic manipulations were carried out in a medium of dry nitrogen gas. All solvents were degassed and purified prior to use according to standard methods: toluene, hexane, and tetrahydrofuran were distilled from sodium benzophenone ketyl.[15]

Synthesis of Poly[trimethoxy(vinylphenethyl) silane

3 g of polystyrene pallet with molecular weight of 320,000 (g/mol) were dissolved in 7 g of 30% absolute toluene and were left for 1 day. Then the same amount of absolute toluene was added, because the sample was still viscous.

3 g of dissolved polystyrene were placed in a 250 mL two-necked flask and 4.02 g (0.03 mol) of $AlCl_3$ were added under constant stirring by small portions till a light red color appeared at the bottom of the flask. After a delay, on the same condition, we added 4.45 g (0.03 mol) trimethoxyvinylsilane. After a short time, was started heating for 3 hours. The solution turned dark brown and a black precipitate was formed at the bottom. The heating was stopped and left to cool down and added 4.18 ml (0.03 mol) triethylamine. 4.62 g of substance (yield 62%), a transparent viscous.

3 g of dissolved polystyrene were placed in a 250 mL two-necked flask and 4.02 g (0.03 mol) of $AlCl_3$ were added in small portions under constant stirring and cold conditions until a light red color appeared at the bottom of the flask. After some delay, 4.45 g (0.03 mol) of trimethoxyvinylsilane were added under the same conditions. After some time, heating was started for 3 hours. The solution turned dark brown and a black precipitate formed at the bottom. The heating was stopped, the mixture was cooled and 4.18 mL (0.03 mol) of triethylamine was added. A clear viscous product with the 62%yield (4.62 g) was obtained.[16,17]

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.

Thermogravimetric investigations were carried out using an analyzer Netzsch Instruments (model TG 209 F1 Taurus). It measures mass change as a function of temperature and has an operating temperature range of 10–1100°C. The rate of temperature increase during tests was ≈10 deg/min in an open area.

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

To investigate the microstructure of the materials the sample was prepared as. The sample was polished on a surface with a length of about 1 cm, after which it was transferred to sandpaper and the process was continued for 1 hour. Then the sample was polished on a coarse calico and transferred to an optical microscope slide. Separate parts of the sample were examined according to the above method.

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, and the resolution was 2.0 nm. The microscope was also equipped with an energy-dispersive spectrometer for X-ray-induced electron beam samples (EDS, Oxford Systems). EDS was used to determine the sample compositions.

2.2. Preparation of Composites

Bamboo is one of the most common wood species used as lumber. The composites were obtained by hot pressing highly dispersed (20-30 μm) dry bamboo powder with trimethoxysilylated polystyrene (with 1 % dicumyl peroxide) as a binder and reinforcing agent. The composites were created under a pressure of up to 15 MPa in the temperature range of 473–493 K for 5 min.

Preparation of Samples for Analysis

Two types of samples have been prepared: cylindrical samples with the diameter of 1.5 cm and height of 2 cm (for the study of water absorption); and parallelepiped samples with the length of 12 cm, height of 0.7 cm, and width 1.5 cm (for the determination of bending strength, impact strength, and thermal stability).

2.3. Investigation of Mechanical and Other Properties

Water absorption test was carried out by immersion a sample in a water bath at room temperature for definite time. After 3 hours, the water absorption index

was calculated. The same manipulation was carried out after 24 hours.

The percentage of water absorption (WA) was calculated by the weight difference between the samples exposed to water and the dried samples according to the following equation: $WA(\%) = \frac{M_e - M_0}{M_0} \cdot 100$ where: M_e and M_o (g) is the sample weight after and before immersion (g), respectively.[18]

Bending test (also known as flexural test) was performed using parallelepiped samples with a length of 10 cm and a vertical cross-section of 1 cm^2. Each sample 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 sample. Bending strength (or flexural strength) is defined as the stress needed to create a breaking point (a crack) on the outer surface of the sample.[19]

Impact strength is a technique applied to soft solids[20,21] 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 weight 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 sample $W = mg (h_1 - h_2)$.[22]

Vicat softening test, also known as Vicat hardness, is the determination of the depth of the indentation with respect 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.

Shore Hardness test was performed for bamboo-based composites. In the Shore hardness test, the indentation depth is measured using a spring-loaded indenter made of hardened steel to indent the material/sample. The indentation depth is a measurement for Shore hardness, that is determined on a scale of 0 Shore (2.5 millimeter indentation depth) to 100 Shore (0-millimeter indentation depth).

3. Results and Discussion

3.1. Obtaining Bamboo-Based Composite Materials

The aim of our study is to obtain new wood-polymer composites (WPCs) based on bamboo materials with different environmentally friendly binders. In this work, we investigated some physical and mechanical properties of bamboo-based WPCs.

We prepared polymeric composites based on bamboo powder with organic/inorganic binders, antioxidants, and flame retardant (antipirene) at temperatures of 473–493 K and pressures of 10–15 MPa. The percentage of binders in the composites is in the range of 15–35%.

The composites were obtained in the following order: 1. weighing the components on an analytical balance; 2. dry mixing of components; 3. loading the mixture into standard pressure molds; 4. heating the mixture in pressure molds at a certain temperature for a certain time; 5. removing the samples from the pressure molds. Samples were obtained by the hot-pressing method, where poly[trimethoxy(4-vinylphenethyl)] silane was taken in the amount of 3.5% of the composite total mass. During the dry mixing of composites, trimethoxy(vinylphenethyl)silane was mixed with benzoyl peroxide until a homogeneous mass was obtained, and then pine wood (both screened and unscreened) sawdust was added and mechanical stirring was continued. Subsequently, the composite mixture was placed in special molds. Pressing was carried out under a pressure of 15 MPa (other pressures were also tried, namely 5 and 10, but the optimal conditions were selected), from 413K to 493K, with successive temperature increases of 274K.

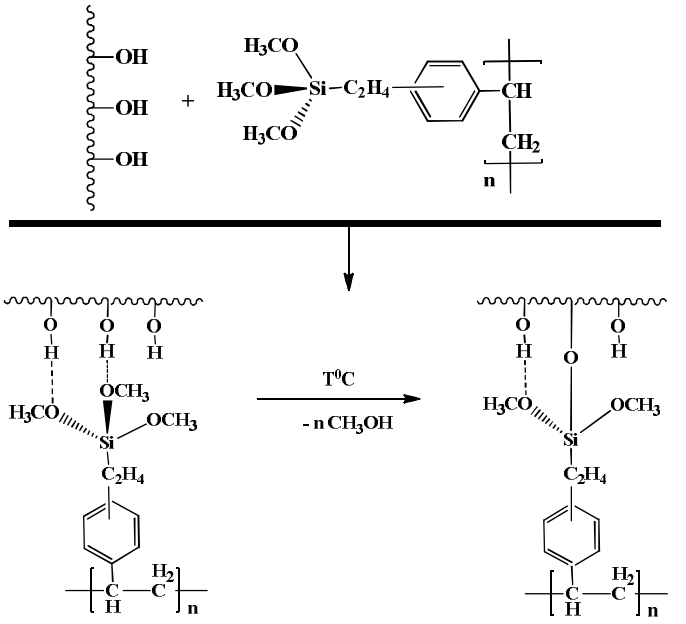
3.2. Probable Chemical Reactions

It is known that bamboo contains lignin, hemicellulose and cellulose structural rings with hydroxyl groups. Poly[trimethoxy(vinylphenethyl)silane, which contains methoxy groups, is one of the substances used as a binder. The mentioned groups participate in the etherification reaction with a binder via the macromolecular and intra-molecular reactions. Etherification reactions proceed analogically with the use of vinyltriemtoxisilane.[23] Processes that occur during the curing are complex and varied.

We expect that the following reactions may occur between the pulverized bamboo and some of the binders. Thus, in powdered bamboo, the following reactions can occur when silylated polystyrene binder is introduced:[24]

$$\text{-OH} + \text{CH}_3\text{O-Si} \equiv \rightarrow \text{-O-Si} \equiv + \text{CH}_3\text{OH}$$

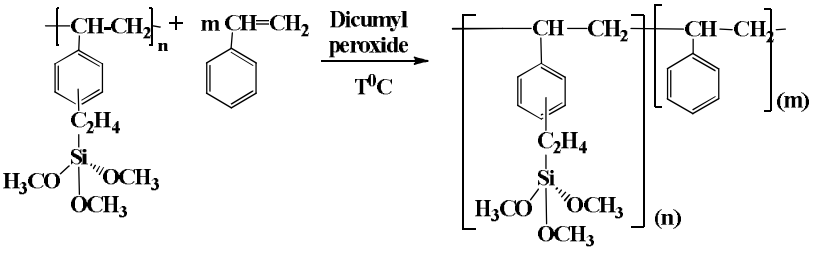
Methoxy groups of trimethoxysilylated polystyrene react with the cellulose hydroxyl groups of the filler to form donor-acceptor bonds. The etherification reaction results in the creation of new covalent C-O-Si bonds between the filler and the binder; it proceeds according to the following scheme:[25]



Scheme 1. Interaction and etherification reactions of triemthoxysilylated polystyrene and cellulose with the formation of hydrogen bonds

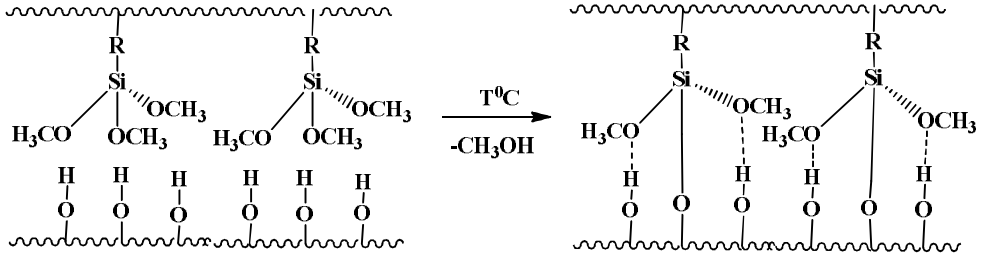
During hot-pressing, the initiator in the mixture may initiates the polymerization reaction of vinyl groups of styrene. The bamboo powder impregnated with poly-TMWPE and styrene forms chemical bonds with the hydroxyl groups of the bamboo surface during hot pressing. As a result, an active filler is likely to be formed, followed by occurring esterification reactions[24-26] and in-situ polymerization.

In the case of using dicumyl peroxide during hot pressing, in *situ*- polymerization and copolymerization by the formation of different ring polymers are possible according to the following scheme:



Scheme 2. Co-polymerization of poly[(trimethoxy(4-vinylphenethyl) silane and styrene

Also, it is possible to continue the proceeding of probable reaction according to Scheme 3:



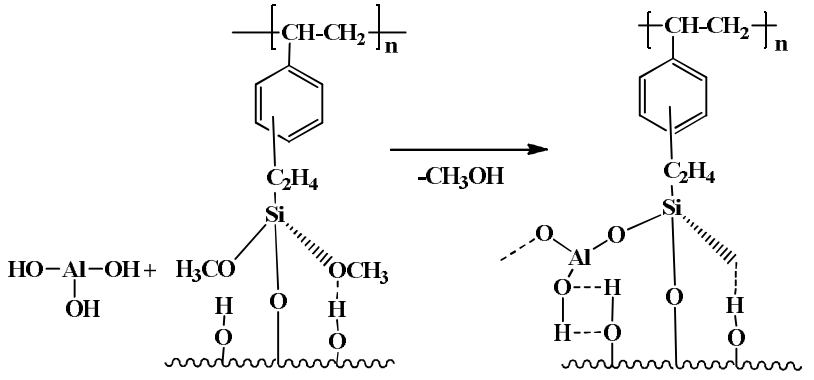
Scheme 3. Etherification and intermolecular interaction reactions of trimethoxysilylated polystyrene with powder; where R = $-C_2H_4C_6H_4-$

It is possible that the resulting copolymer will react to form hydrogen bonds in esterification reactions with hydroxyl groups present on the surface of bamboo to form covalent chemical bonds, as shown in Scheme 1.

A flame retardant is also used in the manufacture of composite materials; in our case, aluminum hydroxide $Al(OH)_3 \bullet xH_2O$ was chosen. Many inorganic flame retardants are known, such as magnesium hydroxide, aluminum hydroxide, phosphates and hydrophosphates, and salt halides. But from this list, we chose aluminum hydroxide as the cheapest additive, which, when decomposed at high temperatures, forms an environmentally friendly substance. At a temperature of 273-293K, aluminum hydroxide separates crystallization water and reduces the degree of heating in the ignition zone. The resulting gas reduces the amount of oxygen and inhibits combustion and ashing processes.

Aluminum hydroxide is a white crystalline substance with passive chemical properties. It is a non-toxic flame retardant capable to suppress flame, prevent ignition and reduce the speed of flame propagation. Aluminum hydroxide is used as a flame-retardant additive in the production of glass, ceramics, polyvinyl chloride, wood composites, and other polymeric materials. It is also included in the decorative and protective coating.

In addition, aluminum hydroxide was specially selected because it is known to be harmless to the environment and has no effect on the human body; it can react with the binder used to make composites, releasing methanol or forming hydrogen bonds, as shown in Scheme 4:



Scheme 4. Probable chemical reactions of aluminum hydroxide with binder and cellulose surface

Interaction with the hydroxyl group of the flame retardant is possible in reactions occurring at deeper stages of transformation. Aluminum hydroxide was taken in the amount of 0.1-10% in composite materials. Aluminum hydroxide, trimethoxysilylated polystyrene (TMSPSt), together with the initiator, were added to bamboo sawdust and mixed until a homogeneous mixture was formed, and then subjected to hot pressing at various temperatures and a pressure of 15 MPa. It is known that the use of dicumyl peroxide during hot pressing initiates the polymerization of styrene, which to a certain extent gives the composition mechanical strength, i.e., plays the role of a reinforcing agent.

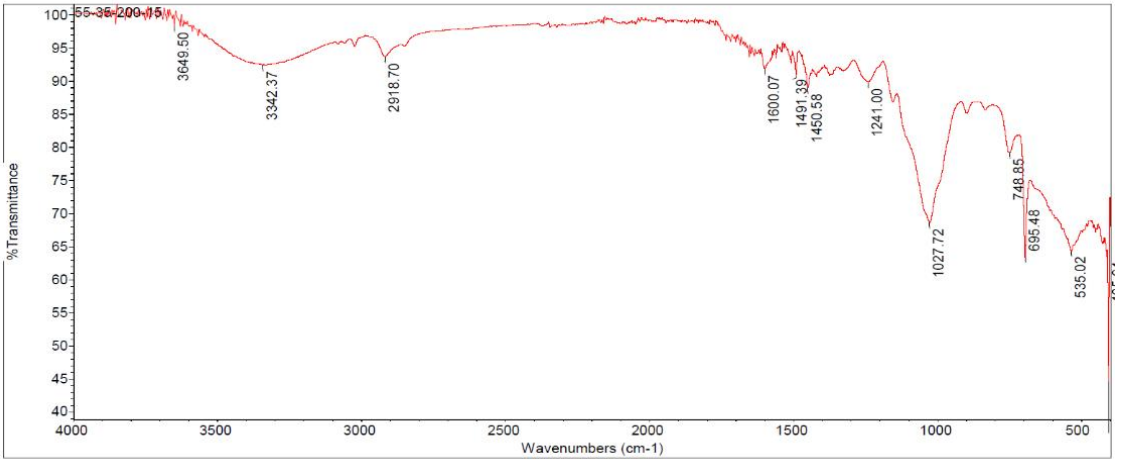
The composites were measured using the following characteristics: 1) Fourier transform infrared spectroscopy (FTIR), 2) bending strength, 3) impact strength, 4) Thermo Vicat method and thermogravimetric analysis, and 5) water absorption coefficient. The results and analysis are presented below.

3.3. Fourier Transform Infrared Spectroscopy (FTIR)

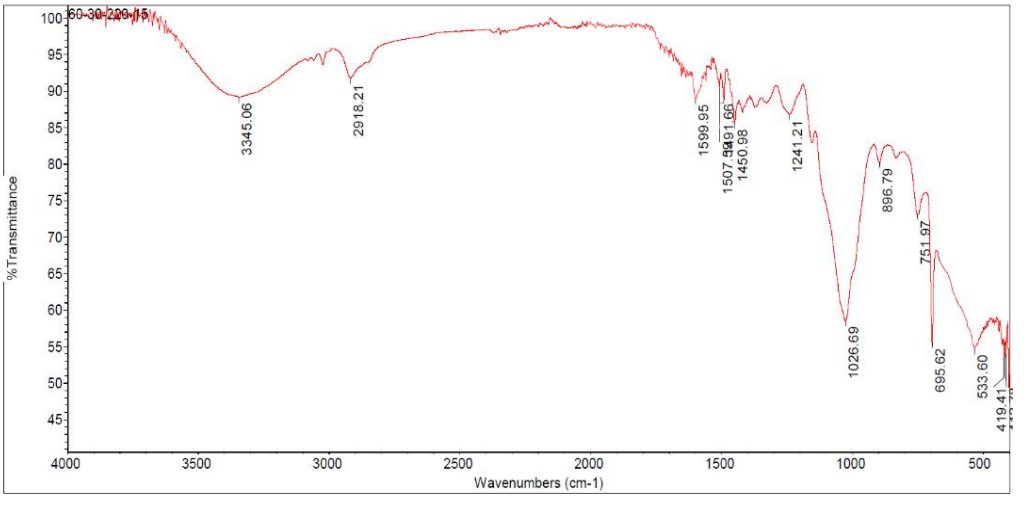
Fourier transform infrared (FTIR) spectroscopy is a versatile technique for the characterization of composite materials. FTIR investigations of composites have been carried out.[27]

In the IR spectra of Figs. 1a and 1b, the stretching vibrations characteristic of the aromatic ring is clearly visible in the region of 1600, 1599 and 1450 cm^{-1}. Deformational and stretching vibrations of C-H bonds are observed in the region of 1241 cm^{-1}. The presence of $-CH_2-$ and $-CH_3$ groups in the molecule is obvious in the region of 2919 cm^{-1}. C-H stretching vibrations of the aromatic bond are observed in the region of 3059 cm^{-1} as a weak intensity absorption band. The presence of the $Si-O-CH_3$ group in the molecule is confirmed by absorption bands in the range of 1027-1026 cm^{-1}. The absorption peak of Si-C is fixed in 896 cm^{-1} area. The O-H bonds in bamboo

cellulose are clearly visible in the 3330 cm^{-1} range. The given infrared spectra (Figs. 1a, and 1b) are completely suitable for the compositions of the specified mixture (60% bamboo, 30% binder, 10% aluminum hydroxide at 293K and 55% bamboo, 35% binder, and 10% aluminum hydroxide at 273K).[25]



a



b

Fig. 1. FTIR spectra of bamboo composites at15MPa. (a) for bamboo 55%, (Poly-TMVPES) 35%, Al $(OH)_3$, 10%, 473 K; (b) bamboo 60%, (Poly-TMVPES) 30%, Al $(OH)_3$ 10%, 493K

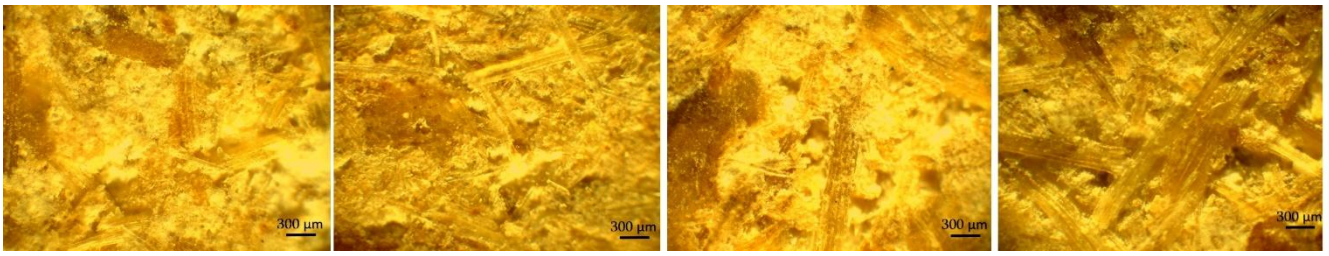
3.4. Study of the Microstructure of Composite Materials

3.4.1. Optical Microscopic Investigations

The investigation of the composite microstructure was carried out using an OMAX-type polarized microscope equipped with a high-resolution digital camera A35140U3 14 MP.

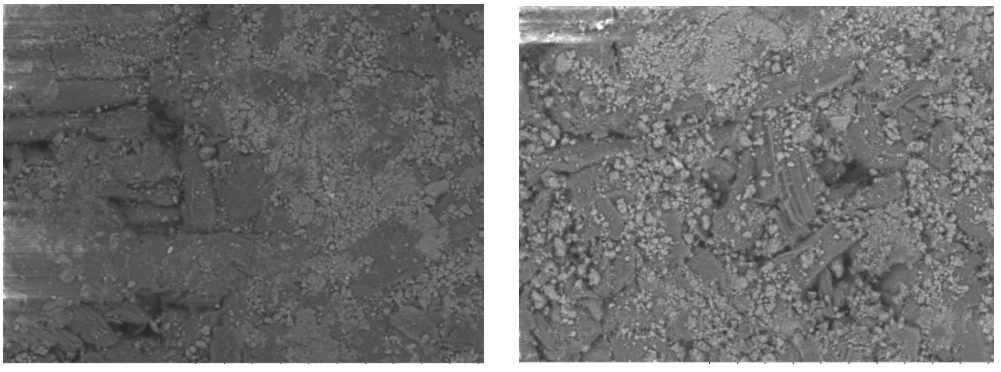
An optical microscope, also called a light microscope, uses visible light and lenses to create a magnified image of small objects that could not otherwise be seen with the naked eye. The magnification range of optical microscopy ranges from 10x to 100x, which means that details in the 0.2-micrometer size range can be observed.

We investigated the microstructure of the composites by examining their surfaces. The samples under study were prepared at a pressure of 15 MPa, temperature of 493 K and different binder concentrations. As can be seen in the photos, the surface is homogeneous. The fibrous nature of the supramolecular structures is noticeable in the composites.



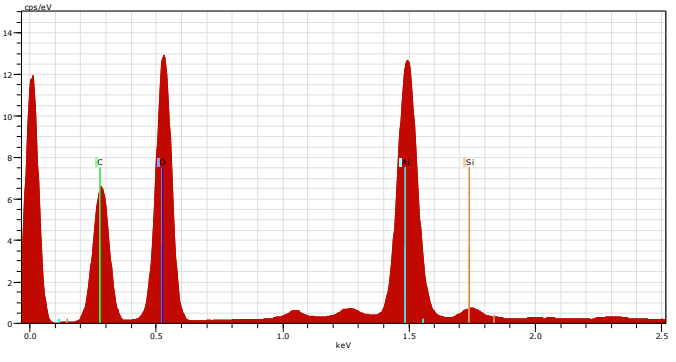
a b c d

Fig. 2. Photos of the transverse surface of composite bamboo: (a) Poly-TMVPES-15%, (b) Poly-TMVPES-20%, (c) Poly-TMVPES-25%, (d) Poly-TMVPES-30%



a b

Fig. 3. SEM pictures of the composites obtained at 493 K and 15 MPa: IV (a) TMSPSt 20% + Bamboo sawdust 70% + $Al(OH)_3$ 10%, and composite X (b) TMSPSt 35% + Bamboo sawdust 55% + $Al(OH)_3$ 10%



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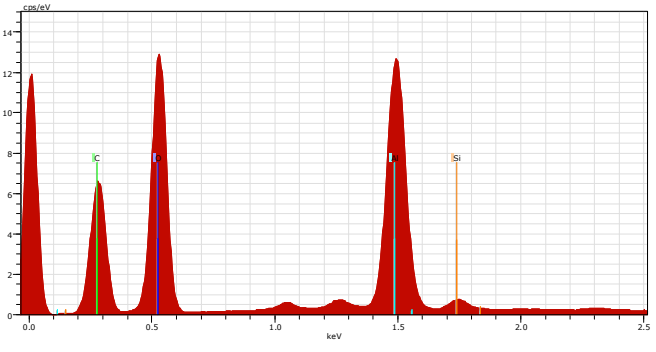


b

Fig. 4. EDS of composites obtained at 493 K and 15 MPa: IV (a) TMSPSt 20% + Bamboo sawdust 70% + $Al(OH)_3$ 10%, and composite X (b) TMSPSt 35% + Bamboo sawdust 55% + Al $(OH)_3$ 10%

3.5. Scanning Electron Microscopic and Energy Dispersion Micro X-Ray Analysis

The morphological characterization of the bamboo fibers and the biocomposites was examined by scanning electron microscopy (SEM). This technique was used to observe the surface morphology and analyze the microstructure in both natural and chemically treated forms.

Composites IV and X, obtained at 15 MPa and 493 K with different degrees of silylation, were studied at different magnifications (×100–×1000). Also, energy-dispersive X-ray microanalysis was carried out for different parts of the sample.

Figs. 3a and 3b shows SEM micrographs at different magnifications and in different parts of the composite, where its fibrous structure, small inclusions of 10–20 μm in size, and holes are visible. The variation of the microscopic pattern varies depending on the type and concentration of the ingredients. It can be assumed that the white areas and spherical light spots in Figs. 3a and 3b correspond to trimethoxysilylated polystyrene with different concentrations, including the flame retardant (aluminum hydroxide) on the background of bamboo tissue. The figure clearly shows the chaotic distribution of ingredients in the composite.

For bamboo composites energy dispersive X-ray spectroscopy (EDS) have been carried out in parallel. This is an analytical technique used to determine the chemical characteristics/elemental composition of materials.

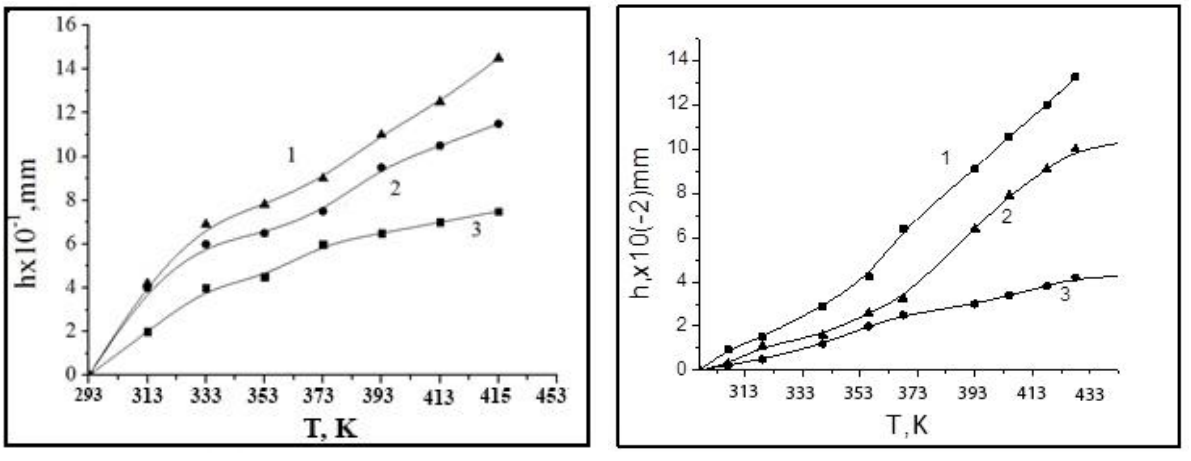
The spectra (Fig. 4) describe the elemental composition of composites IV and X; the percentage distribution of the elements is indicated by peaks. It can be seen that the main elements in the composite are C, O, Si, and Al, where the largest amountis represented by O.

3.6. Investigation of the Thermal Characteristics of the Composites

We investigated thermal stability of obtained composites by the Vicat method.

The curves in Fig. 5a show that the change in pressure affects the thermal stability of composites quite significantly. Partially, a change in pressure in the range of 10-15 MPa leads to an increase in the stability of composites. This depends on the density of the bonds formed between the ingredients, as well as on the mechanical properties of these composites, which also increase. One of the reasons is the so-called Frank and Rabinowitz cellular effect. This effect is explained as follows: the volumes of the reaction volumes decrease with increasing pressure, which leads to a decrease in the movement of the reactant particles and, as a result, the reaction rate decreases, or, accordingly, the amount of reaction products decreases. This fact influences the mechanical and thermal properties of the materials. The composites containing different amounts of bamboo and silylated polystyrene (Fig. 5b), show an increase in thermal stability with an increase in concentration of the binder used.

Thermogravimetric investigations were carried out. The rate of temperature increase was ≈10 deg/min in an open area. Fig. 6 (a, b, c, d) shows TG curves of the composite with binders and different degrees of silylation.



a b

Fig. 5. Dependence of the softening point on the temperature for bamboo-based composites obtained: (a) at constant temperature of 473K, 35% TMSPSt and different pressures: 15 (1), 12 (2) and 10 (3) MPa and (b) at 15 MPa, 493K and different content of TMSPSt 1) 25%, 2)30%, 3) 35%

It is evident that with an increase in temperature, the mass losses of composites increase. About 10% mass loss can be observed in the temperature range up to 400-500 K. In this temperature range, condensation processes can occur both with unreacted hydroxyl groups and with hydroxyl and methoxyl groups. The main destruction process occurs in the temperature range of 500-650 K, and after 700 K, complete destruction of composite materials occurs. It was found that the concentrations of the binders used do not significantly affect the thermal oxidation resistance of the composites.

So, we can conclude that, thermooxidative stability is almost the same for all obtained composites.

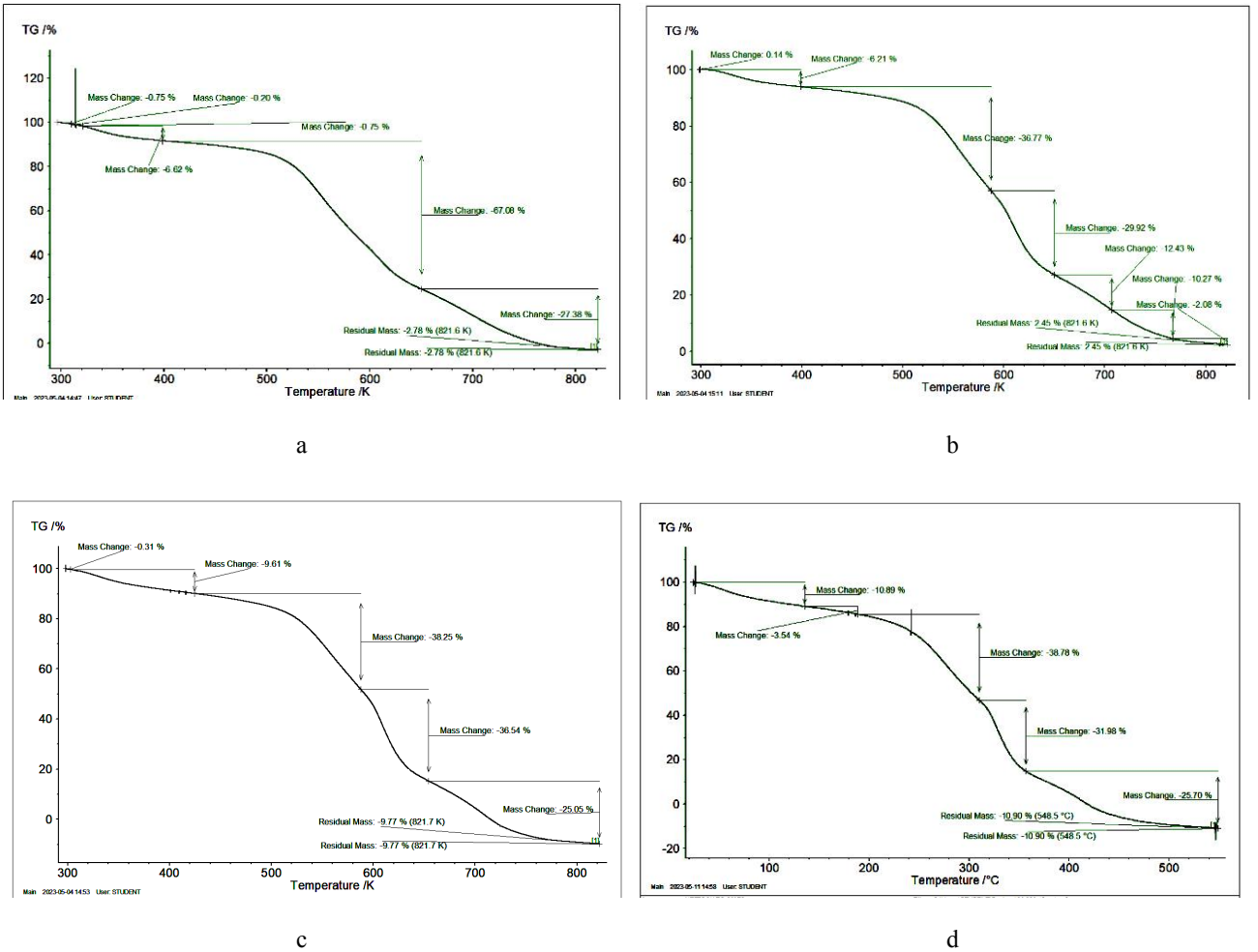


Fig. 6. Thermogravimetric curves of bamboo-based composites obtained at 493 K and 15MPa: a) TMSPSt-15%, b) TMSPSt-20%, c) TMSPSt-25%, d) TMSPSt-30%

3.7. Physical-Mechanical Properties of Composites

Among the physical and mechanical properties, bending strength and impact strength were studied.

Bending test was performed at different temperatures and binder concentrations. Bending test was performed according to a standard for wood polymer composites.[19,28]

For a three-point test, the flexural strength σ_f can be calculated as follows:

$$\sigma_f = 3FL / 2wd^2 \quad (1)$$

F is the maximum force applied, **L** is the length of the sample, **w** is the width of the sample and **d** is the depth of the sample. Thus, to calculate the flexural strength σ_f, we multiply the force by the length of the sample and then multiply this by three. Impact strength was determined using an apparatus of the Charpy type. The numerical data of the noted parameters for these composites are summarized in Table 1.

Table 1. Dependence of bending strength and impact strength values of bamboo-based composites on the preparation conditions (temperature, pressure, and binder concentration) of the sample (exposition time 15 min).

#	Composite, %	Temperature, T, K	Pressure, MPa	Bending strength, MPa	Impact strength, kJ/m^2
I	TMSPSt 15% + Bamboo sawdust 75% + $Al(OH)_3$ 10%	473	10	36.959	13.917
II	TMSPSt 15% + Bamboo sawdust 75% + $Al(OH)_3$ 10%	493	10	44.307	14.894
III	TMSPSt 20% + Bamboo sawdust 70% + $Al(OH)_3$ 10%	473	10	66.851	13.318
IV	TMSPSt 20% + Bamboo sawdust 70% + $Al(OH)_3$ 10%	493	10	68.966	13.027
V	TMSPSt 25% + Bamboo sawdust 65% + $Al(OH)_3$ 10%	473	10	61.425	15.189
VI	TMSPSt 25% + Bamboo sawdust 65% + $Al(OH)_3$ 10%	493	10	71.530	15.598
VII	TMSPSt 30% + Bamboo sawdust 60% + $Al(OH)_3$ 10%	473	10	36.799	28.749
VIII	TMSPSt 30% + Bamboo sawdust 60% + $Al(OH)_3$ 10%	493	10	59.364	29.707
IX	TMSPSt 35% + Bamboo sawdust 55% + $Al(OH)_3$ 10%	473	10	55.077	30.034
X	TMSPSt 35% + Bamboo sawdust 55% + $Al(OH)_3$ 10%	493	10	56.928	30.435
XI	TMSPSt 15% + Bamboo sawdust 75% + $Al(OH)_3$ 10%	473	15	39.574	14.253
XII	TMSPSt 15% + Bamboo sawdust 75% + $Al(OH)_3$ 10%	493	15	45.776	15.041
XIII	TMSPSt 20% + Bamboo sawdust 70% + $Al(OH)_3$ 10%	473	15	58.083	11.769
XIV	TMSPSt 20% + Bamboo sawdust 70% + $Al(OH)_3$ 10%	493	15	67.444	12.152
XV	TMSPSt 25% + Bamboo sawdust 65% + $Al(OH)_3$ 10%	473	15	78.937	16.054
XVI	TMSPSt 25% + Bamboo sawdust 65% + $Al(OH)_3$ 10%	493	15	79.652	15.001
XVII	TMSPSt 30% + Bamboo sawdust 60% + $Al(OH)_3$ 10%	473	15	75.771	30.729
XVIII	TMSPSt 30% + Bamboo sawdust 60% + $Al(OH)_3$ 10%	493	15	87.880	32.303
XIX	TMSPSt 35% + Bamboo sawdust 55% + $Al(OH)_3$ 10%	473	15	50.423	42.071
XX	TMSPSt 35% + Bamboo sawdust 55% + $Al(OH)_3$ 10%	493	15	68.338	31.915

Table 1 shows that the reaction conditions has a mixed effect on the bending strength and impact strength. Generally, with increasing pressure, temperature, and binder concentration, both properties of bamboo-based composites increase except for some data. The minimal value for bending strength is 36.799 at 473 K, 10 MPa, 75% content of bamboo sawdust, and 15% content of TMSPSt; the maximum value is 87.880 at 493 K, 15 MPa, 60% content of bamboo and 30% content of TMSPSt.

As for the impact strength, this characteristic is a really important performance parameter. It attracts attention, especially in the processes of instantaneous loading.

Tests of the obtained composites for impact strength are also shown in Table 1. According to Table 1, an increase in the binder concentration and the pressing temperature increases the impact strength. The effect of pressure does not play a significant role.

The main reason for such different dependencies for both studies is the degree of heterogeneity of the binder distribution in the composites. At a relatively high binder content, the binders create their own structural phase in the form of clusters, which generally leads to a weakening of the mechanical properties of the composite.

Table 2. Water absorption of the samples at various binder concentrations, temperatures, and pressures

#	Composite, %	Tempe-rature, T, K	Pressure, MPa	Weight, g	Volume, m^3	Density, g/cm^3	Weight after 3 h of exposure in water (g)	Weight after 24 h of exposure in water (g)	Water absorption after 3 h exposure in water (wt.%)	Water absorption after 24h of exposure in water (wt.%)
I	TMSPSt 15% + Bamboo sawdust 75% + $Al(OH)_3$ 10%	473	10	3.509	2.361	1.486	3.562	3.661	1.51	4.33
II	TMSPSt 15% + Bamboo sawdust 75% + $Al(OH)_3$ 10%	493	10	3.623	2.508	1.445	3.649	3.699	0.72	2.10
III	TMSPSt 15% + Bamboo sawdust 75% + $Al(OH)_3$ 10%	473	15	3.402	2.287	1.488	3.459	3.506	1.68	3.06
IV	TMSPSt 15% + Bamboo sawdust 75% + $Al(OH)_3$ 10%	493	15	3.390	2.273	1.491	3.482	3.482	2.71	2.71
V	TMSPSt 20% + Bamboo sawdust 70% + $Al(OH)_3$ 10%	473	10	3.262	2.358	1.383	3.289	3.310	0.83	1.47
VI	TMSPSt 20% + Bamboo sawdust 70% + $Al(OH)_3$ 10%	493	10	3.190	2.278	1.400	3.224	3.226	1.07	1.13
VII	TMSPSt 20% + Bamboo sawdust 70% + $Al(OH)_3$ 10%	473	15	3.241	2.231	1.453	3.318	3.326	2.38	2.62
VIII	TMSPSt 20% + Bamboo sawdust 70% + $Al(OH)_3$ 10%	493	15	2.860	2.036	1.405	2.907	2.989	1.64	4.51
IX	TMSPSt 25% + Bamboo sawdust 65% + $Al(OH)_3$ 10%	473	10	3.281	2.399	1.368	3.349	3.463	2.07	5.55
X	TMSPSt 25% + Bamboo sawdust 65% + $Al(OH)_3$ 10%	493	10	2.817	2.271	1.240	2.885	2.990	2.41	6.14
XI	TMSPSt 25% + Bamboo sawdust 65% + $Al(OH)_3$ 10%	473	15	2.842	2.181	1.303	2.903	2.986	2.15	5.07
XII	TMSPSt 25% + Bamboo sawdust 65% + $Al(OH)_3$ 10%	493	15	2.766	2.137	1.294	2.783	2.851	0.61	3.07
XIII	TMSPSt 30% + Bamboo sawdust 60% + $Al(OH)_3$ 10%	473	10	2.847	2.082	1.367	2.891	2.984	1.55	4.81
XIV	TMSPSt 30% + Bamboo sawdust 60% + $Al(OH)_3$ 10%	493	10	2.802	2.151	1.303	2.877	2.961	1.68	5.67
XV	TMSPSt 30% + Bamboo sawdust 60% + $Al(OH)_3$ 10%	473	15	2.541	2.003	1.269	2.590	2.681	1.93	5.51
XVI	TMSPSt 30% + Bamboo sawdust 60% + $Al(OH)_3$ 10%	493	15	2.211	1.892	1.169	2.240	2.302	1.31	4.12
XVII	TMSPSt 35% + Bamboo sawdust 55% + $Al(OH)_3$ 10%	473	10	2.700	2.112	1.278	2.739	2.838	1.44	5.11
XVIII	TMSPSt 35% + Bamboo sawdust 55% + $Al(OH)_3$ 10%	493	10	2.652	2.346	1.130	2.691	2.811	1.47	6.00
XIX	TMSPSt 35% + Bamboo sawdust 55% + $Al(OH)_3$ 10%	473	15	2.622	2.282	1.149	2.655	2.754	1.26	5.03
XX	TMSPSt 35% + Bamboo sawdust 55% + $Al(OH)_3$ 10%	493	15	2.678	2.180	1.228	2.700	2.771	0.82	3.47

3.8. Water Absorption Measurement

The water absorption behavior is intensively studied because it is an important characteristic that determines the end use of wood-polymer composites. Poor resistance of wood to moisture absorption can cause dimensional instability and undesirable effects on the mechanical properties of these materials.[29] A detailed study of this property is fundamental, as wood-based composites are often exposed to environments where humidity conditions change rapidly.[18,30] The results of experimental measurements of water absorption are presented in Table 2.

Table 2 shows that the water absorption coefficient depends on the binder concentration, temperature, and pressure of composites preparation. Bamboo-based composites with a relatively low binder concentration are more stable in moisture absorption. As the binder concentration increases, the stability of water absorption decreases. Temperature and pressure have a positive effect on water absorption properties.

4. Conclusions

A new composite material based on bamboo sawdust and silylated polystyrene as a binder with varying degrees of silylation, and aluminum chloride as a flame retardant was obtained at different temperatures and pressures. The directions of obtaining a composite structure and such physical properties as mechanical strengthening (bending strength and impact strength), thermostable properties, and water absorption were investigated.

To determine the morphology of the composites and the nature of ingredients distribution in the composite body, structural studies were performed using optical and scanning electron microscopy (SEM).

Energy dispersive X-ray microanalysis (EDS) was used to determine the elemental composition of the materials under study. As for the mechanical properties, the bending strength and impact strength were studied. Vicat and thermogravimetry methods were used to study the thermal stability of the composites. The water absorption of the composites was studied according to a standard method.

In general, it has been shown that the mechanical properties of composites significantly depend on the conditions of composites preparation. The strengthening of bamboo-based composites increases with increasing process temperature in the range of 473-493K at a constant (10.15 MPa) pressure.

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References

[1] Mohanty, B.N.; Sujatha, D.; Uday, D.N. Bamboo Composite Material: Game-changer for Developing Economies; 10th World Bamboo Congress, Korea 2015.
[2] Chen, H.C.; Chen, T.Y.; Hsu, C.H. Effects of Wood Particle Size and Mixing Ratios of HDPE on the Properties of the Composites. *Holz Roh Werkst* **2006**, *64*, 172–177. https://doi.org/10.1007/s00107-005-0072-x
[3] Laemlaksakul, V.; Kaewkuekool, S. Laminated Bamboo Materials for Furniture – A Systematic Approach to Innovative Product Design. *WSEAS Transactions on Advances in Engineering Education* **2006**, *3,* 424–430.
[4] Li, S.H.; Zeng, Q.Y.; Xiao, Y.L.; Fu, S.Y.; Zhou, B.L. Biomimicry of Bamboo Bast Fiber with Engineering Composite Materials. *Mater. Sci. Eng. C* **1995**, *3,* 125–130. https://doi.org/10.1016/0928-4931(95)00115-8
[5] Zhu, J.X.; Sheng, S.L. Discussing the Ecological Quality of Bamboo Structural Building. *Journal of Building Science* **2005**, *21*, 92–94.
[6] Shen, Z.R.; Ni, Y.; Hu, Z. Material Test and Structural Analysis For "Germany and China-Together Cooperation" Bamboo Structure Exhibition Hall. *Journal of Structural Engineers* **2009,** *25*, 51–54.
[7] Wen, Y.; Xu, K.; Tang, J.; Li, Y. Research Status and Development trend of Steel-Bamboo Composite Structure. *Adv Mat Res*, **2014**, *893*, 716–719. https://doi.org/10.4028/www.scientific.net/AMR.893.716
[8] Shin, F.G.; Xian, X.J.; Zheng, W.P.; Yipp, M.W. Analyses of the Mechanical Properties and Microstructure of Bamboo-Epoxy Composites. *J Mater Sci* **1989**, *24*, 3483–3490. https://doi.org/10.1007/BF02385729
[9] Okubo, K.; Fujii, T.; Yamamoto, Y. Development of Bamboo-Based Polymer Composites and Their Mechanical Properties. *Compos. Part A Appl. Sci. Manuf.* **2004**, *35*, 377–383. https://doi.org/10.1016/j.compositesa.2003.09.017
[10] Janssen, J.J.A. *Building with bamboo* (2nd ed.); Intermediate Technology Publication: London, 1995.
[11] Amada, S.; Ichikawa, Y.; Munekata, T.; Nagase, Y.; Shimizu K. Fiber Texture and Mechanical Graded Structure of Bamboo. *Compos. B. Eng.* **1997**, *28*, 13–20. https://doi.org/10.1016/S1359-8368(96)00020-0
[12] Abdulkareem, S.A.; Adeniyi, A.G. Production of Particleboards Using Polystyrene and Bamboo Wastes. *Niger. J. Technol.* **2017***, 36*, 788–793. http://dx.doi.org/10.4314/njt.v36i3.18
[13]. Mukbaniani, O.; Aneli, J.; Buzaladze, G.; Markarashvili, E.; Tatrishvili, T. Composites on the Basis of Straw with Some Organic and Inorganic Binders. *Oxid. Commun*. **2016**, *39*, 2763–2777.
[14] Mukbaniani, O.; Aneli, J.; Tatrishvili, T.; Markarashvili, E.; Londaridze L.; Kvinikadze, N.; Kakalashvili, L. Wood Polymer Composite Based on a Styrene and Triethoxy(Vinylphenethyl)silane. *Chem. Chem. Technol*. **2023**, *17,* 35–44. https://doi.org/10.23939/chcht17.01.035
[15] Aneli, J.; Shamanauri, L.; Markarashvili, E.; Tatrishvili, T.; Mukbaniani, O. Polymer-Silicate Composites with Modified Minerals. *Chem. Chem. Technol*. **2017**, *11*, 201–209. https://doi.org/10.23939/chcht11.02.201
[16] Tolentino, M.S.; Carpena, J.F.; Javier, R.M.; Aquino, R.R. Thermal Treatment Temperature and Time Dependence of Contact Angle of Water on Fluorinated Polystyrene as Hydrophobic Film Coating. *IOP Conf. Series: Mater. Sci. Eng.* **2017**, *205*, 012024. https://doi.org/10.1088/1757-899X/205/1/012024
[17] Mukbaniani, O.; Tatrishvili, T.; Markarashvili, E.; Londaridze, L.; Pachulia, Z.; Pirtskheliani, N. Synthesis of Triethoxy(Vinylphenethyl)silane with Alkylation Reaction of Vinyltriethoxysilane to Styrene. *Oxid. Commun*. **2022**, *45*, 309–320.
[18] Iulianelli, G.; Bruno Tavares, M.; Luetkmeyer, L. Water Absorption Behavior and Impact Strength of PVC/Wood Flour Composites. *Chem. Chem. Technol.* **2010**, *4*, 225–229. https://doi.org/10.23939/chcht04.03.225
[19] Lee, S.-H.; Ohkita, T. Mechanical and Thermal Flow Properties of Wood Flour-Biodegradable Polymer Composites. *J. Appl. Polym. Sci*. **2003**, *90*, 1900–1905. https://doi.org/10.1002/app.12864
[20] Liu, C.; Tanaka, Y.; Fujimoto Y. Viscosity Transient Phenomenon during Drop Impact Testing and Its Simple Dynamics Model. *World J. Mech.* **2015**, *5*, 33–41. https://doi.org/10.4236/wjm.2015.53004
[21] Chudzik, J.; Bieliński, D.M.; Bratychak, M.; Demchuk, Y.; Astakhova, O.; Jędrzejczyk, M.; Celichowski, G. Influence of Modified Epoxy Resins on Peroxide Curing, Mechanical Properties and Adhesion of SBR, NBR and XNBR to Silver Wires. Part I: Application of Monoperoxy Derivative of Epoxy Resin (PO). *Materials* **2021**, *14*, 1320. https://doi.org/10.3390/ma14051320
[22] Mukbaniani, O.; Brostow, W.; Aneli, J.; Londaridze, L.; Markarashvili, E.; Tatrishvili, T.; Gencel, O. Wood Sawdust Plus Silylated Styrene Composites with Low Water Absorption. *Chem. Chem. Technol*. **2022**, *16*, 377–386. https://doi.org/10.23939/chcht16.03.377

[23] Mukbaniani, O.; Aneli, J.; Londaridze, L.; Markarashvili, E.; Tatrishvili, T. Ecologically Friendly Polymer Composites on the Base of Leafs. *Oxid. Commun.* **2021***, 44*, 908–921.
[24] Mukbaniani, O.; Brostow, W.; Aneli, J.; Markarashvili, E.; Tatrishvili, T.; Buzaladze, G.; Parulava, G. Sawdust Based Composites. *Polym Adv Technol* **2020**, *31*, 2504-2511. https://doi.org/10.1002/pat.4965
[25] Mukbaniani, O.; Tatrishvili, T.; Kvinikadze, N.; Bukia, T.; Pachulia, Z.; Pirtskheliani, N.; Petriashvili, G. Friedel-Crafts Reaction of Vinyltrimethoxysilane with Styrene and Composite Materials on Their Base. *Chem. Chem. Technol*. **2023**, *17*, 325–338. https://doi.org/10.23939/chcht17.02.325
[26] Mukbaniani, O.; Brostow, W.; Hagg Lobland, H.E.; Aneli, J.; Tatrishvili, T.; Markarashvili, E.; Dzidziguri, D.; Buzaladze, G. Composites Containing Bamboo with Different Binders. *Pure Appl. Chem.* **2018**, *90*, 1001–1009. https://doi.org/10.1515/pac-2017-0804
[27] Xu, G.; Wang, L.; Liu, J.; Wu, J. FTIR and XPS Analysis of the Changes in Bamboo Chemical Structure Decayed by White-Rot and Brown-Rot Fungi. *Appl. Surf. Sci*. **2013**, *280*, 799–805. https://doi.org/10.1016/j.apsusc.2013.05.065
[28] Kickelbick, G. Concepts for the Incorporation of Inorganic Building Blocks into Organic Polymers on a Nanoscale. *Prog. Polym. Sci*. **2003**, *28*, 83–114. https://doi.org/10.1016/S0079-6700(02)00019-9
[29] Bledzky, A.; Letman, M.; Viksne, A.; Rence, L. A Comparison of Compounding Processes and Wood Type for Wood Fibre–PP Composites. *Compos. Part A Appl. Sci. Manuf.* **2005**, *36*, 789–797. https://doi.org/10.1016/j.compositesa.2004.10.029
[30] Shi, S.Q.; Gardner, D.J. Hygroscopic Thickness Swelling Rate of Compression Molded Wood Fiberboard and Wood Fiber/Polymer Composites. *Compos. Part A Appl. Sci. Manuf.* **2006**, *37*, 1276–1285. https://doi.org/10.1016/j.compositesa.2005.08.015

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ЕКОЛОГІЧНО ЧИСТІ КОМПОЗИТИ НА ОСНОВІ БАМБУКА

Анотація. *Дослідження присвячено отриманню композиційних матеріалів на основі бамбука та нових екологічно чистих в'яжучих речовин з різним ступенем силілювання (15-35 %) за різних тисків і температур. Синтез проводили з використанням силільованого полістирену (полі[триметокси(4-вінілфенетил)]силану) та стирену як в'яжучої речовини й армувального агента в присутності органічних/неорганічних добавок, антиоксидантів та антипірену. Полі[триметокси(4-вінілфенетил)]силан, тверду речовину коричневого кольору, було синтезовано реакцією алкілування вінілтриметоксисилану та полістирену в присутності безводного $AlCl_3$. У цій статті представлено розробку композитів екологічного призначення (екокомпозитів) з використанням бамбукових волокон та їхні основні механічні властивості. Поверхневі структури нових композитів досліджували кількома методами, включаючи електронну мікроскопію, енергодисперсійний рентгенівський мікроаналіз, випробування на згин, ударний тест Шарпі, термогравіметричні дослідження та визначення водопоглинання. Нові композити характеризуються добрими механічними властивостями, термостійкістю, екологічною чистотою та водопоглинанням, значно меншим за водопоглинання існуючих деревостружкових плит.*

Ключові слова: *композити, полі[триметокси(4-вінілфенетил)] силан, антиоксиданти, бамбукові волокна, ІЧ-спектроскопія, рентгенівський мікроаналіз, термогравіметричні дослідження.*