

NEW ENVIRONMENTALLY SAFE COMPOSIT

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Abstract

The aim of the work is to obtain composite materials on the basis of pine needles and investigation the properties of composite materials: water absorption, physical-mechanical investigations: (hardness, flexural and stretching and thermal properties, Vicat, FTIR, SEM, energy dispersive X-ray microanalysis and optical microscopic studies. Study of resistance of composites to microorganisms. The pine is one of the more extensively used types of wood used as lumber. The composites were prepared by hot pressing of highly dispersed (20-30 μm) dry pine needles sawdust with triethoxysilylated styrene (in the presence of 1% benzoyl peroxide). Fourier transform infrared spectroscopy (FTIR) confirmed the composition of composites. Optical microscopic examinations showed amorphous clusters on the micrographs, and concentration heterogeneity is also observed. Mostly obtained composites are anisotropic and are characterized by the fibrous structure of supramolecular structures. The surface morphology of the composites was studied by scanning electron microscopy (SEM).

Keywords: ecology, composite, filler, binder, property

I. Introduction

Agro-industrial waste removal is a serious issue of concerning in developing countries. Cellulose is a polysaccharide polymer. This present review [1] explores cellulose history, structure, worldwide production, and extraction of cellulose from agro-waste. A wide spectrum of researches in the arena of properties of cellulose, hemicellulose and lignin; their degradation; sources and composition of cellulosic and its derivatives from agro-industrial wastes; present status of converting them into value-added products of food and pharmaceutical applications. Cellulose is a tremendous product due to its abundance and characteristic structural properties. The major industrial source of cellulose is vascular plants. The lignocellulosic materials, especially agro-industrial residues, are important as reinforcement products for building construction material industry, in terms of environmental preferences of the modern society. Most paper products generate from wood pulp, while textile fibers are commonly not isolated from woody fibers. The materials based on cellulose and its derivatives have been used for a wide variety of applications, such as food additives, paper manufacturing, pharmaceuticals, or other chemical engineering uses, such as chromatography, paints, and explosives.

Waste is defined as any material, which has not yet been fully utilized, i.e., the leftovers from production and utilization. The waste contains three main constituents: Cellulose, hemicellulose, and lignin, and it can contain various compounds [2]. Cellulose and hemicellulose are carbohydrates that can be broken down by enzymes and acids and then fermented to produce ethanol renewable electricity, fuels, and biomass-based products [3, 4]. However, waste is an expensive and generally unavoidable result of human activity. It includes plant materials, agricultural, industrial and municipal wastes, and residues [5]. Food processing wastes food in spillage, spoilage, discarding substandard edible materials, or removing edible food parts in inefficient processing [6]. Waste

significantly impacts environmental, economic, and community health [7]. Plants produce about 180 billion tons of cellulose manufacture annually, and it is the largest reservoir of organic carbon on the earth. Cellulose constitutes the most abundant, renewable polymer resource available today worldwide. It has been expected that by photosynthesis, 10^{12} tons are synthesized annually in a rather pure form, for example, in the seed hairs of the cotton plant but mostly are common with lignin and other polysaccharides in the cell wall of woody plants. Cellulose is the structural part of the primary cell wall of green plants, many forms of algae, and the oomycetes. Cellulose is the most common organic compound on the earth. About 33% of all plant material is cellulose (cotton is 90% and wood is 40–50%). For industrial use, cellulose is mainly obtained from wood pulp and cotton. It is mainly used to manufacture paperboard and paper [8] and it is transformed into a wide variety of derivative products such as cellophane and rayon. Converting cellulose from energy crops into biofuels such as cellulosic ethanol is under exploration as an alternative fuel source.

In recent years great interest in the development of new composites is derived from thermoplastic polymer matrices reinforced with wood filler, because of their environmental and economic benefits [1, 2]. Their renewability, biodegradability, low density, high stiffness and relatively low price are established [3]. Among of these various thermoplastic matrices mainly used in the manufacture of plastic / wood composites was polystyrene [4], which is very popular because of its inapparency, fluidity and good electrical insulating properties [5].

The use of lignocellulosic fibers has certain disadvantages such as degradation at low temperatures with poor compatibility between the polar lignocellulose filler and the non-polar polymer matrix [6]. Due to the strong intermolecular hydrogen bonding between the lignocellulose fibers, which tend to agglomerate during mixing with the polymer matrix in the compounding process, resulting composites with low mechanical and thermal properties [7].

The improving of the interface compatibility between thermoplastic polymers and lignocellulosic filler has attracted much attention from researchers [8]. Several modifications of the fiber surface such as reaction with acid compounds [9, 10], alkali treatment [11, 12] and the incorporation of compatibilizer, such as malleated polymer [13, 14] or treatment with coupling agents [15, 16] are reported in the literature.

Among the different coupling agents, functional organosilanes [$\text{RSi}(\text{OR}')_3$] are often used. These bifunctional molecules with their alkoxy-silane groups are used to modify the surfaces of natural fibers. After hydrolysis reactions of the fibers, surfaces rich in OH groups can be created. Chemical bonds on the surfaces of the fibers through a siloxane bridges, organofunctional groups bond to the polymer matrix. These groups improve the compatibilization between the fibers and the polymer matrix by formation of covalent bonds. The silane coupling agents provide bridges between the fibers and the matrix [17-19].

II. Experimental part

Processing. The composites were prepared by hot pressing of highly dispersed (50 μm) components under pressures up to 15 MPa and temperatures up to 100°C in molds for 15 min. We have created two types of samples: cylindrical (for investigation of water absorption) and rectangular (for mechanical testing).

Fourier transform infrared spectra were determined with a Varian 660-IR FT-IR Spectrometer. The KBr pellets of samples were prepared by mixing (1.5–2.0) mg of samples, finely grounded, with 200 mg KBr (FTIR grade) in a vibratory ball mixer for 20 s.

Microstructure of the samples was studied by NMM-800RF/TRF type of optical microscope SEM and EDS observations were conducted. Measurements were performed under a microscope - Tescan Vega 3, LMU, LaB 6 cathode. Maximum accelerating voltage was 30 kV, resolution 2.0 nm. The

microscope was also equipped with an energy dispersive spectrometer of X-ray-induced electron beam specimens (EDS, Oxford Systems). EDS was used to analyze the sample compositions.

Bending testing also known as flexural testing, was performed on parallelepipeds with the length of 10 cm and the vertical square cross-section of 1 cm². Each specimen was placed on two prisms, with the distance of 8.0 cm between the prisms. The indenter was a metal cylinder with the diameter of 10 mm applied from above to the midpoint of the specimen. Bending strength (or flexural strength) is defined as the stress needed to create a breaking point (a crack) in the outer surface of the test specimen .

Impact viscosity determination, also called *shock viscosity* determination, is a technique applied to soft solids 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 $mg(h_1 - h_2)$, anormalized with respect to the horizontal cross-section of the specimen.

Vicat softening depth consists in the determination of the depth of the indentation with respect to the top surface caused by a flat ended indenter with the cross-section of 1 mm². The load applied is 10 or 50 N and the cross-section of the indenter end is circular. The term *Vicat hardness* is also in use – really confusing since larger values correspond to lower hardness.

Water absorption is determined simply as the percentage weight change of the sample after submersion in water. We have performed such measurements after 3 hours and 24 hours exposition to water.

III. Results and discussions

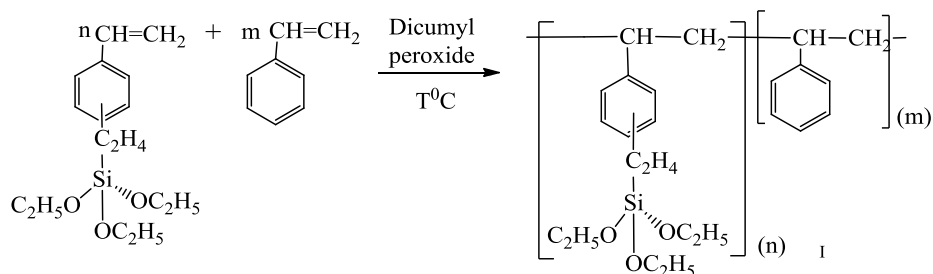
Wood has been an essential material for human survival since the primitive state, for its wide abundance, renewable and environmentally benign nature, relative ease of working it, and outstanding mechanical properties. With the development of technology, wood came to be used for shelter, fuel, tools, boats, vehicles, bridges, furniture, engineering materials, weapons, and even raw materials for energy. Now, wood is widely used in various corners of human life. The wood-polymer composites (WPC) are materials of relatively new generation, in which the role of the binder performs such thermo-plastics polymers as polyethylene, polypropylene, polyvinyl chloride, polystyrene and others. These materials sometimes are called as liquid wood. There are known rather wide assortment of the products made from WPC. Using such methods as extrusion, hot pressing, rotation formatting one obtained such goods as terraces, floor desks, wall panels, roofs coatings, pipes and so on. WPC are distinguished from analogs by high stability to atmospheric influences, mechanical and chemical sustainability, water proofing, which allows to use these materials as coatings of washing rooms, sauna, terraces, and docks and so on. Wood-polymer composites (WPC) are substances or items made up of one or more natural materials or flours but one or a mixture of polymers, such as polyamide, rayon, or latex. Their cheap and superior efficiency, as well as their elevated sustainable development, low moisture absorption, sturdiness against ecological impact such as insects and fungi when compared to timber, high-dimensional data stability over their entire life, and high relative stiffness, have attracted the attention of manufacturers and researchers in recent decades ⁵.Introduction inorganic nanoparticles have found numerous applications in fields such as medicine, design of electronic devices, catalysis, and polymers reinforcement. Grafting polymer chains endow them with unique functional properties and allow tailoring of their surface characteristics to obtain materials with novel properties and applications. The wood polymer composite on the basis of triethoxy (vinylphenethyl) silane and sawdust via in-situ polymerization has been obtained earlier. The aim of the work was to obtain and research new environmentally safe wood polymer composites (WPC) - based on a new environmentally safe binder and reinforcing agent triethoxy- (vinylphenethyl) silane

and styrene and in the presence of antioxidant aluminum hydroxide, study physical-mechanical, thermal properties, and water absorption.

Composites based on dry sawdust on the basis of pine with triethoxy (vinylphenethyl) silane and styrene as a binder and reinforcement agent which was obtained via hydrosilylation reaction of divinylbenzene with triethoxyvinylsilane according to the have been created. The pine is one of the more extensively used types of wood used as lumber. The composites were prepared by hot pressing of highly dispersed (20-30 μm) dry sawdust on the basis of pine with agent. The composites have been created under pressures up to 15 MPa and in the temperature range 140-220°C in samples for 5 min. Two types of samples have been created: cylindrical (for investigation of water absorption) and rectangular (for mechanical testing).

It is known that the wood sawdust contains cellulose, hemicellulose derivatives, and lignin structural rings with hydroxyl groups. In our binder triethoxy(vinylphenylethyl) silane we also have ethoxyl groups as well as a vinyl group. Those groups were expected to participate in the etherification reaction with a binder through inter-molecular and intra-molecular reactions and the vinyl group may polymerize. So, used a coupling agent.

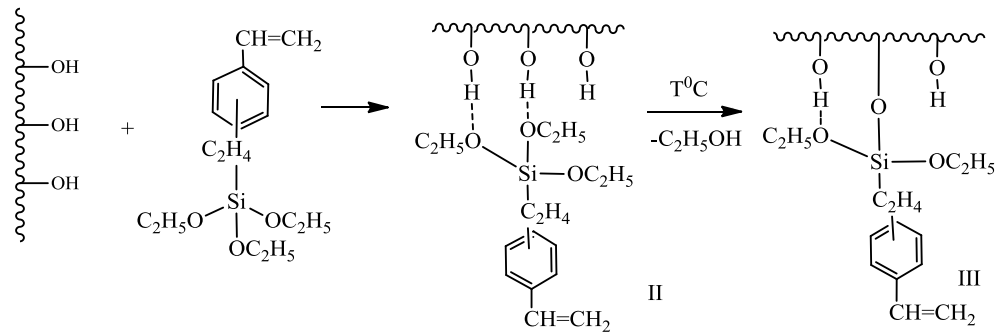
Composites were prepared in the following ratio: 3% triethoxy(vinylphenethyl)silane, 27% styrene, and dicumyl peroxide, 60% pine sawdust. As filler two types of wood sawdust have been obtained sifted sawdust medium size particle 0.614 mm and unsifted sawdust particle size 1.615 mm The triethoxy(vinylphenethyl)silane (TEVPES) and styrene were stirred with dicumyl peroxide (DP) (1% by weight) and this homogeneous mixture (3-5% (TEVPES) - 27-25 %) was added to a predefined weight ratio of pine sawdust. Then the mixture was stirred for 5 minutes until it became homogeneous, placed in a press form, and pressed at several temperatures. During hot-pressing, the initiator existing in the mixture may initiate the polymerization reaction of vinyl groups of TEVPES and styrene. Wood sawdust impregnated with TEVPES and styrene, at the moment of hot pressing, forms chemical bonds with the hydroxyl groups of a wood surface. Active filler is likely formed, then etherification and in-situ polymerization reactions take place. In the case of dicumyl peroxide during hot pressing, in situ polymerization and copolymerization by the formation of different ring polymers (Structure I) is possible according to the following Scheme 1:



Scheme 1: Co-polymerization of triethoxy(vinylphenethyl)silane and styrene

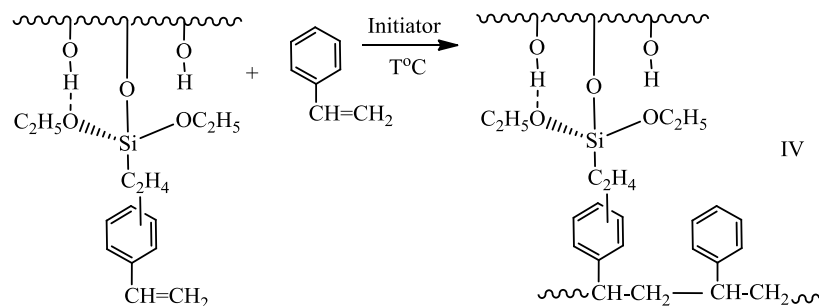
It is not excluded that triethoxy(vinylphenethyl)silane can form hydrogen bonds with or after the polymerization reaction with silane sawdust (Structure II) by etherification at high temperatures to form a chemical bond (Structure III) according to Scheme 2:

In particular, one expects the formation of hydrogen bonds before the onset of the etherification reaction with triethoxysilylated styrene and also the formation of ethyl alcohol.



Scheme 2: Formation hydrogen bonds and etherification reactions of triethoxy(vinylphenethyl)silane with sawdust surface.

It is possible that the product of the interaction of triethoxy(vinylphenethyl)silane with cellulose will undergo a polymerization reaction with styrene (Structure IV) according to Scheme 3:



Scheme 3: Co-polymerization reaction of TEVPES and cellulose interaction product II with styrene

For obtaining composite materials were performed Fourier transform infrared spectra investigation, likewise, optical microscopic examinations, scanning electron microscopy and energy dispersive X-ray spectral analysis.

In the FTIR spectra of composite materials, one can see the adsorption bands for the asymmetric valence oscillations characteristic of the $\equiv\text{Si-O-Si}\equiv$ bond, up to a maximum of 1026 cm^{-1} , corresponding to siloxane bonds. The absorption band at 1150 cm^{-1} area corresponds to the asymmetric absorption bands characteristic of the Si-O-C and C-O-C bonds, where the absorption bands overlap. Absorption bands at 1262 , 1370 , 1419 , 1507 , 1600 - 1650 , 1720 , 2800 - 2950 , and 3346 cm^{-1} correspond to the methyl groups, CH bond absorption in ($-\text{C} / \text{C}- / \text{CH}_3$), CH_2 cellulose - lignin, C=C aromatic, C=C alkene, (C=O ester bonds), phenyl groups and -OH groups.

Mostly obtained composites are anisotropic with different sizes of particles. Cracks and dividing lines are also observed. Whose dimensions can be easily determined using the scale bar.

The surface morphology of the composites was studied by scanning electron microscopy (SEM). In Fig. 1 one can observe indicate pores, indentations, and inserts with the sizes in the range of 0.01 - 0.5 mm .

For composites, physical-mechanical investigations have been performed. In particular, the determination of the bending strength and impact viscosity with respect to temperature and triethoxy(vinylphenethyl)silane and styrene concentrations has been studied.

As have shown investigation results, with increasing temperature from 140 to 220° C , at 20 -degree intervals, the values of bending strength decrease from 10.6 up to 20.9 MPa . With an increase in the TEVPES concentration the values of bending strength increase from 23.6 up to 29.6 MPa . With an increase in temperature, the impact viscosity slightly increases.

The thermal properties of composites have been studied via the Vicat method. The Vicat softening temperature is the temperature at which a flat-ended needle penetrates the specimen to the depth of 1 mm under a specific load. The temperature reflects the point of softening to be expected when a material is used in an elevated temperature application.

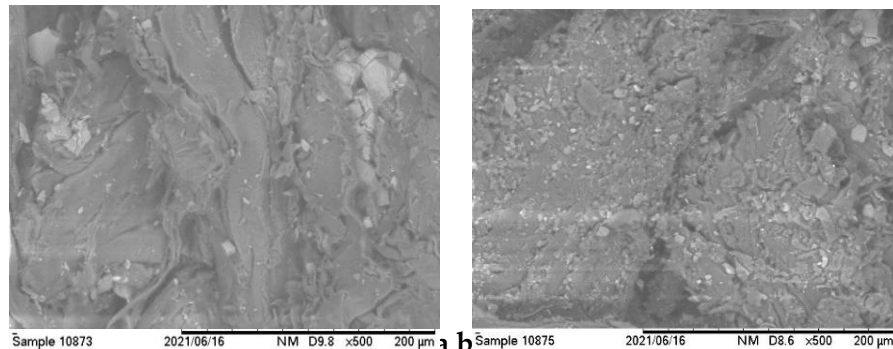


Figure 1: Scanning electron microscope micrograph of a composites: Sawdust (sifted)-60%+TEVPES -5%+ St -25% +Al(OH)₃ -10%, 160 °C (a), Sawdust (sifted) 60%+TEVPES-5%+ St -25% +Al(OH)₃ -10% (220°C) (b).

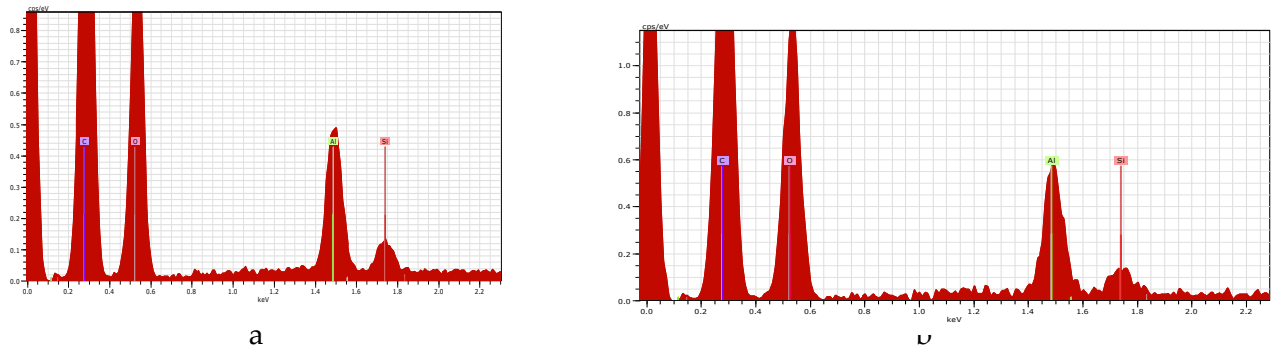


Figure 2: Energy dispersive X-ray microanalysis of composites: Sawdust (sifted)-60%+TEVPES -5%+ St -25% +Al(OH)₃ -10%, 160 °C (a), Sawdust (sifted) 60%+TEVPES-5%+ St -25% +Al(OH)₃ -10% (220°C) (b).

The composites based on TEVPES, styrene, and Al (OH)₃ with sawdust are characterized by improved thermal stability with increasing temperature. This result is expected for two reasons. The total volume of connected empty micro spaces distributed randomly in the composite has been reduced by the pressure application. Consequently, the rigidity and thermal stability of the WPC material increase, and the density of micro-structure increases again TEVPES creates new heterogeneous chemical bonds in the composites via etherification reaction at high temperatures not only with sawdust surface but with used antioxidant Al (OH)₃. In parallel, TEVPES reinforce composite materials, by in-situ copolymerization reactions with styrene. The higher this pressure, the higher is thermal stability compositions.

Water-absorption test is a test to determine the moisture content of the soil as a percentage of its dry weight Water absorption is one of the significant magnitudes used to determine the amount of water absorbed under specified conditions.

The results of investigations were shown, that with an increase in pressing temperature from 140° up to 220°C the water absorption decreases from 54-60% up to 0.95-1.07 %. It must be noted that the WPC obtained from sifted sawdust is characterized by less water absorption. WPC prepared from unsifted sawdust is characterized by increased density compared with sifted sawdust. Both phenomena may be explained with relatively low values in the last column show low volumes of the empty intermolecular spaces.

During the current study composition of composite materials, as well of composition plant materials, used for the preparation of these materials were determined. Specifically, content of Calcium, Magnesium, Sulfur and Silicon were determined. Quantitative analysis were performed using ISO methods. Experimental results comply with theoretically expected results.

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