

RIGA TECHNICAL UNIVERSITY
Faculty of Materials Science and Applied Chemistry
Institute of Design Technologies

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**EXTENSION OF ASSORTMENT OF HEMP-
BASED COMPOSITE AND TECHNOLOGY
OPTIMIZATION**

Summary of the Doctoral Thesis

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DOCTORAL THESIS PROPOSED TO RIGA TECHNICAL UNIVERSITY FOR THE PROMOTION TO THE SCIENTIFIC DEGREE OF DOCTOR OF ENGINEERING SCIENCES

To be granted the scientific degree of Doctor of Engineering Sciences, the present Doctoral Thesis has been submitted for the defence at the open meeting of RTU Promotion Council on April 26, 2019 at the Faculty of Materials Science and Applied Chemistry of Riga Technical University, 6 Kipsalas Street, Room 117.

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DECLARATION OF ACADEMIC INTEGRITY

I hereby declare that the Doctoral Thesis submitted for the review to Riga Technical University for the promotion to the scientific degree of Doctor of Engineering Sciences is my own. I confirm that this Doctoral Thesis had not been submitted to any other university for the promotion to a scientific degree.

Name Surname (signature)

Date:

The Doctoral Thesis has been written in Latvian. It consists of Introduction; 3 chapters; Conclusion; 121 figures; 29 tables; the total number of pages is 163. The Bibliography contains 189 titles.

CONTENTS

Abbreviations	5
1. Overall review of the thesis.....	6
1.1. Introduction	6
1.2. Goal of the Thesis	6
1.3. Tasks of the Thesis	6
1.4. Scientific novelty.....	7
1.5. Thesis to be defended.....	7
1.6. Practical significance of the Thesis	7
1.7. Approbation of the results	8
2. Overview of the thesis.....	11
2.1. Situation analysis.....	11
2.2. Technologies of experiment and sample testing methods.....	13
2.2.1. Composite components	13
2.2.2. Methods of chemical treatment of reinforcing components.....	13
2.2.3. Composite preparation	15
2.2.4. Sample testing methodology	18
2.3. Results	20
2.3.1. Properties of composite reinforcing components	20
2.3.2. Properties of hemp reinforced composites	22
2.3.3. Surface and aging studies of composites.....	25
Conclusions	29
Proposals and recommendations	30
References	31

ABBREVIATIONS

A – primary processing waste of hemp “Białobrzesskie” fiber
 a^* , b^* – color coordinates in CIELab-76 color space
WRC – waste-reinforced composite
APTES – γ -aminopropyltrialkoxysilane
 C – chroma
 d – diameter
 D – determination factor
EDS (EDX) – energy-dispersive X-ray spectroscopy
 E_k – extruded composite
 E_t – modulus of elasticity in tension, MPa
 ϵ_t – elongation at break, %
FTIR – Fourier-transform infrared spectroscopy
GU – specular reflection gloss, gloss units
 H – hue
 KI – melt flow index, g / 10 min
 L^* – lightness
LLDPE – linear low-density polyethylene
MAPE – maleated polypropylene as coupling agent
wt % – weight percent
 R – correlation coefficient
RMS – root mean square
SEM – scanning electron microscopy
Si – silanized reinforcing component
Sol – reinforcing component treated with sol-gel method
Š – technical fibres of hemp “Białobrzesskie”
FRC – fiber-reinforced composite
TEOS – tetraethyl orthosilicate
V – mixing of the components on two roll-mills
HV – Vickers hardness, MPa
 Δa^* , Δb^* – color numerical values
 ΔC – color saturation difference
 ΔE – just-noticeable difference between two colors
 ΔH – hue difference between two colors
 ΔL – lightness between two colors
 ρ – density, g/cm³
 σ_t – maximal tensile strength, MPa
ZAD – zinc acetate dihydrate

1. OVERALL REVIEW OF THE THESIS

1.1. Introduction

Due to the increasing production of various composites in the world and decreasing of fossil resources, methods are being sought and new materials created that could improve the properties of existing materials, or replace them with biological, eco-friendly composites that can be recycled and reused, while also saving resources. High density polyethylene and polypropylene are polyolefins with a wide range of applications, thermoplastic matrices can be easily recycled and made of various composites. The linear low density polyethylene is used because its main advantage is the regular structure and high elasticity that can be successfully used to increase the natural fiber content of the composite, thus improving both the composite properties and reducing the polyethylene consumption and material price. As a reinforcing component, waste of hemp fiber first stem treatment and high quality fibres have been selected. Hemp growing in Latvia is gradually developing, so the amount of processing waste will increase in the future. Thanks to suitable cultivation and harvesting methods, hemp has high mechanical properties. The cultivation and use of industrial fiber hemp can make a major contribution to supplementing natural resources in Latvia and developing new business areas, as hemp is a fast growing culture and does not require a large amount of chemicals in the growth process. The use of waste in hemp processing and textile processing for the production of natural fiber composites significantly saves fossil resources and the natural fiber composite is a semi-biodegradable environmentally friendly material.

1.2. Goal of the Thesis

1. To expand the assortment of natural fiber reinforced polymer composites by integrating hemp fibers and waste into a linear low-density polyethylene matrix for composite design with reduced water absorption and mechanical properties for predictable applications.
2. To adjust chemical treatments for reinforcing hemp components that promote adhesion of the polymer matrix and reinforcing components and durability of the coating.

1.3. Tasks of the Thesis

1. Selection and analysis of published literature sources on composites containing natural vegetable fibers (hemp, flax, etc.) and their properties.
2. Review of natural fiber surface modification techniques, their analysis and selection of suitable application technologies.
3. Optimization of the selected natural fiber surface modification methods.
4. Modification of hemp fiber waste and evaluation of coating properties.
5. Manufacture of reinforced composites with the highest quality modified hemp.

6. Testing and analysis of the obtained composite properties, improvement of manufacturing technologies.
7. Predicting possible application of the investigated composites and identification of recycling options.

1.4. Scientific novelty

The effect of chemical treatment of hemp “Białobrzegie” fiber and of first-stage processing waste on hemp properties and properties of modified low-density polyethylene composites containing modified hemp fiber has been investigated in the work. As a result of the study, the possibility of increasing the hemp fiber content in the composite has been demonstrated, while simultaneously improving the physical and mechanical properties of the composite, significantly reducing the water absorption capacity of the material and retaining good rheological properties that allow the composites to be recycled with conventional polymer processing techniques (extrusion, die casting, etc.). Customized and improved sols provide a high quality hemp surface modification.

1.5. Thesis to be defended

1. The study shows that the use of sol-gel technology to modify the surface properties of hemp fibers ensures that the properties of LLDPE composite are improved. It is possible to increase the content of modified fiber residues in the composite while maintaining a sufficiently good melt flow for composite and allowing optimization of composite manufacturing parameters.
2. The optimum composition of the sol forms a coating that does not damage hemp waste during the fixation process. The synthesized sols can be modified to give the desired properties to both fiber residues and natural fiber composites.
3. Modified hemp fiber residues can be integrated into thermoplastic polymer composites, have good mechanical strength and reduced water absorption, allowing for more predictable material usage.

1.6. Practical significance of the Thesis

Hemp fibers obtained in Latvia have good properties thanks to the weather conditions that are suitable for their cultivation, and the harvest is good enough, but the relationship between the producer of the hemp fiber and manufacturer is not properly organized. Exporting to other countries is not economically viable, so the production of high-quality fiber materials on site would contribute to the economic development of the industry and would not pose a major threat to the environment. The use of residues for the production of new composite saves resources and addresses waste disposal in line with the circular economy guidelines.

In the course of the Doctoral Thesis, a hemp and LLDPE-based composite has been created in which the integrated components have increased adhesive activity. This allows to

supplement both the practical knowledge and the technological and operational properties of the composite, as well as to significantly expand the range of possible uses of the material.

The improved composite has melt flow properties that allow it to be processed using conventional polymer processing techniques (extrusion, die-casting, rolling, pressing, etc.). Generally, the processing of high-performance natural fiber composites in articles is difficult because by incorporating the fiber-reinforcing components into the polymer matrix, the composite melt flow index is rapidly diminishing. The resulting natural fiber composites can not be used for the production of heavy duty structural components but other products, such as car door panels, car bumpers, body casings, packaging and other areas where polyethylene is widely used.

1.7. Approbation of the results

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*Scientific articles indexed in Web of Science and/or SCOPUS data bases.

** Scientific articles in proceedings with ISBN code indexed in Web of Science Conference Proceeding Citation Index and/or SCOPUS data bases.

2. OVERVIEW OF THE THESIS

2.1. Situation analysis

Plant-based fiber composites can be divided into three groups: filled, reinforced and laminated composites. Depending on the type, it should be taken into account that they have different fiber preparation processes, composite manufacturing methods and processing options [1]. The production of composites is limited by the heat treatment temperature, which should not exceed 180–200 °C for a long time. This factor reduces the choice of potential polymers that can be used as matrix natural fiber reinforced composites [2], [3]. The demand for petroleum-derived polymers is growing, but bio-materials are also of great interest and importance, thanks to their lower production costs and the ability to conserve nature. Natural fibers have several important advantages: they are a renewable resource with low density, relatively low price, easily recyclable and biodegradable, with good thermal and acoustic properties [4], [5].

Plant-based fibers mainly consist of cellulose, lignin and hemicellulose. Even within one species, the chemical composition of hemp fibers varies depending on the place of growth, changing weather conditions and respective agrotechnical complex. Comparing the chemical composition of fibers and woody part (shives), there are significant differences, with more than half the number of cellulose lower in the shives, but the use of more water-soluble components that affect their properties and the most suitable treatment methods. The total fiber content in the dry stem of the hemp plant varies between 25 % and 35 % depending on the variety [6], [7].

In composites using short fibers as reinforcing components, the percentage of fiber, length of fibers or waste, and the most appropriate method of manufacture are relevant for each matrix. The hemp variety has no particular impact on the mechanical properties of the LWBPE composite, but the length of fibers significantly affects them. In the case of hemp fibers, the optimum fiber content of the LWBPE in composite is 30 % by weight, and the length of the fiber used is up to 1 mm [8]. The external load is transferred to the reinforcing components due to the interphase linkage between the matrix and the hemp, strong interphase adhesion guarantees an increase in mechanical properties.

A significant drawback of natural fibers is the tendency to attract water, therefore a wide range of chemical treatments are used to reduce it and give it additional features. Depending on the intended use of the composite, various methods of pre-treatment of fibers or combinations thereof are used – chemical and mechanical treatment, effect of microorganisms, etc. Modification of hemp fibers is most often done by treatment with alkali, acetylation, silanization, or the application of various nano-coatings. Modification of reinforcing components to be integrated in composites by applying sol-gel technology [9], [10] has been little studied in sources.

Adapting the sol-gel method to hemp fibers is a prerequisite for qualitative coating on natural fibers, with different plant species being more sensitive to the chemical composition

of the sole used. Hemp fibers do not withstand the acidity of cotton fibers as they contain less cellulose [11].

The sol-gel process is influenced by a variety of factors: precursor selection, H_2O : Si ratio, solvent, sol pH, catalyst type, temperature, etc. To obtain nanoparticles within the range of 1–4 nm, a low temperature at which the precursor solubility is slow and pH close to 2 or 7 should be used to slow the growth of the nanoparticles. Polymerization is easier to control in an acidic environment because the changes in particle growth do not take place as fast as in a basic environment [12].

Plant lignocellulosic, fibrous reinforcing components are mainly used for reinforcing thermoplastic polyolefin matrices, as thermoplastic polymers can be recycled, have relatively low processing temperatures and good mechanical properties. Polyethylenes, such as LDBPE, are suitable for making natural fiber reinforced composites because of their low melting point (from 120 °C), high melt flow index (up to 50 g / 10 min), which is essential to increase fiber percentages, maintain performance and reduce matrix consumption. In the global polymer market, LDBPE predicts an increase in consumption of 6.0–5.5 %, as it is relatively cheap [13].

Hemp fiber reinforced composite properties are used not only for fiber modifications, but also for various additives for matrix modification – plasticizers, nanoparticles, processing agents, pigments, etc. In recent years, hybrid composites combining different modifying techniques, different reinforcing components and nanoparticles have been extensively studied [14], [15].

The tensile and bending properties of hemp-containing composites significantly increase the interphase modifier maleinized polyethylene wax (MAPE) and nanoparticle additives, which can also be achieved with silage treatment of hemp. Silanization also reduces water absorption, with some sources also achieving positive results using fiber treatment with alkali and acetylation. The chemical composition of the fibers, lignin, cellulose and hemicellulose in different parts of plants are very different, and it also has a strong influence on the mechanical properties of composites. It has been stated that the mechanical properties of fiber-reinforced composites are higher than those of the waste-filled composites [8], [16].

The properties of natural fiber composites have a significant impact on the preparation techniques of the composition and methods of obtaining the finished product. There are currently two composite product preparing technologies in the world: combined and split, depending on the desired result. Generally, mixing and scattering of the components in the matrix depends on the technology and parameters selected during the preparation of the composition, such as temperature, time, stirrer speed, shear rate, etc. Functional lubricants and other additives also have a significant effect on the viscosity of the mixing environment, polymer melt, and the quality of the resulting composite material [17], [18].

2.2. Technologies of experiment and sample testing methods

2.2.1. Composite components

A linear low density polyethylene (LLDPE) is used as a composite polymer matrix. LL6201 grade polyethylene is used for fiber-reinforced composites (FRC) used, while LL6201 XR is used for waste-reinforced composites (WRC).

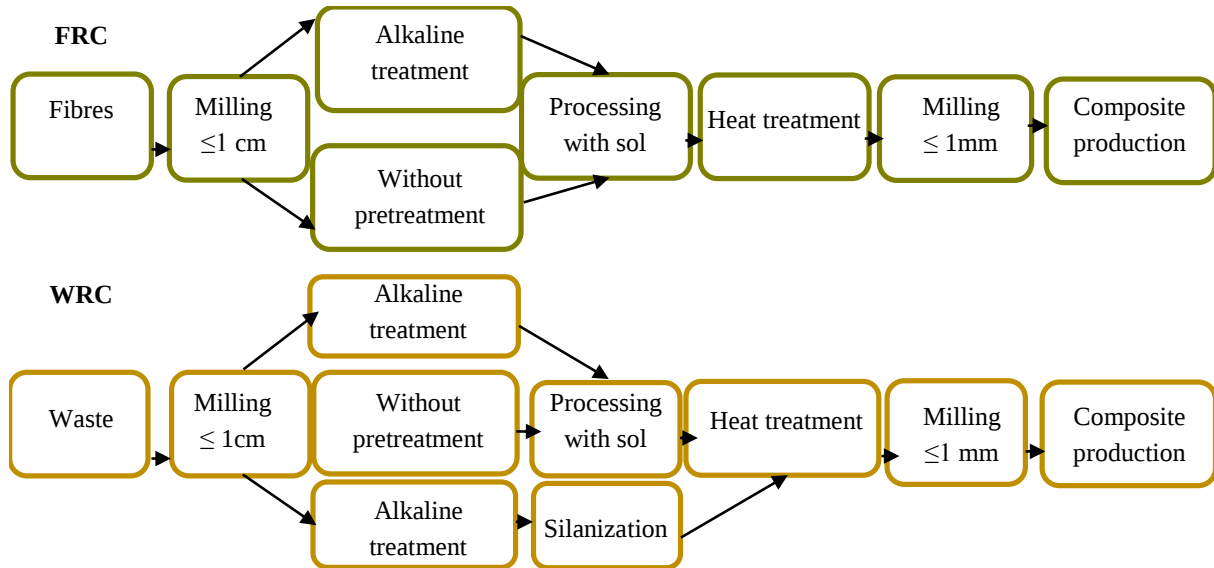


Fig. 2.1. Schemes for preparing reinforcing components.

Two types of lignocellulose-containing reinforcing components were used in the study. The treatment schemes for the *Bialobrzeskie* variety fiber (Š) harvested in 2014 and the first processing of hemp waste (A) collected in Latvia are shown in Fig. 2.1. Initially reinforcing components are screened using a 1 cm mesh sieve, then treated according to the selected chemical treatment and milled a second time with a 1 mm mesh sieve in the *RETSCH ZM-200* mill, rotor speed 1800 rpm (Fig. 2.1). Grinding after chemical treatment is necessary to remove clumped particles A or S.

2.2.2. Methods of chemical treatment of reinforcing components

Treatment with alkali

Hemp particles are treated with 0.0025 or 0.05 mol of NaOH and distilled water for 30 minutes at 20 °C, then rinsed in distilled water to neutral pH.

Silanization

To 80 % ethyl alcohol solution was added 2 mol of silane (TEOS or APTES) and hydrochloric acid to pH 4 (Table 2.1). A is passed for 1 h in the prepared solution, then dried in a thermal oven for 24 h at 60 °C, then held in a vacuum oven for 2 h at 110 °C (1 bar).

Sol-gel synthesis

Table 2.1

Reagents Used for Sol-gel Synthesis

Reagents	Formula	Manufacturer	Concentration
Tetraethyl orthosilicate (TEOS)	$C_8H_{20}O_4Si$	Germany (Alfa Aesar)	99 %
Ethanol	C_2H_5OH	EU (SIA “Enola”)	99 %
Hydrofluoric acid	HF	EU (SIA “Enola”)	40 %
Hydrochloric acid	HCl	EU (SIA “Enola”)	27 %
Zinc acetate dihydrate	$Zn(CH_3COO)_2 \cdot 2H_2O$	EU (SIA “Enola”)	98 %
γ -aminopropyltriethoxysilane (APTES)	$H_2N(CH_2)_3Si(OC_2H_5)_3$	Sigma Aldrich	99 %

The reagents used to synthesize the sols combinations are shown in Table 1. The sol is synthesized according to the planned combinations using the selected silane as a precursor (APTES or TEOS). Water and/or ethyl alcohol are added to the hydrolysis and condensation processes, the chosen acid serves as a catalyst for adjusting the environmental acidity to the required pH. Zinc acetate dihydrate (Table 2.2) has also been added as a modifier in some combination of sols. The reinforcing components are soaked in the sol to ensure even coverage.

Table 2.2

Variations of Synthesized Sols and Heat Treatment

Sol variant: silane, mol: catalyst, mol: modifier, mol or wt %* / pH	Mixing the sol		Drying	Heating	
	°C	min	°C	°C	min
TEOS 0,09 : HF 0,8/2	50	30	90	120	10
TEOS 0,13 : HF 0,8/2,2				90	30
TEOS 0,14 : HF 1,6/2				120	10
TEOS 0,09 : HF 0,8 : ZAD 8/ 5,3		40		90	30
TEOS 0,09 : HF 0,8 : ZAD 7,5/4,6				120	10
TEOS 0,09 : HF 0,5 : ZAD 7,5/5,5					
TEOS 0,09 : HF 0,8 : ZAD 8 un APTES 0,009/5					
APTES 0,07 : HF 2,8/2,2		30			
APTES 0,06 : HCl 0,23/4,5		23		720	60
APTES 0,1 : HCl 0,25/9,6					
APTES 0,06 : HCl 0,23/ZAD 7,5/6,5					

* ZAD indicates wt % but APTES mol

The following combinations of sol are assigned according to the following principle (commas are used as decimal separators in sample designations): silane, mol: catalyst, mol: modifier, mol/pH.

2.2.3. Composite preparation

The reinforcing components are dried at 60 °C for 12 h before being introduced into the composite to minimize the amount of moisture in the uncoupled water and to prevent air intake during the pressing.

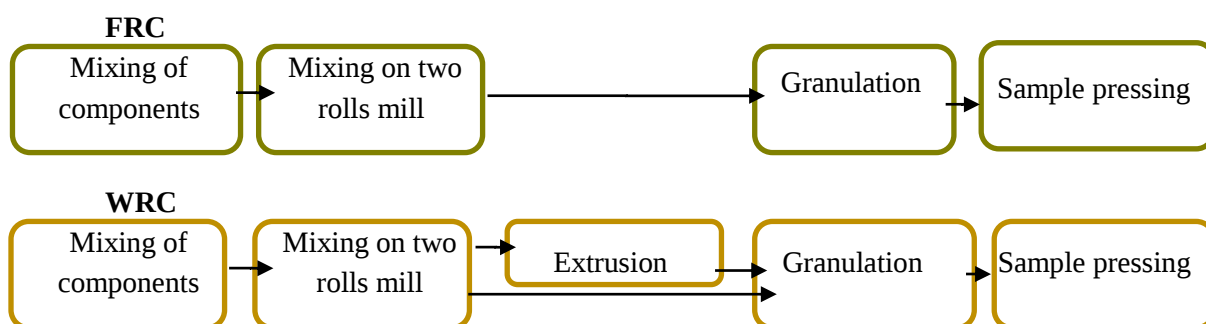


Fig. 2.2. Composite manufacturing schemes.

Composites are made with heated two-rollers mill. Part of the sample is modified with 5 wt % of Licocene PE MA 4351: maleinised polyethylene wax (MAPE) or 1–3 wt % of PRIEX 15005 MAPE granules and 2 wt % by weight of zinc oxide nanoparticles (ZnO). For some composites, plasticizer functional lubricant *Struktol TPW709* 1 wt % is added to facilitate extrusion process. Composite modifiers are added in the rolling process by calculating the percentage of the matrix weight.

After rolling, the material is milled in a knife mill to give irregularly shaped granules. To improve the mixing quality, part of the material is further extruded after rolling (PRISM TSE 16TC extruder) by mixing the 2-chin extruder (Ek) at the temperature of the extruder cylinder heating zones 160–165–175–185–195 °C and spinning speed 25–75 min⁻¹ [19],[20]. After extrusion, the finished profiles are granulated, cut into pieces of up to 3 mm in length.

Samples of composites are marked upon the following principle (commas are used as decimal separators in sample designations): reinforcing component, wt % / (reinforcing component processing) / manufacturing method / matrix modifier in manufacturing process, wt % (Tables 2.3 and 2.4)

The production, selection and number of samples conform to the methods specified in the standards. At least 10 samples were tested for each composite variant. Tensile deformation was tested for 15 to 20 samples, as the relative error could be up to 15 % when testing an insufficient number of samples. Mathematical processing of data was done by calculating mean values of parameters and estimating their confidence intervals according to probability 0.95, as well as relative errors. Correlation analysis (correlation and determination coefficient matrices) is suitable for estimating the correlation intensity between the parameters characterizing the sample properties. Graphic images were created in the *Microsoft Excel for Windows 2010* technology environment with built-in functions and data analysis applications

for computation and comparison. To optimize the most important properties of the composites (water absorption, surface hardness, density, modulus of elasticity), a first rate full-scale experiment of factors was performed describing the influence of production parameters and their interaction with both statistically adequate equations and their graphical interpretations in the form of echo surfaces and two-dimensional slices.

Table 2.3

Fiber-Reinforced Composite Parameters

Fiber wt % / (processing of reinforcing component) / manufacturing method / matrix modifier in manufacturing process						
	Processing of reinforcing component			Adds to the manufacturing process		
Composite designation	NaOH, 0.05 mol	Sol	ZAD, wt %	MAPE, 5 wt %	Struktol, 1 wt %	Mixing on two rolls mill/ extruded
Š30/-/V/-	–	–	–	–	-	roll-milled
Š30/NaOH/V/-		–	–	–	-	roll-milled
Š30/-/V/MAPE	–	–	–		-	roll-milled
Š40/-/V/-	–	–	–	–	-	roll-milled
Š40/-/V/MAPE	–	–	–		-	roll-milled
Š40/(TEOS 0,14 : HF 1,6/2)/V/-	–	TEOS 0,14 : HF 1,6/2	–	–	-	roll-milled
Š40/(TEOS 0,14 : HF 1,6/2)/V/MAPE	–	TEOS 0,14 : HF 1,6/2	–		-	roll-milled
Š40/(TEOS 0,09 : HF 0,8 : ZAD 7,5/4,6)/V/-	–	TEOS 0,09 : HF 0,8 : ZAD 7,5/4,6		–	–	roll-milled
Š40/(TEOS 0,09 : HF 0,8 : ZAD 7,5/4,6)/V/MAPE	–	TEOS 0,09 : HF 0,8 : ZAD 7,5/4,6				roll-milled
Š40/(NaOH 0,05 and TEOS 0,14 : HF 1,6/2)/V/-		TEOS 0,14 : HF 1,6/2	–	–	-	roll-milled
Š40/(NaOH 0,05 and TEOS 0,14 : HF 1,6/2)/V/MAPE		TEOS 0,14 : HF 1,6/2	–		-	roll-milled
Š40/(NaOH 0,05 and TEOS 0,09 : HF 0,8 : ZAD 7,5/4,6)/V/-		TEOS 0,09 : HF 0,8 : ZAD 7,5/4,6		–	–	roll-milled
Š40/(NaOH 0,05 and TEOS 0,09 : HF 0,8 : ZAD 7,5/4,6) /V/MAPE		TEOS 0,09 : HF 0,8 : ZAD 7,5/4,6			–	on two roll- mills
Š40/-/V/Struktol	–	–	–	–		roll-milled
Š40/-/V and Ek/Struktol	–	–	–	–		roll-milled / extruded
Š50/-/V/-	–	–	–	–	-	roll-milled
Š50/-/V/MAPE	–	–	–		-	roll-milled
Š50/(TEOS 0,14 : HF 1,6/2)/V/-	–	TEOS 0,14 : HF 1,6/2	–	–	-	roll-milled
Š50/(TEOS 0,09 : HF 0,8 : ZAD 7,5/4,6)/V/MAPE	–	TEOS 0,09 : HF 0,8 : ZAD 7,5/4,6			–	roll-milled

Table 2.4

Waste Reinforced Composite Parameters

Fiber wt % / (processing of reinforcing component) / manufacturing method / matrix modifier in manufacturing process								
Composite designation	Processing of reinforcing component				Adds to the manufacturing process			Mixing on two rolls mill/ extruded
	NaOH, mol	Silanizēts, 2 mol	Sol	ZAD, 7.5 wt %	MAPE, wt %	Struktol, 1 wt %	ZnO, 2 wt %	
A40/-/V/-	—		—	—	—	—	—	roll-milled
A40/-/V/Struktol	—		—	—	—		—	roll-milled
A40/-/V+ Ek/Struktol	—		—	—	—		—	roll-milled / extruded
A40/NaOH 0,025/V/-	0,025		—	—	—	—	—	roll-milled
A40/NaOH 0,05/V/-	0,05		—	—	—	—	—	roll-milled
A40/-/V/MAPE 1	—		—	—	1	—	—	roll-milled
A40/-/V/MAPE 2	—		—	—	2	—	—	roll-milled
A40/-/V/MAPE 3	—		—	—	3	—	—	roll-milled
A40/(NaOH 0,05 and TEOS 0,09 : HF 0,8 : ZAD 7,5/4,6)/V/-	0,05		TEOS 0,09 :HF 0,8 :ZAD 7,5/4,6		—	—	—	roll-milled
A40/NaOH 0,05/V/ZnO	0,05		—	—	—	—		roll-mill
A40/NaOH 0,05 and TEOS 0,14 : HF 1,6/2/V/-	0,05		TEOS 0,14:HF 1,6/2	—	—	—	—	roll-milled
A40/NaOH 0,05 and sil APTES 2/V/-	0,05	APTES	—	—	—	—	—	roll-milled
A40/NaOH 0,05 and sil TEOS 2/V/-	0,05	TEOS	—	—	—	—	—	roll-mill
-/-/V/ZnO	—	—	—	—	—	—		roll-milled
A40/(APTES 0,06 : HCl 0,23/4,5)/V/-	—	—	APTES 0,06: HCl 0,23/ 4,5	—	—	—	—	roll-milled
A40/(APTES 0,06 : HCl 0,23/ ZAD 7,5 6,5)/V/-	—	—	APTES 0,06:HCl 0,23/ZAD 7,5/6,5		—	—	—	roll-milled

2.2.4. Sample testing methodology

1. Plate samples are obtained by compression of prepared composite pellets. Initially, the material is pressed in the press without pressure for 3 minutes at 150 °C, then pressed under a pressure of less than 5 MPa for 3 minutes, and then cooled under a pressure for 3 minutes. 1 mm thick samples were made for the micro-hardness test but 0.5 mm thick samples were made for tensile deformation tests with the shape of double-blade.
2. The pH is determined with a waterproof *AD14 pH* meter at a fixed temperature of 22 °C with possible measurement error $\text{pH} \pm 0.01$ and ± 0.1 °C.
3. High Definition Scanner *Silverfast-se Epson perfection 4870* (resolution 1200 dpi) with sliding tape and *FibreShape*, an auto particle analysis software, was used that allows to measure thousands of objects simultaneously. On the surface of the sliding tape is obtained a two-dimensional image in black and white – the length, diameter and length of fibers and the thickness of the shingles are automatically is read by the program as the length and width of fractions, and statistical indicators are automatically determined.
4. Size distribution of reinforcing component fractions was measured (by milling through a 1 mm mesh sieve) according to standard LVS EN 933:2012 [21] with sieve shaker *A059-11/AE/0062* using 1000 μm , 500 μm , 355 μm , 150 μm and 90 μm sieve mesh size.
5. Energy dispersive X-ray spectroscopy was used to analyze the surface of chemical composition of fiber with *SEM Mira Tecsan HF* and with the *Oxford Inca X-sight EDX* detector.
6. The material density was determined according to ISO 1183-1:2012 [22] using hydrostatic weighing equipment *YDK 01* and scales *Sartarius* (accuracy 0.00001 g) at 20 °C in alcohol.
7. Fiber and residue size differences for particles < 90 μm were estimated using an optical microscope with magnification by 4 $\times$, while the surface and cross-section of the aged composites are magnified by 4 $\times$ and 10 $\times$. The formation of composite agglomerates and air inlets after compression were evaluated organoleptically.
8. The kinetics of water absorption of composites by fixing the changes in mass of the samples in time was determined in accordance with LVS EN ISO 62:2008 [23].
9. Melt flow index according to ASTM D 1238-90b [24] shall be evaluated by the mass of the polymer, in grams, passing through a cylindrical capillary of a certain size ($d = 2.06$ mm, $L = 8$ mm) placed in a capillary viscometer under specified conditions (temperature, load) and that is recalculated for a 10-minute run time.
10. The micro-hardness (HV) of the sample surfaces (by Vickers M-41) is determined by pressing a regular square diamond pyramid at a 136° angle between the faces on the sample surface. For determination of micro-hardness, a 1 mm thick pressed flat and smooth composite material with the lowest possible surface roughness is used. The applied load during loading is 200 g. Voltage is not exceeding 10 V.

11. The properties of deformation in tension are determined according to ISO 527:2012 [25]. The universal dynamometer *Zwick / Roell Z020* was used. The test was performed at a deformation speed of 20 mm/min and the tensile strength (σ_t), elastic modulus (E_t) and relative elongation (ε_t) were determined.
12. For the investigation of cross-sectional fracture plane of composite samples and surface coatings of reinforcing components, micrographs were taken with scanning electron microscope (*SEM Mira Tescan*, *SEM Hitachi S-3400*, *Hitachi VP-SEM SU3500* and *Helios Nanolab, FEI*).
13. Fourier-transform infrared spectroscopy (attenuated total reflection) was used to determine the presence of functional groups on the surface (range 400 cm^{-1} to 4000 cm^{-1}).
14. Sample surface topography analysis was performed with atomic force microscope *Bruker Dimension Edge* in tapping mode using silicon nanoprobe with spike radius of 3.75 μm , spring constant 26 N/m, frequency 300 kHz, length 160 μm , and aluminum coating 100 nm. Surface topography was measured at 25 $\mu\text{m} \times 25 \mu\text{m}$, 20 $\mu\text{m} \times 20 \mu\text{m}$. Samples were taken at 2.6 V $\pm$ 0.2 V. Images were processed in the *NanoScope Analysis 1.5* technology environment for 3D models. Root mean square roughness (RMS) for comparing surface roughness changes was automatically calculated. RMS was calculated from the roughness average (ARS) by drawing a square root.
15. The kinetics of the aging process of film-type composites was studied in a UV chamber (model *Q-UV spray* with solar *Eye Irradiance control*) equipped with a UVA-340 radiation lamp. The dominant wavelength of UV radiation was 340 μm . UV aging was performed according to ASTM G 154 [26] with periodic water quenching (80 cycles: 8 h irradiation at 60 $^{\circ}\text{C}$, 4 h at 50 $^{\circ}\text{C}$ in vapor, 0.89 w/m^2 irradiation capacity). Duration of one cycle was 12 h, and total length of aging process was 1000 h.
16. After aging, changes in sample colour, lightness and gloss, surface microhardness and comparison with the relevant non-aged samples were determined. Surface colour on one pressed composite side was fixed with the *X-Rite PANTONE Capsure MR200* Colorimeter. Coordinates of colour vectors a^* , b^* and L^* in CIELab-76 colour coordinate space, as well as lightness differences between samples (ΔL^*), colour vector coordinates (Δa^* , Δb^*), possible resolution difference (ΔE), chroma (C) and hue (H) were calculated.
17. The surface gloss of the pressed composites was determined by the *NOVO-GLOSS LITE TM Statistical Glossmeter* according to ASTM D523 [27], at measuring angle 60 $^{\circ}$ both before and after aging.

2.3. Results

2.3.1. Properties of composite reinforcing components

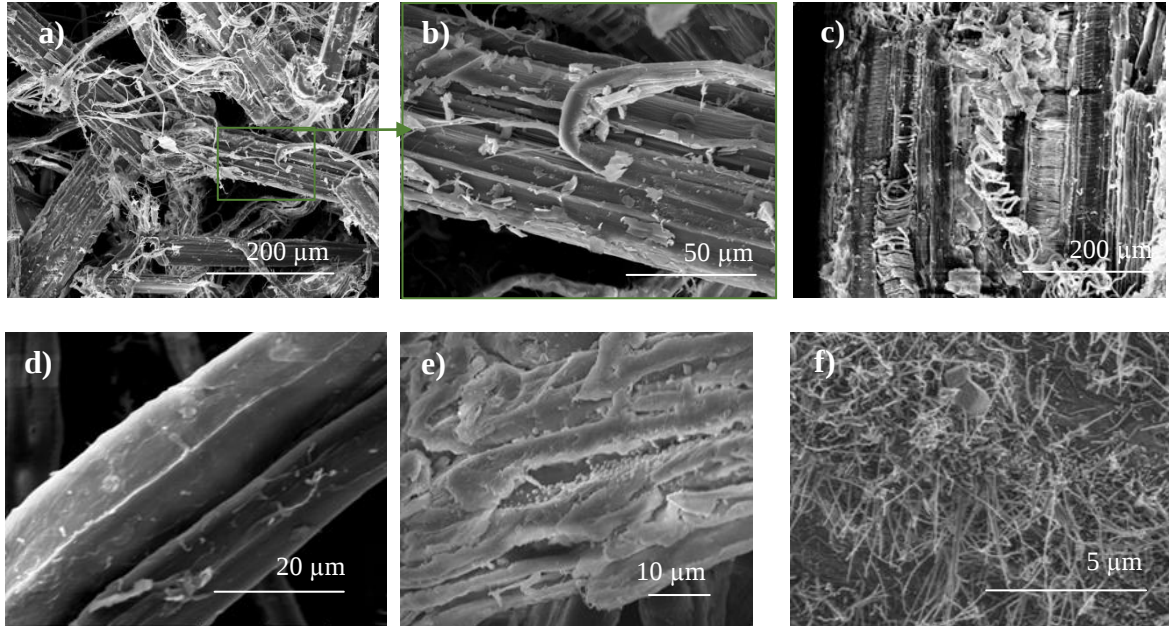


Fig. 2.3. SEM micrographs: a), b) ground hemp fiber, b); c) waste; d) with 0.05 mol NaOH treated fibers; e) waste with 0.05 mol NaOH and silanization (2 mol TEOS) treatment; and f) sol TEOS 0,14 : HF 1,6/2 treated hemp.

The microstructure of the surface of the reinforcing components is very diverse, so it is difficult to identify the applied coatings (Fig. 2.3 a–c). Treatment with NaOH cleans the surface of hemp (Fig. 2.3 d) by preparing it for further processing, while silanization can be identified by cubic formations on the surface (Fig. 2.3 e). The surface structure of modified hemp fibers and waste of sol-gel technology varies according to the composition of the sol: the surface treated with the APTES sols is smooth (Fig. 2.6 b), but the TEOS sols forms a relief starting from small rounded growths to longs and openwork silicon branches (Fig. 2.3 f).

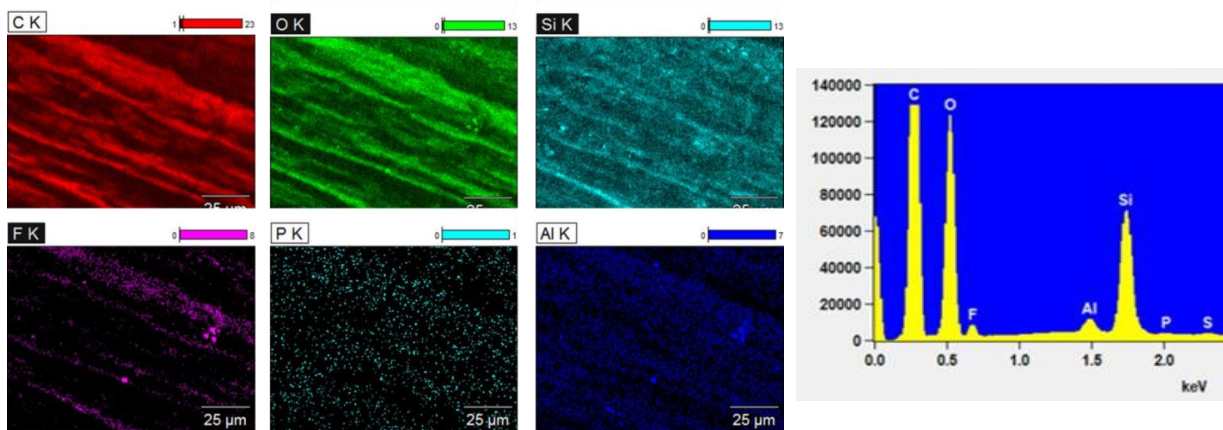


Fig. 2.4. Chemical elements of coating TEOS 0,14 : HF 1,6/2 on the hemp fibre surface.

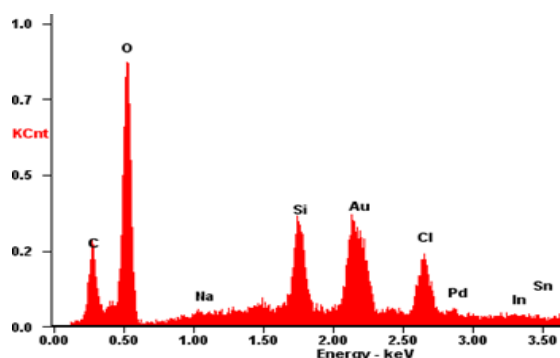
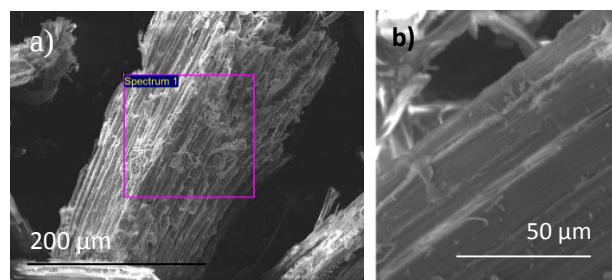


Fig. 2.5. Chemical elements on hemp waste surface after treatment with sol APTES 0,06 : HCl 0,23/4,5.



a)	Elements	C	O	Si	Cl	Ca	Zn	Mg	Al
	Wt %	44.5	38.6	3.9	4.4	0.5	7.8	0.1	0.2

Fig. 2.6. Chemical elements on the hemp waste surface after treatment with sol APTES 0,06 : HCl 0,23 : ZAD 7,5/6,5.

The EDX analysis shows that the dispersion of chemical elements on the surface depends on both surface relief and sol quality (Figs. 2.4–2.6). Based on the results of SEM and EDX reinforcement component surface modification analysis, NaOH 0.05 mol pre-treatment with subsequent silanization with 2 mol TEOS or APTES and modification of reinforcing components with the following precursor TEOS and APTES bases is considered more appropriate:

- TEOS 0,14 : HF 1,6/2
- TEOS 0,09 : HF 0,8 : ZAD 7,5/4,6
- APTES 0,06 : HCl 0,23/4,5
- APTES 0,06 : HCl 0,23 : ZAD 7,5/6,5.

Table 2.5

The Ratio of Length and Width of the Particles of Reinforcing Components Depending on Treatment

Sample	Length/width ratio	±
Untreated fibers	10.91	0.16
Untreated waste	16.01	0.10
Waste treated with sol APTES 0,06 : HCl 0,23/4,5	14.69	0.12
Waste treated with sol APTES 0,06 : HCl 0,23 : ZAD 7,5/6,5	13.27	0.14

Granulometric and particle size analysis shows that the particle size of the untreated crushed particles is greater than that of the fibers, with the length and width dimensions of the sol-modified reinforcing components decreasing as compared to the untreated (Table 2.5). Increase in fine fractions content of modified components (Fig. 2.7 b) during milling and reduction of tensile strength values of corresponding composites (from 11.2 MPa to untreated WRC to 10.8 MPa and 8.9 MPa) in too acidic environment (about pH 2) (Fig. 2.8) shows that hemp destruction can occur during the modification process. The distribution of silanized (pH 4 treatment) waste particles is close to the distribution of untreated waste (Fig. 2.7 a).

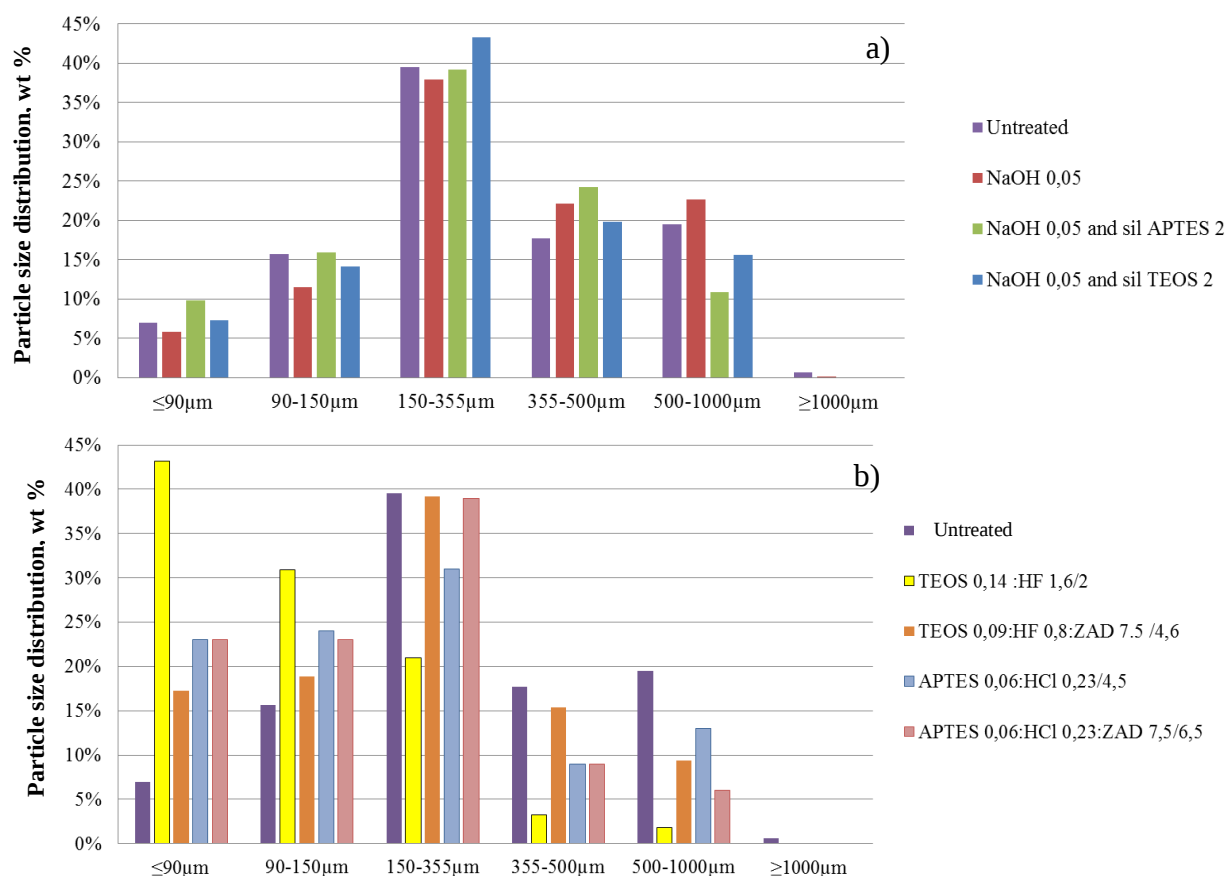


Fig. 2.7. Waste particle size distribution by fraction after chemical treatment: a) NaOH treated and silanized; b) Treated with sol-gel technology.

2.3.2. Properties of hemp reinforced composites

Compared to the corresponding properties of the polymer matrix used, the elongation on break of 40 wt % of the composite reinforcing components of the composite is reduced by 12.55 (FRC) and 5.02 (WRC) respectively, while the maximum tensile strength is 1.23 (FRC) and 1.24 (WRC). The tensile elastic module, on the other hand, increases by 8.13 (FRC) and 5.36 (WRC) respectively (Table 2.6).

Table 2.6

Effect of Polymer Matrix Mechanical Properties on 40 wt % Hemp Fibers and on the Mechanical Properties of Waste-Reinforced Composites

Reinforcing components	Elastic modulus in tension, MPa		Increases, times	Maximal tensile strenght, MPa		Decrease, times	Elongation at break %		Decrease, times
	LLDPE	40/-V/-		LLDPE	40/-V/-		LLDPE	40/-V/-	
S	49.0	398.3	8.13	12.8	10.5	1.23	59	4.7	12.55
A	81.7	438.3	5.36	13.9	11.2	1.24	21.1	4.2	5.02

With 50 wt % fiber-reinforced composite with 5 wt % MAPE additive tensile strength (Fig. 2.8 a) according to EN 622 is approaching load bearing construction requirements for fiber boards (24 MPa), and its tensile modulus is 0.9 GPa (Š50 /-V/MAPE 2).

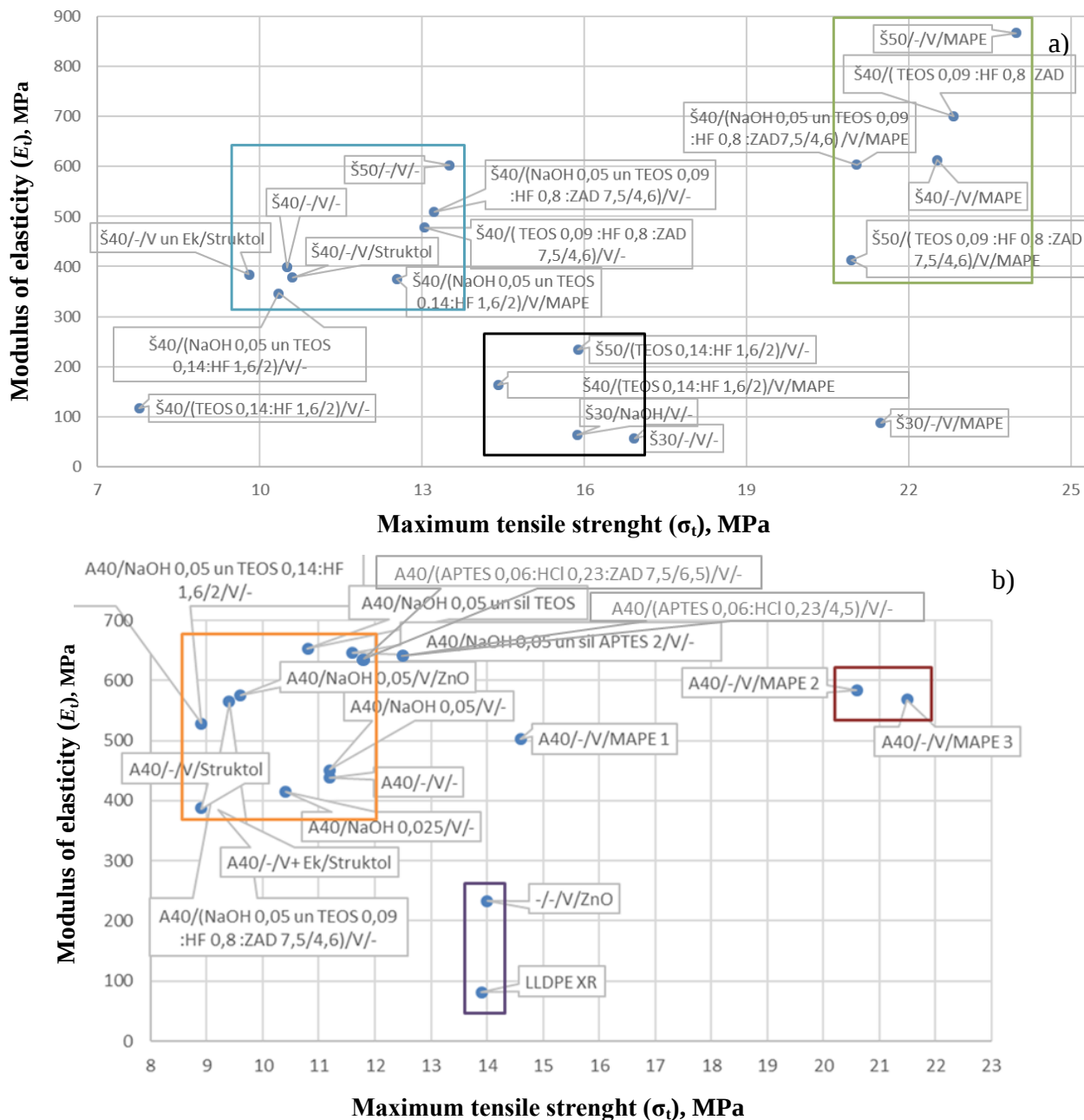


Fig. 2.8. Composite modulus of elasticity (E_t) and maximum tensile strength (σ_t), MPa: a) fiber reinforced composites; b) waste reinforced composites.

Based on water absorption, 40 wt % hemp reinforced composites can be divided into 3 groups (Fig. 2.9).

- Very low water absorption – between 5 % and 8 %: (Š40/-V/MAPE; A40/(NaOH 0,05 un TEOS 0,09 : HF 0,8 : ZAD 7,5/4,6)/V/-; A40/NaOH 0,05 un TEOS 0,14 : HF 1,6/2/V/-; A40/-V/Struktol, A40/-V+ Ek/Struktol).

- Low water absorption – 8 to 12 %: (Š40/(TEOS 0,14 : HF 1,6/2)/V/-; Š40/(TEOS 0,14 : HF 1,6/2)/V/MAPE; A40/-/V/MAPE 1; Š40/(TEOS 0,09 : HF 0,8 : ZAD 7,5/4,6)/V/MAPE; Š40/(NaOH 0,05 un TEOS 0,09:HF 0,8:ZAD 7,5/4,6)/V/MAPE; Š40/(NaOH 0,05 un TEOS 0,14:HF 1,6/2)/V/-).
- Medium high water absorption – between 12 % and 17 % (the other experimental composite variants correspond).

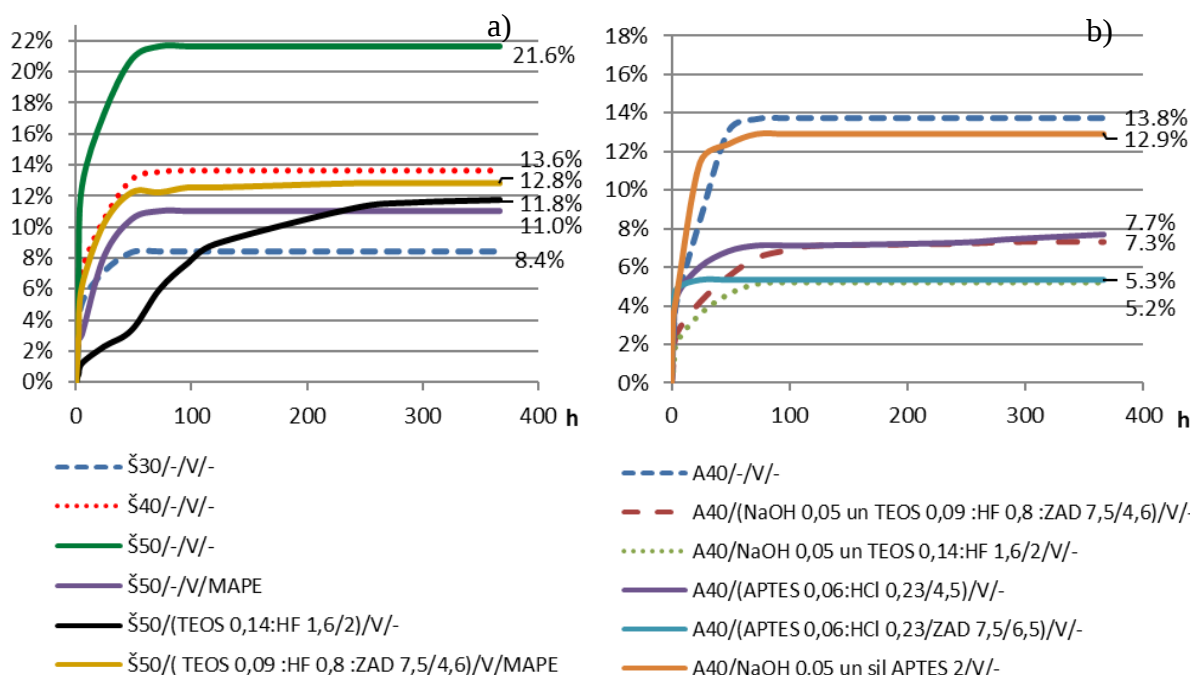


Fig. 2.9. Water absorption kinetics of LLDPE composites: a) hemp fiber reinforced; b) waste reinforced.

The water absorption of unmodified fiber composites increases rapidly from 8 % to 21.6 % by weight with a fiber content of 30 wt % to 50 wt %; it can be reduced to 11 % with MAPE 5 % by weight of additive within low absorption range or up to 12 % by modifying fibers with TEOS 0.14 mol sol (Fig. 2.9a). With 40 wt % of waste, the water absorption of reinforced composites decreases more than 2 times when residues are modified with APTES 0,06 : HCl 0,23 : ZAD/ 6,5 and TEOS 0,14 : HF 1,6/2, as well as by modifying the waste with the APTES and TEOS sols, the water absorption of the composites obtained falls within the very low absorption range (Fig. 2.9 b). The residual alkali pretreatment in combination with silanization does not significantly reduce the water absorption of composite.

The extrusion and mixing on two-roll mill combination reduces composite E_t , σ_t , ε_t and HV compared to mixing on two-roll mill without Struktol additive. To ensure a smooth profile of the extruded granules, the Struktol TPW709 concentration in the composite must be higher than 1 wt %.

The addition of both the unmodified waste and fibers increases the density of the composite 1.2 times compared to the matrix. Depending on the chemical treatment of waste, the addition of waste at 40 wt % increases the density of composites in the range of

1.059 g/cm³ to 1.244 g/cm³, and the addition of fibers in the range of 1.052 g/cm³ to 1.122 g/cm³ (Fig. 2.10).

If we compare the properties of all the composites we have made, the regularities between several of the parameters can be seen. Dependence of surface micro-hardness on fiber-reinforced composite density (Fig. 2.10 a) is described by a non-linear equation (2.1):

$$y_{HV} = 23651x_b^2 - 50337x_b + 26865, (R = 0.79), \quad (2.1)$$

where y_{HV} – composite surface micro-hardness, MPa;
 x_b – composite density, g/cm³.

As the composite density increases, the surface micro-hardness also increases. In contrast, the impact of waste-reinforced composite density on microc-hardness is relatively weaker ($R = 0.46$, $D = 0.21$; Fig. 2.10 b).

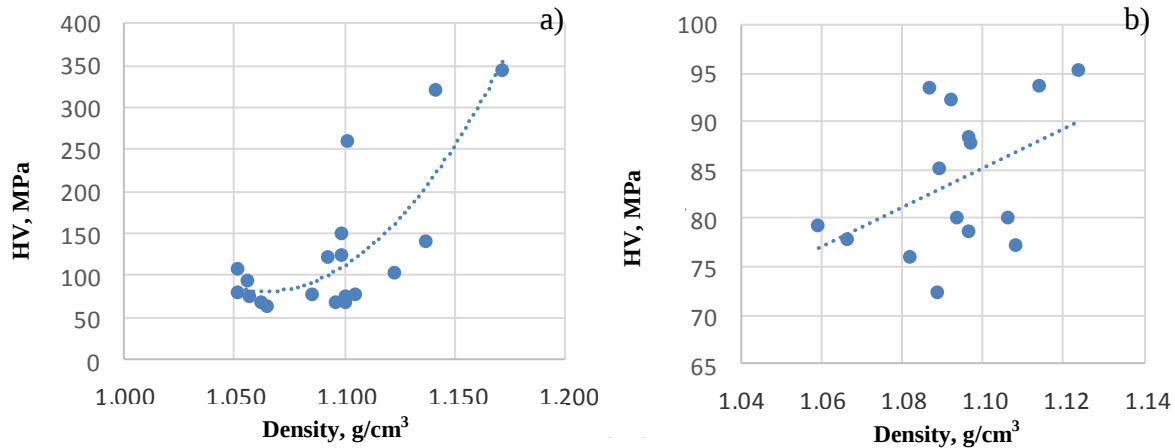


Fig. 2.10. Micro-hardness and density interaction of composite: a) fiber-reinforced; b) reinforced with waste.

Compared to the matrix, 40 % by weight of WRC surface micro-hardness increased only 2.1 times, and FRC 5.8 times. By modifying fibres with TEOS 0.14 mol, it is possible to obtain composites with comparatively high HV (Š40/(TEOS 0,14 : HF 1,6/2)/V/MAPE (260 MPa) and Š50/(TEOS 0,14 : HF 1,6/2)/V/- (345 MPa).

Untreated S 40 wt % of composite MFI is small – 0.59 g / 10 min, but WRC practically net – 0.03 g /10 min. Both WRC and FRC melt flow indexes can be successfully saved and increased by using sol processing, the impact on MFI is similar (WRC MFI increased 0.4 times, and FRC 0.5 times).

2.3.3. Surface and aging studies of composites

The LLDPE matrix is characterized by the formation of spherulites in a linear direction with little branching. From the spherulite centres up to 2 µm long lamellas are formed and amorphous polymer areas are visible between them. The processed fiber composite (NaOH 0.05 mol and TEOS 0,14 : HF 1,6/2) shows better adhesion of the fiber complex to the matrix than untreated because more ordered lamellar self-orientation without distinct amorphous areas is formed (Fig. 2.11).

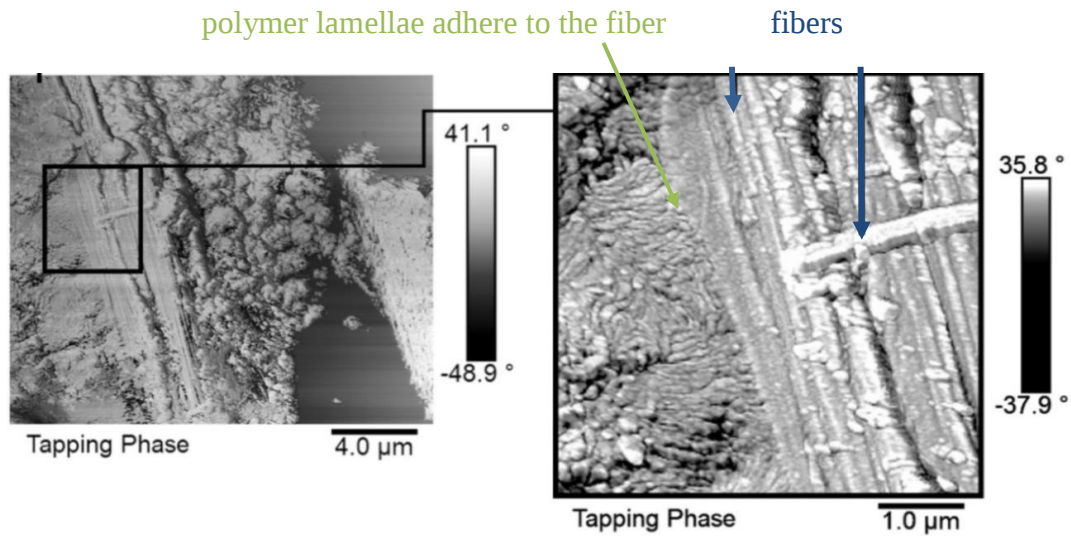


Fig. 2.11. Surface nanostructure-phase and amplitude of composites Š40/NaOH 0.05 and TEOS 0.14 : HF 1.6 /2 /V/.

The surface roughness of the aged sample is twice as high as before. Cracks appear on the surface of the aged composite (Fig. 2.12).

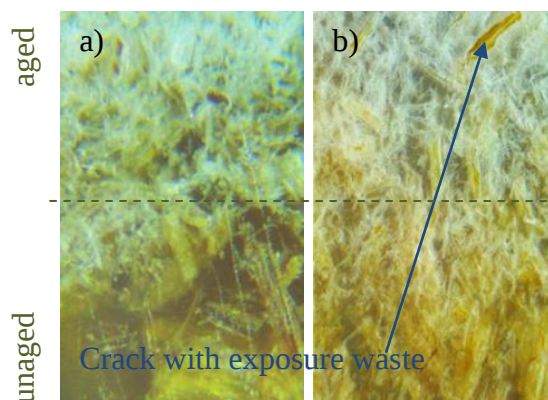


Fig. 2.12. Boundary surface of aged and unaged composites: a) A40/-/V/-; b) A40/NaOH 0,05/V/ZnO.

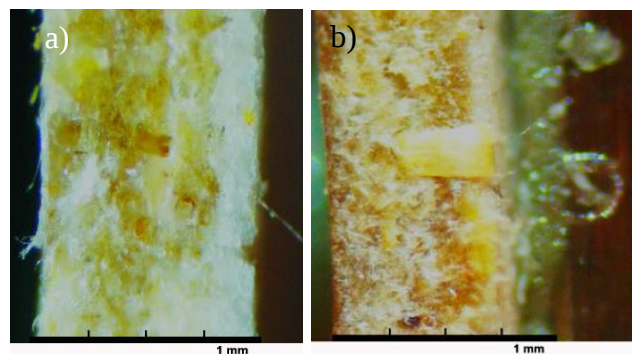


Fig. 2.13. Cross-sectional surface of composite after aging, optical microscope images at 4× magnified (aged part to the right): a) A40 /-/V/-; b) A40 /-/V/MAPE 2.

Pressed composite thickness before aging is 1mm. Aging footprints of untreated waste in the composite are visible at a depth of 0.23 mm (Fig. 2.13 a); similar results are found for the composite with the treatment of alkaline waste and the ZnO nanoparticles additive – 0.24 mm.

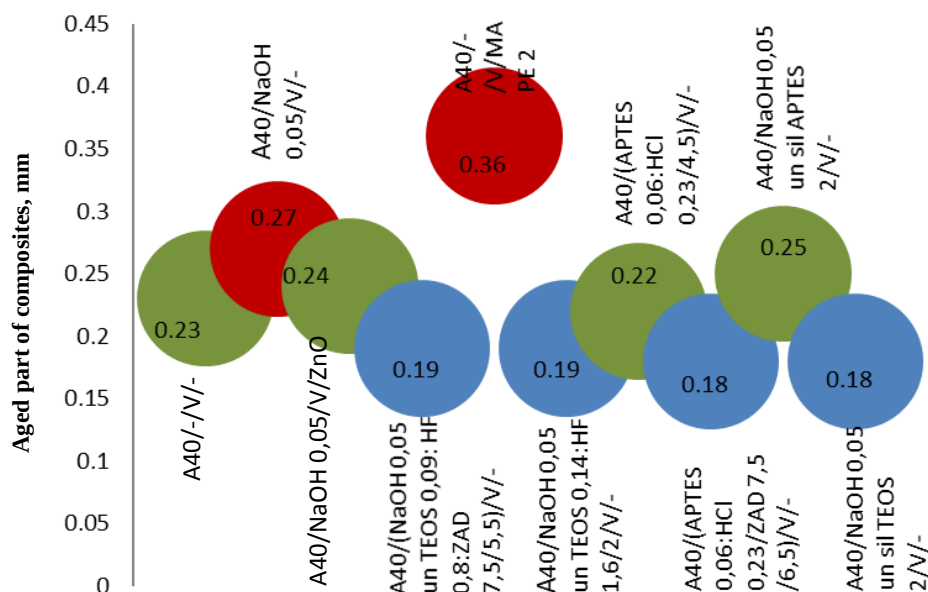


Fig. 2.14. Depth of aged part of composite, mm.

Composites which are waste treated with the APTES sol and silanized have aging footprints – 0.22 and 0.25 mm (Fig. 2.14). Composite with a MAPE additive at a depth of 0.36 mm (Fig. 2.13 b) and a treatment of NaOH residues (0.27 mm) is faster than an untreated waste composite. Composites with residues treated with ZAD-containing sols or treated with TEOS (0.18–0.19 mm) have less aging footprints.

The surfaces of non-aged composites are medium-gloss, semi-matt. After aging, the surface gloss of the composite declines rapidly – the surface becomes matt. Increase in surface elevation height differences due to aggressive effects of outdoor environment is the main reason for shine changes.

After aging, the greatest change in gloss, with 88 % and 87 %, respectively, is for composites with 2 wt % of MAPE additives and waste treatment with APTES. The interactions between aged glossy surface gloss and micro-hardness are described by the equation

$$y_{GU} = -0.056x_{HV} + 7.5381, (R = 0.71), \quad (2.2)$$

where

y_{GU} – composite surface gloss after aging, GU;

x_{HV} – surface hardness of aged composites, MPa.

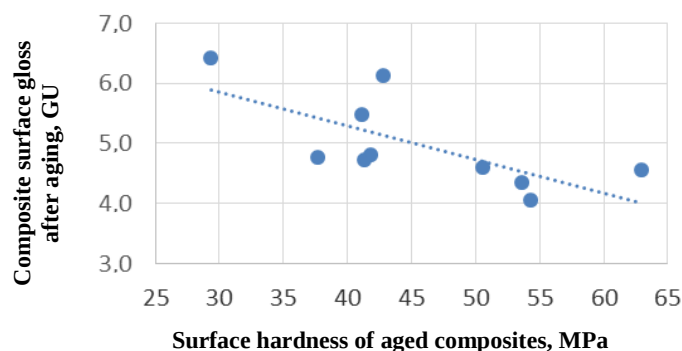


Fig. 2.15. Interaction between the gloss and micro-hardness of the WRC surface.

The surface gloss of the experimental variants ranges from 4 GU to 6 GU and surface micro-hardness from 38 MPa to 51 MPa. As the surface gloss of the aged samples decreases, the surface micro-hardness also decreases (Fig. 2.14).

As a result of aging, visual changes occurred: composites bleached, lost colour, saturation and tone (Fig. 2.12). Changes in colour occurred mainly due to increased lightness. The composite with ZnO nanoparticle additive had the smallest changes in colour, hue, brightness and tone.

The micro-hardness of the composite surface after aging is rapidly decreasing, losing hardness in the range of 31 % to 62 %. Composites with residual alkali pretreatment and subsequent silanization, with less alkali pretreatment and subsequent treatment with sol TEOS 0,14 : HF 1,6/2, lose the surface micro-hardness more rapidly.

The damaged layer of aged composite cross-sections varies from 0.18 mm to 0.36 mm. Deeper defects can be seen in the composite modified with MAPE and waste, but the smallest traces of damage are in the composites waste modified with ZAD-containing sol, or modified only with TEOS precursor sol.

CONCLUSIONS

1. Hemp fiber and waste can be successfully integrated as a reinforcing component in a linear low-density polyethylene matrix, improving its mechanical and operational properties.
2. The highest percentage of chemically untreated reinforcing fibers of hemp components that can be introduced into the matrix while retaining the melt flow index required for composite formation and increased mechanical properties is 40 wt %.
3. By applying different treatments and additives to fiber and waste components, it is possible to change the properties of the LLDPE matrix composite within wide limits and to improve the most important properties of the intended use.
4. By adjusting the natural fiber-like modification temperature, time, and environmental pH, sol-gel technology can provide efficiently functioning reinforcing nanocoatings for the design of composite performance.
5. The moisture and water absorption capacity of composites with high natural fiber content can be effectively reduced by adjusting treatments for hemp hydrophobization.
6. By modifying fiber components with a suitable sol, it is possible to create 50/50 wt % of composites with limited moisture absorption. The research allows us to predict that by improving the composition of sols, the proportion of hemp component could be increased up to 60 wt % in the future.
7. Higher mechanical properties of the composites are obtained by the MAPE additive or by reinforcing components that are modified by TEOS and ZAD containing sol (fibers) and APTES sol (residues). However, it should be noted that composites with MAPE additive are aging more intensively.
8. By experimentally adjusting the composition of sols, it is possible to modify not only hemp, but also other natural fibers and fabrics made of them.
9. The methods of modification of reinforcing components can be successfully applied by forming other thermoplastic matrix composites provided that their melting temperature does not exceed the destructive temperature of the reinforcing components.

PROPOSALS AND RECOMMENDATIONS

1. For the production of composites as a reinforcing component, it is more economically advantageous to use crude straw and primary fiber processing waste rather than fibers, as they are produced as a by-product of production and are priced mainly in transport and storage costs.
2. From a composite manufacturing point of view, less technological process is required for composites that include untreated reinforcing components and a MAPE additive for improving composite properties. In this case, the chemical pre-impregnation of the hemp component is not required, it can be ground in one process preparation process.
3. Modification of the surface of hemp component by sol-gel technology increases the total number of composite manufacturing operations, but ensures faster and more even mixing of components in the rolling process, significant improvements in composite properties, as well as the ability to increase the content of reinforcing components to 50 wt % and, possibly, further more.
4. The positive effect of the optimal composition sols studied (APTES 0,06 : HCl 0,23/4,5; APTES 0,06 : HCl 0,23 : ZAD 7,5/6,5; TEOS 0,09 : HF 0.8 : ZAD 7,5/5,5 and TEOS 0,14 : HF 1,6/2) has been tested with modified hemp waste in reinforced composites. Given that the internal cavities of the hemp shells are large, impregnation of the component with a vacuum in the sol could be applied to improve the composite properties.
5. The process of TEOS-based sols studied in the Thesis is more energy-intensive compared to sols containing APTES, since the synthesis of TEOS-containing sols takes 30 to 40 minutes at 50 °C, followed by drying at 90 °C and heating at 120 °C. APTES containing sols are mixed at room temperature (23 °C) and do not include ethyl alcohol in the sol, but the mixing time (720 min) increases significantly.
6. In order to predict the sphere of application of the composite material more accurately, the composites should also be tested for biological stability against microorganisms such as pathogenic fungi. It is reported in the literature that the zinc acetate dihydrate used in the work of the sols modifier can serve as a reducing agent for various microorganisms.
7. Depending on the desired performance of the material, low water absorption composites and slow aging can be used under outdoor conditions. Packaging materials have low density, all the resulting composites are suitable if they are not intended to be used in contact with food. Composites with the most appropriate mechanical properties and lower resistance to ultraviolet radiation can be selected for non-structural constructions (except for rooms with high humidity), panels, moldings, gaskets, housings and other household products, in accordance with the requirements of the relevant standards.

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