



TALLINN UNIVERSITY OF TECHNOLOGY
SCHOOL OF ENGINEERING
Department of Materials and Environmental Technology

**INFLUENCE OF FIRE RETARDANT TREATMENT ON
THE FIRE RESISTANCE AND MECHANICAL
PROPERTIES OF HEMP FIBRE REINFORCED PLA
COMPOSITE**

**TULETÕKKEAINE MÕJU KANEPIKIUGA ARMEERITUD PLA
KOMPOSIIDI TULEKINDLUSELE JA MEHAANILISTELE
OMADUSTELE**

MASTER THESIS

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Tallinn 2021

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THESIS TASK

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Main speciality: Wood technology

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Thesis topic:

(in English) Influence of fire retardant treatment on the fire resistance and mechanical properties of hemp fibre reinforced pla composite.

(in Estonian) Tuletõkkeaine mõju kanepikiuga armeeritud PLA komposiidi tulekindlusele ja mehaanilistele omadustele.

Thesis main objectives:

1. Surface pretreatment of hemp fibres with alkali and combined treatment with silane.
2. Fire retardant treatment of untreated and chemically modified fibres.
3. Fabrication of hemp reinforced polylactide composites at fibre loading of 50 wt.%
4. Investigation of the effect of fire retardant treatment on the hemp fibre surface morphology.
5. Determination of the influence the fibre fire retardant treatment on the composite mechanical performance.

Thesis tasks and time schedule:

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1.	Review previous research on topic and preparation of literature review	6.2.20
2.	Obtain additional information about project if necessary (clarification of unclear terms and areas)	20.2.20
3.	Selection hemp fibres from the bundle and cleaning them	25.2.20
4.	Preparation of materials and reporting	10.3.20
5.	Preparation of materials and reporting	20.3.20

6.	Presentation of results	20.4.20
7.	Preparation of final project 1 report	24.5.20
8.	Preparation of materials – Hemp fibres	4.10.20
9.	Treating by NaOH and Silane	9.10.20
10.	Applying fire retardants Palonot® and Borax	13.11.20
11.	Fabrication of the composite	18.01.21
12.	Preparing samples for mechanical test	25.02.21
13.	Fire test with cone heater	09.04.21
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PREFACE

The author is grateful to the laboratory of wood technology, department of materials and environmental engineering, Tallinn University of Technology, particularly my supervisor Percy Festus Alao, for their help and dedication in ensuring the success of this research.

While this study aims to evaluate the "Influence of fire retardant treatment on the fire resistance and mechanical properties of hemp fibre reinforced PLA composite". Hemp fibres prepared with pretreatment with alkali and combined treatment with silane. Also, borax and Palonot® applied as fire-retardant applications.

The results from a reaction to fire of these composites' composites and mechanical tests were evaluated showed that fire performance properties, tensile and flexural properties of the hemp fibres composites, and conclusion and recommendations were drawn from this performance.

Key words: hemp fibre; PLA; mechanical properties; fire test; master thesis

INTRODUCTION

The use of hemp fibres as reinforcement in composite materials has increased in recent years due to the increasing demand for developing biodegradable, sustainable, and recyclable materials. Hemp is one of the most promising materials for replacing glass fibres and other carbon-based composite reinforcements (Placet, 2009). Hemp is also well-known for its strength and environmental friendliness. Industrial hemp is made from natural fibres found in the local area and can create new products. Hemp in the Cannabis sativa group and known for its high potency while remaining affordable. Cannabis is much less expensive to grow than cotton, flax, or other plant fibres, and it is a more complex plant that grows well without pesticides or herbicides. Cannabis is also regarded as an easy-to-process and-recycle product.

Fibres, whether natural or synthetic, are used to create composite materials. The fibres increase the composite's tensile strength and, as a result, its performance. Natural fibres are bound and kept together by lignin within a composite matrix, so a single natural fibre does not entirely make up the fibre composites (Shahzad, 2012). Hemp is a natural resource that is less harmful to the environment than synthetic fibres while also being less expensive. The most popular and oldest fibre reinforcers are glass fibres. Hemp fibres have similar mechanical properties to glass fibres (Varghese, 2018).

This study investigates the influence of fire-retardant treatment on the fire resistance and mechanical properties of hemp fibre reinforced PLA composite. Given this, frost retted hemp fibres were first treated with alkali and combined alkali and silane, followed by fire retardant treatment with Palonot[®] or Borax. The treated fibres were subsequently used in the reinforcement of polylactide at a fibre loading of 50wt.%. The performance of the composite was then evaluated based on the fire resistance and mechanical properties. Besides, understanding the changes in mechanical properties after treating, such as improving or drawbacks in structures. The research objectives are the following:

- Surface pretreatment of hemp fibres with alkali and combined treatment with silane.
- Fire retardant treatment of untreated and chemically modified fibres.
- Fabrication of hemp reinforced polylactide composites at fibre loading of 50 wt.%
- Investigation of the effect of fire retardant treatment on the hemp fibre surface morphology.

- Determination of the influence the fibre fire retardant treatment on the composite mechanical performance.

The first chapter of this study reviews previous studies on the topic, highlighting various shortcomings, properties, and advantages of natural fibre reinforced composites and contrasting them with composites made of synthetic materials. The materials and methods used to achieve the study's desired goal discussed in Chapter 2, and the composites' output discussed in Chapter3.

1. LITERATURE REVIEW

1.1 Natural fibres

Natural fibres (NF) are non-artificial or synthetic fibres derived from various sources, including plants, animals, and minerals (Aravinthan et al., 2010). Natural fibres from both renewable and non-renewable resources, such as oil palm, sisal, flax, and jute, have received much attention in recent decades for use in composite materials. Plants that produce cellulose fibres include bast fibres (jute, flax, ramie, hemp, and kenaf), seed fibres (cotton, coir, and kapok), leaf fibres (sisal, pineapple, and abaca), grass and reed fibres (rice, corn, and wheat), and core fibres (hemp, kenaf, and jute), as well as all other types like wood and roots (Faruk, 2012). The most common and commercially natural fibres in the world and world production have been shown in Table 1.

Table 1. NF in the world and globaly production (Faruk, 2012)

Fibre sources	World production (ton)
Bamboo	30
Sugar cane bagasse	75
Jute	2300
Kenaf	970
Flax	830
Grass	700
Sisal	375
Hemp	214
Coir	100
Ramie	100
Abaca	70

1.2 Hemp fibre

Natural lingo cellulosic fibres (NFLs) have drawn attention for reinforcing and producing Polymer Composites in the enlightenment of bio-based products for energy saving and natural, recyclable fibres (Sanjay, et al., 2015). One of the most famous NLF is hemp fibre for recent years. Hemp tensile strength is remarkable (900 MP and modulus of 70 GPa), provides the ability to use in thermoset polymeric matrices, epoxy, and polyester (Callister, et al, 2018). Hemp fibres are recognised as one of the bast natural fibres categories from the hemp plant under the class of Cannabis, producing fibres, shives, and seeds. Bast fibres are

used as raw materials for thermal insulations, cigarette papers and bio-composites. Its stalks have surface layers. Its bark layer with 20-50 bast fibre bundles and a woody core with a central lumen, as seen in Figure 1. Hemp fibre (HF) is a low-cost, high-quality natural fibre gaining popularity in various industries, including construction, aerospace, and automotive interiors. Since it has better mechanical properties than other natural fibres used in the manufacture of fibre-reinforced thermoplastic (RFP) composites (Suardana et al., 2011).

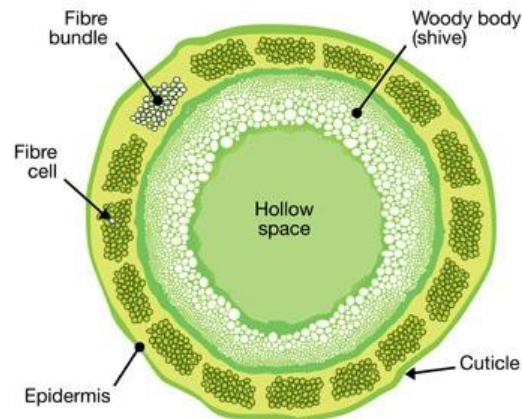


Figure 1. Cross section of hemp stalk

The hemp plant is grown for fibre, oil and drug production purposes. Hemp is an annual herb plant growing around 4 to 5 m high and thickness from 4 to 20 mm. Before flowering, male and female plants are equal. Female plants are often shorter and have more branches than male plants. The male flowers dangle in long and loose, multi branched and clustered panicles, which can be up to 30 cm long, while female flowers are tightly crowded in the axils (Carus et al., 2013). Industrial hemp can grow on very different soil types, and it is considered one of the strongest and adaptable crops and environmentally friendly. It will be ready to harvest in four months. Therefore, maintaining the field is not necessary, and hemp can grow without using any pesticides. Table 2 shows different fibres Chemical composition.

Table 2. Chemical composition of plant fibres (Mochan, 2019)

Fibre	Origin	Cellulose (%)	Lignin (%)	Hemicellulose (%)	Pectin (%)	Wax (%)	Ash (%)	Microfibrillar Angle (°)
Hemp	Bast	70-74	3.5-5.7	15-20	0.8	1.2-6.2	0.8	2-6.2
Jute	Bast	61-72	12-13	18-22	0.2	0.5	0.5-2	8
Sisal	Leaf	78	8	10	-	2	1	-
Flax	Bast	64-72	2-2.2	18-20	1.8-2.3	-	-	5-10
Ramie	Bast	69-91	0.4-0.7	5-15	1.9	-	-	7.5
Harakeke	Leaf	56-64	7.8	23-31	-	-	-	-
Coconut Coir	Fruit	36-43	0.15-0.25	41-45	3-4	-	-	30-49
Kenaf	Bast	45-57	22	8-13	0.6	0.8	2-5	2-6.2

1.2.1 Thermal and flammability characteristics of hemp

The main components of hemp as natural or plant fibres are cellulose, hemicellulose, lignin, pectin and wax (Kim et al., 2018). Cellulose has a high level of crystallizing that glucose units connected in long chains in the matrix of hemicellulose. Polysaccharide, acts as a cementing matrix between micro-cellulose fibrils and forming the main structural component of the fibre cell (Figure 2). Cellulose is thermally decomposed in several steps as follow (Horrocks, 1983):

- Desorption of absorbed water
- Cross-linking of cellulose chains with the evolution of water to form dehydrocellulose
- Decomposition of the dehydrocellulose to yield char and volatiles,
- Formation of laevoglucose
- Decomposition of the levoglucosan to yield flammable and non-flammable volatiles, gases, tar and char

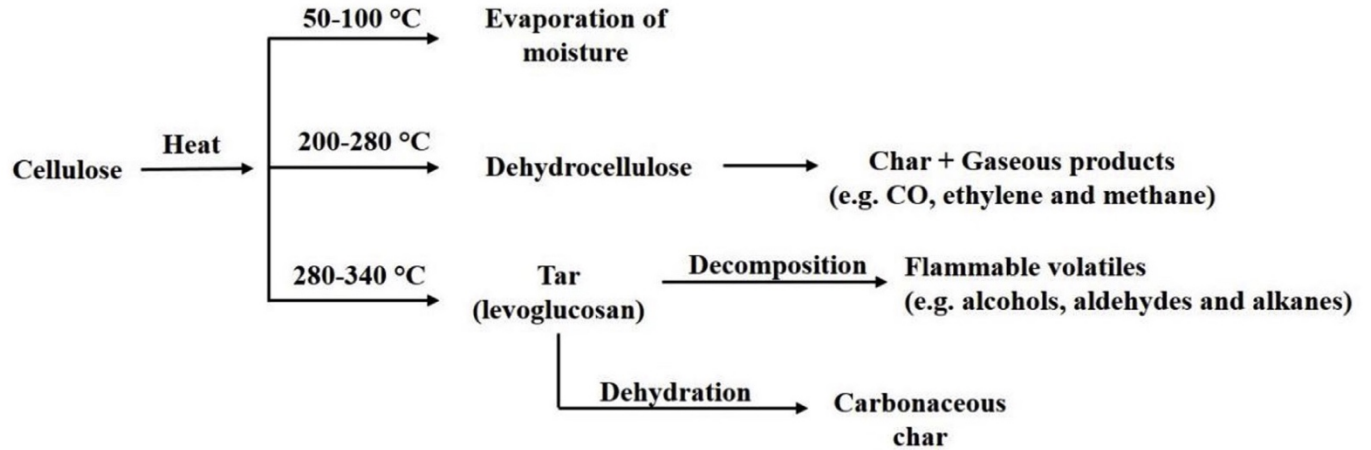


Figure 2. Basic schematic representation of cellulose degradation process (Horrocks, 1983).

Table 3. Thermal properties of natural fibres and synthetic polymers obtained (Kandola, 2012)

Material	T _g (°C) Glass transition	T _m (°C) Melting	T _p (°C) Pyrolysis	T _c (°C) Ignition	LOI (%)
Wool	NA	No melting	245	600	25.2
Cotton	NA	No melting	350	350	18.4
Silk	NA	No melting	320	600	22 - 23
Flax	NA	No melting	371	NA	NA
Hemp	NA	No melting	346	NA	NA
Nylon 6	50	215	431	450	20 - 21.5
Polypropylene	-20	165	469	570 - 600	18.6
Polyethylene	-120	110 - 130	340	350	17.4
Polyester	80 - 90	255	420 - 477	480	20 - 21.5
Epoxy	60	No melting	360 - 430	550	23
Phenolic	300	No melting	440 - 520	614	25
*NA: NOT APPLICABLE					

1.2.2 Morphology of temperature effect on the mechanical properties of hemp fibres

When hemp fibres were exposed to 100 °C for 24 hours, their tensile strength increased by about 18 per cent, while their Young's modulus decreased (Teixeira, 2018). Hemp fibres became brittle and inelastic after 24 hours at 200°C, decreasing mechanical stiffness. (figure 3). Hemp decomposition began at 150 °C, hemicelluloses and pectin decomposition began at 260 °C, and cellulose decomposition began at 360 °C. (Shahzad, 2013). Moreover, it was found that the cross-section of hemp fibres was polygonal, and the tensile strength of a *single hemp fibre was 277 ± 191 MPa, also, a tensile modulus and a strain to failure of 9.5 ± 5.8 GPa and $2.3 \pm 0.8\%$, separately. *single hemp fibre = width of 67 ± 26 μm

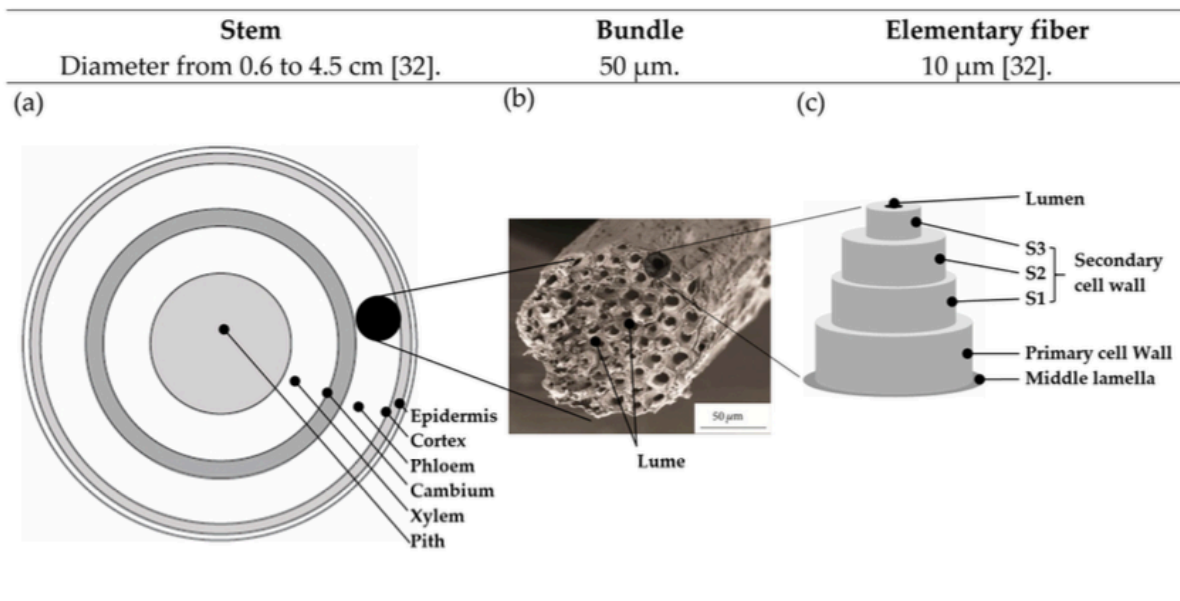


Figure 3. Structure of hemp fibre: (a) transverse hemp stem (b) cross-section morphology of the hemp fibre bundle, and (c) schematic depiction of hemp elementary fibre (adapted from Nunes, 2017).

1.2.3 Advantages of using hemp

Using natural fibres also by focusing on hemp have lots of advantages as follow (Palumbo. *et al.*, 2015):

- We can prepare them yearly (wood has long generation cycles)
- Bio-degradable, which results in the reduction of harmful waste materials in the environment
- Easily reachable
- Price fixing helps to differentiate the market for farmers
- The natural structure provides lower thermal conductors
- Their hygroscopic behaviour helps to maintain comfort in buildings

1.2.4 Different usage of hemp plant's parts

Almost every part of the hemp can be used in different industries. All of it can be used as fuel.

Hurds. The non-fibrous layer of the stem can use in paper pulp, rayon, cellophane, food additives

Bast Fibres. Using building materials, carpeting, insulation, clothing and paper (cigarette paper)

Hemp Gain. This is a source of food, oil and meal. Also, there is a unique mixture of omega-6 and omega-3 in its body.

1.2.5 Growing and utilization hemp in Europe

Climatic conditions in all parts of Europe are suitable for hemp fibre growing approximately but show that hemp is grown and harvested only in several countries in Europe. This limitation is based on some issues because growing hemp in some countries is illegal because of the possibility of using it as a drug substance. The top producers of hemp in Europe are listed below in Table 4.

Table 4. Most important European hemp producers (IAL Consultants, 2013)

European Countries	Hemp producing share in Europe (%)
France	72%
Germany	10.5%
Netherlands	9.4%
United kingdom	4.4%
Austria	1.8%
Poland	0.8%
Denmark	0.6%
Latvia	0.6%

1.3 Composites

Composites are the category of materials that include load-carrying solid material that we know as reinforced, fixed in weaker material, known as the matrix. Reinforcement is a process that helps to sustain the structural load and provides strength and rigidity. The reinforcement's location and orientation are maintained by the matrix, which can be organic or inorganic. Composites provide a unique combination of properties that individual constituents would be unable to achieve on their own. Natural fibre reinforced polymers (NFRP) have been provided as an alternative to glass fibre reinforced polymers (GRP) for building construction and other industries. GRP has a weak environmental impact, and it does not have any place in the modern view of the circular economy. However, from an economic point of view, GRPs have a longer life cycle than NFRPs. However, natural fibres are less harmful to humans (Naughton, 2014).

1.3.1 Natural fibre reinforced composites (NFRC)

Natural fibre-reinforced composites are composite materials (presenting as NFRC in this article). The reinforcing fibres are derived from renewable and carbon dioxide neutral resources such as wood and plants. For NFRC to minimize disadvantages and ensure that fibres are entirely protected and surrounded by the matrix to provide stronger interfacial bonding, it is essential to use a good technique for fibre distribution. Temperature and pressure during processing can affect fibre dispersion, and longer fibres have a greater chance of having lower dispersion than shorter fibres (Pickering et al., 2016). Mechanical properties of NFRC improves when it has a better orientation, and it would have the best performance if the fibres would be aligning to the loading direction. Randomly directed fibre composites have been shown to have better formability and cost less to manufacture than highly directional fibre composites (Zampaloni et al., 2007). Therefore, the direction of the fibres provides a more mechanical advantage.

1.3.2 Hemp fibre in the production of effective Composite

Numerous studies have been conducted on figuring out the interfacial bonding between natural fibres and matrix, which can be classified into three types (Shalwan, 2013):

1. Hybridization
2. Physical treatment
3. Chemical treatment

Cellulose, hemicelluloses, lignin, and pectin are all abundant in hemp fibres. As long as polymeric materials have a hydrophobic, long aliphatic primary chain, they will be polar, hemp has hydroxyl groups in its structure and acts as a polar hydrophilic fibre (Safri, 2018). In composite production, combining hydrophilic and hydrophobic materials results in deficient matrix–fibre interfacial adhesion, inadequate stress transfer between matrix and fibre, and a loss of the composite materials' final properties (Satyanarayana, 2009).

In thermoplastics and thermosets, the tensile properties of natural fibre reinforced polymers are highly impacted by the interfacial adhesion between the matrix and the fibres. Several chemical modifications are employed to improve the interfacial matrix–fibre bonding resulting in the enhancement of tensile properties of the composites. In general, the tensile strengths of the natural fibre reinforced polymer composites increase with fibre content, up to a maximum or optimum value; the value will then drop. However, Young's modulus of the natural fibre reinforced polymer composites increases with increasing fibre loading. The tensile strength and Young's modulus of composites reinforced with bleached hemp fibres increased incredibly with increasing fibre loading (Ku, 2013). Figure 4 shows a comparison of natural fibre composites tested based on mechanical properties. Natural fibre composites have specific properties that are often superior to glass fibre composites. According to recent studies, natural fibre composites can replace glass in a variety of applications and finished goods that do not need very high load-bearing capabilities (Wambua, 2003).

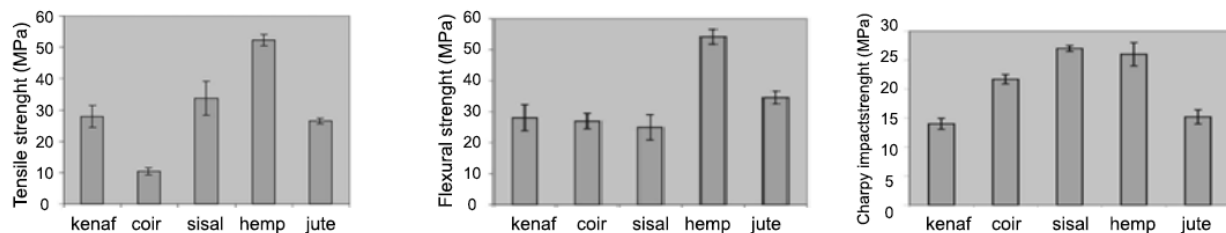


Figure 4. Tensile, Flexural and Charpy impact (Wambua, 2003).

1.4 Polymers

There are two standard polymeric matrices for the composites, first, thermo-plastic and second thermoset polymers. The structural differences of the two polymer types impact thermal decomposition and combustion (Price, 2009). There is a linear structure in the thermoplastic polymers (Horrocks, 2005). On the other hand, thermoset polymers contain a three-dimensional cross-linked molecular structure. Thus forming under heating is prevented (Price, 2009). The polymer burning includes different steps (Azwa, 2013):

1. Heating,
2. Decomposition,
3. Ignition,
4. Combustion

Both polymer types start the change of molecular structures at the early step of heating. Additional heat decomposes the polymers to break the molecular bonds and produce varying types in the pyrolysis stage. Free radical formed by the bond scission with flammable products under high temperature ignites the polymer with oxygen availability in the environment. Enough energy and combustible volatiles can establish the combustion cycle (Price, 2009). Polymers with essential flame resistance, phenolic and polyamide resins can yield char during the combustion. The phenolic resin releases water due to phenol-phenol condensation, and then the oxidation of methylene groups leads to carbonyl linkage. Further decomposition liberates CO, CO₂ and other volatiles, ultimately yielding char (Price, 2009).

1.4.1 Important factors for selecting materials for metrics

Using Polymeric material in metrics are the most common matrices for producing fibre-reinforced composites. They have lightweight and need low temperature for processing. At temperatures above 200 °C, natural fibres become brittle and degrade. Thermoplastic and thermoset polymers have also been used as matrices to create composites with natural fibres such as HF as reinforcement (Holbery et al., 2006). Natural fibres, on the other hand, are a natural substitute made by plants (cellulose or lignocellulose), animals (protein), and minerals. Figure 5 demonstrates how NFRP composites can be constructed using a cellulosic plant fibre combined with either a thermoplastic or thermosetting matrix content.

Figure 5 shows that a mixture of plant/cellulose fibre with either a thermoplastic or thermosetting matrix material may be used to make natural fibre reinforced polymer (NFRP) composites.

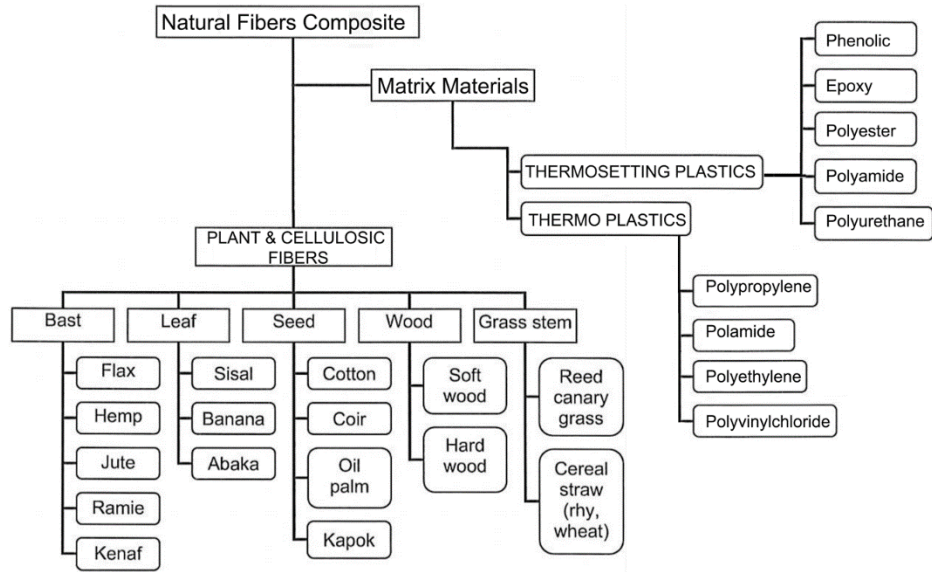


Figure 5. Natural fibres, matrices for PC. (Sanjay., 2010).

Table 5 shows the beneficial usage of natural fibres usually overcomes the drawbacks (Malkapuram et al. 2008). It is discussed that weight reduction is essential because of their low density (Table 6). Besides, based on availability, they are cost-effective. It degrades quickly and allows for easy machining with minimal tool wear. However, natural fibres have low thermal performance, poor compatibility, and poor resistance to the environment. By the way, if some treatments can fix these technical problems, natural fibres can be a suitable replacement instead of glass fibre and other synthetic fibres even for use in outdoor applications. Additionally, Table 6 compares the properties of natural and glass fibres.

Table 5. Advantages and Disadvantages of Natural Fibres (Malkapuram et al. 2008).

Advantages	Disadvantages
Lightweight	Low thermal stability
Biodegradability	Lack of interfacial adhesion
Ease of machinability	Quality variation
Non-toxic	Poor resistance to environment
Availability and low cos	Poor compatibility with polymer matrix
Non-abrasive	
Less dependency on non-renewable energy	
Low pollutant emission	
Energy recovery	

Table 6. Comparison between natural and glass fibres. Source: (Wambua et al., 2003).

Properties	Natural fibres	Glass fibres
Density	Low	Twice than of NF
Cost	Low	Low, but higher than NF
Renewability	Yes	No
Recyclability	Yes	No
Energy consumption	Low	High
Distribution	Wide	Wide
CO ₂ neutral	Yes	No
Abrasion to machines	No	Yes
Health risk when inhaled	No	Yes
Disposal	Biodegradable	Not Biodegradable

1.5 Fire retardant

To improve the fire resistance of wood-based panels and wood surface, usually adding fire retardant is common among producers and end-users. Also, mechanical and sorption properties could be important when considering their usability for construction in a building. The chemical formula of fire retardant that adds to the fibres and matrix during panel production or spraying the chemical fire retardant on the finished panels' surfaces is essential (Medved, et al., 2020). The most common substance for improving fire resistance is borates (borax, boric acid) (Nagieb et al., 2011). Good mechanical properties are significant for boards treated by fire retardant, and it would be more considerable when wants to use in residential buildings, kindergarten or hospitals. After using fire retardant usually, two types of changes appear on the treated products. Reducing mechanical properties is an adverse effect, and thickness swelling is a positive effect for treated products. Heating, decomposition, fire, combustion, and propagation are the five initial stages in the burning process. Fire retardant can be accomplished by disrupting the burning phase at each stage, resulting in the process being terminated before actual ignition. Incorporating an additive that can interfere with combustion at a specific stage of the burning process is the quickest way to achieve fire retardancy. Inorganic compounds, halogenated compounds, and phosphorous compounds are the most commonly used additive groups. Antimony oxide, sodium borate, and dicyandiamide are also used, boric acid, ammonium phosphates and borates, ammonium sulphate chlorides, zinc chloride and borate, antimony oxide, sodium borate, and dicyandiamide. Fire retardant action mechanisms can occur in both the condensed and gas phases, with the condensed phase involving polymer degradation and the gas phase involving the combustion of volatile materials. Chemical or physical processes may be used in both situations. Release of water

and gas, which dilutes the gases emitted by the flame; cooling the material surface; formation of a resistant and non-flammable layer on the material surface, which acts as a heat and volatile fuels insulator (Boccarusso, 2016). The fire retardants can be incorporated directly into the polymer matrix during the manufacturing process, or they can be impregnated or grafted onto natural fibres.

2. MATERIALS AND METHODOLOGY

2.1 Materials

The hemp fibres (*Cannabis sativa*, Tisza, Hungarian) was obtained from the hemp plant grown in Saaremaa, Estonia (Figure 6). However, these hemp fibres are not clean and therefore contain many shives. It was necessary to separate these shives from hemp fibres to properly clean the fibres for a homogenous outcome. PLA fibres (Ingeo™4043D) from NatureWorks was used as the polymer matrix. The polymer was 60 mm long and a density of 1.24 g/cm^{-3} .



Figure 6. Bundle of hemp

2.2 Methods

2.2.1 Preparation of hemp fibres

The shives and stalks were manually separated from the hemp fibres. The obtained fibres were weighed with a digital electronic weighing balance (Brand: College, Modell: B2002), then carded (carding was done thrice to improve fibre homogeneity and separation of strands). For every 300 g of hemp fibre material (shives + fibres) from the bail, $110.7 \pm 6.3 \text{ g}$ of fibre is obtained after cleaning and carding. Figure 7 shows the image of the classic drum carder and the hemp fibres after 3 carding cycles.



(a)



(b)

Figure 7. (a) Classic drum carder; (b) hemp fibres after carding

2.2.2 Fibre treatment

Alkali pretreatment. Hemp fibres were treated with 5 wt.% sodium hydroxide solution (NaOH) purchased from Sigma-Aldrich. NaOH granules were dissolved in a solution of water (5g of NaOH:95ml of water). Hemp fibres were soaked in the solution at room temperature (23 °C) for 4 hours. Fibres were then washed in tap water to remove residual alkali by measuring the wastewater's pH until it was about 7. Finally, the fibres were oven-dried at 80 °C until constant weight.

Silane treatment. The alkali pretreated hemp fibres were subsequently treated with an ethanol and water solution (80/20 vol %) containing 3 wt.% silane coupling agent (3-Aminopropyl-triethoxy silane). The amount of silane was relative to the weight of hemp fibres (for every 100 g of hemp fibres, 3g of silane is used). Prior to the treatment, the solution was stirred for 2 hours to pre-hydrolyzed silane, while acetic acid was added to control the pH to 5. The hemp fibre treatment was done for 2 hours by soaking. The hemp fibres were subsequently filtered and oven-dried at 80 °C until constant weight.

Borax application. Sodium tetraborate $\text{Na}_2\text{B}_4\text{O}_7$ (borax) is soluble in water. It has a wide range of usage as a part of the formulation of washing powders. Borax is used in glassmaking for wax emulsions and gums. Borax can release water from its crystalline structure, which

helps as a fire retardant and acts as a buffer to protect a product during contact with fire. For the fibre borax treatment, the untreated, pretreated and treated hemp fibres were soaked in a solution of 53 g of borax in 1000 ml. Borax was previously dissolved in the water for 5 minutes at a temperature of 43 °C (for every 100 g of hemp fibres). The soaking duration was 24 hours at room temperature. After the borax application, the excess water was drained, and the fibres were oven-dried at 80 °C for 24 hours. Figure 8 shows the borax treated hemp fibres. The weight of the borax deposited on the fibre was approximately 12 ± 1.2 g. To obtain the exact amount of fibre components removed during treatment, two replicas of the dried hemp fibres (10 g) was soaked separately in distilled water for 24 h and then oven dried at 80 °C. The results show that approximately 3% of the hemp fibre component was removed as shown in Table 7.

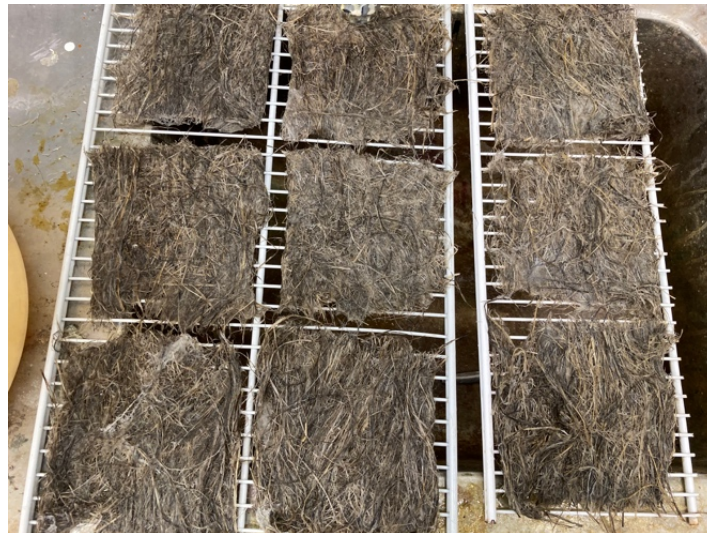


Figure 8. Dried hemp layers with Borax

Table 7. Calculating reduction of soaking materials in water

	Before soaking (g)	After soaking (g)
Hemp samples	10.11 ± 0.03	$9.78 \pm 0,08$

Palonot[®] treatment. Palonot[®] is a sustainable, safe and non-corrosive fire retardant solution for engineered wood products, construction timber and cellulose fibre based products. Also, it is discussed that wood building requires low cost of fire protection without any drawback in fire safety. Palonot[®] gives the highest Euroclass B-s1,d0 (EN 13501-1) fire retardancy while, Palonot[®] F1 is ionic liquid (ILs) based. Based on the manufacturer's information, Palonot[®]

does not have any adverse effect on the mechanical properties of wood or its' products. For the hemp fibre treatment, Palanot[®] was supplied by Palonot[®] company in Finland. The palonot[®] was diluted to 50% using water the hemp fibres treatment. The hemp fibres (untreated, alkali pretreated and combined alkali and silane treatment) were soaked for 3 mins until full area coverage and absorption. After treatment, fibres were dried for 24 hours at room temperature, and then subsequently oven-dried at 60 °C until constant weight.

2.2.3 Fabrication of the composite

For this study, the composites were fabricated by thermo compression at a temperature 180 °C and pressure 3 MPa for 10 min. The composites were produced from combining 50 wt.% hemp fibres with the PLA fibres (i.e 50 g of hemp fibre + 50 g of PLA) in a classic drum carder. For the fire retardant treated fibre reinforced composites, only the top layer fibres were treated to ensure optimal protection and to reduce the negative impact on the composite mechanical performance. For the samples, the top layer hemp fibres were combined with the PLA in the form of a mat, while the core layers were mixed with the PLA using the classic drum carder. Figure 9 shows the mixture in the oven, dried for 4 hours before the hot-pressing process. Table 8 presents the abbreviation for the prepared composite specimen.



Figure 9. Half and half hemp fibers and PLA

Table 8. List of samples abbreviations

Abbreviation	Composite description
Un	Untreated hemp fibre reinforced PLA composites
Na	Alkali pretreated hemp fibre reinforced PLA composites
Sa	Alkali + silane treated hemp fibre reinforced PLA composites
UnBr	Composites from fibres (Un, Na, Sa) treated with Borax
NaBr	
SaBr	
UnPal	Composites from fibres (Un, Na, Sa) treated with Palonot®
NaPal	
SaPal	

2.2.4 Experimental

Table 9 shows the list of tests and standards that took place in this study.

Table 9. Tests names and Standards

No	Test	Standard
1	Scanning Electron Microscopy SEM analysis	Laboratory method
2	Fire test	ISO 5660-1 2015
3	Tensile test	EN – ISO 527-4
4	Flexural test	EN-ISO 14125

2.2.4.1 SEM analysis

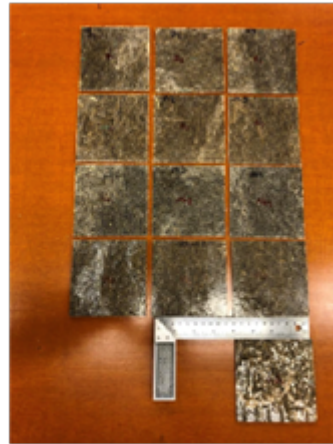
The SEM images of the fibres were observed using a Zeiss Ultra 55 (FELMI-ZFE, Steyrergasse, Austria) at 20 kV, depth of 20µm and resolution of 50,000. For this observation, samples were carbon glued on an aluminium stub and then coated with an alloy of 2 nm thick gold (Au)/palladium (Pd) layer (80/20).

2.2.4.2 Reaction to fire test

Figure 10 presents the composite samples sizes (surface area, 100 mm²) for the reaction to fire test.



(a)



(b)

Figure 10. (a) Composite sample 100 x 100 mm; (b) Prepared samples for fire performance test

The specimens were prepared on a timber (surface area 100 mm² and 50 mm thickness) The composite specimen and timber block are held together with a self-binding aluminium (see Figure 11a). Also, a type K Pentronic AB thermocouple (0.25 mm in diameter) was inserted between the composite layer and timber at the centre point (50 mm) (see Figure 11b). The Thermocouple was maintained at 300 mm in length to ensure accurate connection to the data logger. Prior to the fire test, specimens were conditioned for 7 days at a temperature of 23 °C and relative humidity of 50%.



(a)



(b)

Figure 11. (a) composites held on timber block (b) thermocouple between the composite and the timber surface in contact with the composite.

The test was performed according ISO 5660-1 2015 by subjecting the specimen, fixed in the metal cast to a heat flux of 50 kW/m² from a cone heater. The exposed surface of the specimen was maintained at a distance of 60 mm from the cone heater. To obtain the surface temperature, a thermocouple was also attached on the top of the test specimens. Figure 12 presents the set-up of the test.



Figure 12. Sample testing in cone heater

The outcome of the composite fire reaction is presented in the form a temperature-time curve at intervals of 5 seconds. The performance of the composites was determined from the ignition time, ignition temperature and weight loss. The thickness and density of all the specimens was measured for effective analysis of the results.

2.2.4.3 Tensile test

The tensile test was performed following EN – ISO 527-4. A total of 30 specimens were examined for all variants, with 5 replicas per sample groups. The test specimen was 250 mm x 25 mm in size, and the thickness of each sample was measured and reported after testing at the point of fracture. Testing was conducted using the Zwick/Roell shown in Figure 13, at a temperature of 20°C, 30% relative humidity, and a test rate of 5 mm/min The specimen was kept between two grips during the procedure (150 mm distance between grips) and load was applied until failure.

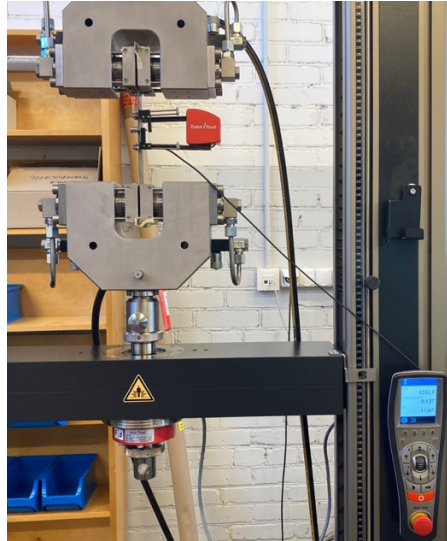


Figure 13. Zwick/Roell machine for mechanical testing

The tensile stress (σ) and strain (ε) of the specimens was calculated as shown:

$$\sigma = \frac{F}{A'} \quad \varepsilon = \frac{\Delta L_0}{L_0'}$$

where

σ – is the tensile stress value, MPa;

F – is the measured force concerned, N;

A – is the initial cross-sectional area, mm²;

ε – is the strain value in question, expressed as a dimensionless ratio, or in percentage;

L₀ – is the gauge length of the test specimen, mm;

ΔL_0 – is the increase in the specimen length between the gauge marks, mm;

Furthermore, the nominal strain (ε_t) and Young's modulus of elasticity (E_t) was calculated as shown below.

$$\varepsilon_t = \frac{\Delta L}{AL'}$$

$$E_t = \frac{\sigma_1 - \sigma_2}{\varepsilon_2 - \varepsilon_1'}$$

where

ϵ_t – nominal tensile strain, expressed as a dimensionless ratio or percentage, %;
 L – initial distance between grips, mm;
 ΔL – increase of the distance between grips, mm;
 E_t – is Young’s modulus of elasticity, MPa;
 σ_1 – is the stress; 0.0005 mm/mm – 0.0025 mm/mm; σ_2 – is the stress; ϵ_1 – is the strain;
 ϵ_2 – is the strain;
 $\Delta\sigma$ – Difference in applied tensile stress between the two strain points, MPa;
 $\Delta\epsilon$ – Difference between the two strain points

2.2.4.4 Flexural test:

The test standard for the flexural test was EN-ISO 14125. Except for the hemp changed variables of fibre lengths 60 mm and width 15 mm, which used eight specimens for each group samples. Thicknesses of each specimen determined before the start of the test. This test was carried out using the Zwick/Roell machine shown in figure 19, at a standard laboratory atmosphere of 20 °C and 30% relative humidity.



Figure 14. Zwick/Roell machine for flexural stress

The following equation is for the flexural stress parameters:

$$\sigma_f = \frac{3FL}{2bh^2}$$

where

σ_f – is the flexural-stress parameter in question;

F – is the applied force N;

L – is the span (mm);

b – is the width (mm) of the specimen;

h – is the thickness (mm) of the specimen

The following equation was used to calculate the flexural strain parameters:

$$\varepsilon_f = \frac{6sh}{l^2} \times 100\%$$

where

ε_f – is the flexural strain parameter in question, expressed as a dimensionless ratio or as a percentage;

s – is the deflection(mm);

h – is the thickness(mm)of the test specimen;

l – is the span(mm)

For calculating deflection:

$$S_i = \frac{\varepsilon_{fi}L^2}{6h} (i = 1 \text{ or } 2)$$

where

S_i – is one of the deflections, mm;

ε_{fi} – is the corresponding flexural strain, whose values ε_{f1} and ε_{f2} are given above;

L – is the span, mm;

h – is the thickness, mm, of the specimen

The flexural modulus:

$$\varepsilon_f = \frac{\sigma_{f2} - \sigma_{f1}}{\varepsilon_{f2} - \varepsilon_{f1}}$$

where

σ_{f1} – is the flexural stress, MPa, measured at deflection s_1 ;

σ_{f2} – is the flexural stress, MPa, measured at deflection s_2

3 RESULTS AND DISCUSSION

3.1 SEM Analyses

Observation of the SEM images presented in the following figures. Figures 15, 17 and 19 show a cleaner and more precise surface for the borax application and Palonot[®] application in Un, Na, Sa treated fibres. Also, it shows that there were clear differences between the borax and palonot[®] applications. Thus, untreated fibres with borax application show align and parallel fibres in comparison with NaBr and SaBr. SaBr shows a hemp fibres alignment, but there is no good borax distribution. NaBr shows an unorganised fibre alignment with Inhomogeneous borax distribution. Palonot[®] seems to capsulate the Sa treated fibres, and parallel alignment is distinguished. This capsulation has happened for Na treated, but the alignment of the fibres is not good in a parallel direction. The density of hemp fibre can vary depending on how much the cellulose content is in the fibres because the higher the cellulose content, the denser the fibre would be (Madsen, 2008). UnPal seems lignin combined with Palonot[®] and modifying a surface that the fibres are not distinguished.

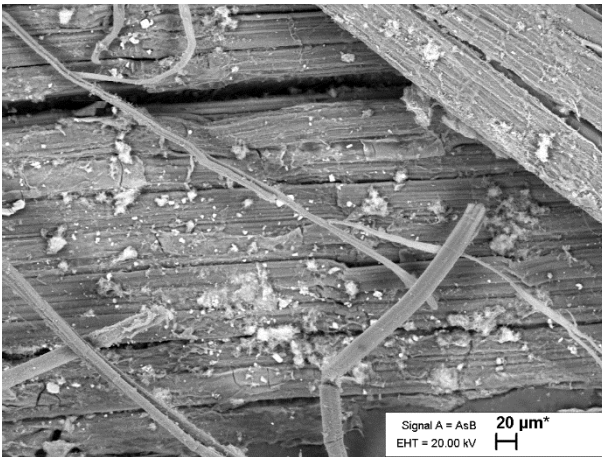


Figure 15. Alkali Borax (NaBr)

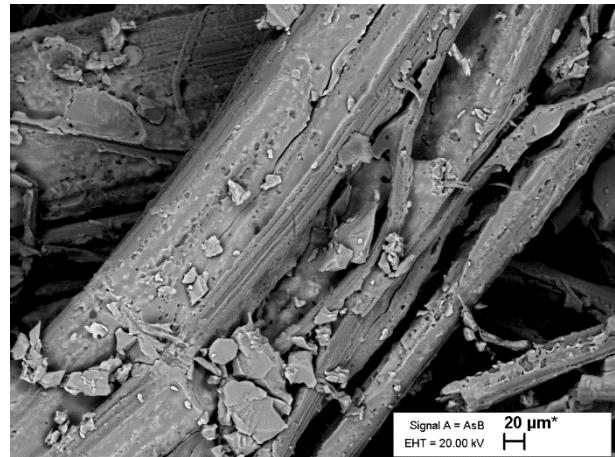


Figure 16. Alkali Palonot[®] (NaPal)

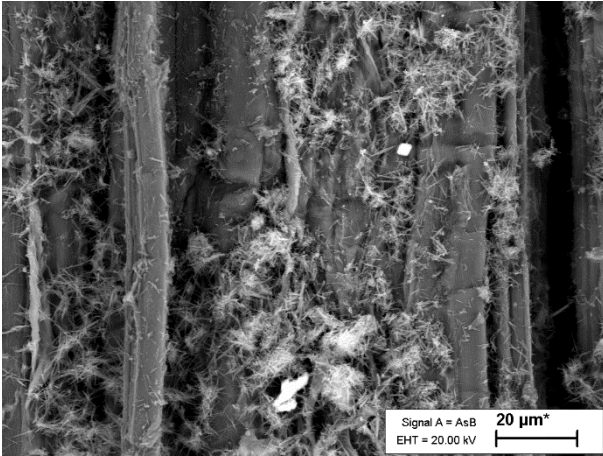


Figure 17. Silane Borax (SaBr)

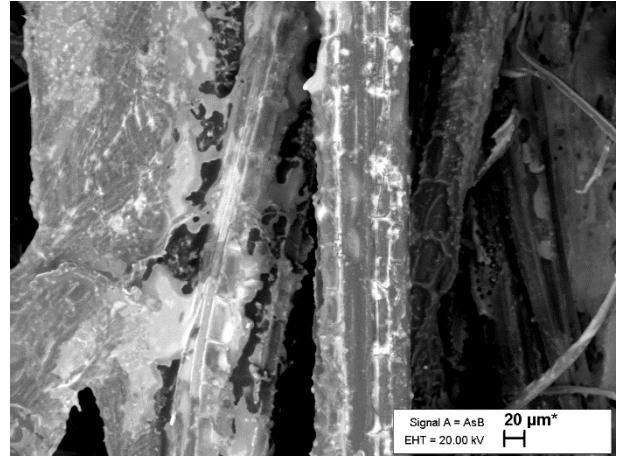


Figure 18. Silane Palonot® (SaPal)

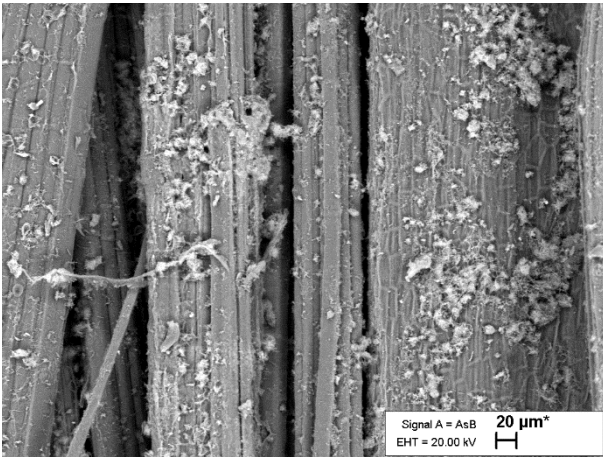


Figure 19. Untreated Borax (UnBr)

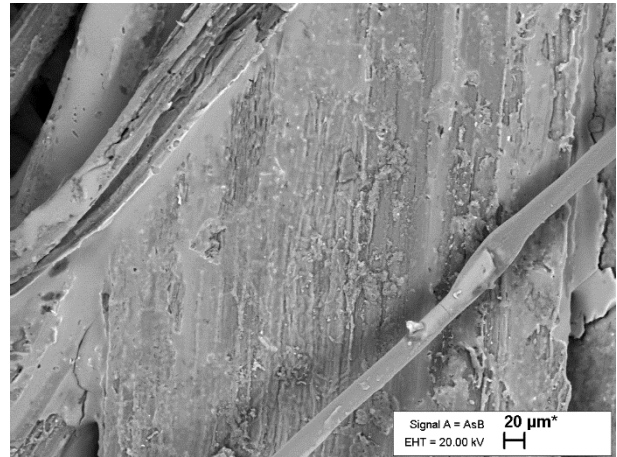


Figure 20. Untreated Palonot® (UnPal)

3.2 Reaction to fire of the composites

Figure 21, shows the reaction to fire of the composites Un, Na, Sa, UnBr, NaBr and SaBr in 480 sec. At first glance, the curves differ significantly for samples without fire-retardant application and borax application; it can be seen that the Na sample absorbed the most heat and stopped to reach the thermocouple that was located down part of the samples. This record could be the essential protection time that shows how long does heat take to pass the sample and reach to timber surface. On the other hand, Un samples had the lowest capability of absorbing heats from cone heater. This result is similar to previous studies that untreated hemp fibres do not have good fire resistance properties.

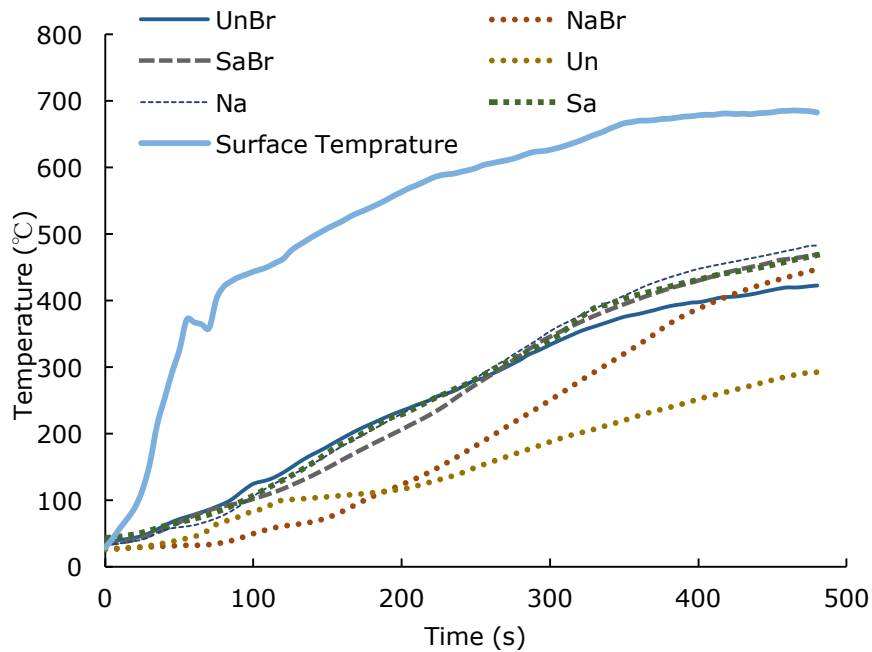


Figure 21. Fire test results, Time and Temperature for Un, Na, Sa, UnBr, NaBr and SaBr in 480 sec.

Figure 22, shows the graph of time and temperature for samples with palonot[®] FR. Among these three samples, UnPal has the highest capability to keep the heat and stop it from reaching the thermocouple. Also, NaPal acted very poorly, and the result for this sample is strange. Some fluctuation at the first steps of some samples, like NaPal have been caused by realising water.

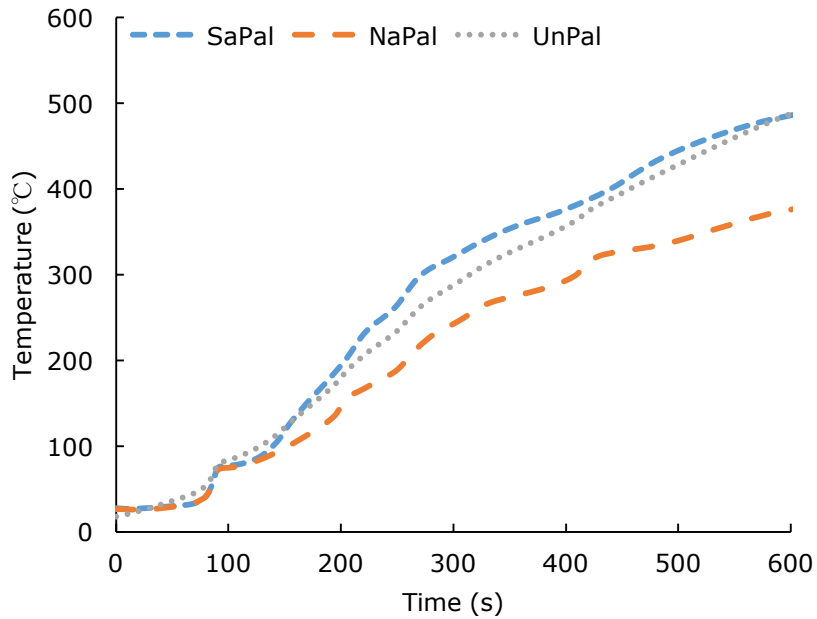


Figure 22. Fire test results, Time and Temperature for UnPal, NaPal and SaPal in 720 sec.

3.2.1 Ignition Time

In this study, ignition time measured the time it took for the composite's surface to reach the critical ignition temperature during the fire tests. It depended on the thermal inertia of the material (a product of heat capacity, thermal conductivity, and density), which changed due to incorporating all different types of materials in its construction (Hull *et al.*, 2011). The differences in the burning behaviour of the untreated composites and composites with borax fire retardant application can be observed from the ignition time and burning behaviour tests. Figure 22. shows the ignition time among untreated and borax application samples. There were no ignition or fire for palonot[®] samples. Figure 22. shows the ignition time of the specimens. These data do not follow any unique pattern and are relatively scattered. This shows that ignition time is not an appropriate characteristic for recognizing standard and fire retarded types in cone calorimeter test. In the UnBr sample, the time taken for the composite to ignite was longer than the other samples. One-way analysis of variance (ANOVA) tests indicated that as an external group analysis among 2 main groups of samples without FR and samples with borax, there are no significant differences (see Appendix 1, Table 11). Inside of the groups, T-test has confirmed that there is no significant difference between each groups items.

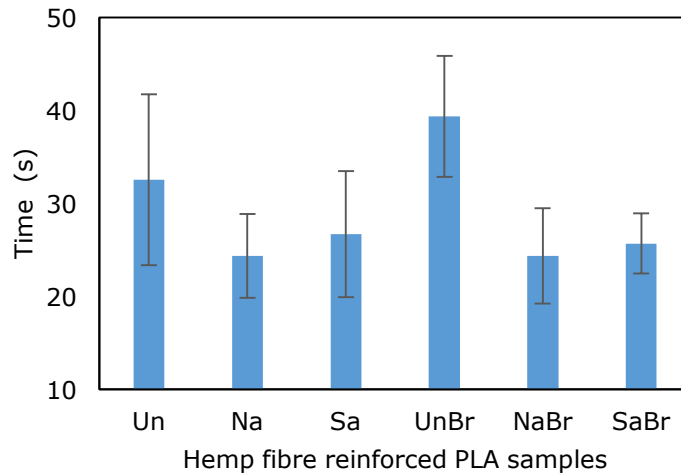


Figure 23. Ignition time for samples without FR and with borax

Table 10. Ignition time and surface temperature

Samples	Ignition time (sec)	Surface temperature
Un	33	213
Na	24	115
Sa	27	154
UnBr	39	252
NaBr	24	115
SaBr	26	115

3.2.2 Density

Figure 23. shows the results of the density observation of composite samples reinforced with untreated and pretreated hemp with alkali and silane with borax and palonot[®] application. Among them, NaPal has the highest density, and the lowest is NaBr.

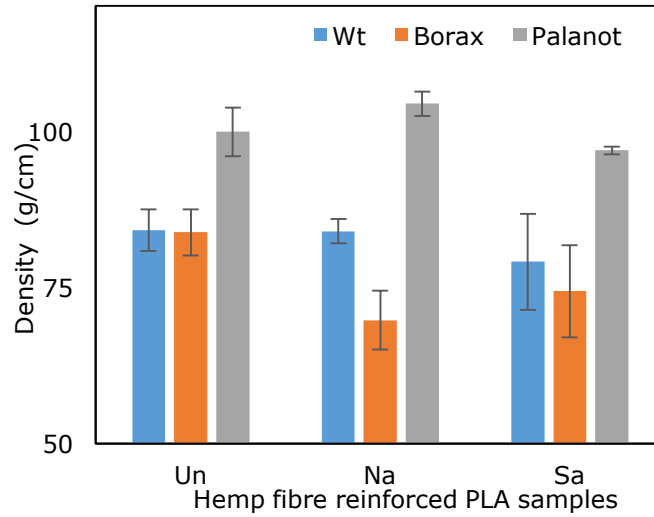


Figure 24. Density for hemp fibre reinforced samples whit Borax and without (Wt) FR.

3.2.3 Comparing weight lost in samples

The fire resistance test revealed a reduction in weight loss for all samples, as presented in Figure 24. The highest loss is for untreated samples without any FR applications. The palanot[®] group has a lower rate, and among them, Na pre-treated hemp fibre samples have the lowest rate. FR treatment concentration is noticeable with borax, and palanot[®] especially palanot[®] samples, show a perfect improvement.

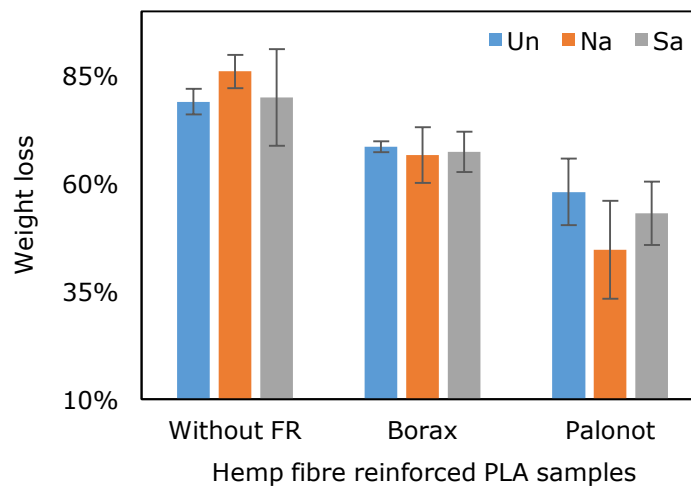


Figure 25. weight loss for hemp fibre composites samples.

3.3 Mechanical test

3.3.1 Tensile stress

Figure 25. shows the tensile test results for composite samples reinforced with untreated and pretreated hemp with alkali and silane with borax and palonot[®] application. According to the obtained results, the composite sample reinforced with alkali fibers and borax application has the highest tensile. From these diagrams it can be concluded that silane composites with borax application are brittle under tensile load, because soaking in the water for combined pretreatment of alkali and silane and after that 24 hours soaking in borax 5 wt.% changed that to be more brittle than other samples because of losing some structural elements and reduction in mechanical properties. NaBr shows the highest outcome with 40.78 ± 2.27 MPa. On the other hand, the lowest outcome recorded by SaBr 28.98 ± 4.36 MPa. One-way analysis of variance (ANOVA) tests indicated that the tensile strength significantly differed between the borax and palonot[®] groups (see Appendix 1, Table 12). Also, inside group borax there are some significant differences between firstly, NaBr and SaBr, secondly, UnBr and SaBr. Inside of palonot[®] group, there is a significant difference between UnPal and SaPal (see Appendix 1, Table 13).

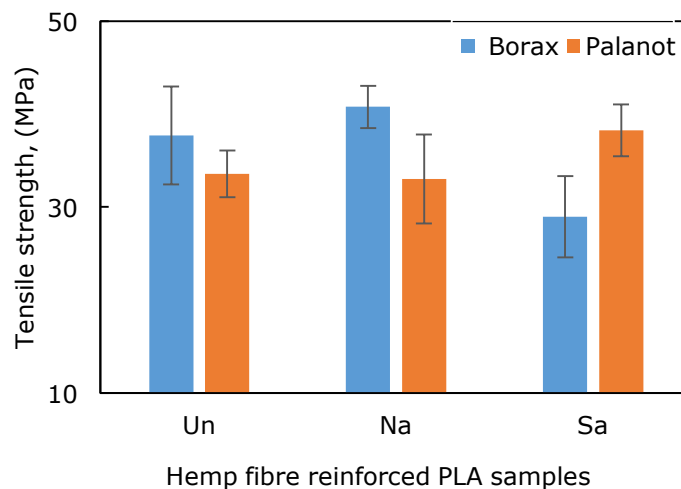


Figure 26. Tensile Strength for hemp fibre composites samples.

Figure 26 depicts Young's modulus of hemp fibre composites. The same result is obtained with Young's modulus as with Tensile power, as can be shown. and NaBr received the highest

outcome with 11.03 ± 1.37 GPa. Also, just as in the case of tensile strength, there was no significant difference in the elastic modulus of borax and palanot[®] application. The lowest outcome related to NaPal with 9.80 ± 1.21 GPa. However, some previous studies show that when silane alone was used, the tensile modulus was significantly higher (10% and 15%) than untreated and alkaline treated fibre composites. The decrease in tensile strength is purely attributed to an extreme removal of lignin and hemicellulose. However, in the modulus case, growth for silane treated fibres was attributed to the developed bonding between the matrix and fibre. One-way analysis of variance (ANOVA) tests indicated no significant difference among borax and palanot[®]. Also, no significant differences within groups (see Appendix 1, Table 14).

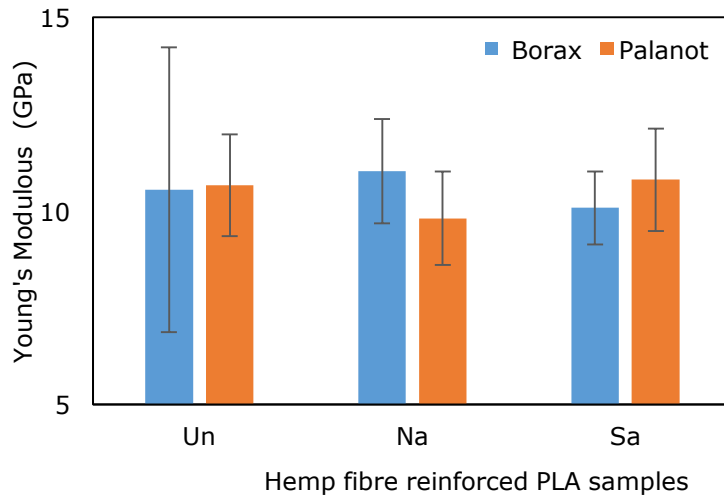


Figure 27. Young's Modulus of hemp fibre composites samples.

3.3.2 Flexural stress

By performing flexural stress (three-point bending test) on composite samples reinforced with hemp fibers, the results obtained are presented in the diagrams of Figure 27. The most important factors affecting the flexural strength and modulus of the fibre-reinforced composite are (a) the interphase adhesion between the matrix and the fibres and (b) the rate of stress transfer between the matrix and the fibres. Unlike tensile strength, the flexural strength of fibre-reinforced composite depends largely on Interfacial shear stress (IFSS) rather than fibre strength. Results show that Silane Borax is very poor in flexural stress with 39.31 ± 2.90 MPa. Another side, UnBr with $67,78 \pm 7.48$ MPa. Has the highest flexural stress. One-way

analysis of variance (ANOVA) tests indicated that the flexural stress has a significant difference between the borax and palonot[®] group (see Appendix 1, Table 18). Also, in group borax and palonot[®] there are no significant differences.

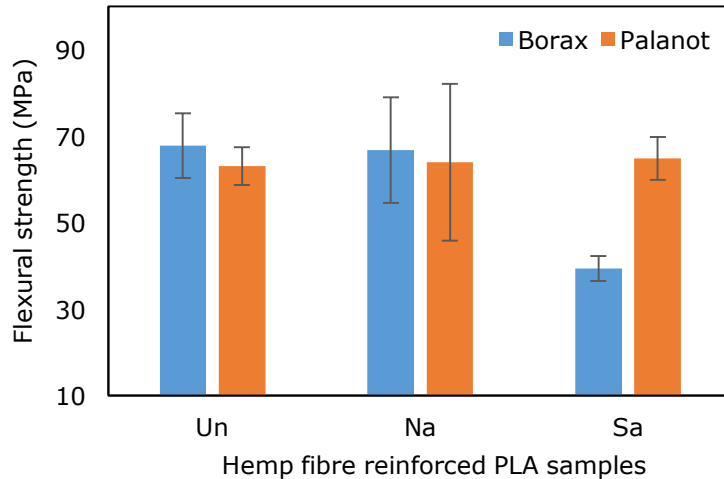


Figure 28. Flexural Strength for hemp fibre composites samples.

Figure 28. shows the flexural modulus of hemp fibre reinforcement composites with palonot[®] and borax application. The highest outcome is UnBr with 9.50 ± 1.40 GPa, and the lowest one is for UnPal with 7.69 ± 2.30 MPa. Previous studies show that combined treatments of hemp fibre with NaOH and silane have improved the bonding between fibre surface and matrix, leading to improved flexural properties even compared to single treatments with NaOH. Nevertheless, for the borax application, mentioned samples soaked in 5 wt.% borax for 24 hours, which could be the reason for the reduction in the results of the flexural modulus test. This soaking could be solved some structural parts and decrease the flexural modulus stress. One-way analysis of variance (ANOVA) tests declared no differences among borax and palonot[®] groups. Also, based on the t-test, there are no differences within groups (see Appendix 1, Table 20).

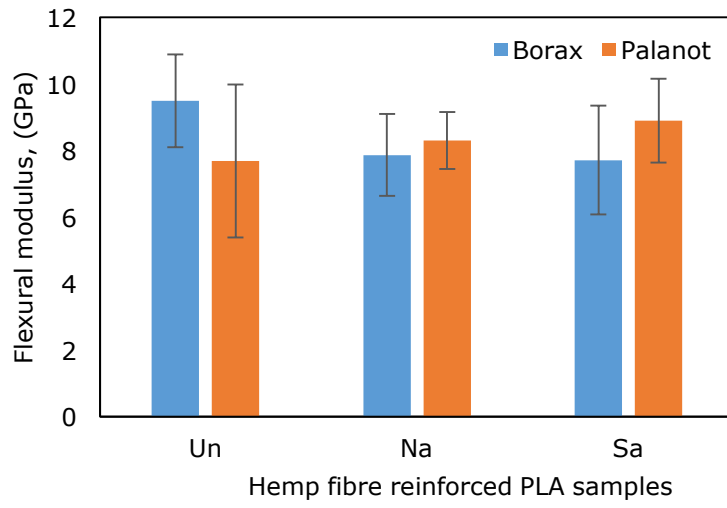


Figure 29. Flexural modulus for hemp fibre composites samples.

CONCLUSION

In this study, as described in the previous sections, composite samples reinforced with natural hemp fibre, were examined from the reaction to fire performance; mechanical properties. Natural fibres have unique properties such as abundance, biodegradability, low weight and low cost, less energy consumption for easy production and recycling than synthetic fibres. However, low fire resistance is one of the critical weaknesses of natural fibres. Using in industrial scales, it has to improve by some chemical pretreatment and fire retardant applications that have set as a part of the aims of this study. For this study, objectives include surface pretreated by alkali and combined treatment with a silane covered in chapter 3 and the literature review part. Using borax and palonot[®] as a fire retardant to understand improving hemp fibres' fire performance, as discussed in chapter 3 in FR applications. Mechanical tests described, and relative results also discussed.

This study shows that by applying FR applications, some pretreatments would be changed. For instance, applying borax on combined alkali and silane pretreated hemp fibre composite has poor outcomes in mechanical tests. This was suspected as the main reason for the reduction in mechanical properties of the FR treated composite, as they reduced the fibre-contact area discussed in SEM analysing. The reduction of the mechanical properties may be overcome with additional hemp fibre treatment and additional in the matrix. However, further study to ensure the compatibility of the materials is required.

SUMMARY

In summary, the influence of fire retardant treatment on the fire resistance and mechanical properties of hemp fibre reinforced PLA composite was studied in the master thesis. The hemp fibre surface was pretreated with alkali (5wt.% solution) and with combined treatment with silane (3wt.% by fibre weight). Composite specimens were prepared in six categories based on the fibre treatment: untreated (Un), alkali (Na) and silane (Sa), combined with borax and Palonot[®] applied as Fire retardants. Additionally, 3 groups of controls were fabricated from the non-fire retardant treated fibres (Un, Na & Sa) for the reaction to fire test. All samples were tested in reaction to fire, but only the fire retardant modified composites were tested in tensile and flexural properties. Results showed that samples with Palonot[®] have good fire resistance behaviour. Analysing the effect of the fire retardant treatment to the mechanical properties of the hemp composite the Palonot[®] treatment for untreated (Un) and (Na) pre-treated specimens had higher negative impact to the performance than specimens treated with borax. However, specimens pre-treated with (Sa) had better impact of the fire retardant treatment (palanot[®]) to the mechanical performance of the hemp fibre composite material compared to the borax treatment, that may be attributed to possible detachment of silane from the fibre surface, and weakening of the fibre properties as a result of the additional soaking in the borax solution. The SEM analysis confirmed the deposition of borax and the palanot[®] on the treated hemp fibre surface, which are seen as salt particles and grafting, respectively. Solving the problem of the reduction of mechanical properties' needs further research.

KOKKUVÕTE

Kokkuvõtlikult uuriti magistritöös tuletõkkeainetega teostatud töötamise mõju kanepikiuga tugevdatud PLA komposiidi tulekindlusele ja mehaanilistele omadustele. Kanepikiudude pinda töödeldi leelise (5% lahusega) ja kombineeritult silaaniga. (3% kiumassist). Katsekehad jagati tuletõkkeainetega töötlemiseks vastavalt kanepikiudude eeltöötamise kolme põhirühma: töötlemata (Un), leelisega töödeldud (Na) ja silaaniga töödeldud (Sa) kiud. Kanepikiust eeltöötlemata (Un) ja eeltöödeldud (Na) ja (Sa) katsematerjale töödeldi booraksi ja Palonot[®] tuletõkkeainetega ning seejärel valmistati nendest koos PLA kiududega kanepikomposiidid. Tulepüsivusomadusi testiti nii eeltöödeldud kui töötlemata kanepikiudusest valmistatud kanepikomposiidist katsekehadel, kuid mehaanilisi omadusi (tõmbetugevust ja paindetugevust) testiti ainult tuletõkkeainetega töödeldud kiududest kanepikomposiididel. Katsetulemused näitasid, et Palonotiga töödeldud katsekehadel oli hea tulekindlus. Kanepikiuga armeeritud komposiididest katsekehade (Un) ja (Na) mehaaniliste omadustele avaldas kanepikiudude Palonotiga töötlemine suuremat negatiivset mõju. Kuid (Sa) katsekehade mehaanilistele omadustele avaldas Palonotiga töötlemine väiksemat mõju kui booraksiga töödeldud katsekehadele, mis võib olla tingitud silaani võimalikust eraldumisest kanepikiude pinnalt ja kiu omaduste nõrgenemisest täiendava leotamise tagajärjel booraksilahuses. SEM-analüüs kinnitas booraksi ja Palonoti sadestumist töödeldud kanepikiudude pinnale, mis olid kiu pinnal nähtavad vastavalt, kas soolaosakeste või teradena. Kanepikiust komposiidide mehaaniliste omaduste vähenemine kanepikiudude tuletõkkeainetega töötlemise tagajärjel vajab probleemile lahenduse otsimiseks täiendavad uuringuid.

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APPENDICES

Appendix 1 Anova analysing for tests results

Table 11. Anova single factor test for fire test (ignition time) test

Groups	Count	Sum	Average	Variance		
Without	3	83,51	27,83666667	17,66723333		
Borax	3	89,35	29,78333333	68,93963333		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	5,684266667	1	5,684266667	0,131265958	0,735453829	7,708647422
Within Groups	173,2137333	4	43,30343333			
Total	178,898	5		<i>F < F crit</i>		

Table 12. Anova single factor test for tensile test (Br and Pal groups)

Groups	Count	Sum	Average	Variance		
UnBr	5	188,5575958	37,71151916	27,46649744		
NaBr	5	203,9190614	40,78381228	5,164153213		
SaBr	5	144,8905534	28,97811068	18,94160304		
UnPal	5	167,8834524	33,57669049	6,246557531		
NaPal	5	165,1481947	33,02963894	22,83834017		
SaPal	5	191,3343391	38,26686782	7,810573421		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	463,653718	5	92,73074359	6,289123663	0,0007	2,620
Within Groups	353,8708992	24	14,7446208			
Total	817,5246172	29				
				<i>F > F crit</i>		

Table 13. Anova single factor test for tensile test (Br group)

Groups	Count	Sum	Average	Variance		
UnBr	5	188,5575958	37,71151916	27,46649744		
NaBr	5	203,9190614	40,78381228	5,164153213		
SaBr	5	144,8905534	28,97811068	18,94160304		
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	375,1433314	2	187,5716657	10,91119656	0,0019	3,885
Within Groups	206,2890148	12	17,19075123			
Total	581,4323462	14				
			F>Fcrit			

Table 14. Anova single factor test for tensile test (Pal group)

Groups	Count	Sum	Average	Variance		
UnPal	5	167,8834524	33,57669049	6,246557531		
NaPal	5	165,1481947	33,02963894	22,83834017		
SaPal	5	191,3343391	38,26686782	7,810573421		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	82,87599202	2	41,43799601	3,3693563	0,0689	3,885
Within Groups	147,5818845	12	12,29849037			
Total	230,4578765	14				
			F<Fcrit			

Table 15. t-Test: Two-Sample Assuming Equal Variances (UnBr, NaBr)

	UnBr	NaBr
Mean	37,71151916	40,78381228
Variance	27,46649744	5,164153213
Observations	5	5
Pooled Variance	16,31532533	
Hypothesized Mean Difference	0	
df	8	
t Stat	- 1,202637617	
P(T<=t) one-tail	0,131749981	
t Critical one-tail	1,859548038	
P(T<=t) two-tail	0,263499963	
t Critical two-tail	2,306004135	
	P > alpha	

Table 16 . t-Test: Two-Sample Assuming Equal Variances (NaBr, SaBr)

	NaBr	SaBr
Mean	40,78381228	28,97811068
Variance	5,164153213	18,94160304
Observations	5	5
Pooled Variance	12,05287813	
Hypothesized Mean Difference	0	
df	8	
t Stat	5,376707655	
P(T<=t) one-tail	0,000332124	
t Critical one-tail	1,859548038	
P(T<=t) two-tail	0,000664248	
t Critical two-tail	2,306004135	
	P < alpha	

Table 17. t-Test: Two-Sample Assuming Equal Variances (NaBr, SaBr)

	<i>UnBr</i>	<i>SaBr</i>
Mean	37,71151916	28,97811068
Variance	27,46649744	18,94160304
Observations	5	5
Pooled Variance	23,20405024	
Hypothesized Mean Difference	0	
df	8	
t Stat	2,866631568	
P(T<=t) one-tail	0,010468491	
t Critical one-tail	1,859548038	
P(T<=t) two-tail	0,020936981	
t Critical two-tail	2,306004135	

Table 18. Anova: Single Factor for flexural test (Br and Pal groups)

Groups	Count	Sum	Average	Variance		
UnBr	5	47,4906057	9,498121141	1,961408706		
NaBr	5	39,35555195	7,871110389	1,499897144		
SaBr	5	38,56103921	7,712207842	2,662204043		
UnPal	5	38,42816024	7,685632048	5,294399691		
NaPal	5	41,52736162	8,305472325	0,734289555		
SaPal	5	44,47569491	8,895138983	1,579010126		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	13,45961136	5	2,691922273	2,620654148	0,3497	1,176
Within Groups	54,92483706	24	2,288534877			
Total	68,38444842	29				
				<i>F > F crit</i>		

Table 19 Single Factor for flexural test (Br samples)

Groups	Count	Sum	Average	Variance		
UnBr	5	338,9078457	67,78156914	55,9039292		
NaBr	5	333,594979	66,7189958	149,0597733		
SaBr	5	196,5390554	39,30781108	8,402216247		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	2605,428347	2	1302,714174	18,31662031	0,0002	3,885
Within Groups	853,4636751	12	71,12197292			
Total	3458,892023	14				
				<i>F > F crit</i>		

Table 20. Single Factor for flexural test (Pal samples)

Groups	Count	Sum	Average	Variance		
UnPal	5	315,2800992	63,05601984	19,00884988		
NaPal	5	319,8081532	63,96163065	328,545167		
SaPal	5	324,0274408	64,80548815	25,06461659		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	7,654776377	2	3,827388189	0,0308	0,9697	3,885
Within Groups	1490,474534	12	124,2062112			
Total	1498,12931	14		<i>F < F crit</i>		

Table 21. t-Test: Two-Sample Assuming Equal Variances (UnBr, NaBr)

	UnBr	NaBr
Mean	67,78156914	66,7189958
Variance	55,9039292	149,0597733
Observations	5	5
Pooled Variance	102,4818513	
Hypothesized Mean Difference	0	
df	8	
t Stat	0,16596077	
P(T<=t) one-tail	0,436152689	
t Critical one-tail	1,859548038	
P(T<=t) two-tail	0,872305378	
t Critical two-tail	2,306004135	
	P > alpha	

Table 22. t-Test: Two-Sample Assuming Equal Variances (NaBr, SaBr)

	NaBr	SaBr
Mean	66,7189958	39,30781108
Variance	149,0597733	8,402216247
Observations	5	5
Pooled Variance	78,73099478	
Hypothesized Mean Difference	0	
df	8	
t Stat	4,884554292	
P(T<=t) one-tail	0,000608659	
t Critical one-tail	1,859548038	
P(T<=t) two-tail	0,001217319	
t Critical two-tail	2,306004135	
	P < alpha	

Table 23. t-Test: Two-Sample Assuming Equal Variances (UnBr, SaBr)

t-Test: Two-Sample Assuming Equal Variances (UnBr, SaBr)		
	UnBr	SaBr
Mean	67,78156914	39,30781108
Variance	55,9039292	8,402216247
Observations	5	5
Pooled Variance	32,15307272	
Hypothesized Mean Difference	0	
df	8	
t Stat	7,939690139	
P(T<=t) one-tail	2,30555E-05	
t Critical one-tail	1,859548038	
P(T<=t) two-tail	4,61111E-05	
t Critical two-tail	2,306004135	
	P>alpha	