TALLINN UNIVERSITY OF TECHNOLOGY
Department of Materials and Environmental Technology

INVESTIGATION OF REACTION TO FIRE AND PHYSICO-MECHANICAL PROPERTIES OF FIRE-RETARDANT TREATED HEMP-PLA COMPOSITES

TULEKAITSEVAHENDIGA TÖÖDELDUD KANEPI-POLÜPIIMHAPPE KOMPOSIIDI FÜÜSIKALIS-MEHAANILISTE KARAKTERISTIKUTE JA TULETÕKKEOMADUSTE UURIMINE

MASTER THESIS

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Tallinn 2023

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Department of Materials and Environmental Technology

THESIS TASK

Student: Raimond Press, 211970KVEM

Study programme: KVEM12/21 - Technology of Wood, Plastic and Textiles

Main speciality: Wood technology

Supervisor: Dr. Percy Festus Alao

Thesis topic:

(in English) *Investigation of Reaction to Fire and Physico-Mechanical Properties of Fire-Retardant Treated Hemp-PLA Composites*

(in Estonian) *Tulekaitsevahendiga töödeldud kanepi-polüpiimhappe komposiidi füüsikalis-mehaaniliste karakteristikute ja tuletõkke omaduste uurimine*

Thesis main objectives:

1. Effectively apply fire-retardant treatments to hemp-PLA composites.
2. Investigate the combined influence of surface modifications and fire-retardant treatment on the mechanical and functional properties of hemp-PLA composites.

Thesis tasks and time schedule:

No	Task description	Deadline
1.	Designing of fire-retardant treatment procedure	20.12.2021
2.	Literature review	22.12.2022
3.	Fabrication of composite samples	10.02.2023
4.	Mechanical strength testing	22.12.2022
5.	Hygroscopicity and reaction to fire testing	25.02.2023
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PREFACE

This thesis aims to investigates how a novel fire-retardant solution combined with hemp fibre surface modifications affects the hemp fibre reinforced PLA biocomposites mechanical and functional characteristics, such as reaction to fire and moisture resistance. The fire retardant (Palonot F1) has not been tested for fibre treatments and there is a lack of research done regarding the treatment of hemp fibres with such fire retardants. Biocomposites have the potential to reduce pressure on the renewable resources and are a competitive alternative to unsustainable petroleum-based materials in certain applications. Green materials have numerous environmental and financial advantages, but their use is restricted due to their, unsatisfactory reaction to fire, lower mechanical properties, and poor moisture resistance. Fabrication of the composites and characterisation of the properties was done in Taltech Laboratory of Wood Technology, while the necessary parameters for reaction to fire classification were obtained in Meka, Latvia. Best results were obtained in combination with surface modifications. Fire retardant treatments enhanced the reaction to fire of the composites significantly. While tensile strength was strongly affected, the flexural strength suffered only minor decrease. However, the fire-retardant composites were vulnerable to high moisture conditions. The investigation demonstrates that the fire-retardant properties of biocomposites can be improved without fully negating functional characteristics of the material, enabling the use of biocomposites on wider scale in the future.

Keywords: hemp fibre; composites; fire performance; mechanical properties; master thesis

List of abbreviations

CC	Cone calorimeter
CPR	Construction Products Regulation
DTG	Derivative thermogravimetry
EMC	Equilibrium moisture content
E	Young's modulus
F1	Palonot fire-retardant
FIGRA	Growth rate of the burning intensity
FR	Fire retardant
FTIR	Fourier-transform Infrared
HRR	Heat release rate
HRRav	Average heat release rate
LOI	Limiting oxygen index
MOR	Ultimate flexural strength
MOE	Flexural modulus
NaOH	Sodium hydroxide
P2; P4	Palonot 2; Palonot 4
PHRR	PHRR: Peak heat release rate
PHRRav	Average peak heat release rate
PLA	Polylactic acid
RH	Relative humidity
SEM	Scanning Electron Microscopy
SBI	Single Burning Item
SMOGRA	Smoke production as smoke growth rate index
SPR	Smoke production rate
T_{char}	Beginning of charring of timber
T_{depth}	Temperature transfer through depth
T_{ig}	Time of ignition
T_{prot}	Basic protection time
T_{surf}	Surface temperature
Taltech	Tallinn University of Technology
THR	Total heat release
TSP	Total smoke production
TSR	Total smoke release
TGA	Thermogravimetric analysis
ig_{temp}	Temperature at the time of the ignition
σ	Ultimate tensile strength

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1. INTRODUCTION

Natural fibres have been in use for thousands of years [1] and have seen a large growth of attention and technological advancement in last decades. Growing interests are due to increasing consumption of non-renewable materials in the context of environmental crisis the world must face with. The use of natural fibres on a larger scale has the potential to reduce the pressure on the renewable resources, minimise the use of water, timber, and carbon emissions, thus mitigating the overall environmental impact of materials use on the nature [2]. Production of natural fibre composites is also highly energy efficient, as it uses 60 % less energy compared to glass fibre production [3].

Using as high volume of natural fibres as possible in biocomposites materials offers greatest financial, environmental benefits, due to low price of natural fibres [2] as well as ecological and carbon footprint [3].

Prospective fields of use where natural fibres can be utilized for higher value applications, are automotive industry and construction materials industry as well as packaging and retail sectors. Taking advantage of naturally and renewably produced materials offers a wide range of benefits for the society in general as it creates job opportunities, especially in rural regions [2]. Therefore, widespread adoption of natural materials, such as hemp fibres directly contributes to many of the EU green deal objectives.

Extensive use of natural fibres is mainly restricted by several factors like being highly flammable without previous treatment and the hydrophilic properties, that cause problems with unsatisfactory interfacial adhesion between matrix and the fibre [4].

Therefore, current thesis aims to apply fire-retardant treatment and investigate the combined influence of fire-retardant treatment and surface modifications on the mechanical and functional characteristics (moisture resistance and reaction to fire) of hemp fibre reinforced PLA biocomposites.

The novelty of this study is because the fire retardant examined (Palonot F1 [5]) has not been previously studied for hemp fibre treatments, especially in combination with chemical modifications (e.g., alkali treatment). Besides, there are no publications regarding combining such fire retardant with hemp fibre surface treatment. Therefore, this thesis provides essential data for the vast application of biocomposites.

The study is based on the following hypothesis:

1. Hemp (natural fibre) is flammable due to its’ high levoglucosan content.
2. The mitigation of the hydrophilic properties of hemp fibres with surface treatment such as alkali treatment will results in an increase in levoglucosan content due to higher crystallinity (cellulose) from the removal of amorphous content.
3. The reaction to fire properties of biocomposites can be improved with fire retardant treatment, but this may lead to unsatisfactory mechanical performance and moisture resistance because of the presence of the FR salts (phosphorus).

Based on this hypothesis, the following activities were planned to achieve the aim of the study:

- The hemp fibres were cleaned and carded.
- Surface treatment to reduce the hemp fibre hydrophilic properties was done with 5 wt.% NaOH solution.
- Examination of the most effective FR products and development of a functional FR treatment method suitable for fibre reinforced PLA composites.
- Fabrication of composites from polylactic acid reinforced with 50 wt.% hemp fibre.
- Investigation of the reaction to fire properties of the composites.
- Investigation of the mechanical performance of the composites.
- Investigation of the hydroscopic properties of the composites before, and after the treatments.

2. LITERATURE REVIEW

2.1 Natural fibres

The woody core of certain dicotyledonous plants [6] contains bast fibres, that have great physical properties that can be used in many ways [7]. Depending on the origin of the fibres in the plant itself, the structure and therefore the properties of the fibre differ, which are the main parameters to consider if producing polymer composites as different fibres suit for different applications [2]. Common plants used for obtaining natural fibres are flax, jute, hemp, kenaf and sisal. According to Ochi [8] the properties of kenaf fibres in the distinct parts of the plant have significantly different strength properties. The fibres obtained from the upper part of the plant the fibres showed about 80 % of the mechanical strength than variants from the lower section of the plant. Furthermore, the length of the fibre is reported to affect its tensile strength, due to the possibility for inherent defects as length increases. Long fibres contain shorter elemental fibres, which are connected by weaker pectin bonds [9].

Table 2.1 lists chemical composition and the mechanical and physical properties of natural fibres and conventionally used manufactured fibres.

Table 2.1. Chemical composition of commonly used natural fibres [10]

Name of fibres	Hemp	Flax	Jute	Ramie	Sisal	Cotton	E-glass	S-glass	Aramid
Cellulose	70,2	71	61-71,5	68,6-76,2	-	-	-	-	-
Lignin	3,7-5,7	2,2	12-13	0,6-0,7	-	-	-	-	-
Hemicellulose	17,9-22,4	18,6-20,6	13,6-20,4	13,1-16,7	-	-	-	-	-
Pectin	0,9	2,3	0,2	1,9	-	-	-	-	-
Wax	0,8	1,7	0,5	0,3	-	-	-	-	-
Density g.cm-^{3}	1,14	1,5	1,3-1,4	1,5	1,45	1,5-1,6	2,5	2,5	1,4
Tensile strength *MPa*	690	345-1100	393-773	400-938	468-640	287-800	2000-3500	4570	3000-3150
Young's modulus *GPa*	30-60	27,6	13-26,5	61,4-128	9,4-22,0	5,5-12,6	70	86	63-67

Table 2.1 continued

Name of fibres	**Hemp**	**Flax**	**Jute**	**Ramie**	**Sisal**	**Cotton**	**E-glass**	**S-glass**	**Aramid**
Specific strength *GPa/g.cm^{-3}*	0,6	0,2-0,7	0,3-0,5	0,3-0,6	0,3-0,4	0,2-0,5	0,8-1,4	34,4	2,1-2,2
Specific modulus *GPa/ g.cm^{-3}*	26,3-52,6	18,4	10-18,3	40,9-85,3	6,4-15,2	3,7-7,8	28	34,4	45-47,8
Elongation at break %	1,6	2,7-3,2	1,16-1,5	1,2-3,8	3-7	7,0-8,0	2,5	2,8	3,3-3,7

2.2 Industrial hemp (Cannabis Sativa L.)

Cannabis Sativa L. is an annual and dioecious plant that has an upright stem and reaches up to 5 meters in height. The plant requires a moderate level of soil and air humidity and high light intensity for optimal growth. It is naturally occurring as a persistent weed in the edges of crop fields [5] Hemp, unlike many other crops grown in Europe, can be grown without the use of any agrochemicals [12].

In temperate climate, as in Europe hemp is considered the best option to obtain natural fibres, as it is a subject of European union subsidies of agriculture [8] and has an incredibly competitive price, especially when compared to synthetic fibres [2]. The fibres (Figure 2.1) are extracted from the stalk in a process called retting. There are several passive methods of retting – water-, dew-, frost retting etc, where the environment, climate and naturally occurring anaerobic bacteria is used, which are used to produce the highest quality fibres compared to mechanical extraction [2].

Hemp is widely grown in Estonia as well, for the purpose of obtaining cannabis oil. Hemp fibres are not widely used however and are currently disposed as residues or waste. Using hemp fibres as a reinforcement in the fabrication of bio compounds therefore allows to add not only economical value and promote regional development, but also to preserve the environment by reducing the use of petroleum-based materials [14].

Figure 2.1 Hemp bast fibres

In 2017 the price range of hemp fibres was around 0,5-0,75 €/kg depending on the shive content (woody non-fibre) [12]. In central and southern Europe, hemp seeds have been a by-product in the past, however, there has been a fast increase of hemp seeds used as human food (60 %) in the last decade. Therefore, nowadays hemp is mostly grown for their seed production. Hemp seeds are highly valued for their nutritional concentration, culinary versatility, pharmaceutical and food supplement applications [12]. The largest producer of hemp fibres is Russia, producing 255 000 tons of fibres a year. In Europe, France and Italy are the largest producers of hemp fibres [15].

The most widely used natural fibre currently being flax, as it has high mechanical properties and good thermal resistance. However, when choosing the fibres for certain applications the price plays a vital role. Flax is used for higher value-added textile markets and for composite panels in automotive industry. Conversely, Jute is the cheapest natural fibre and has highest production volume of the currently grown fibres. Jute is substantially grown in Asia, where it offers the best growth conditions [7].

Hemp fibres are more competitive also for lower value products than flax fibres due to the cheaper price range [17]. Hemp fibres show one of the best properties among the rest of the natural fibres considering specific Young's moduli and tensile strengths [8] [19]. Hemp compared to flax has a lower environmental and carbon footprint, due to hemp plants less demanding growing conditions and nutritional needs [20]. Hemp fibres contain hemicellulose and lignin, which are amorphous and make it possible for water to be absorbed and thus making fibres hydrophilic. Hemp bast fibres have many advantages over synthetic fibres, like sufficient length to use as replacement, low density and cost, high stiffness, and strength to weight ratio [6]. Land coverage for growing hemp has increased by 70 % from 2015-2019 and by 62 % in quantity of hemp grown. Growing hemp offers several environmental benefits like preventing soil erosion, production of pollen when environmentally friendly growth methods are used. Hemp can also act as a potential carbon storage, as it can sequester 9 to 15 tonnes of CO_2 in a period of 5 months, similarly to a young rapidly growing forest [4].

Hemp fibres show an enormous range of variability in mechanical properties, that are dependent on many factors. Hemp fibre density ranges from 1,14-1,6 $g.cm^{-3}$ [10][21], glass and carbon fibres have higher density of 2,55 $g.cm^{-3}$ and 1,8 $g.cm^{-3}$ respectively. Though glass fibres have better mechanical properties, the specific strength properties of hemp fibres that take density into account are superior to that of glass fibres. Therefore, in applications where weight of the material is of importance hemp fibres are a viable option as a substitute to petroleum based raw materials [21]. However, factors other than mechanical and physical properties, such as availability in the region and optimal price-performance ratio must be considered when choosing the natural fibre reinforcement for composite materials.

2.3 Polymer matrices

Polymers can be thermoset or thermoplastic in their nature, depending on the structural chemical bonds. Thermoset matrices have an advantage when chemical and thermal stability is needed. Thermoset plastics cannot be remelted and reformed and decompose only if heated to a high enough temperature and therefore cannot be recycled. Conversely, thermoplastic polymers provide high damage tolerance and can be recycled, as they can be reshaped or softened by heat. Polymer materials in general have low density a low melt temperature. There is vast variety in composite materials from low to high strength, high flexure, and high durability. Most of the polymer materials are poor conductors of electricity and some can be used as electrical insulators. Plastics have a wide range of applications and are in some cases irreplaceable due to their variance in properties and low price. Two of the most widely used fibre-reinforcement plastics in matrices are unsaturated polyester and epoxy resins [23].

Polymer matrices in reinforced composites serve the purpose of distributing the forces to the fibres evenly, holding the reinforcement in place and protecting the reinforcement (fibres) providing rigidity. Choosing a correct matrix depends on availability and the application, requirements and the desired properties of the composite material being developed [24]. However, in terms of low environmental impact, recyclability, and sustainability the synthetic adhesives cannot compete with some of the adhesives of natural origin, such as Polylactic acid (PLA) [25].

Since the 2nd World War, the effort put into development of technology to convert petrochemicals into plastics has been overwhelmingly superior to that of natural sources. This has led to a situation where the price, ease of manufacturing, mechanical and physical properties cannot be matched with their natural alternatives. Natural adhesives are sourced of carbohydrates (starch, cellulose), plant-based proteins (soybeans etc.), animals (hides, bones, milk) or lignocellulosic extracts (lignin, tannins) [25]. Because of enormous potential, lignin-based resin derivatives have been thoroughly researched since the 1800 s, but due to complex structure, difficulty of extraction and high melting temperatures have been limited in their use [25].

Another source for biobased adhesives that have the potential for use in composite manufacture are soy proteins. Soybeans contain about 40 % of protein, soy flours as an adhesive have been widely used in the past for plywood production but are currently unable to compete with synthetic adhesives. Soy resins have issues with high viscosity and long press time but are potentially useable as spray-dried powders in use with compression moulding methods [25].

Adhesives derived from starch are made from glucose found in various plants like potatoes, tubers, fruits, and grains (corn and wheat) [25].

2.4 Polylactic acid

Even though it is questionable if the currently available natural or renewable materials alone will be able to substitute the high quantities of synthetic materials presently used as matrices in composite materials [25], they certainly play a vital role in terms of reducing the non-renewable materials in certain applications.

Polylactic acid is the first widely used renewable plastic that is produced from annually grown natural resources [26]. PLA offers a suitable alternative in substitution of petroleum based non-renewable polymers that are not biologically degradable, considering growing awareness of enormous environmental threat that these plastics can cause eventually [27]. It is a biodegradable polymer that is produced by microbial fermentation of carbohydrate rich substances [28] like corn, cassava, sugar cane or beets. The glucose is extracted by milling, converted into dextrose via hydrolysis and is then fermented into lactic acid [29]. The leading producer of Polylactic acid during the last decades has been NatureWorks LLC. PLA has been shown to degrade biologically in 30 days in the right conditions. The carbon footprint of PLA is around 60-80 % lower than that of petroleum-based alternatives [30].

Carothers et al [31] introduced a novel ring opening polymerization method in 1932. The method consists of first the polymerization of lactic acid to a low molecular weight oligomer, which is catalytically depolymerized through internal transesterification to lactide using the "back-biting reaction. Then, the ring of lactide opens to form high molecular weight PLA. Despite the efforts made to improve the technique, on an industrial level there has been no significant advancements. Thus, ring opening method (see Figure 2.2) is still the most used method to produce PLA that has high molecular weight and purity, suitable for long-duration applications [32].

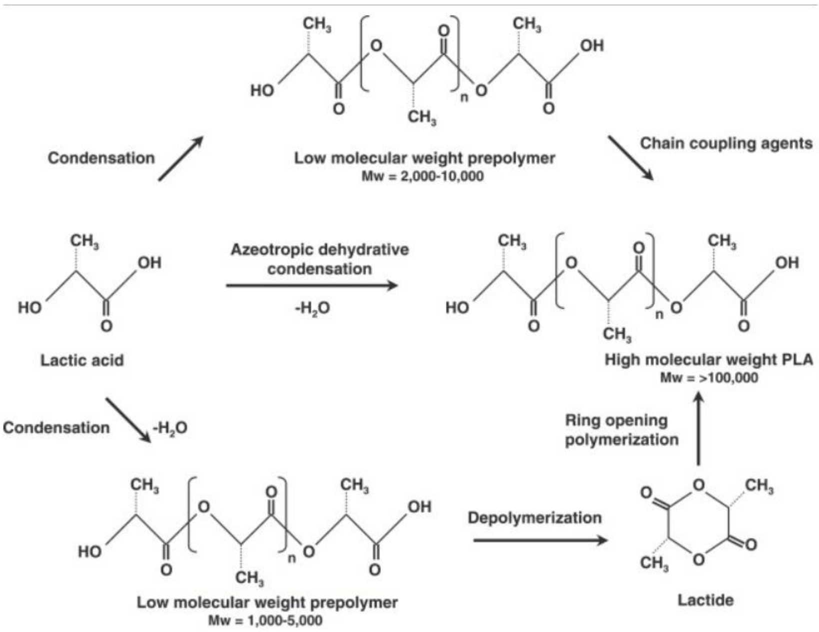


Figure 2.2 Methods used to produce polylactic acid [33]

The properties of PLA enable it to be used in various applications as it has low moisture absorption, high wicking; low flammability and smoke generation; good resistance to UV light in outdoor applications and low density. As it is melt-spun, easy to process and can be used in fabrics it is an appealing choice to produce varied materials [33]. Unfortunately, the price of PLA is currently much higher than the conventional matrices such as polypropylene (PP) and polystyrene (PS) [34].

2.5 Hemp biocomposites

The use of biocomposites has potentially extensive environmental and economic impact in various industries. According to Seile et al [35], green composites from hemp-PLA have lower CO_2 emissions, significantly reduce global warming leading to about 81 % reduction in carbon footprint. The environmental benefits can be further improved by using sustainable growing methods.

Hemp fibres have low density and high stiffness, which results in relatively high specific strength/stiffness properties that allow them to be used in applications where weight of the material is important. The main limitations affecting incorporation of biocomposites/green composites is the economic viability of the matrices and adequate performance of these materials [36].

In case of glass fibres, the fibre content can be as high as 80 %, providing very high strength properties [23]. However, in natural fibre composites the fibre content is limited, because of insufficient wetting of the reinforcement at such high fibre content [37] [26].

The use of hemp and natural fibres in general is currently limited by several challenges that must be addressed [38]

- Limitation in quantity of fibre reinforcement
- Hydrophilic and non-polar nature of fibres
- Limited temperature and therefore material selection
- Lower mechanical performance compared to currently used petroleum-based reinforcements
- Unsatisfactory fire-resistant properties

Natural fibre composites (NFC's) properties are affected by many factors like fibre type, harvesting time, fibre extraction method, treatments, bonding of the matrix and fibres, orientation of the fibres [39]. Another issue is variability in quality of fibres which can be affected by the growing location and climate; crop variety, seed quality, soil, harvesting time. Extraction and processing will also affect the outcome of the produced NFC [40]. Therefore, the properties of fibres in a specific geographical location must be evaluated and tested separately and considered in production to ensure uniform quality.

Hemp fibres contain cellulose and hemicellulose, which makes the fibres hydrophilic by nature. This hampers the adhesion between the hydrophobic materials used in the matrices of composite materials and the reinforcing fibres, consequently reducing the mechanical properties of such composite products [41].

Therefore, chemical treatments are used to remove the non-cellulosic subjects such as hemicellulose, lignin, pectin, fat and wax from the composition of the fibres to achieve optimal bonding between the fibres and the matrix due to increased surface area and surface roughness. Various treatment methods are used to enhance the properties of the fibres. Chemical treatments being the most widely used to reduce the hydrophilic properties. The hydrophilic properties of natural fibres also make it possible for modification of fibre properties as needed for given applications [39].

Sawpan et al [26] studied the impact of different treatments on the mechanical performance of a 35 wt. % hemp fibre reinforced composites. The results show that alkali treatment of the hemp fibre improved the tensile strength the most and the following mechanical properties were reported: tensile strength of 85,4 MPa, Young's modulus was 12,6 GPa and impact strength of 7,4 kJ.m^{-2}, which were increased by the treatments about 10,5 % and 8,2 % higher, respectively.

2.5.1 Fibre treatment methods

Although, surface treatments using mechanical or chemical methods can improve fibre to matrix interfacial adhesion, chemical approach is dominating in because it offers the best results. Most widely used chemical methods are alkali, acetyl treatments and addition of silane and maleated anhydride coupling agents [42]. Silane and Alkali treatments have shown great results in improvement of the mechanical properties of NFC [43].

Alkali treatments aim to remove the non-cellulosic substances like hemicelluloses, lignin, and pectin on the surface of natural fibres, which are all contributing to the reduced adhesion between the matrix and the fibres. Hemicellulose being the most hydrophilic in nature [40]. Alkali treatment tends to also affect the cellulose structure. Efficient alkali treatments can improve the crystallinity of the cellulose in natural fibres and therefore the strength of the fibre, while too harsh treatments weaken the fibres by converting the crystalline structure into amorphous form [42].

Georgiopoulos et al [44] has found that silane treatments have a significant effect on the mechanical properties of natural fibre composites. Flax fibres and PLA film was used in compression moulding of the composites with a 22 wt. % flax fibre content. An improvement in the quality of fibre to matrix interface was noted on all treatments (1-5 %). The optimal silane treatment was found to be using a 2 wt. %, that improved the flexural strength and modulus the most, although flexural modulus was higher for 1 % solutions [45]. It has been pointed out by Mazzanti et al [46] that even though alkaline treatments are often conducted to improve the adhesion between the matrix and fibres, the main improvement of mechanical strength is caused by the separation of thick fibre bundles during the treatment.

2.6 Hemp PLA composites

The alignment of fibres and fibre matrix ratio is dependent on the desired properties and intended application as it affects the mechanical properties of the composite [47]. In terms of mechanical optimization, a fibre fraction of 30—35 wt. % has been shown to be optimal to be used in production hemp-PLA composites [43][48].

Hu et al [49] compared different fibre fractions and treatments and concluded that alkali treated fibres performed best at 40 wt. % showed tensile strength of 54,6 MPa, flexural strength 112,7 MPa and tensile modulus of 8,5 GPa. Oksman et al [50] reported insufficient wetting of fibres when 40 wt. % of fibres were used.

Sawpan et al [43] investigated the impact of different treatments on the mechanical performance and found that 35 wt. % hemp fibre reinforced composites showed best mechanical strength. The results show that 5 % alkali treatment of the hemp fibre improved the tensile strength up to 85,4 MPa, Young's modulus was 12,6 GPa and impact strength of 7,4 $kJ.m^{-2}$. Baghaei et al [51] studied different composite production methods of hemp/PLA composites (direction of fibres and the effect of alkali treatment). In the production, compression moulding and fibre mass fraction of 30 % was used. It was found that alkali treated composites produced using hemp/PLA yarn with an off-axis angle of 0º had the best mechanical properties from the tested techniques (results are presented in Table 2.3). Nonwoven hemp/PLA fibres showed significantly poorer performance than yarn fibres (at 0º off-axis), [51].

Besides, another study by Baghaei et al [52] reported that hemp-PLA yarns provide better adhesion between the components and improve the alignment of reinforcing fibres, thereby enhancing the mechanical properties when fibre volume was increased.

Table 2.2. Tensile properties of PLA/hemp composites [51]

Sample	**Tensile strength MPa**	**Young's modulus GPa**	**Elongation at break %**
PLA	41,21 ± 2,25	2,91 ± 0,39	1,92 ± 0,26
Hemp/PLA yarn (off axis angle 0º)	72,75 ± 6,26	8,77 ± 1,44	1,24 ± 0,36
Hemp/PLA yarn (off axis angle 45º)	34,75 ± 4,63	4,62 ± 1,04	0,66 ± 0,18
Hemp/PLA yarn (off axis angle 90º)	22,01 ± 3,38	3,70 ± 0,65	0,53 ± 0,11
Hemp/PLA nonwoven	53,63 ± 1,22	5,60 ± 0,95	1,10 ± 0,30
Akali hemp/PLA yarn (off-axis angle 0º)	77,08 ± 2,60	10,27 ± 1,36	1,58 ± 0,26

The results of the mechanical tests showed a significantly higher tensile strength and an increase in young's modulus between woven and nonwoven composite materials. Alkali treatment of the fibres in nonwoven composites show further increase in the properties of the material. Similarly, to tensile strength increase, the impact strength increased compared to pure PLA, as the yarn (off axis angle 0º) reinforced composites showed better performance, especially with alkali treated fibres [51].

Another study [8] that used kenaf fibres selected from the lower section of the plant stem, compared to previous tests showed the great strength properties. A matrix of PLA emulsion-type resin was used and combined with the 70 wt. % fibre volume. The kenaf fibres were previously heat treated at 160 ºC for 60 minutes and the boards were produced using compression moulding by using 10 MPa of force for 10 minutes. Ochi [8] was able to produce composite boards that showed high strength properties. The tensile strength test results showed remarkable 223 MPa and flexural strength of 254 MPa was presented.

Durante et al [53] have studied mechanical properties of bio-composites produced from PLA, reinforced by woven hemp fabric using compression moulding and 20 %, 30 % and 40 % fibre fractions. Composites with 20 and 30 wt. % showed similar flexural strength, a significant reduction occurred in case of 40 wt. %, even though impact strength increased. Creep tests showed that NFC with 30 wt. % fibre content has the best creep behaviour. The flexural and impact strength results are listed in Table 2.3.

Table 2.3 Woven hemp and PLA composites flexural and impact strength [53]

Type	**20 wt. %**	**30 wt. %**	**40 wt. %**	**100 % PLA**
Flexural strength *MPa*	118,6 ± 8,0	116,6 ± 6,9	77,9 ± 8,5	56,2 ± 7,3
Impact strength *kJ.*m^{-2}	20,5 ± 0,9	24,9 ± 1,2	29,3 ± 1,4	8,9 ± 0,7

Combined treatment method using alkali and silane treatments on hemp fibres have shown significant increase in mechanical properties of hemp-PLA composites by Alao et al [37]. In the research, 30 wt. % and 50 wt. % hemp fibre composites were prepared using compression moulding technique.

The mechanical properties were higher for 30 wt. % alkali treated specimens. The composites without modified hemp fibres achieved much lower tensile and flexural strength compared to PLA, especially with higher fibre content. Combined alkali and silane treatment was shown to improve the properties the most, notably flexural properties. Composites with 30 wt. % alkali-Silane treated hemp fibres achieved the highest flexural performance that was 100 % and 53 % more than that of the untreated hemp fibre composites at 50 wt. % and the 30 wt. %, respectively. Tensile strength and Youngs modulus of alkali-silane treated specimens had the most significant increase in case of 30 wt. % composites. Tensile strength and Youngs modulus decreased with increase of fibre fraction-[37].

Pappu et al [15] fabricated hybrid composites from sisal and hemp (30 wt. % fibre fraction) using PLA as the matrix; and achieved tensile strength of 46,3 ± 6,6 MPa, Young’s modulus of 6,1 ± 0,6 GPa and flexural strength of 94,8 ± 11,2 MPa. The composite had low density of 1,14 g.cm^{-3}.

2.7 Fire resistance of biocomposites

Natural fibres are considered to increase the poor thermal conductivity of polymer composites and are therefore highly flammable. As the use of such materials is gaining popularity and their poor thermal properties pose a hazard, the improvement of their flammability is of high importance [54]. Therefore, various methods have been developed that can be used to increase the durability against decomposition [55] [56].

Refractory additives reduce the amount of heat released during the initial stages of fire by physically or chemically limiting certain phases of the burning process and therefore delaying the spread of the fire. Due to the nature of biocomposites, the improvements that can be made regarding the duration of fire resistance are limited, however significant advancements can be made in this regard by using fire retardants (FR) [54].

The main problem that occurs when fire retardant treatments are carried out on natural fibres is the deterioration of mechanical properties. Therefore, the difficulty lies in the treatment of the fibres in a manner that provides both satisfactory fire resistance and mechanical properties. In achieving optimal mechanical properties of NFCs, the composite structure should not be compromised and the adhesion between the fibre and the matrix should not be reduced. Many of the methods that are used to achieve improved thermal stability of natural fibres has been adapted from treatments used on textiles, thermoplastic, and thermoset polymers [57].

High crystallinity of natural fibres is responsible for increased flammability, which is caused by higher rate of levoglucosan. Increased orientation of fibres decreases pyrolysis, however increased crystallinity of cellulosic fibres escalates the formation of levoglucosan during the process of pyrolysis. Therefore, higher cellulose content in fibres constitutes for higher flammability. Higher lignin and ash content enables increased char formation during burning, which results in better thermal resistance and mechanical durability in case of fire, although some parts of lignin start to decompose at lower temperatures (160 ºC), whereas cellulose decomposition starts at 250 ºC. In case of sufficient duration of heat, natural fibres decompose into flammable and non-flammable gases, tar, and char. Due to large heterogeneity of natural fibres, the composites fire resistance is dependent on the specific fibres that are used [55].

To be eligible for use in various applications, no matter what the industry, a material must comply with certain standards. Hemp biocomposites are no exception; therefore, the fire resistance must be tested according to the standards necessary for certain application. Previous tests have shown that the fire resistance of natural fibre composites without any enhancement are inadequate to resist fire for needed periods of time and contribute to the spread of fire [55]. Even in relatively low temperatures, naturally reinforced composites can soften, creep and their mechanical properties can change and cause sudden distortion in when used in load-bearing structures. At around 300-500 °C polymer matrices decompose, which causes them to release heat and toxic substances [58].

Increased fire performance can be achieved by using fillers in NFC production. Fillers can be added to the polymers in final stages of composite manufacturing, grafted or deposited on the surface of natural fibres. However, they cannot be used on all polymers, as compatibility is necessary with the selected filler. Fillers are widely used as they are cost effective in improving fire resistance. Treatment agents can be used to achieve different results, as they have various effects on the composites [58].

Fillers can improve the fire-retardant properties by [55]:

- Diluting the combustible organic materials in reinforcing fibres
- Reducing the temperature of composites, functioning as a heat sink
- Reducing heat release rate (HRR)
- Increasing the aromaticity of the polymer matrices making it possible to turn into an insulating surface layer of carbonaceous char that slows heat conduction into the composite and reduces flammable gas release.

However, there are several issues in usage of fillers. Filler use is limited by compatibility with the polymers that are used in composites as they can have a degrading effect on the mechanical and environmental durability properties. Some have been shown to gradually break down if exposed to moisture, give off toxic gases or may be environmentally hazardous. Fibre surface modification with FR has been found to be more effective than incorporation into matrix, but the amount of FR that can be used is limited [55].

Flame retardants containing halogen have been widely used, but have been losing popularity, because of toxicity and environmental risks linked to it. Therefore, phosphorus-based fire retardants have gained research focus in the last decades [59]. Biocomposites made from biodegradable materials such as hemp and PLA, treated with environmentally friendly phosphorus-based FR systems could even be potentially used as fertilizers after their end use [60]. Phosphorus mainly acts as a fire retardant in the gas phase in most thermoplastics by releasing phosphorus radicals from the polymer elevated temperature [55]. Treatments using phosphorus containing products also promotes the formation of char. Char can reduce the release of the flammable substances; through promoting melting and dripping of thermoplastics the heat loss can be accelerated [61].

The requirements for construction products marketed in EU are set by the European Construction Products Regulation (CPR), while providing harmonised standards to assess the performance of construction products [62]. Design of timber structures is regulated by Eurocodes, from which Eurocodes 5-2 describes the fire design of timber structures [63]. Standard EN 13501-1 [64] provides a classification and testing system to evaluate the fire performance of individual building materials and building elements. Classification is divided into seven in regards of reaction to fire (A1, A2, B, C, D, E, F), into three for smoke production (s1, s2 and s3) and flaming droplets (d0, d1, d2). Official classification of materials according to EN 13501 that have a non-negligible contribution can be determined can be determined by SBI test or ignitability test [65].

Growth rate of the burning intensity (FIGRA) is one of the main parameters that has been created to determine Eurocode fire class for materials and is calculated based on the heat release rate and test duration according to single burning item test EN 13823 [66]. Important parameters in evaluation of fire performance are ignition time, spontaneous ignition, flash point temperature, rate of heat release, thermal stability index, smoke toxicity, extinction flammability index, mass loss, limiting oxygen index (LOI), flame propagation on the surface and fire resistance [57].

2.7.1 Fire resistance test methods

Fire resistance parameters can be evaluated using various test methods and analysis. Thermogravimetric analysis (TGA) is used to determine the thermal stability and the changes occurring in material weight during decomposition at the microscopic level, considering the temperature or duration of decomposition; or a combination of the two [55]. Derivative thermogravimetry (DTG) is used to simplify and graphically present a the thermogram peaks of the rate of material weight changes simultaneously with the heat that is applied [67].

Cone calorimeter (CC) is a widely used testing device that allows to measure the fire reaction of test samples. It is composed of an electric heater, an ignition source, and a gas collection system [55]. Cone calorimetry is considered one of the most effective tests to evaluate the combustion behaviour of materials, while enabling it to be done on small-scale, which is especially beneficial for material development purposes [68].

Reaction to fire test (ISO 5660-1:2015), can be used to evaluate composite materials resistance to fire using cone calorimetry. According to the standard [69] the test is used to "assess the contribution that the product under test can make to the rate of evolution of heat during its involvement in fire". The test method is based on the amount of oxygen required for combustion, which is generally the net heat of combustion. During the tests, measurements of oxygen concentrations, changes in mass and exhaust gas flow rates are being made. The test enables to determine the peak heat release rate (PHRR), total heat release (THR), heat release rate (HRR), total smoke production (TSR) etc. PHRR is an important parameter in evaluation of fire resistance [68].

Conical heater provides uniform heat flux and similar conditions to real life fires and is therefore widely used. However, the orientational positioning of the test specimens is not often considered. Tsai [70] analysed the orientational placement of material during testing and concluded that vertical position should be used as it might provide more accurate results, as the materials end use is most likely vertical. It was found that in case of horizontal testing lower critical heat flux is needed, ignition time may be shortened, peak heat release is lowered and burning time is extended [70]. Heat flux ranges from 25-50 $kW.m^{-2}$ have been used to evaluate the materials reaction to fire. Hapuarachchi et al used 25 $kW.m^{-2}$ and 50 $kW.m^{-2}$ to simulate an ignition source and fully developed fire conditions respectively [71].

Fanfarová et al [60] highlighted 65 % less mass loss for fire retardant treated hemp fibre insulation test specimens exposed to direct flame for a period of 5-minutes. The objective was to define the reaction to fire of the material. Alao et al [72] also identified that the fire resistance of hemp-PLA composites increased with higher fibre fraction due to lower amount of PLA that has a lower decomposition temperature. The key parameter values of reaction to fire found in previous research for the natural fibre composites are listed in Table 2.4.

Table 2.4 Comparison of reaction to fire results from past researches

Composite	**PHRR $kW.m^{-2}$**	**THR $MJ.m^{-2}$**	**TSR $m^2.m^{-2}$**	**Mean CO_2 kg.kg**
PLA [73]	485	104	5	150
PLA-HEMP [73]	361	120	26	1,58
PLA-HEMP nanocomposite [73]	340	122	57	1,57
PLA-hemp untreated [74]	344	76		
HEMP-polyester [71]	362			
HEMP-polyester + ATH FR [71]	180			
PLA-FLAX + FR [75]	149	57,5		

2.8 Applications

Due to high strength properties considering the low density, NFC can be considered for a wide range of applications. However potential fields of use possess their individual issues that must be addressed. Hemp biocomposites produced using injection moulding and short fibres have reduced mechanical properties, which are used in high volume automotive industry where they are able to provide sufficient performance for low price. Hemp composites offer better mechanical properties for structural use when fibres are aligned unilaterally, non-crimped or in woven structure [8]. Long hemp fibres offer better directional reinforcement, which makes them applicable in automotive and construction industry as well as using in internal finishes [38]. Woven and short fibres offer lower specific mechanical strength, but the properties are better divided in all directions [23].

The first automotive components from hemp fibres were introduced by Henry Ford in the 1940s. Nowadays it is driven by importance to use renewable, recyclable raw materials in production [76]. Hemp fibres have low density and therefore using them in automotive and aerospace industries enable to improve fuel efficiency and emissions, by reducing weight of the materials used [77] and have low environmental impact during their life cycle. The 30 wt. % natural fibre reinforced composites have about 6% lower weight compared to glass fibre counterparts [78], therefore using 50 wt. % of natural fibres reduces the material weight by around 10 %. Natural fibres in combination with PP matrices are mostly used in automotive applications to produce various interior parts of vehicles. Examples of use include covered door, instrument panels, armrests, seat back panels, wall panels, pillars, centre consoles, load floors etc. The use NFC in other sectors is significantly lower than in automotive industry, however they find use in building and construction industries, sports, aerospace applications. In construction sector NFC are used to produce door and window frames, wall panels etc. Bcomp Ltd. is a leading producer of lightweight natural fibre solution for applications such as automotive interiors, motorsports, marine and satellite panels [79]. Hemp-PLA composites are financially viable and competitive with currently mainly used polyamide-glass fibre composites in automotive applications [35].

While significant advances have been made in past decade regarding technical development, the NFC market must still evolve and prove its value to scale on industrial levels and reach sectors of high inertia on wider scale [80]. The use of NFC in a wider range of applications is restricted before such materials and products can meet set regulatory requirements for specific applications, such as mechanical strength [81], flammability, release of smoke and toxic gases [82][83].

The wider and faster adaptation of NFC materials in other sectors is also highly reliant on political incentives, development of standards and characterizing the properties of the available natural fibre materials [76]. NFC market size was expected reach market size of 6,5 billion by 2021 [81].

3. MATERIALS AND METHODS

3.1 Materials

3.1.1 Hemp Fibres

Hemp fibres (*Cannabis sativa*, dioecious Hungarian variety *Tisza*) used in this project are locally grown in Saaremaa, Estonia in the year 2016. The fibres were frost-retted and decorticated from stems by a mechanical process [14]. The chemical composition of the hemp (Table 3.1) and other properties: physical and mechanical (Table 3.2) of the hemp fibre used in this study are already published [84].

Table 3.1 Properties of hemp fibres used in the project [84]

Cellulose %	**Hemicellulose %**	**Lignin %**	**Soluble content %**	**Inorganic matter**
77,4 ± 0,3	8,3 ± 0,3	1,4 ± 0.0	12,6 ± 0,4	0,3 ± 0,0

Table 3.2 Physical and mechanical properties [84]

Density g.cm^{-3}*	**Diameter μm**	**Modulus GPa**	**Strength MPa**	**Strain at break %**
1,26 ± 0,04	18 ± 5	16.6 ± 8.5	500 ± 239	18 ± 5

*Density was determined in this thesis by immersion method using ethanol

The hemp fibres were manually cleaned to remove the woody core (shives) and subsequently carded (twice) in preparation for composite fabrication, with a classic drum carder with (width of 300 mm and 72 teeth per inch).

3.1.2 PLA

Polylactic acid (PLA) fibres (Ingeo™ bicomponent bonding fibre SLN2450CM) from NatureWorks LLC was used in the project (Figure 3.1). The PLA has a density of 1,24 g.cm^{-3} and a peak melting point of 145-160 ºC [85].

Figure 3.1 PLA fibre bundle

3.1.3 Chemicals

3.1.3.1 Alkali treatment

Sodium hydroxide (NaOH) solution was prepared using NaOH granules from STANCHEM (CAS: 1310-73-2: “STANCHEM” Sp. Z o.o, Boduszyn, Poland).

3.1.3.2 Palonot FR

Palonot fire-retardant (F1) technology is based on protic ionic liquid (ILs). The fire-retardant is composed of an aqueous solution of bisphosphonate acid, and alkanol amine, and optionally an alkaline agent. The solvent used is water. F1 contains no substances of very high concern and is a sustainable and non-corrosive fire-retardant solution for wood-based panels and natural-fibre based products. F1 provides the highest B-s1, d0 fire retardancy according to EN 13501-1 while allowing quick and effortless treatment [86]. F1 has a pH range of 4,0 to 7,0. Palonot can additionally be used to protect wood against mould, rot, blue stain, insect attacks and dimensional changes [87].

3.2 Methods

3.2.1 Fibre treatments

Alkali treatment: Hemp fibres were first dried for 24 hours at 80 °C. The alkali treatment of the hemp fibres was performed by soaking in a 5 wt. % NaOH solution for 1 hour as it was determined to offer best overall mechanical performance [48]. After treatment the fibres were washed thoroughly with water and dried in oven at 80 °C until constant weight.

Fire retardant (Palonot F1) treatment: 5.5 g (130 mm x 130 mm) of the hemp fibre mat was prepared by carding and treated with 20 ml of FR product provided by Palonot [5].

This amount of FR was decided upon by first performing a series of trials using six (6) Palonot products and solutions of 5ml, 10ml; 15 ml, which did not improve the thermal properties significantly.

After conducting reaction to fire and mechanical strength tests it was decided that the amount of FR will be increased to 20 ml per fibre mat to delay the ignition further and improve the fire-retardant properties. The designing process of FR treatments is described in appendix 1. Two Palonot products (Palonot 2; Palonot 4, designated P2 & P4) achieved the best results, which were comparable.

FR was diluted by adding 10 ml of distilled water to 20 ml of FR. Solution was thoroughly mixed before coating and the treated fibres were dried for 48 hours at 40 ºC. The mat was treated by spraying (Figure 3.2) the FR, while weighting the fibre mat, until desired quantity was applied. Current method used enabled to ensure a precisely desired amount of FR and provide a uniform distribution throughout the fibre mat.

Figure 3.2 Fire retardant treatment spraying technique

3.2.2 Fabrication of composite boards

The variants of composites fabricated are presented in Table 3.3.

Table 3.3 Composite variations

Control/Composite	Non-FR	With FR	
		Treatment with Palonot 2	Treatment with Palonot 4
PLA	PLA	-	-
Untreated hemp fibre PLA	UT	UTP2	UTP4
NaOH treated hemp fibre PLA	Na	NaP2	NaP4

The hemp fibres were first oven-dried at 80 ºC for 24 hours to achieve constant weight. The hemp fibre fraction of 50 wt. % was used for all specimens. For the non-FR composites, the PLA and hemp fibres were carded together in the drum carder previously described, to form unidirectionally aligned fibre mats. Mats were then cut into size of 130 mm x 130 mm. For a moulding template of 130 mm x 130 mm x 2 mm, 44 g of hemp fibre (22 g) and PLA (22 g) was used. The composites were produced by compression moulding using a CARVER hot press (Figure 3.3) with a 3-minutes preheating phase under no pressure and a temperature of 180 °C, followed by a compression phase with a pressure of 3 MPa for 7 minutes at the same temperature. The mould with the resulting composite was allowed to cool down under weight for 15 minutes before removing the composite.

Previously prepared fibre mats were stacked unidirectionally in correct order and placed between a film and hot pressed into boards.

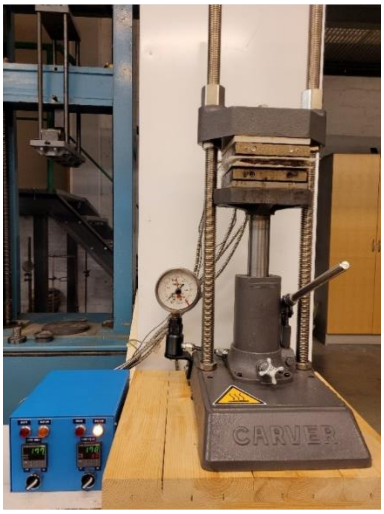


Figure 3.3 Compression moulding of test specimens

Regarding FR treated boards, the core layer consisted of hemp/PLA mix (22 g), while the face layers were with FR treated hemp fibre mat (5.5 g) sandwiched between PLA top mat (5.5 g) and the core mix (hemp and PLA mix). This was the most practical approach to ensure the treatment of the hemp fibres and to mitigate any negative impact that may occur compared to treating 22 g of hemp fibres. The boards were fabricated using similar processing parameters described above.

3.2.3 Evaluation of the composite density

The density of the composites was determined according to EN ISO 1183-1 with ethanol (97 % concentration). Test specimens were prepared, conditioned to 50 % RH and temperature of 23 °C. The apparent mass of specimens in air and in the ethanol was measured using a METTLER TOLEDO AX and MX/UMX analytical scale. The density was then calculated according to the formula presented in equation 3.1 [88].

$$\rho_s = \frac{m_{S,A} \times \rho_{IL}}{m_{S,A} \times mS_{,IL}} \qquad (3.1)$$

where,

$m_{S,A}$ is the apparent mass of the specimen in air, in g;

$mS_{,IL}$ is the apparent mass of the specimen in the immersion liquid, in g;

ρ_{IL} is the density of the immersion liquid at 23 °C

3.2.4 Evaluation of hygroscopicity

The moisture sorption was assessed in accordance with the standard EVS-EN ISO 12571:2021 at a constant temperature of 23 $\pm$ 0,5 °C and relative humidity of 30 %, 45 %, 60 %, 80 % and 95 %. Prior to the test, the samples were oven dried at 60 °C until a constant weight. The equilibrium moisture content (EMC) at the specific RH of adsorption and desorption were determined by weighing the samples until the mass change was less than 0,1 % in the past 24 hours. The EMC is calculated based on the equation 3.2.

$$EMC\ (\%) = \frac{M - M_0}{M_0} \text{x } 100 \quad (3.2)$$

where

M_0 is the mass of oven dry sample; M is the mass of the specimens at any given RH.

3.2.5 Fourier-transform Infrared (FTIR)

FTIR spectroscopy was performed using INTERSPEC 200-X (Spectronic Camspec, Leeds, UK), directly on the surface of the materials to assess the fibre and the composites surface after alkali and FR treatment. The analysis was carried out after conditioning in the scanning room for about 7 days. All the FTIR spectra were taken at a resolution of 4 cm. Before scanning the samples, a background scan of a clean Zn–Se diamond crystal was performed. A total of 30 scans on 5 replicas were recorded for each sample at wavelength of 500-4000 cm^{-1}.

3.2.6 Scanning Electron Microscopy (SEM)

SEM (Scanning Electron Microscopy analysis) was conducted by cutting small cross sections of the prepared composites, which were then coated by silver metallic paint; poured into liquid EPO, which also penetrated the material. The surface was then sanded smooth and coated with an 80 Gold-20 Palladium (2 Nm thick) layer. Surface was analysed by Zeiss FEG-SEM Ultra 55 and Bruker Espirit 1.82 EDS systems at a 20 kV of accelerating voltage. Mainly reflective electron detector was used (AsB – mass sensitive), as well as secondary electrons (SE2 - surface sensitive).

3.2.7 The reaction to fire test

Reaction to fire was conducted according to ISO 5660-1:2015, using a cone calorimeter. This test assesses the contribution to fire of the specimens [69]. Figure 3.4 shows the test set-up in Tallinn University of Technology (Taltech). A concurrent test was also done in Meka, Latvia.

The samples were conditioned prior to the testing to a constant mass at a temperature of 23 °C and 50 % relative humidity. A heat flux of 50 $kW.m^{-2}$ was used with a 25 mm distance between the test specimen and heat source. The test specimens were placed on birch wood blocks cut from the same board to imitate the placement of wooden structure covered with composite boards. For the test conducted at the facility in Taltech, a 0,25 mm diameter type K thermocouple was attached to the top of the samples and at the bottom face of the samples in contact with the birch block. The sides of the sample were covered with aluminium foil tape.

Figure 3.4 Reaction to fire test using cone heater

In Taltech parameters such as the temperature transfer through the depth of the boards (T_{depth}), time of ignition T_{ig} and surface temperature at the time of the ignition (ig_{temp}) were recorded during the test. The test duration was 300 seconds in most tests, NaP4 tests were conducted for 600 seconds. The effectiveness of FR treatment was assessed by ability to perform as a fire barrier through the basic protection time (T_{prot}) and beginning of charring of timber (T_{char}), which is considered to be at temperatures of 270 °C and 300 °C consequently (EN 1995-1-2:2004), measured from the surface of the timber block, as it has been done in previous research [89].

In Meka values such as PHRR, HRR, THR, TSR, CO_2 release, and mass loss were determined with the objective to predict a fire classification for the composites. The fire resistance classification was determined according to EN 13501-1 [64], however for official classification Single burning item (SBI) tests [66] are required, which require large samples in bigger quantities. Therefore, for material development purposes the SBI test results were predicted based on cone calorimetry test results, which has been proven to provide trustworthy outcomes in previous studies [90][65].

Based on a model [65] created to predict the Eurocode classification, the prediction was made. As stated, if the PHRR values of cone calorimetry tests are lower than 75 $kW.m^{-2}$ then class B can be predicted. Further calculations were not performed.

Essential parameters for Eurocode classification are fire growth rate index (FIGRA), total heat release during 600 seconds (THR600), smoke production as smoke growth rate index (SMOGRA) and total smoke production [65]. These values were calculated as described in EN 13823 [66].

3.2.8 Mechanical properties

The FR treatment are known to have a degrading effect on the natural fibres. To determine the effect that specific chemicals and treatments have on the mechanical properties flexural and tensile tests were performed. Flexural strength tests were done according to EVS-EN ISO 14125:2000; and tensile tests according to EVS-EN ISO 527 (Type 1BA). For each variation 3 boards were fabricated, from which 4 flexural and tensile test specimens were cut using a laser cutting machine, as shown in Figure 3.5.

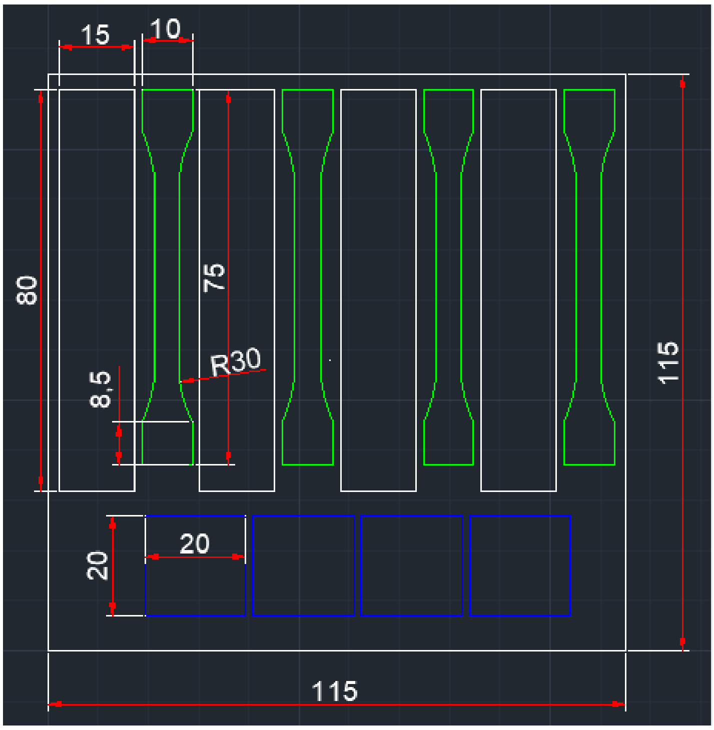


Figure 3.5 Composite board mechanical strength and density test specimen cut plan: Flexural test specimens are presented using white lines, tensile specimens are shown with green lines and density specimens are marked as blue.

4. RESULTS

Results presented in current thesis have already been partially published [48].

4.1 Density and alkali treatment

4.1.1 Weight reduction due to alkali treatment

The 5 wt. % NaOH treatment removed 8,9 ± 1,9 % of hemp fibre chemical composition, which is slightly less than shown in previous studies [91][92]. Suardana et al found that when hemp fibres were treated for a duration of 1 hour, using 2 %, 4 %, and 6 % alkali solution at 95 ºC, the removal of weight was 8,0 %, 9,8 % and 13,6 % respectively [92]. Kostic et al reported a 4,4 % weight reduction during a 30-minutes treatment time using a 5 wt. % alkali treatment, however when boiling temperatures were used the reduction was significantly increased [91].

Hemp fibres used compose of 22,6 ± 0,7 % of non-cellulosic content, as 8,9 % was removed, the amount remaining within the fibres is 13,7 ± 2,3 %. On visual examination the fibres appeared to be lighter coloured and well separated, having less bundles, indicating that the surface area of the fibres was increased.

4.1.2 Density of composites

Figure 4.1 shows that the density was lowest for the UT composites (1,00 $g.cm^{-3}$), Na specimens had a significantly higher density of 1,03 $g.cm^{-3}$. Pure PLA specimens had a density of 1,22 $g.cm^{-3}$. The slightly higher density of alkali treated composites is most likely related to the better separation of hemp fibres due to removal of pectin, wax and intercellular components caused by the alkali treatment [37].

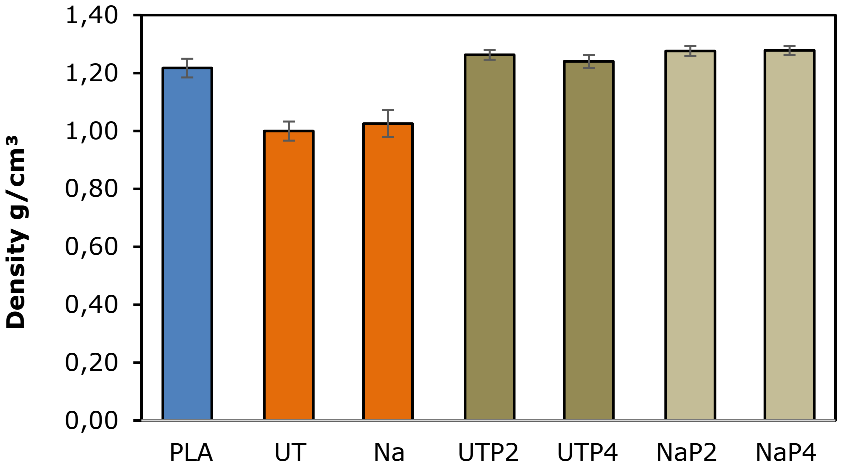


Figure 4.1 Density of produced composite variants.

Sawpan et al [93] also found that fibre treatments increase the density of hemp fibres, which could be the reason of higher density of the Na composite. However, as the void content of the composite is unknown, the lower density of UT composite could be caused of voids. Better separation of fibres likely improved interfacial adhesion between the fibres and matrix enabling to form less voids in the composite. The FR treated composites had much higher density due to added material of FR to the board.

4.2 FTIR analysis

Figure 4.2 shows the vertically shifted spectra of hemp fibre variants used in this thesis. No difference was observed between UTFP2 and UTFP4, therefore UTFP2 is presented. At 1516 cm^{-1} there is a peak representing the tensile vibration of the aromatic skeleton of lignin [94]. A peak shifting was observed at 2925 cm^{-1} due to alkali treatments in NaF. The reduction and shifting of these peaks in NaF compared to UT refers to the successful removal of lignin [95]. A smoothening of the peak in the region of 1739 cm^{-1}, which corresponds to C=O stretching in the acetyl groups of hemicelluloses. The absence of this peak in NaF suggests that hemicelluloses were removed due to alkali treatment [96]. The Peak at 1430 cm^{-1} describing the C-H bending of crystalline cellulose and the peak at 1373 cm^{-1} are responsible for stretching of the hydrogen bond intensity of cellulose [41]. These peaks were not affected, meaning that alkali treatments did not affect the cellulose structure. Peak at 1655 cm^{-1} is assigned to the absorbed water by hemicellulose [97]. This region was reduced due to alkali treatments, indicating the increased hydrophobicity of hemp fibres.

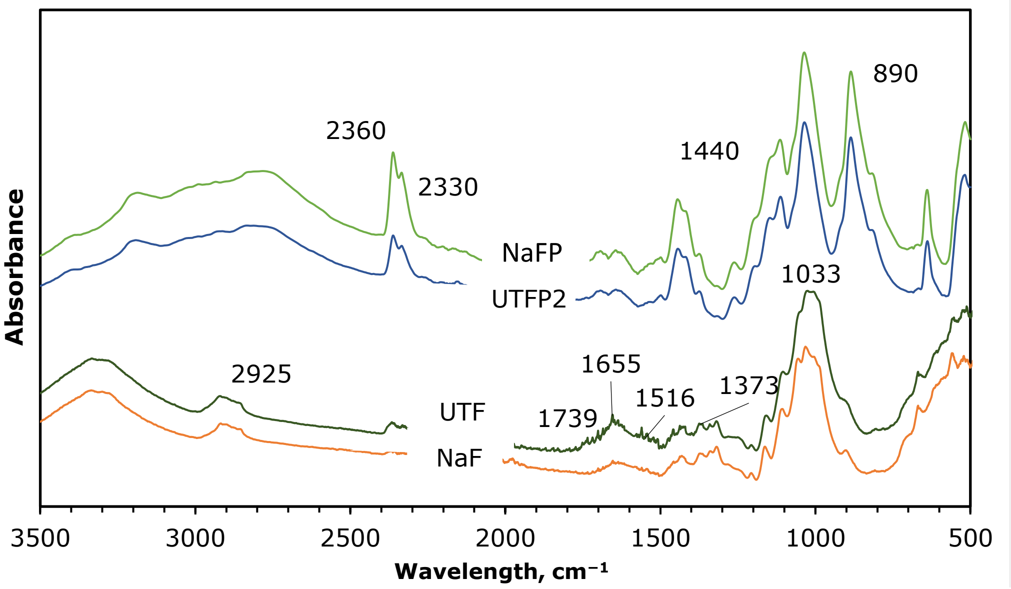


Figure 4.2 FTIR of hemp fibres that were used for fabrication of the composites: NaFP2 (alkali treated hemp fibres treated with P2), UTFP2 (untreated hemp fibres treated with P2), UTF (untreated hemp fibres), NaF (alkali treated hemp fibres).

FR treatments had a clearly visible effect on hemp fibres absorption peaks. Most drastic changes in the fibres appear at wavelengths of 890 cm^{-1}, 1440 cm^{-1} and 2330–2360 cm^{-1}, as the peaks were intensified in those regions. The peak at 2360 cm^{-1} correspond to P-H bonds and a shoulder at 810 cm^{-1} is attributable to P-O-C bonds [98], which may refer to phosphorylation of the fibres by the FR treatments. These peaks were intensified in NaFP2, referring to improved phosphorylation of the alkali pre-treated fibres [98]. Peaks appearing at 890 cm^{-1} and 1440 cm^{-1} were assigned to C-H bending of amorphous and crystalline cellulose respectively [41]. Broadening of the region of 2695–2830 cm^{-1} in FR treated fibres was attributed to C-H stretching of aldehyde [99].

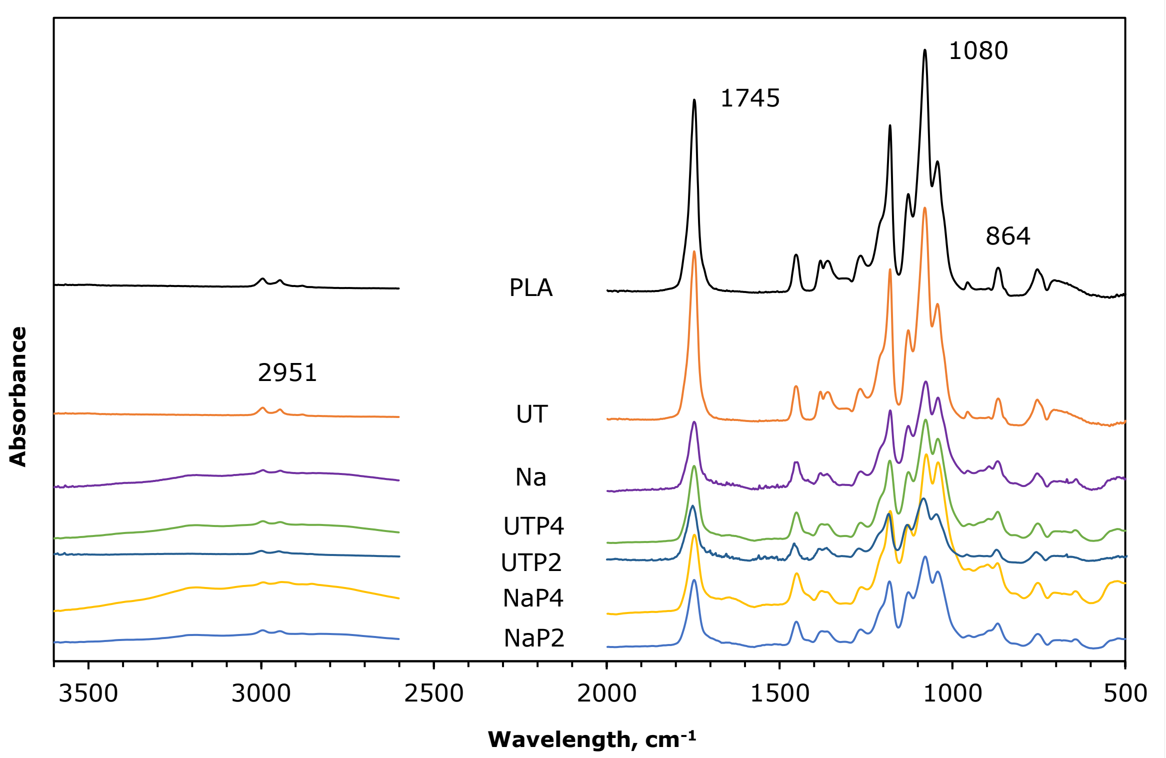
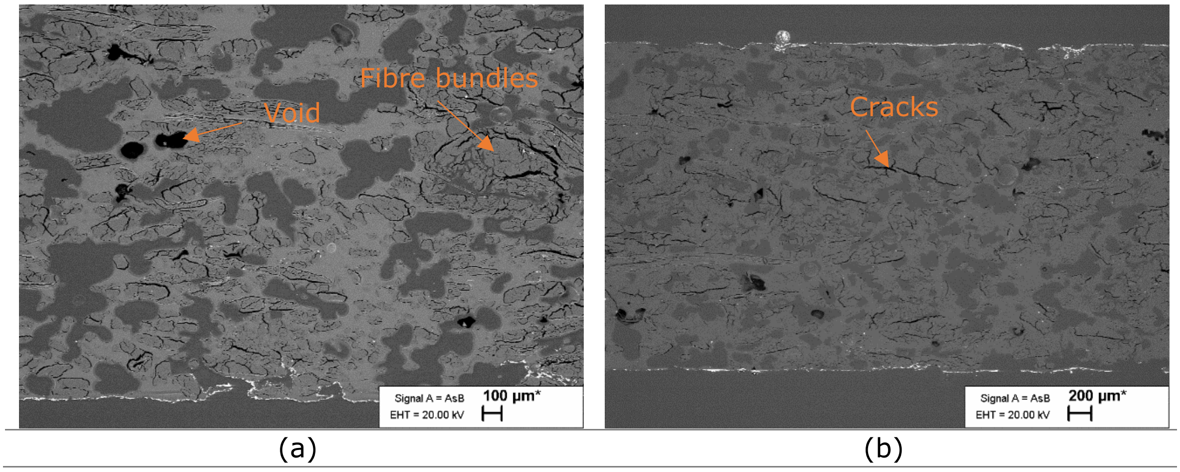


Figure 4.3 The shifted FTIR spectrum of the fabricated composites

Clear peaks at 864 cm^{-1}, 1078 cm^{-1} and 1745 cm^{-1} are attributed to C-C, C-O, C=O stretching vibrations respectively, that indicates the presence of PLA in the composites [100], which were not observed in fibre scans. These peaks appeared sharper in PLA and UT, because there was less PLA by volume present in the rest of the variants. However, there were no significant differences apparent by FTIR in the structure of the composites.

4.3 SEM analysis

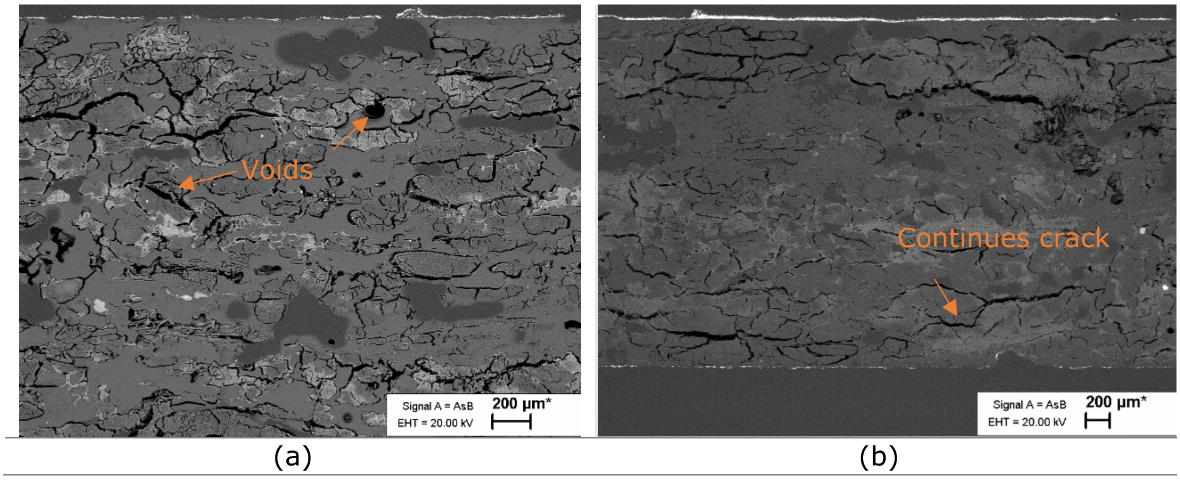
SEM images show that alkali treatments have increased the fibre separation by reducing the amount of large fibre bundles in the matrix (shown in Figure 4.4).



(a) (b)

Figure 4.4 Cross sectional images of UT (a) and Na (b)

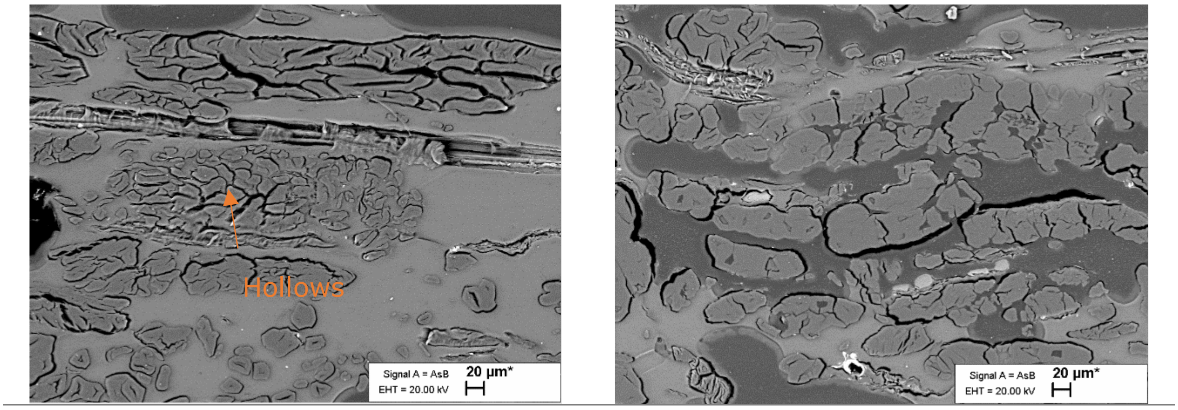
FR treated composites appear to have formed more cracks as can be seen on Figure 4.5. The FR layer is clearly visible from both sides of the composites, as there is reduced adhesion between FR treated fibres and matrix, which has created continues cracks near FR layer. The interfacial adhesion and fibre separation seems to be better in the core of NaP2 composite. UTP2 has more fibre bundles present and cracks than NaP2. Better separation of fibres and less cracks is caused by the alkali treatment that separates the fibres and enables better adhesion as was also reported previously by Alao et al [101]. Improved bonding between the matrix and FR treated fibres would be beneficial as this could avoid delamination of layers when exposed to heat.



(a) (b)

Figure 4.5 Cross sectional images of (a) UTP2 and (b) NaP2

In Figure 4.6 (a) the close-up view of an unseparated hemp fibre bundle is shown. It is visible that hollows are present in between the fibres. Figure 4.6 (b) shows that fibres have been more uniformly distributed in Na, consequently the composite has better distribution of fibres in the matrix. Therefore, the fibre surface area has been increased in alkali treated composites, as noted by Sair et al [102].



(a) (b)

Figure 4.6 Cross sectional image of (a) hemp fibre bundle in UT composite (b) fibre distribution in Na

4.4 Impact of Fire-Retardant treatments

4.4.1 Reaction to fire tests

To evaluate the effect of the FR treatments and multiple parameters were analysed. Average T_{surf} during test period are shown in Figure 4.7 and average T_{depth} in Figure 4.8.

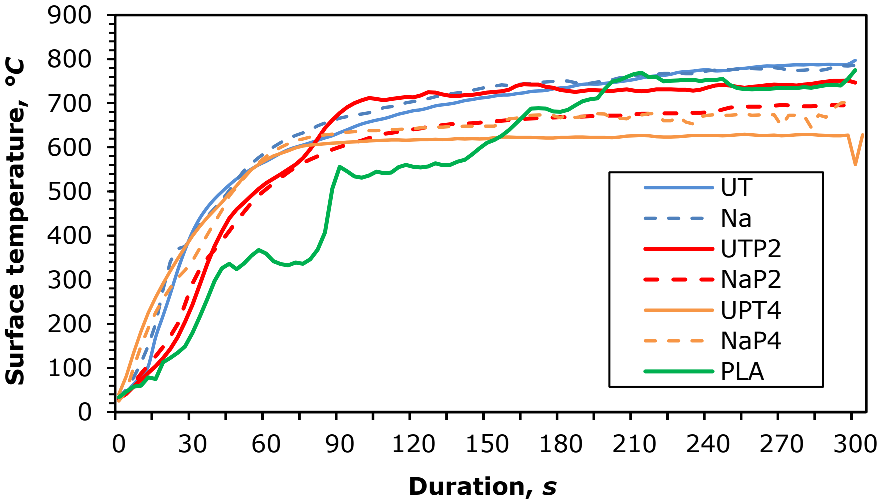


Figure 4.7 Surface temperature of different composite variations during fire tests

UTP4 showed significantly lower surface temperature than other subjects throughout the test period. PLA surface temperature remained lower in the beginning as there was a delay in ignition but increased quickly afterwards.

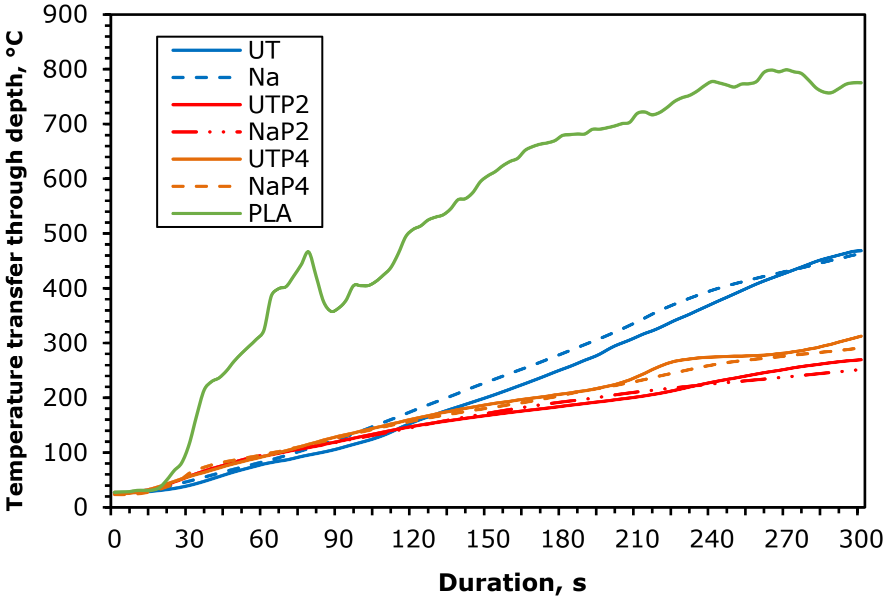


Figure 4.8 Temperature transfer through the composite surface during fire test

The results show a clear significant decrease in the T_{depth} of both (NaP and UTP) FR treated composites. The T_{depth} curve of non-FR treated specimens was similar, although in UT the temperature rise was slightly delayed. In comparison with PLA, composite samples performed much better in protecting the wooden surface from heat. Unlike T_{surf}, the T_{depth} of PLA started rising quickly from the beginning, reaching a peak of 799,18 °C at 270 s. Even though the surface temperature of PLA was initially somewhat lower than Na, UT and UTP, no protection to the wooden block was offered causing the wooden block to ignite. Table 4.1 lists the ignition parameters for non-FR samples. UT and Na both showed similar reaction to fire as T_{ig}, ig_{temp} and t_{char} values were in similar range. PLA ignited 13-14 seconds later but had much lower values of T_{prot} and T_{char}.

Table 4.1 Ignition parameters of non-FR samples

Sample	T_{ig}, s	ig_{temp}, °C	T_{prot}, s	T_{char}, s
PLA	$27 \pm 2{,}5$	155 ± 18	$45 \pm 7{,}9$	$51 \pm 10{,}8$
UT	$13 \pm 2{,}3$	138 ± 26	$194 \pm 18{,}1$	$210 \pm 21{,}0$
Na	$14 \pm 1{,}7$	150 ± 19	$177 \pm 27{,}5$	$192 \pm 27{,}5$

The FR contributes to 29 %,8-33 %,7 % of total material mass of FR treated composites (See Appendix A4.6). UTP2 samples had slightly lower FR %. All parameters measured except mass loss were increased in FR treated samples in comparison of non-FR samples. In UTP2 ignition occurred significantly sooner, which could be associated to lower FR deposited. The improvement in T_{ig} was much greater in NaP2, UTP4, NaP4 samples, as some of the samples did not ignite during test period of 300 seconds. However, despite the low T_{ig} in UTP4, UTP2 performed similarly in regards of protection time to the wooden surface, while UTP4 had the poorest results. Overall, the alkali variants showed the best results in regards of reaction to fire, while NaP2 performed slightly better than NaP4 in regards of protecting the wood from fire.

The measurements were also confirmed by visual examination. PLA offered no protection to the wood, resulting in heavy charring of the block. FR treated samples had significantly less decomposition of the composites and offers an almost full protection to the timber, preventing charring compared to the non-FR batch (UT and Na). Wooden blocks under UT and Na meanwhile showed more charring. It was observed (see Figure 4.9) that NaP2 and NaP4 avoided crack propagation much better during the test duration of 300 s, which could be the reason these variants were able to protect the wooden surfaces much better.

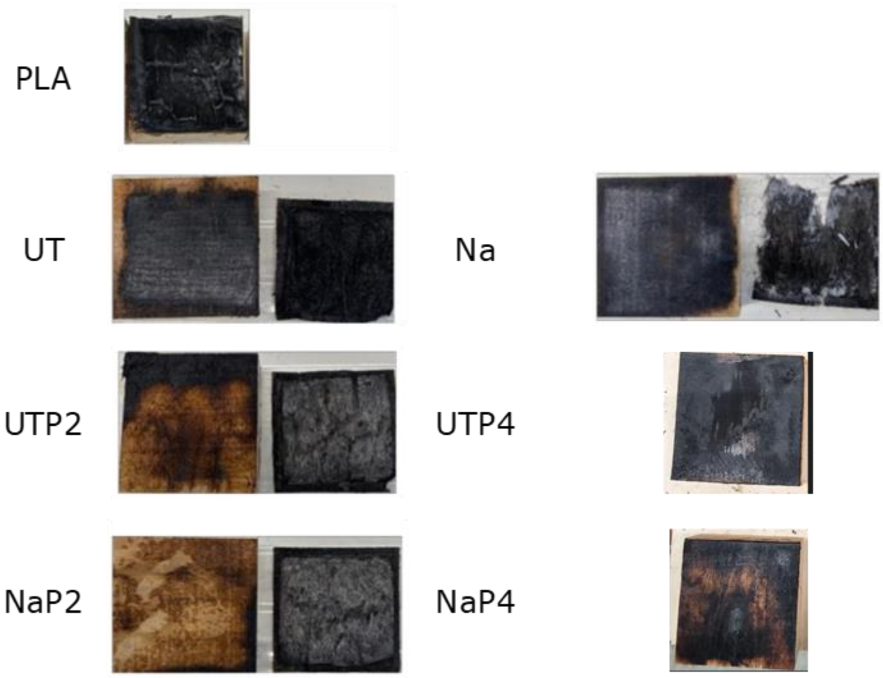


Figure 4.9 Composites and wooden blocks after the reaction to fire test

4.4.2 Eurocode fire class estimation

The key fire performance characteristics such as PHRR, THR, TSR and CO_2 yield of non-FR treated composites was investigated in this thesis had mostly similar values as reported in previous studies (listed in Table 2.4), except for slightly higher TSR found.

The main fire reaction characteristics were analysed to describe and compare the reaction to fire and fire resistance of the composites under investigation more accurately and to predict the fire class. As the alkali treated samples NaP2 and NaP4 performed the best, the number of variants tested was reduced to three (3). Best performing groups based on previous findings of the investigation in Taltech and for control Na was used. The FR fraction compared to total mass (FR, %) and ignition parameters are presented in Appendix A4.7.

The performance of the specimens in Meka is similar to the outcome in Taltech. The non-FR composites exhibited short T_{ig}. NaP2 however had a much lower T_{ig} during the test while NaP4 did not ignite in most cases.

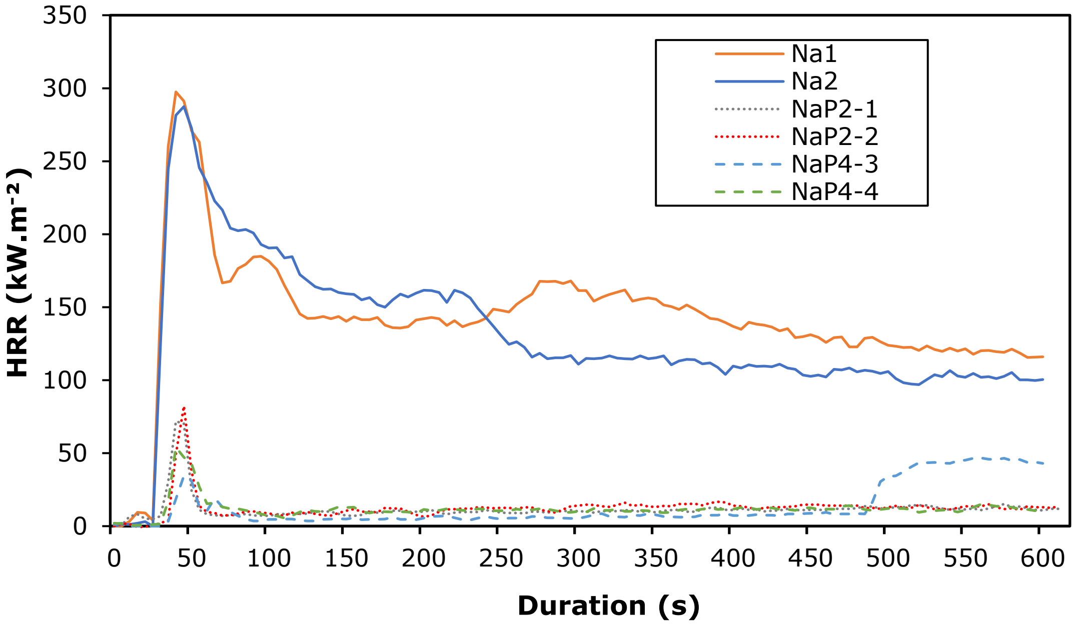


Figure 4.10 Comparison of HRR

Figure 4.10 clearly shows a large decrease in the HRR peak values at preliminary stages (45 s) of the test of all FR treated samples compared to non-FR samples. NaP2 samples exhibited slightly higher HRR values in the initial stages, which might have caused the unexpected early ignition. Early stage PHRR was on average lowered by 380 % in NaP2 and by 661 % in NaP4. However, NaP4-3 achieved the PHRR at 560 s after the occurrence of ignition at 493 s. This is likely due to the integrity of the FR treated layer was broken and the advancement of fire into the core, providing additional fuel, which was also observed by Hapuarachchi and Peijs [56].

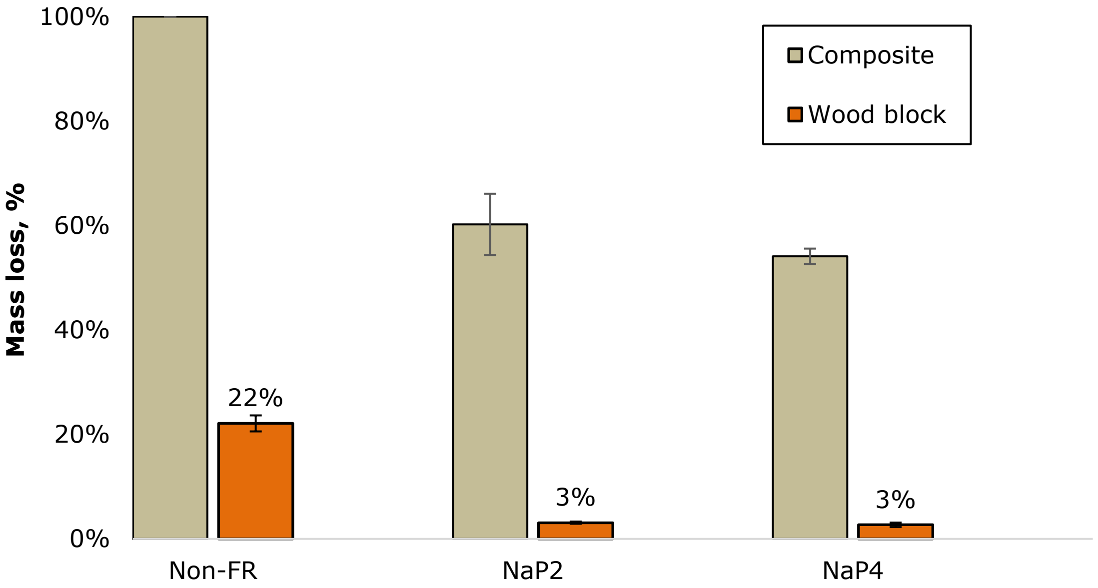


Figure 4.11 Mass loss of composites and wood blocks during fire test

The mass loss of non-FR samples differentiates a lot from FR treated boards. FR composites lost almost half of their weight during the test period, while non-FR samples were completely degraded. Wooden blocks placed underneath the non-FR composite lost 733 % more mass in comparison of FR-treated samples. NaP4 composite lost an insignificant 6 % less mass than NaP2. The data was confirmed by visual examination (shown in Figure 4.12) as both FR treated variants provided much more protection to wooden blocks and significantly reduced the decomposition of it. While non-FR composites were completely decomposed, FR-treated composites were still in one piece, although there were cracks and openings apparent, revealing the core layer.

As observed in tests done with the duration of 300 s, it was apparent that NaP2 and NaP4 were able to avoid crack formation, while UTP2 and UTP4 exposed the core layer much sooner, resulting in lower protection to the wood as described above.

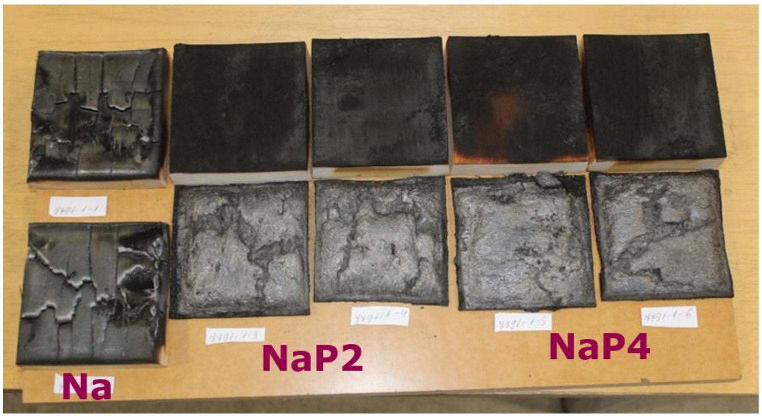


Figure 4.12 Composite and wood specimens after cone calorimetry test

Similarly, Hapuarachchi and Peijs [103] experienced delamination of PLA-hemp layered structure during cone calorimeter tests, causing the fire to breach deeper into the material and increasing the HRR. This problem could be avoided by using short fibres or partially.

Even though NaP2 ignited early in the test and had slightly higher PHRR the other key characteristics were slightly lower than for NaP4., Average HRR (HRRav) was reduced due to FR treatments with readings about 11 times lower, which corresponds to the charring of timber blocks as charring rate is related to HRR [65]. Similar outcome was noted for the average PHRR (PHRRav), FIGRA and THR600.

HRR values and classifications predicted for the studied composites are listed in Table 4.2.

Table 4.2 HRR values and classification

	THR MJ.m^{-2}	PHRR kW.m^{-2}	PHRRav kW.m^{-2}	FIGRA W.s^{-2}	THR600 MJ.m^{-2}	**Class**
Na-2	78,4	287,4	292,4 ± 7	232,1 ± 14,1	82,0 ± 5,1	D
Na-1	85,6	297,5				D
NaP2-1	6,89	71,8	77 ± 7,4	20,3 ± 1,3	7,2 ± 0,4	B
NaP2-2	7,51	82,3				B
NaP4-1	8,01	46,7	50,4 ± 5,2	21,4 ± 2,1	7,5 ± 0,7	B
NaP4-2	7,03	54,03				B

Na was classified into class D. Both samples of NaP4 had a PHRR < 75 kW.m^{-2} and were classified to the highest class-B, meaning the material had a very limited contribution to the fire intensity. In case of NaP2 samples, one of the samples showed slightly higher PHRR than 75 kW.m^{-2}. However, FIGRA limit (shown in appendix 3.) for classification into class B was about 6 times lower for all FR treated samples and THR600 values were also within the limit. Therefore, further calculations described in the model [65] were not done, as the values would be lowered even further due to the lower heat flux used in SBI test. NaP2 samples were also estimated to be suitable for class B.

FR-composite samples had a much higher 313 % total smoke release during 600 s (TSP600), which is caused due to the impure burning conditions created by the addition of FR into composites, as also found by Hapuarachchi and Peijs [56]. Smoke release results and the classifications are shown in Table 4.3.

Table 4.3 Smoke release results and classification

Variation	**SPR $m^2.s^{-2}$**	**SMOGRA $m^2.s.^{-2}$**	**TSP600 m^2**	**CO_2 kg/kg**	**Class**
Na	0,001	11,2 ± 1,0	75,4 ± 5,6	1,45 ± 0,03	S2
NaP2	0,004	35,0 ± 5,8	236,1 ± 38,7	0,65 ± 0,13	S3
NaP4	0,003	34,9 ± 0,5	235,2 ± 4,0	0,93 ± 0,27	S3

SMOGRA calculated was much lower than what is needed for class S2, however TSP600 was above the limit of <200, meaning that both NaP2&4 fall into class S3. NaP2 had slightly lower CO_2 release.

Hapuarachchi et al [73] studied hemp-PLA composites and presented slightly higher PHRR and similar CO_2, TSR found was lower. Gallos et al [74] also measured similar PHRR and THR in untreated hemp-PLA composites. Hapuarachchi et al [71] achieved a significant reduction of PHRR in FR treated hemp-polyester composites, as twice as low values were recorded after treatments. Bocz et al [75] produced FR treated flax-PLA treated composites and noted a PHRR of 149 kW^{-2} and THR of 57,5 $MJ.m^{-2}$, which is lower than in previously mentioned papers.

The key fire performance characteristics such as PHRR, THR, TSR and CO_2 yield of non-FR treated composites was investigated in this thesis had mostly similar values as reported in previous studies (listed in Table 2.4), except for slightly higher TSR. Results show that FR treated composites provided much lower values than Na and previous studies related to biocomposites fire reaction, apart from TSR, which was significantly higher. On average the PHHR results found in this thesis were about 64 % [71] and 57 % [75] lower, while THR measured was 87% lower than in previous papers. TSR of NaP2 and NaP4 was about three times higher than in Na. Mean CO_2 yield was significantly lower in FR composites compared to Na.

Additionally, a few trials were made regarding FR treatments from one side. Results were promising as the protection to wood offered and mechanical strength was similar when treatment was carried out only on one side. Furthermore, increasing the thickness and higher density of the material might improve the mechanical and functional properties of the composites. Using a resin as a matrix in the composite might enable to use higher fibre [39] volume and therefore increase the mechanical strength, thermal stability, and heat release rates. As noted by Hapuarachchi and Peijs [103] woven fibre mats might provide improved HRR values compared to nonwoven mats.

A few tests were done also during the thesis by using woven flax fabric for the surface FR treated layers. In these composites only protection to the wooden surface and $\mathrm{t_{ig}}$ were evaluated. The hybrid hemp-flax composites did not ignite during 600 second period, but the T_{prot}, T_{char} values were found to be lower than in NaP2. However, to be certain, additional testing and measurement of HRR values should be done. The results found should be confirmed by large scale SBI tests to officially acquire a fire class for such FR treated hemp-PLA composites.

4.5 Mechanical properties

The mechanical properties were analysed through evaluating the ultimate tensile strength (σ) and flexural strength (MOR), Young's modulus (*E*) and flexural modulus (MOE).

4.5.1 Tensile strength results

Tensile strength (σ) results are shown on Figure 4.13. The reinforcement of the PLA matrix with the hemp fibres increased σ by 17 % (UT) compared to the PLA control (51.5 MPa). Alkali treatment further improved the σ by 27 %, which suggest improved interfacial adhesion of the matrix and reinforcing fibres. Lower tensile σ of UT refers to inferior transfer of stresses from the matrix to the fibres [104].

Incorporation of FR had a negative effect on all the composites variants. This resulted in a 13 % decrease of σ for UTP2 compared to UT. The deterioration in σ was more noticeable with NaP2 with a 42 % decrease compared to the corresponding non-FR variant (Na), which is likely caused by the combined degrading effect of alkali and FR treatments, which weakened the natural fibres. NaP4 had an even larger 45 % decline in σ, however the difference between NaP2 and NaP4 was not statistically significant. UTP4 showed a notable 20 % lower σ than UTP2, which refers to more damaging properties of P4. Overall, UTP2 exhibited significantly better σ than the rest of the FR treated variants.

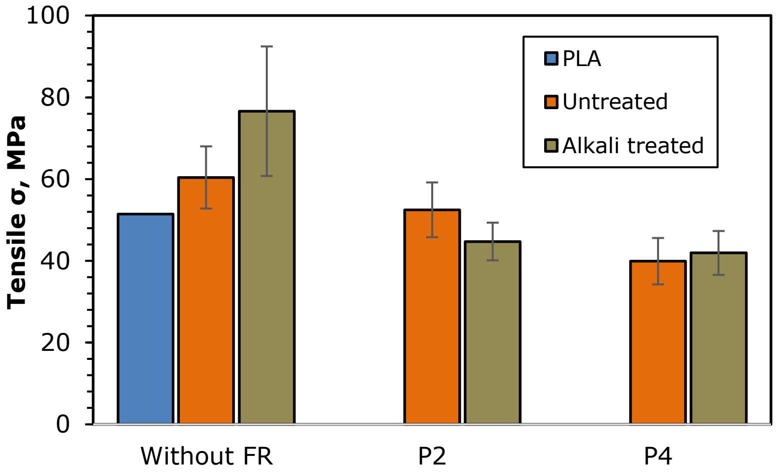


Figure 4.13 Comparison of tensile strength; FR chemical Palonot 2 (P2), FR chemical Palonot 4 (P4)

Introduction of natural fibres to PLA resulted in large increase of the material stiffness (shown in Figure 4.14), as *E* was increased by 86 % in UT and 139 % in Na. FR treatments showed an increasing effect on the *E* of both P2 variations. Young's modulus was significantly higher in NaP2 (10,6 GPa) and UTP2 (10,4 GPa) than in PLA specimens, while there was no significant difference between the two variants. UTP4 and NaP4 samples showed *E* that are 46 % and 58 % lower than UTP2 and NaP2, respectively. Treatments with P4 did not reduce the elongation at break (shown in Table 4.9) as much as in the case of P2, therefore *E* was not increased as much.

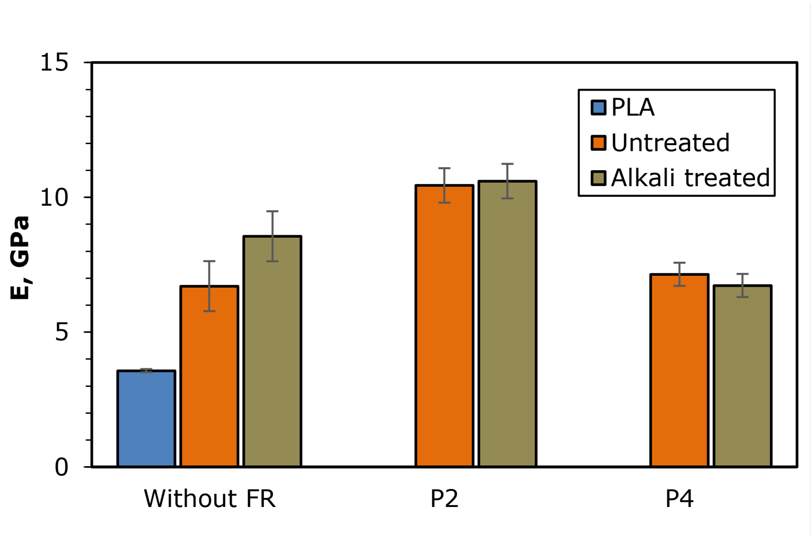


Figure 4.14 Comparison of Young’s modulus

4.5.2 Flexural strength results

Flexural strength of the composites is presented in 4.15. Composite materials MOR was a notably higher, 19 % in UT and 29 % higher compared to PLA. MOR of P2 specimens was slightly, but insignificantly lowered in comparison of non-FR treated specimens in both variations. UTP2 and NaP2 had 6 % and 8 % lower MOR, respectively. However, compared to PLA there was still a considerable improvement of bending strength, 12 % in UTP2 and 19 % in NaP2. NaP2 showed an insignificant 6 % higher MOR than UTP. P4 experienced a more negative effect on the MOR, as compared to P2 variants both UTP4 and NaP4 had a pronounced reduction of 21 % and 22 %, respectively.

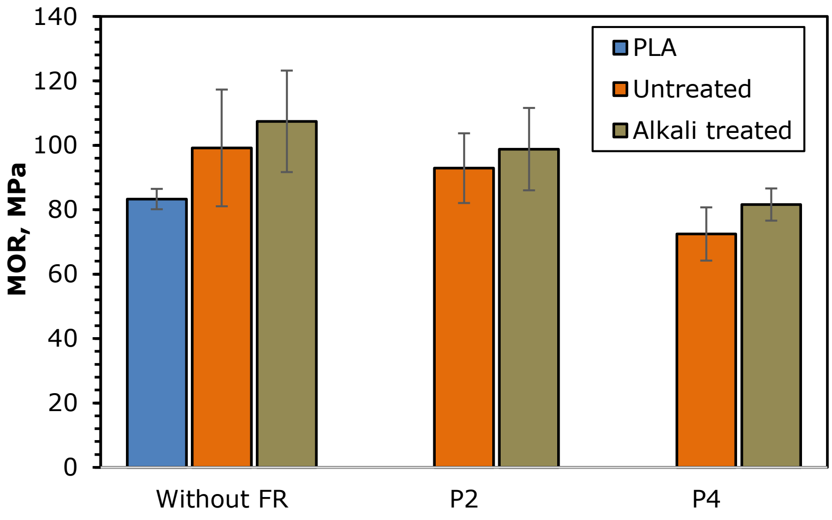


Figure 4.15 Comparison of MOR

An almost three-fold increase in MOE occurred in both cases compared to PLA. UTP4 had a significantly lower MOE than UT, UTP2 and UTP4. There was no statistically significant difference between the MOE of NaP2 and NaP4.

Both E and MOE were significantly increased in P2 samples due to the reduction of hemp fibre elasticity (shown in Table A4.9), which increased the stiffness of the composite. Elongation at break was not as lowered as much in P4. Suardana et al [105] also reported increased stiffness, while significant reductions occurred also for σ and MOR when diammonium phosphate FR was incorporated.

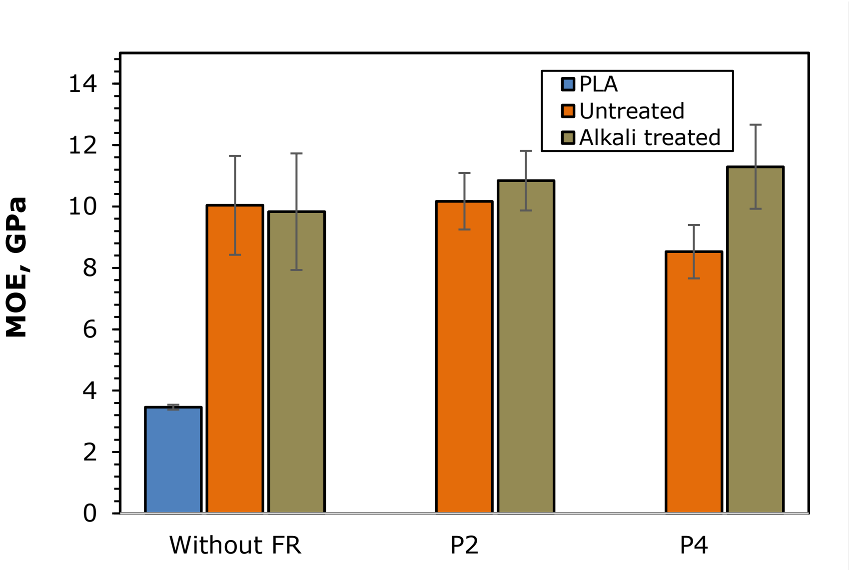


Figure 4.16 Comparison of MOE

The Reinforcement of PLA using natural fibres has been reported to increase mechanical properties of it in numerous papers [43], [84], [106], [107]. Alkali treatments have also shown to further improve the mechanical properties due to removal of soluble content and improvement of interfacial adhesion, as the fibres are better separated, impurities (waxes and oils) are partially removed, and the surface area is increased. Sawpan [43] documented tensile strength of 85,4 MPa and *E* of 12,6 GPa. Baghei [51] found that Alkali treated composites reinforced with hemp-PLA yarn fibres show superior mechanical performance than untreated, nonwoven hemp-PLA yarn composites. Alkali hemp-PLA yarn composites had σ of 77,1 MPa, *E* of 10,3 GPa, while untreated nonwoven composites had σ of 53,6 MPa and *E* of 5,6 GPa. As regarding maximal mechanical strength, the fibre fraction best results are achieved at 30-35 wt. %, considering that 50 wt. % fibre volume and PLA fibres were used, the performance of the produced composites is noteworthy, compared to studies where PLA was used as the matrix [39]. Felix Sahayaraj et al [108] reported 23 % lower tensile σ, but 32 % higher flexural strength. *E* and MOE found were significantly lower, however the manufacturing method included much longer pressing times and higher pressures. The mechanical properties of biocomposites could be further improved by using hemp or hemp-PLA yarns [51], [52], which might improve the adhesion between the two and further improve the alignment of fibres.

FR treatment did not have as drastic effect on the MOR as examined in tensile σ, which was strongly affected, likely due to damage caused to the cellulose structure.
Unlike σ, flexural results, both MOR and MOE were not changed as much and remained in similar range to that of the non-FR composite variations (Figure 4.15 & 4.16). While FR treatments reduced the mechanical strength of the composite considerably, the composites still exhibited mechanical strength comparable to many NFC where FR were not integrated [109].

Overall, mechanical properties found suggest P2 offers better mechanical performance, while the material is turned brittle by both fire retardants. FR treated composites would provide better performance in applications where flexural properties are of importance.

4.6 Hygroscopic properties

Figures 4.17 and 4.18 show the change of equilibrium moisture content (EMC) at different RH % of non-FR treated and FR treated composites. The results for UT and PLA previously published [110] are also shown for comparison.

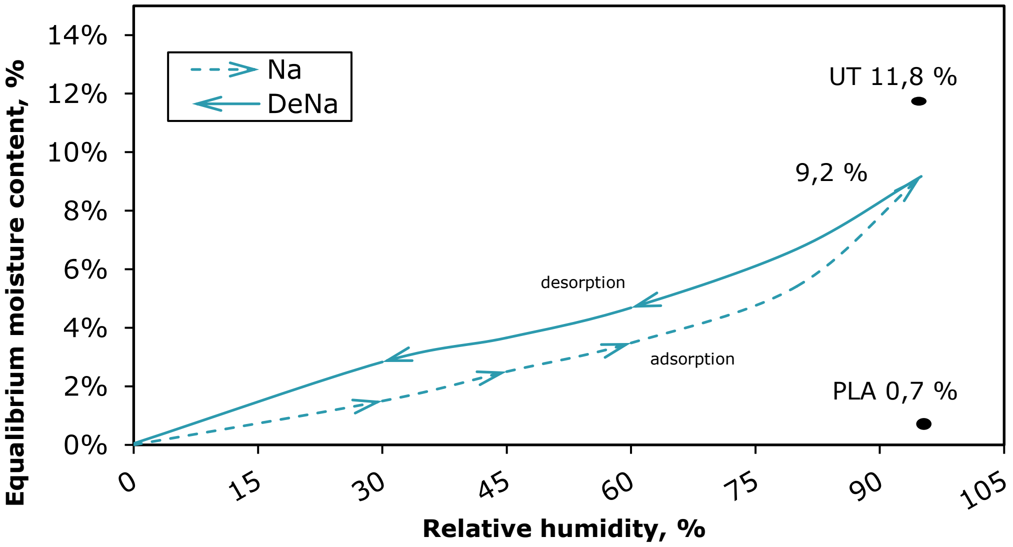


Figure 4.17 Equilibrium moisture content (%) at RH (%) of 30, 45, 60, 80 and 95 in alkali treated specimens: Na (- -) absorption values, DeNa (–) desorption values, arrow direction shows either the absorption (forward) or desorption (backwards) of the samples, absorption values are indicated with dashed lines.

Until 60 % RH the mass change of the boards was relatively uniform. Initially Na had a slighting higher moisture absorption than NaP2 & 4, but after exceeding 60 % RH the FR-treated boards started absorbing increasing amount of moisture. At 60 % RH the FR treated specimens were observed to start leaching (see Figure 4.17) and absorbed significantly more water since then than Na due to presence of FR salts. NaP4 absorbed significantly more moisture than NaP2. During the desorption process, as RH was reduced, the equilibrium moisture content (EMC) of Na samples remained ca 1,5 % higher than during absorption, due to some water being bound into cell walls after reaching the fibre saturation point [111]. Alkali treatments reduced the EMC compared to UT as the same hemp fibres were shown to have EMC of 11,8 % [110].

Flame retardants are known to increase sensitivity to water of composites. Celino et al found that hemp fibres absorbed 10,5 % of water at 80 % RH [112]. Na had EMC of 5,4 % at that level of RH, meaning that fabricated composites have lower EMC than hemp fibres.

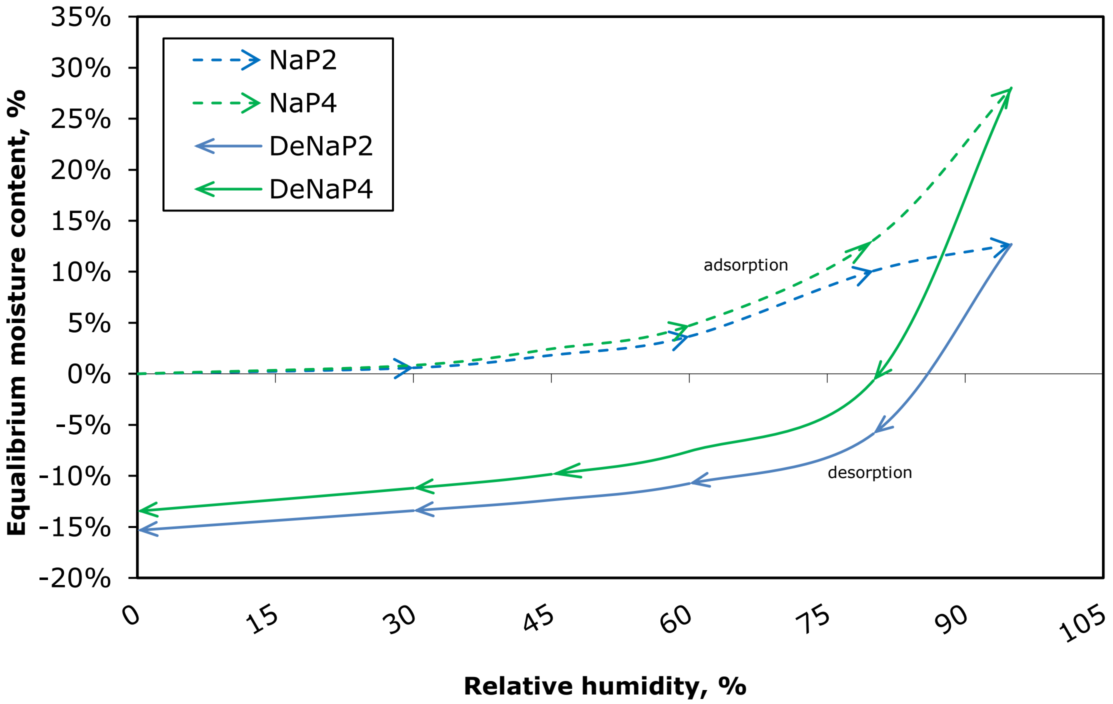


Figure 4.18 Equilibrium moisture content (%) at RH (%) of 30 %, 45 %, 60 %, 80 % and 95 % in FR treated specimens: NaP2 & NaP4 (- -) absorption values, DeNaP2 & DeNaP4 (–) desorption values, arrow direction shows either the absorption (forward) or desorption (backwards) of the samples, absorption values are indicated with dashed lines.

Due to sweating of FR treated samples the weight of those samples was extensively reduced during desorption, referring to leaching out of the FR solution at higher than 60 % RH. NaP4 samples lost 13 % and NaP2 lost 15 % of original weight on average. Campana et. [113] also reported the reduction of fire-retardant properties at high RH %. The durability and effectiveness of the FR treatment should be evaluated in future studies.

5. SUMMARY

The aim of the current thesis was to apply fire-retardant treatment and to investigate the impact of the hemp fibre surface modification in combination with fire retardants on the mechanical and functional characteristics (moisture resistance and reaction to fire) of hemp fibre reinforced PLA composites. Fire retardant treatments were carried out using a novel fire-retardant system, which had not been tested for fibre treatments so far. Consequently, there was lack of information regarding the effect of combining such fire retardant with hemp fibres.

Hemp fibres were prepared, and alkali treatments were carried out. Suitable fire retardants and an effective treatment method was selected. Different variations of hemp fibre reinforced PLA composites were fabricated. The mechanical and functional properties of the composites were investigated.

Alkali treatments were able to provide better separation of individual hemp fibres and remove some of the non-cellulosic components from the fibre surface. Consequently, there was better interfacial adhesion between the fibres and PLA and fibres were more uniformly distributed throughout the matrix. Due to these reasons the mechanical properties of the alkali treated composites were improved.

Reaction to fire tests showed that fire retardant treatment substantially increased the fire-retardant properties of the composites, which was further improved when combined with alkali treatments. The composites were predicted to fulfil the requirements for the highest fire class B. Smoke release was increased by the fire-retardant treatments, while the CO_2 release was much lower. The reaction to fire parameters achieved in current thesis were superior to previous studies regarding natural fibre composites.

As predicted, there was a notable negative effect to the mechanical strength, especially to the tensile properties, as tensile strength was reduced by 46 %. Flexural strength was however only a marginally decreased. Slightly larger reduction in mechanical properties was noted when combined treatment was used. However, FR treatment increased the stiffness and brittleness of the composites. FR treated composites were shown to be vulnerable to moisture when exposed to high relative humidity conditions, as they started to leach when RH exceeded 60 %.

The investigation demonstrates that the fire-retardant properties of biocomposites can be improved without fully negating functional characteristics of the material, enabling them to be possibly used for applications where fire retardant properties are of importance. SBI tests must be conducted to acquire official fire classification for the composites. Additional development of the material could furthermore improve the overall performance of biocomposites.

Comprehensively, the characterisation of the FR treated hemp-PLA composite suggests that such composites would be used most purposefully and effectively in dry conditions and for applications where low density, minimal contribution to fire and the ability to withstand flexural forces is required. Widespread adaptation of sustainable materials offers numerous financial and environmental benefits and is essential in achieving the EU green deal goals.

6. KOKKUVÕTE

Käesoleva magistritöö eesmärgiks oli Eestis kasvatatud kanepikiudude modifitseerimine kombineeritult tuletõkkeaine ja naatriumhüdroksiidiga ning selle töötluse mõju uurimine kanepi-polüpiimhappe komposiidi füüsikalis-mehaanilistele karakteristikutele ja tuletõkkeomadustele. Uurimustöö uudsus seisneb asjaolus, et konkreetset tuletõkkevahendit ei olnud veel seni kasutatud looduslike kiudude töötlemiseks, mistõttu puudus arusaam ja teave tulekaitsevahendi mõjust ning tõhususest taoliste komposiitmaterjalide tuletõkkeomaduste parandamisel.

Töö käigus eraldati kanepikiud kestadest, kraasiti ning modifitseeriti keemiliselt kasutades naatriumhüdroksiidi (NaOH). Komposiitmaterjali pindmistes kihtides kasutatud kanepikiudusid töödeldi erinevate tuletõkkeainetega. Seejärel valmistati töötluste poolest erinevad 50 m.% kiusisaldusega sarrustatud PLA komposiidid ning uuriti nende funktsionaalseid ja mehaanilisi omadusi, et selgitada välja parimaid tulemusi pakkuv kombinatsioon ja tuletõkkeaine.

Tulemustest selgus, et leelisega töötlemine parendas kiudude ja maatriksi vahelist nakkuvust ning võimaldas kiudude paremat eraldumist pundardest, mistõttu oli sarruse jaotumine PLA maatriksis ühtlasem. Seejärel paranes oluliselt ka komposiitide mehaaniline tugevus.

Tulekindluse katsed näitasid, et parimad tuletõkkeomadused on saavutatavad kombineerides kiudude eeltöötlust leelisega. Komposiitidele oli võimalik prognoosimise teel omistada kõrgeim tuleohutusklass B, mis tähistab materjale mille panus tule intensiivsusele on väga limiteeritud. Tuletõkketöötlus suurendas komposiidi suitsu eraldumist, kuid vähendas põlemise käigus vallanduva süsihappegaasi hulka. Käesolevas töös tuleohutusparameetrid olid oluliselt paremad kui varasemates biokomposiite käsitlevates uurimustes avalikustatud näitajad. Ootuspäraselt vähenes tulekaitse vahendiga töötlemise tulemusena märkimisväärselt komposiitide mehaaniline tugevus. Seda eriti kombineeritud töötluste puhul, mis vähenesid tõmbetugevust 46 % võrra. Mõju paindetugevusele osutus aga statistiliselt mitteoluliseks. Töötluste tulemusena suurenes materjalide jäikus ja haprus. Tuletõkketöötlus vähendas komposiitide niiskuskindlust, mistõttu kõrge õhuniiskuse tingimustes täheldati märkimisväärset tulekaitsevahendi eraldumist materjalist.

Materjali tulekindluse ametlikuks klassifitseerimiseks tuleks läbi viia suuremahulisemad testimised. Materjali edasine arendamine võib veelgi täiendada biokomposiidi funktsionaalseid ja mehaanilisi omadusi.

Kokkuvõtvalt näitavad tulemused, et sääraste komposiitide tuletõkkeomadusi on võimalik märkimisväärselt parendada, tagades optimaalsed mehaanilised omadused. See omakorda loob eeldused biokomposiitide kasutamiseks valdkondades nagu ehitus- ja autotööstus kus on olulised materjali tuletõkkeomadused. Valmistatud komposiite on kõige otstarbekam kasutada kuivades tingimustes ning rakendusteks kus on oluline materjali kaal, tulekindlus ja paindetugevus. Jätkusuutlike materjalide osakaalu suurendamisel on hulgaliselt keskkondlikke ja majanduslikke eeliseid ning vältimatu osatähtsus ELi rohe-eesmärkide saavutamisel.

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APPENDICES

Appendix 1 Determination of suitable Palonot chemicals

Figure 1. shows the reaction to fire test results of composites treated with 15 ml of different FR. Each of the points indicate the ignition time and temperature of a sample treated with one of the Palonot chemicals. Different Palonot fire retardants that were used are indicated as P1-P6. At this stage, samples were tested with a distance of 60mm from the heat source with the heat flux of 50 kW⁻².

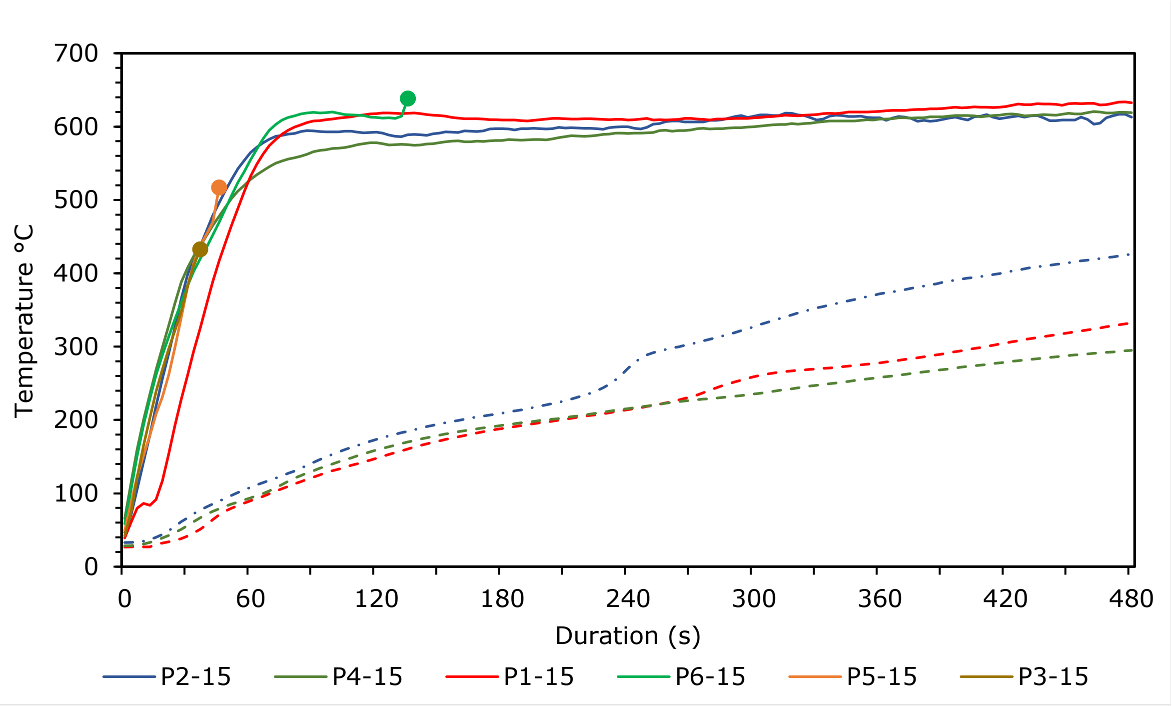


Figure 1. Reaction to fire: Composites treated with 15 ml of different FR (P1-P6), ignition time and temperature results. Lines ending with dots represent the ignition time of the samples, the temperature response underneath the composite is shown with dashed lines for the samples that did not ignite in 480s.

Products 1,2 and 4 did not ignite during the testing period of 8 minutes and charring of the material occurred instead. Temperature underneath the material was lowest for P4 (292 °C) and significantly higher for P2 (426 °C). Chemicals which were able to improve the reaction to fire so that the ignition was avoided were chosen to be used to produce samples for mechanical testing. To determine the suitable chemical that reduces the mechanical strength the least compared to untreated samples, fire retardant treated specimens were prepared and tested (Table 1).

Table 1. Comparison of mechanical performance

FR code	**σ *MPa***	**E GPa**	**MOR *MPa***	**MOE *GPa***
P1	42,7 ± 8,4	9,0 ± 0,1	66,1 ± 19,5	12,1 ± 1,8
P2	47,8 ± 3,4	11,0 ± 0	68,6 ± 14,5	13,5 ± 2,2
P4	48,8 ± 3,4	10,2 ± 0	66,0 ± 10,9	12,7 ± 1,6

P2 and P4 showed higher tensile strength, tensile modulus. P2 showed a slightly higher flexural strength and flexural modulus. As P2 and P4 had better overall mechanical performance, these chemicals were now chosen for further testing.

To further evaluate the effectiveness of the FR treatment, the distance from cone heater was reduced from 60mm to 25mm, the heat flux remained at 50 kW.m^{-2}.
Five (5) samples were prepared consisting of 50 wt. % hemp fibre and FR treatment of 15ml of P2 in outer fibre mats. The data and test results are presented in table 2.

Table 2. Palonot no.2 test sample data and reaction to fire test results

Sample code	**Material weight**	**FR quantity in samples %**	**Ignition time *s***	**Thickness *mm***
P2 - 1	62,40	24%	61	0,31
P2 - 2	61,77	23%	30	0,33
P2 - 3	60,65	22%	50	0,31
P2 - 4	60,60	24%	60	0,31
P2 - 5	62,50	21%	91	0,39
Average	61,60	23%	58	0,33

Unlike at distance of 60mm, all the samples, on average at 58 seconds. Therefore, it was decided that the amount of FR will be increased to 20ml per fibre mat to delay the ignition further and improve the fire-retardant properties.

Appendix 2. Eurocode classification parameters

Table 3. Classification parameters and limits [114]

Class	Test method(s)	Classification criteria	Additional classification
A2	EN ISO 1182 (1) or	$\Delta T \leq 50$ °C and $\Delta m \leq 50$ % and $t_f \leq 20$s	—
	EN ISO 1716 and	PCS ≤ 3,0 MJ.kg^{-1} (1) and PCS ≤ 4,0 MJ.m^{-2} (2) and PCS ≤ 4,0 MJ.m^{-2} (3) and PCS ≤ 3,0 MJ.kg^{-1} (4)	—
	EN 13823 (SBI)	FIGRA ≤ 120 W.s^{-1} and LFS < edge of specimen and THR_{600s} ≤ 7,5 MJ	Smoke production (5), and flaming droplets/particles (6)
B	EN 13823 (SBI) and	FIGRA ≤ 120 W.s^{-1} and LFS < edge of specimen and THR_{600s} ≤ 7,5 MJ	Smoke production (5), and flaming droplets/particles (6)
	ENISO11925-2 (8) *Exposure = 30s*	Fs ≤ 150 mm within 60s	
C	EN 13823 (SBI) and	FIGRA ≤ 250 W.s^{-1} and LFS < edge of specimen and THR_{600s} ≤ 15 MJ	Smoke production (5), and flaming droplets/particles (6)
	EN ISO 11925-2 (8): *Exposure = 30s*	Fs ≤ 150 mm within 60s	
D	EN 13823 (SBI) and	FIGRA ≤ 750 W.s^{-1}	Smoke production (5), and flaming droplets/particles (6)
	EN ISO 11925-2 (8): *Exposure = 30s*	Fs ≤ 150 mm within 60s	
E	ENISO11925-2 (8) *Exposure = 15s*	Fs ≤ 150 mm within 20s	Flaming droplets/particles (7)
F	No performance determined		

(*) The treatment of some families of products, e.g. linear products (pipes, ducts, cables, etc.), is still under review and may necessitate an amendment to this decision.

(1)For homogeneous products and substantial components of non-homogeneous products.

(2)For any external non-substantial component of non-homogeneous products.

(2a) Alternatively, any external non-substantial component having a PCS ≤ 2,0 MJ.m^{-2}, provided that the product satisfies the following criteria of EN 13823 (SBI): FIGRA ≤ 20 W.s^{-1}; and LFS < edge of specimen, and THR_{600} ≤ 4,0 MJ and s1 and d0.

(3)For any internal non-substantial component of non-homogeneous products.

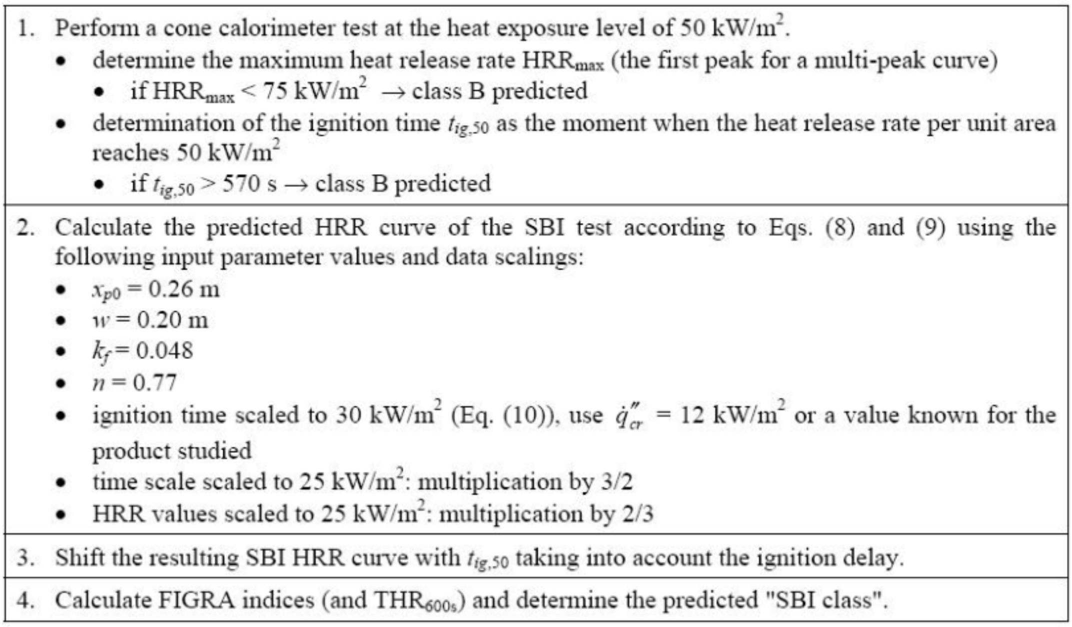
(4)For the product as a whole.

(5)s1 = SMOGRA ≤ 30m^2.s^{-2} and STP_{600s} ≤ 50m^2; s2 = SMOGRA ≤ 180m^2.s^{-2} and TSP_{600s} ≤ 200m^2; s3 = not s1 or s2.

(6)d0 = No flaming droplets/particles in EN 13823 (SBI) within 600s; d1 = no flaming droplets/particles persisting longer than 10s in EN 13823 (SBI) within 600s; d2 = not d0 not d1; ignition of the paper in EN ISO 11925-2 results in a d2 classification.

(7)Pass = no ignition of the paper (no classification); fail = ignition of the paper (d2 classification).

(8)Under conditions of surface flame attack and, if appropriate to the end-use application of the product, edge flame attack.



1. Perform a cone calorimeter test at the heat exposure level of 50 kW/m^2.
   - determine the maximum heat release rate HRR_{max} (the first peak for a multi-peak curve)
     - if $HRR_{max} < 75$ kW/m^2 → class B predicted
   - determination of the ignition time $t_{ig,50}$ as the moment when the heat release rate per unit area reaches 50 kW/m^2
     - if $t_{ig,50} > 570$ s → class B predicted

2. Calculate the predicted HRR curve of the SBI test according to Eqs. (8) and (9) using the following input parameter values and data scalings:
   - $x_{p0} = 0.26$ m
   - $w = 0.20$ m
   - $k_f = 0.048$
   - $n = 0.77$
   - ignition time scaled to 30 kW/m^2 (Eq. (10)), use $\dot{q}''_{cr}$ = 12 kW/m^2 or a value known for the product studied
   - time scale scaled to 25 kW/m^2: multiplication by 3/2
   - HRR values scaled to 25 kW/m^2: multiplication by 2/3

3. Shift the resulting SBI HRR curve with $t_{ig,50}$ taking into account the ignition delay.

4. Calculate FIGRA indices (and THR_{600s}) and determine the predicted "SBI class".

Figure 2. Steps for prediction of SBI test results based on cone calorimetry [65]

Appendix 3 Reaction to fire information

Table A4.6. Taltech reaction fire test data

Sample	**FR, ml**	**FR, %**	t_{ig}, **s**	ig_{temp}, **°C**	t_{prot}, **s**	t_{char}, **s**
UTP2-1	16,49		40	577,09	X	X
UTP2-2	21,46		35	434,25	261	X
UTP2-3	18,2		32	384,03	243	264
UTP2-4	20,61		30	735,99	X	X
Average	19,19	29,8	35	532,84	252	-
Sd.	2,27	2	5	158,21	12,73	-
UTP4-1	21,39		X	-	228	309
UTP4-2	21,59		X	-	231	285
UTP4-3	20,32		220	698,765	156	210
Average	21,1	32,3	-	-	-	268
Sd.	0,68	0,8	-	-	-	51,64
NaP2-1	22,53		96	577,09	X	X
NaP2-2	22,59		X	-	X	X
NaP2-3	22,02		52	434,25	X	X
NaP2-4	23,95		252	735,99	X	X
Average	22,77	33,7	-	582,44	-	-
Sd.	0,83	0,69	-	-	-	-
NaP4-1	22,56		X	X	222	276
NaP4-2	22,49		285	253,3	351	414
NaP4-3	22,57		141	173,65	273	267
Average	22,54	33,7	-	213,475	282	319
Sd.	0,04	0,1	-	56,32	64,97	82,40

Table A.4.7 Meka fire test data

Variation	**Na**		**NaP2**		**NaP4**	
Sample code	Na-2	Na-1	NaP2-1	NaP2-2	NaP4-3	NaP4-4
FR, %	-		34,1 ± 0,2		33,7 ± 0,1	
T_{ig}	23		39	41	493	No ignition

Table A4.9 Elongation at break of produced composite variants

Variant	**Tensile**	**Flexural**
UT	1,2 ± 0,23	1,6 ± 0,12
Na	1,2 ± 0,28	2,1 ± 0,45
UTP2	0,6 ± 0,05	1,1 ± 0,30
UTP4	0,8 ± 0,26	1,6 ± 0,70
NaP2	0,5 ± 0,04	0,9 ± 0,32
NaP4	0,7 ± 0,09	0,8 ± 0,06