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

INVESTIGATION OF LIQUID RESISTANCE AND UV AGEING OF REED-BASED POLYMER COMPOSITES

PILLIROOST VALMISTATUD POLÜMEERIKOMPOSIITIDE VASTUPIDAVUSE UURIMINE VEDELIKES JA UV-VANANEMISELE

MASTER THESIS

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Tallinn 2021

AUTHOR’S DECLARATION

Hereby I declare, that I have written this thesis independently.
No academic degree has been applied for based on this material. All works, major viewpoints and data of the other authors used in this thesis have been referenced.

“24 ” May 2021

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24.05.2021

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THESIS TASK

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main speciality: wood technology
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Thesis topic:
(in English) Investigation of liquid resistance and UV ageing of reed-based polymer composites.
(in Estonian) Pilliroost valmistatud polümeerikomposiitide vastupidavuse uurimine vedelikes ja UV-vananemisele.

Thesis main objectives:

1. Fabricate reed-based composites from polypropylene and polylactide at 50 wt.% loading.
2. Determine the liquid absorption and thickness swelling of the composites.
3. Investigate the influence of UV treatment on the durability of the composites and on the liquid resistance.

Thesis tasks and time schedule:

No	Task description	Deadline
1.	Literature review	30.04.2020
2.	Prepare polymer-reed composite materials.	30.10.2020
3.	Composite UV ageing	19.02.2021
4.	Moisture resistance test	31.03.2021
5.	Determination of composite density	09.04.2021
6.	Additional literature review	30.04.2021
7.	Data collation and analysis	30.04.2021
8.	Final thesis preparation	24.05.2021
9.	Pre-defence of the thesis	14.05.2021
10.	Submission of final thesis	24.05.2021
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CONTENTS

PREFACE

Topic for this thesis was initiated between the research group of the laboratory of wood technology, Tallinn University of Technology, and “Sutu OÜ” Company. All the required experimental work was done at Tallinn University of Technology, mainly in the Laboratory of Wood Technology. I received support from my supervisors, Dr. Heikko Kallakas, Researcher, and Percy Festus Alao, Early Stage Researcher, as well as from Catherine Kilumets, Engineer in the laboratory. And I would like to express gratitude to them for their support on the way to graduation.

This thesis investigated composite materials with reed, treated with color pigments, and two different matrices – polylactide and polypropylene. Their moisture and artificial weathering resistance parameters were studied. As a result of the work done, we can conclude that the resulting material performed adequately in terms of durability parameters and that the combination of reed and polymers can be used in the fabrication of durable sustainable composites.

Keywords: Reed; Composite materials; Polypropylene; Polylactide; UV ageing; Master thesis

List of abbreviations and symbols

NFPC – Natural fiber polymer composites
PP – Polypropylene
PC – Polycarbonates
PLA – Polylactide
PHB – Polyhydroxybutyrate
WPC – Wood polymer composite
PVC – Polyvinyl chloride
HDPE – High density polyethelene
FT-IR – Fourier transform infrared spectroscopy

1. INTRODUCTION

Composite materials are multicomponent materials consisting of a base – a matrix, and fillers that play strengthening and some other roles. They are widely used in various spheres of life from domestic appliances to building materials and structures. One of the major advantages of composite materials is the ability to produce materials with the required qualities, physical characteristics, and mechanical properties by combining various matrices and fillers and changing them quantitatively [1].

In the modern world, more and more interest is shown in "bio-friendly" materials due to the worsened environment. These materials do not leave harmful effects on the environment. The use of natural fibers such as plant fibers, is one of the solutions in this situation because of their ability to decompose after use without polluting the environment. Natural fibers are increasingly used in conjunction with biobased polymers, which makes produced composite materials even more environmentally friendly [2, 3].

The aim of the thesis is to examine suitability of reed in the development of polymer composite. Main objectives of this work were to fabricate reed composites from polypropylene and polylactide, to determine the liquid absorption and thickness swelling of the composites, to investigate the influence of UV treatment on the durability of the composites and on the liquid resistance.

The reed was obtained in October-November 2019 from Saaremaa island and provided by Sutu OÜ, reed particle size was less than 0.3 mm. Composite materials test specimens prepared by hot-pressing contained 50 wt.% of reed (neat untreated reed and reed treated with two color pigment) and 50 wt.% of polymer matrix. The material was characterized by swelling in thickness, liquid absorption, and color and gloss change measurements after immersion to different liquids. Degradation of the materials under UV radiation influence for 12 weeks was followed by color and gloss measurements. Test samples after UV treatment were also immersed in liquids, to investigate the influence of UV degradation on the liquid absorption and swelling in thickness.

2. LITERATURE REVIEW

2.1 Composite materials

Composite materials are multicomponent materials, consisting mainly of a polymer matrix reinforced with a filler or fiber. Composites can be natural, such as wood or artificially created, such as ferroconcrete.

The combination of dissimilar substances in composite manufacture leads to the creation of a new material, the properties of which differ significantly from the properties of each of its components. By varying the composition of the matrix and the filler, their ratio, orientation, using special additional reagents, etc., a wide range of materials with the required physical and mechanical properties are obtained. For example, the necessary values of strength, heat resistance, modulus of elasticity, abrasion resistance, as well as magnetic, dielectric, radar absorbing, and other special properties are achieved [1].

2.2 Types of materials used in composite materials

Matrices in composite materials are metals, polymers, cements, and ceramics. As fillers, a wide variety of artificial and natural substances are used in various forms (coarse, sheet, fibrous, dispersed, finely dispersed, micro dispersed, nanoparticles).

Recently, great interest has been shown in composite materials based on a polymer matrix of artificial and biological origin reinforced with plant fibers. This interest is due to the desire to use biodegradable materials with acceptable properties and to reduce un-decomposable solid wastes.

Polymer matrix composites are widely used in a variety of applications due to enhanced properties such as high specific stiffness and strength, high impact, abrasion and corrosion resistances, and better chemical resistance. They also have a low thermal resistance and a high coefficient of thermal expansion. Polymer composites are made up of a polymer matrix and inorganic or organic fillers, which may be natural or synthetic. Typically, fillers help to improve the necessary properties of polymers while also lowering the associated cost. Because of their improved thermal, mechanical, chemical, and barrier properties, polymer matrix composites are recently used as engineered materials for a wide range of applications in a variety of fields, including aerospace, automobile, sports, medical, electronics, civil, communications, energy, military, marine, construction, industry, and various household item applications [4].

Fibers from plants such as cotton, reed, hemp, jute, sisal, pineapple, ramie, bamboo, banana, etc., as well as wood and seeds of flax and other types of agricultural waste are used as the reinforcing material in plastics. The use of plant waste allows to make eco-friendly and biodegradable materials [1].

Natural fiber polymer composites (NFPC) have gained a lot of attention in numerous applications due to superior advantages of natural fiber compared to synthetic fiber in terms of low cost, abundant sources, biodegradability, low weight, minimal health hazards, improved surface finish of molded parts composites, less damage to processing equipment, and relatively good mechanical properties [5].

In India, natural fibers such as coir, sisal, hemp, jute, date palm, and sugarcane bagasse, as well as fillers such as coconut shells, groundnut shells, and rice husks, are widely available. When mixed in the right proportions with polymers (both thermoplastic and thermosetting), these fibers can be used to improve their mechanical and thermal properties. Waste fiber/fillers are used in a variety of applications, ranging from small mini parts to details in the aerospace industry. It can provide double benefits, such as the replacement of conventional materials providing composite materials at a lower cost and the reduction of agricultural waste [6].

2.3 Natural/crop-based materials for composite

Among all-natural fibers, cellulose fibers are the most often used for polymer matrix composite reinforcement. cellulose fibers are derived from a variety of plant components, including leaves, roots, fruits, seeds, etc. The properties of fibers vary and can be determined by different parameters like crop's location, plant species, climatic conditions, soil type, water supply, fiber age, mode of transportation, and storage conditions [7].

Fibers from plants such as cotton, hemp, jute, sisal, pineapple, ramie, bamboo, banana, etc., as well as wood and seeds of flax have some valuable properties, for example high mechanical strength and excellent biocompatibility. Table 2.1 shows some of the properties of readily utilized plant and synthetic fibers. These materials are used as the reinforcement in polymer matrix composites. They have gained more attention and growing field in materials technology [8].

Table 2.1 Properties of some readily utilized plant and synthetic fibers [8]

Fiber	**Density, g/cm^3**	**Elongation, %**	**Tensile strength, MPa**	**Young's modulus, GPa**
Abaca	1,5	3-10	430-760	12,0
Bagasse	1,25	-	290	17,0
Bamboo	0,6-1,1	-	140-230	11-17
Cotton	1,5-1,6	7,0-8,0	287-597	5,5-12,6
Hemp	1,48	1,6	690	70,0
Jute	1,3	1,5-1,80	393-773	26,5
Kenaf	1,4	1,5	930	53,0
Sisal	1,5	2,0-2,5	511-635	9,4-22,0
Carbon	1,4-1,75	1,4-1,8	4000	230-240
E-glass	2,5-2,55	2,5	2000-3500	73
Viscose	-	11,4	593	11,0

Table 2.2 presents the chemical composition of some selected fibers. It is essential to know the physical and chemical properties of the fibers, since the quality and characteristics of the composite materials obtained on their basis depend on them.

Table 2.2 Chemical composition of plant fibers [8]

Fiber	**Cellulose, %**	**Hemicellulose, %**	**Lignin, %**	**Pectin, %**
Abaca	62,5	21	12	0,8
Bagasse	37	21	22	10
Bamboo	34,5	20,5	26	-
Cotton	89	4	0,75	6
Jute	67	16	9	0,2
Kenaf	53,5	21	17	2
Sisal	60	11,5	8	1,2

Sharma et al. [6] provided information on some important fibers/fillers that are commonly used in polymer composites. Sisal fiber is a versatile fiber that can be used in short or long forms with a variety of resins. For example, it is used with polylactide with surface modifications and coupling agents to improve adhesion with the matrix.

Because coir fiber has a lower cellulose content than other fibers, it must be treated before being processed. The length of the coir fiber has an impact on the composite's strength, and the low interfacial strength between the fiber and the epoxy affects flexural strength [6].

Jute fiber is very compatible with a variety of resins. When compared to sisal fiber composite, jute fiber composite has superior properties. Jute fibers added to both polypropylene and epoxy improves wear resistance under sliding of composites [6].

Bamboo fiber is used in the production of polymer composites in both powdered and fiber forms. It has a wide range of applications in the automotive and building insulation industries. The tensile strength of the bamboo fiber reinforced epoxy composite is higher than that of the jute fiber reinforced epoxy composite. These fibers can also be combined to create a hybrid composite [6].

Various resins have been successfully used to create Kenaf fiber composites. When mixed with polyester, it has a better sliding wear resistance than epoxy [6].

Sugarcane bagasse has a lot of potential for being used as an agriculture waste. After being washed, dried, and chemically treated, bagasse can be used with polymeric material to improve mechanical properties. Alkali-treatment removes impurities and wax of sugarcane bagasse therefore improves properties of the composites [6].

2.3.1 Reed

Reed is one of the most widely distributed and highly productive wetland plant in the world. Since the reed is very fast growing, it is frequently cut, consequently making the raw material widely available [9]. Reed forms extensive thickets along the banks and river deltas in countries with warm and temperate climates. A moisture-loving plant grows along the banks of reservoirs, mostly at a depth of one and a half meters, along swamps and meadows, in the vicinity of groundwater in forests. Often found in forest and forest-steppe regions of the Northern Hemisphere. In the deltas of the Dnieper and Danube, industrial harvesting of common reed (Phragmites australis (Cav.) Trin. ex Steud.) is carried out. It grows in several regions of the Netherlands, mostly in nature conservation areas [10]. Figure 2.1 shows the general view of the reed during growth.

Figure 2.1 General view of the reed [11].

Reed is one of the oldest natural building materials, usually combined with dirt and wood, from which shelters and houses have been created for millennia. Reed has many different uses: for example, its stems or canes are used as a building material for huts, roofs, fences, etc. [2]. Recently, reed is used as a renewable material for construction applications. For example, in flooring and roofing slabs, lightweight cement composite as a filling component to improve mechanical properties [9]. Additionally, it is utilized in landscape design as a material for fences, wind deflector walls, blinds meadows and tree protection [2]. Experimental study on the mechanical properties of reed stalk was carried out and the compression, tensile and bending properties of reed stalk in the harvest time was gained [11]. The specimens were prepared, and experiments were conducted within 72 hours after harvesting. Table 2.3 describes the compression, tensile and bending properties of the reed stalk.

Table 2.3 Mean values of the compression, tensile and bending parameters of reed stalk [11]

Compression experiment	Mean compression force	161,31 N
	Mean compression strength	2,69 MPa
	Mean elasticity modulus	75,52 MPa
Tensile experiment	Mean tensile force	49,87 N
	Mean tensile strength	16,45 MPa
	Mean elasticity modulus	433,19 MPa
Bending experiment	Mean bending force	17,92 N
	Mean bending strength	2,15 MPa
	Mean fracture deflection	5,54 mm

A. Nourbakhsh and A. Ashori [12] investigated the use of agro-waste materials (corn stalk, reed stalk, and oilseed stalk) as thermoplastic reinforcement to analyze and understand their applicability as an alternative to wood fibers for polymer composites. Agricultural byproducts are a great alternative to wood since they are abundant, widely distributed, and easily available. Agricultural wastes can be beneficial to the economy, the climate, and technology, in addition to their availability and renewability. The important chemical components and fiber morphology of reed stalk are presented in Table 2.4 [12].

Table 2.4 Chemical compositions and morphological characteristics of the used materials [12]

Chemical components	**Reed stalk**
Cellulose (%)	48.2 (1.9)
Lignin (%)	22.7 (0.8)
Extractives (%)	3.2 (0.3)
Ash (%)	1.1 (0.3)
Fiber morphology	
Length (mm)	0.98 (0.09)
Aspect ratio (L/D)	46.5 (2.8)

The influence of reed fiber loading on mechanical properties has been investigated. The overall trend showed that adding agro-waste materials improves the composites' tensile and flexural properties dramatically. Pure polypropylene (PP) samples with the same parameters as the composites had tensile and flexural moduli of 1.25 GPa and 1.13 GPa, respectively. While for PP/reed (45% reed fiber, 53% PP, 2% MAPP) composite samples these parameters were 2.3 GPa and 3.3 GPa [12].

2.4 Polymer matrix

For various uses, different kinds of polymers are used in fiber reinforced polymer composite materials. Each polymer has unique properties and different levels of moisture absorption and degradation sensitivity. The polymer selection requirements can range depending on the application areas. The choice of appropriate polymer is critical, particularly in the field of chemical and corrosion conditions. In addition, the polymer matrix plays no significant role in tensile strength improvement in FRP systems. The type of polymer used as a matrix, on the other hand, has a major impact on the interlaminar shear strength and compressive strength [13].

2.4.1 Polypropylene

Polypropylene is a thermoplastic polymer obtained by polymerization of propylene (propene) in the presence of metal complex catalysts.

Polypropylene has the lowest value of density in general for all plastics, it is hard (resistant to abrasion), heat-resistant (begins to soften at 140 °C, melting point 175 °C), almost does not undergo corrosion cracking. It has a high sensitivity to light and oxygen (sensitivity decreases with the introduction of stabilizers) [14]. The indicators of the main physical and mechanical properties of polypropylene are given in Table 2.5.

Table 2.5 Physical and mechanical properties of polypropylene [15]

Physical and mechanical properties	**Values**
Density, g/cm^3	0,90–0,91
Melting point temperature, °C	186
Flexural modulus, MPa	1389
Yield strain, (L/L_0), %	34,5
Izod Impact strength, J·m^{-1}	27

Polypropylene is usually processed by injection molding, pressing and extrusion.

Items made from polypropylene retain their shape at temperatures up to 150 °C, however, at 140 °C the strength modulus is only 10% of this characteristic at room temperature, so that the practical operating temperature does not exceed 135 °C. The use of polypropylene at low temperatures is limited by a relatively high brittle temperature (from -10 to +20 °C) [14].

Abou-Zeid et al. [16] investigated untreated and benzylated reed reinforced polypropylene composites and characterized through mechanical and physical properties (tensile and flexural strength and modulus, water absorption) and scanning electron microscopy (SEM). Flexural and tensile strength of the benzylated reed PP composite was greater than that of the pure polymer, while the same characteristics of composite materials with untreated reed were vice versa lower than that of pure polymer. With increase of fiber content from 30% to 40% slight deterioration in the flexural strength was observed, however, tensile strength increased significantly. Flexural and tensile modulus increased greatly for both fiber content mainly due to the presence of the fibers whether untreated or benzylated. Water absorption of composite materials was higher than of the pure polypropylene. Although, water absorption of benzylated reed composite was significantly lower than the untreated fiber composite. That was because benzylation reduces amount of hydroxyl groups in the molecules of reed fibers, which are responsible for water absorption. Finally, SEM photographs in Figure 2.6.1 showed that untreated reed polymer composites had poor adhesion between fibers and matrix, while polypropylene reinforced with benzylated reed had stronger adhesion. This is evidenced by debonding phenomena of the untreated reed fiber in Figure 2.2 A while in Figure 2.2 B the surface of benzylated reed is embedded with the plastic particles [16].

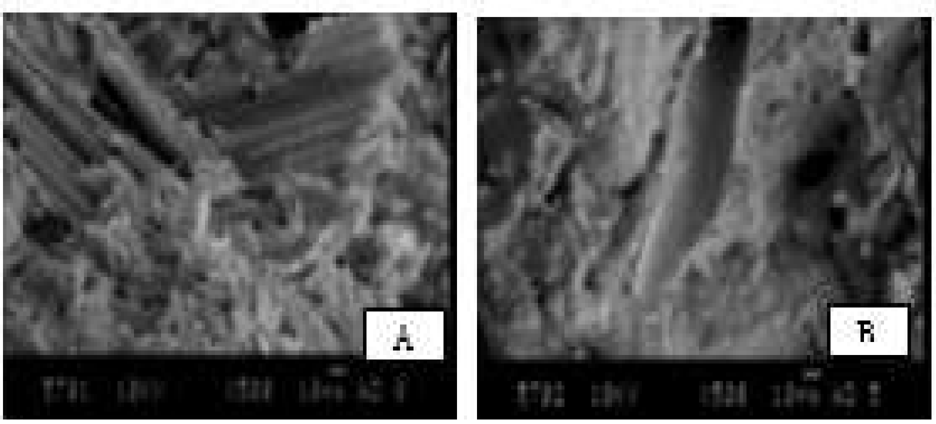


Figure 2.2 SEM photographs of fracture surface of untreated reed filled PP (A) and benzylated reed filled PP (B) [16]

Bartos et al. [17] investigated composite materials made of polypropylene and sugarcane bagasse fibers. Alkali-treated and untreated fibers were used in this study. Latter were used as reference. Alkali treatment increases composite stiffness and strength, according to the observations. At about 5% NaOH content of the treating solution, these properties reach their maximum. The change in inherent fiber characteristics was related to the increase in properties. The fracture initiation stress and fracture energy of composites increase as the inherent strength of the fibers increases. Interfacial adhesion has a minor impact on stiffness, but it has a much larger impact on strength and impact resistance. Alkali treatment improves inherent fiber strength, which is proportional to composite strength.

2.4.2 Polycarbonate

Polycarbonates (PC) – a group of thermoplastics, polyesters of carbonic acid and dihydric alcohols of the general formula $(\text{-O-R-O-CO-})_n$. Of greatest industrial importance are aromatic polycarbonates, primarily Bisphenol A-based polycarbonate. Polycarbonates are highly resistant to heat, oxygen, gasoline, oils. It is quite resistant to the action of acids and alkalis. They are used for the manufacture of fibers, films, varnishes. They are easily processed by extrusion or injection molding into products with good mechanical properties and heat resistance [14].

In the processing of polycarbonates, most of the methods for processing and molding thermoplastic polymers are used: injection molding (manufacturing of products), blow molding (various kinds of vessels), extrusion (production of profiles and films), molding of fibers from melt. In the production of polycarbonate films, molding from solutions is also used – this method allows one to obtain thin films from polycarbonates of high molecular weight, the formation of thin films from which is difficult due to their high viscosity. Methylene chloride is usually used as a solvent. Some values of physical and mechanical properties of polycarbonate are given in Table 2.6.

Table 2.6 Physical and mechanical properties of polycarbonate [15]

Physical and mechanical properties	**Values**
Density, g/cm^3	1,20
Tensile strength, MPa	65,5
Tensile modulus, MPa	2380
Flexural strength, MPa	93,1
Flexural modulus, MPa	2340
Yield strain, (L/L_0) %	6–8
Izod Impact strength, J·m^{-1}	850
Glass transition temperature, °C	150

2.4.3 Polylactide

Polylactide (PLA) is a biodegradable, biocompatible, thermoplastic, aliphatic polyester, the monomer of which is lactic acid. Annually renewable resources such as corn and sugarcane serve as raw materials for production. It is used to produce products with a short service life (food packaging, disposable tableware, bags, various containers), as well as in medicine, to produce surgical sutures and pins [7].

There are two methods for the synthesis of polylactide: polycondensation of lactic acid and polymerization of lactide. A combination of these is used in industry. By polycondensation of lactic acid, only low molecular weight polylactide can be obtained, since a by-product is released in the process – water, which is difficult to divert from the reaction, and therefore the growing polymer chain is destroyed. The resulting low molecular weight polylactide is depolymerized to a lactic acid dimer, lactide. The resulting lactide is polymerized at high temperature with the addition of a tin octanoate catalyst, to obtain a high molecular weight polylactide [7].

Both lactic acid and lactide exhibit optical activity, that is, they exist in the form of two L- and D-stereoisomers, which are mirror images of each other. By varying the relative content of these forms in polylactide, one can set the properties of the obtained polymer, as well as obtain various classes of polylactide materials. Polylactide from 100% L-lactide (L-PLA) has a high degree of stereoregularity, which gives it crystallinity. Glass transition temperature of L-PLA: 54–58 °C, melting point 170–180 °C. Using a mixture of D- and L-forms of lactide during polymerization, an amorphous polylactide (L, D-PLA) is obtained, the glass transition temperature of which is 50–53 °C, and there is no melting, since there is no crystalline phase [7].

The highest melting point of the stereo complex, consisting of pure L-PLA and pure D-PLA. The two chains are intertwined, and the additional interactions formed between them lead to an increase in the melting temperature (up to 220 °C). Some physical and mechanical properties of polylactide are given in Table 2.7.

Table 2.7 Physical and mechanical properties of polylactide [15]

Physical and mechanical properties	**Values**
Density, g/cm^3	1,25–1,29
Tensile strength, MPa	28–50
Tensile modulus, MPa	1200–3000
Elongation at break, %	2,0–6,0
Shear strength, MPa	54,5
Bending strength, MPa	132
Melting point temperature, °C	145–186
Glass transition temperature, °C	53–64

Yu et al. [18] reviewed the effect of surface treatment on the properties of PLA/ramie composites. It was seen that incorporation of ramie fibers into polylactide improved the tensile properties compared to pure polymer. The maximum tensile strength was 66.8 MPa (composite with 30% of ramie fibers treated by NaOH) whereas tensile strength of neat PLA was 45.2 MPa and of composite with untreated ramie fibers was 52.5 MPa. Similarly, impact, flexural and dynamic mechanical properties were improved. This improvement in the properties was due to better compatibility and bonding at the interface between the polylactide matrix and ramie fibers.

Comparative studies between flax fiber reinforced with polylactide and polypropylene composites have been conducted in the [19], which showed significant improvements in tensile modulus for polylactide reinforced with flax. Tensile modulus values for pure PLA and composites with 30% and 40% of flax fibers content were 3.4 GPa, 8.3 GPa and 7.3 GPa respectively.

Bartos et al. [20] presents a study of composite materials from polylactide and sugarcane bagasse fiber. Since the adhesion of the fibers to polymers is often rather poor, it was modified with a maleated PLA binder. Tensile and impact testing were used to determine the mechanical properties of the composites, whereas local deformation processes by acoustic emission testing and microscopy. Even without coupling, good adhesion between the fibers and PLA results in high strength. Acoustic emission testing and microscopy analysis of local deformation processes revealed that three local processes occur in the material during deformation: debonding, shear yielding, and fiber fracture. PLA that has been modified with sugarcane bagasse fibers has significantly increased stiffness, almost constant tensile strength, and slightly increased impact resistance, resulting in a material with a good combination of properties for structural applications.

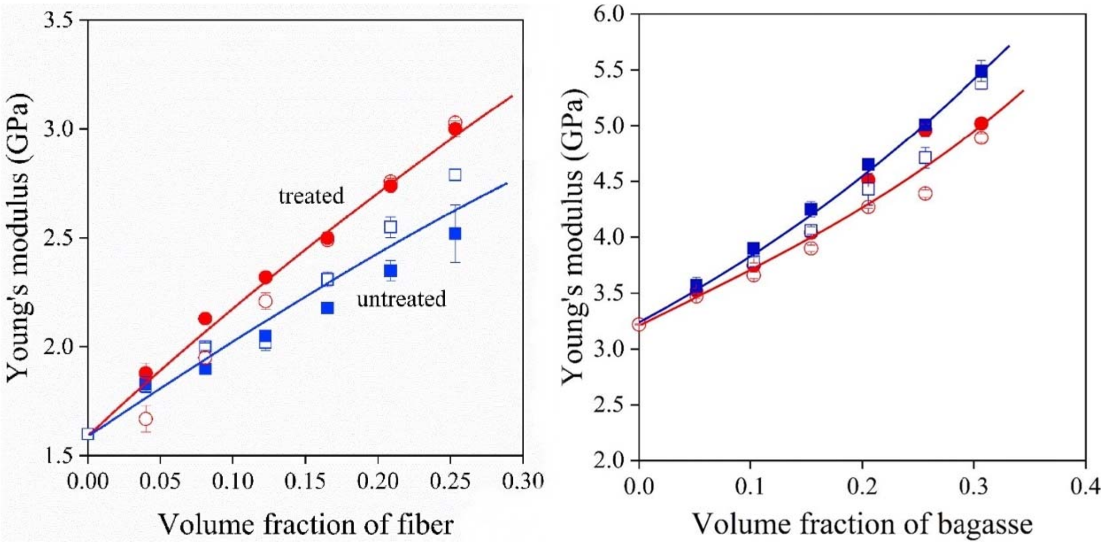
2.4.4 Comparison of PP, PC, PLA.

As PLA has a glass-transition temperature of 53-64 °C and a melting temperature between 145-175 °C it can be processed by conventional methods such as injection molding, blow molding, extrusion and film forming operations. The mechanical properties of PLA are either similar or often superior to petrochemical polymers, such as polypropylene. For this reason, polylactide can be used instead of petrochemical polymers such as polypropylene and polyethylene, for example in the field of single-use packaging. However, polylactide has a low toughness due to its brittle nature and has a molecular weight significantly lower in comparison with other polymers. Adding natural fillers in polymer matrix helps to overcome the brittle nature of polylactide [21].

Composite materials based on a polylactide matrix are widely recognized as a noble substitute for polymer composites obtained from petrochemical raw materials such as polyolefins. They are biodegradable and have high mechanical characteristics. However, the use of PLA is limited by some weak characteristics, such as relatively poor impact properties, due to the brittleness of polylactide, and also by the limited supply and higher cost of PLA compared to conventional polymers such as polyethylene and polypropylene [21]. Prices of PLA, HDPE, PP and PET in 2016 were 1.8 USD, 1.3-1.6 USD, 1.4-1.6 USD and 1.4 USD respectively [22].

Blends of polypropylene with polycarbonate have attracted great attention in the field of polymer research. Addition of polypropylene improves the process ability of polycarbonate. Polypropylene is an extremely versatile plastic, also available as a copolymer (ethylene/propylene). It has the lowest density among all thermoplastics (about 0.9 g/cm^3), high strength, stiffness, as well as excellent fatigue and chemical resistance. All this makes polypropylene attractive for many applications. It is also available in the form of fiber (for ropes, carpet) and in the form of a film (for packaging). Polycarbonate is an engineering plastic which has many advantages over conventional materials in terms of mechanical and physical properties. These plastics are transparent and have good heat resistance and high toughness but are exposed to alkaline solutions and hydrocarbon solvents. Polycarbonate is used in various fields, for example, anti-vandal street lamp covers, baby bottles, car covers and casings, camera parts, electrical components, protective equipment and CDs are made from this polymer [23].

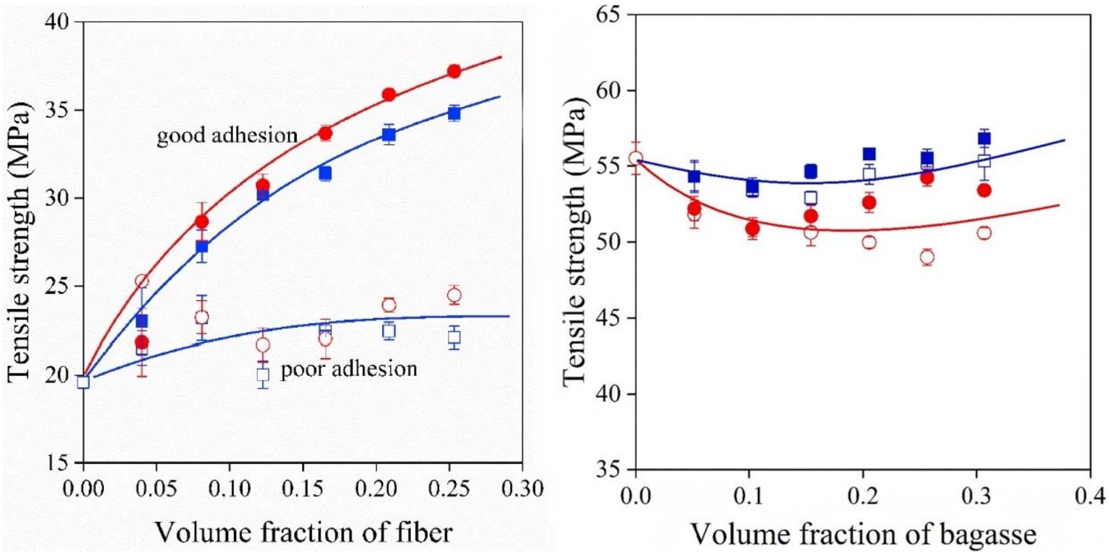
Different studies [17] [20] mentioned earlier investigated composite materials with one filler – sugarcane bagasse fibers, but different matrices - polylactide in one case and polypropylene in the other. Their physical parameters such as tensile strength and stiffness depending on the content of the fibers and its treatment were studied. For the PP/sugarcane bagasse fiber with alkali treatment (5 wt% NaOH) composites, the stiffness value varied from 1.5 to 3.0 GPa according to fiber content, while in the case of the PLA/bagasse fiber composites, these values were from 3.2 to 5.5 GPa according to fiber content. Results for stiffness can be seen in Figure 2.3. Accordingly, the stiffness of the composite material with polylactide is approximately two times higher than for the material with polypropylene as a matrix.



a b

Figure 2.3 The stiffness of PP/sugarcane bagasse fiber composites plotted against fiber content. Effect of alkali treatment (5 wt% NaOH) and coupling. Symbols: (□) untreated, (■) untreated, MAPP, (○) alkali treated, (●) alkali treated, MAPP, [17] (a); Effect of composition, fiber characteristics and interfacial adhesion on the stiffness of PLA/bagasse fiber composites. Symbols: (○) short, no MAPLA, (●) short with MAPLA, (□) long, no MAPLA, (■) long, MAPLA, [20] (b)

A similar dependence is observed in the case of tensile strength (see Figure 2.4). The tensile strength values for composites with polypropylene varied from 30 to 34 MPa according to the fiber content of the composites. For the composites based on polylactide, the values were from 49 to 56 MPa.



a b

Figure 2.4 Correlation between the tensile strength of PP/sugarcane bagasse fiber composites and fiber content. Symbols: (□) untreated, (■) untreated, MAPP, (○) alkali treated, (●) alkali treated, MAPP, [17] (a); Tensile strength of PLA/bagasse fiber composites plotted against fiber content. The influence of fiber dimensions and coupling. Symbols: (○) short, no MAPLA, (●) short with MAPLA, (□) long, no MAPLA, (■) long, MAPLA, [20] (b)

In all cases, with the exception of the tensile strength of the composite material with polylactide, the values of the physical parameters increased with an increase in the content of fibers in the material.

2.4.5 Polyhydroxybutyrate

Polyhydroxybutyrate (PHB) is a biodegradable homopolymer with a high degree of crystallinity and it has consequently stiff and brittle mechanical properties. To increase flexibility of PHB a plasticizer or natural filler materials can be added or a copolymer of PHB, for example, polyhydroxybutyrate-cohydroxyvalerate (PHBV) can be used [24] [25].

The PHB has also properties of special interest like biocompatibility and biodegradability. It is used in fields of the pulp and paper industry including the use as granules for internal sizing. PHB can be completely biodegraded by numerous microorganisms. This polymer is prepared by bacterial fermentation. These bacteria have to be capable of biosynthesizing polyesters as energy storage media [15]. Some physical and mechanical properties of polyhydroxybutyrate are given in Table 2.8.

Table 2.8 Physical and mechanical properties of polyhydroxybutyrate [15]

Physical and mechanical properties	**Values**
Density, g/cm^3	1,262
Tensile strength, MPa	20–60
Tensile modulus, MPa	1400–2200
Extension at break, %	6,0
Flexural modulus, MPa	800–4000
Young’s modulus, MPa	700–3500
Melting point temperature, °C	137–170
Izod Impact strength, J·m^{-1}	35-400

Barkoula [26] studied biodegradability of the flax reinforced to polyhydroxybutyrate composite. It was seen that the presence of fibers improved the biodegradation behavior of the composite as the lignocellulosic fibers can degrade in short period.

Table 2.9 Mechanical properties of natural fiber reinforced biopolymer composites [27]

Matrix / Fiber	PLA/kenaf	PLA/hemp		PHBV-Ecoflex/jute	PHBV-Ecoflex/abaca
Processing method	Compression molding	Injection molding		Injection molding	
Modification	–	–	coupling agent	–	–
Tensile Strength, MPa		72,1	72–74	35,2±1,3	28,0±1,3
Tensile modulus, GPa	5,73±1,20	2,0–2,5	2,2–2,4	7,0±0,26	4,4±0,06
Strain at break, %	1,48±0,05	52	65–70	0,8±0,0	0,9±0,1
Flexural strength, MPa	–	90–100	100–105	–	–
Flexural Modulus, GPa	–	6–7	5,8–6,0	–	–

From various studies it was investigated that reinforcing biopolymers with natural fibers leads to improved biodegradation behavior because of the lignocellulosic nature of the fibers which can degrade in short period. Additionally, it results in improved mechanical properties. Table 2.9 shows some important properties achieved with polymer fiber reinforcement [27]. Mechanical properties of polyhydroxybutyrate-based and polylactide-based composites are presented for comparison.

2.5 Production method

There is a wide selection of methods (hand lay-up, pultrusion, compression molding, injection molding, vacuum bagging, spray up, resin transfer molding, vacuum infusion molding, filament winding, and solution casting) of reinforcement of polymers with plant fibers to form composite materials. These methods typically include wetting, mixing, or saturating of fibers and matrix together into a rigid structure using a chemical and thermal reaction [5].

One of the major factors influencing the mechanical properties of fiber reinforced polymer composites is the production method. As a result, the manufacturing phase is expected to influence the composite's durability. Based on specified values of processing parameters, the properties of the composite can be varied in each manufacturing process. During the processing, control parameters such as pressure levels, speed, curing time, and temperature may be changed. The mechanical properties of compression molded composite materials are less than those of vacuum infusion. This is due to the presence of more microvoids in compression molded composites, which reduce the mechanical characteristics. Since there are far less microvoids in the vacuum infusion process, fiber reinforced polymer composites may have better mechanical properties. Regardless of other factors, it is the safest procedure for producing composites since closed infusion will only produce relatively low levels of dangerous products and vapor during manufacturing [13].

Extraction of plant fibers consists of retting where core tissues are collected by separation of inner stem and outer, after which required single plant fibers separated from core tissues and obtained by manual mechanical separation process or the use of a decorticator [8]. Then plant fibers are pre-treated for further production of composites, which includes drying, baling, and milling [10].

For thermoplastic bio-composites manufacturing process includes defibrillating the plant fiber in resin, followed by impregnation of inorganic fiber in composite and dispersion of fibers to get composites. After combining, composites are formed through injection or compression molding. The last one is preferred, as the impact resistance of composites is higher than in case of injection molded parts [8].

Bio-based fiber-composite from reed-like plant Typha sp. can be produced without additional binding agent. Typha fibers are collected into mats which were compression molded to panels. Role of binder acted naturally occurring constituents of cattails. This "green" composite's mechanical properties due to self-gluing were remarkable [28]. Composite materials made of melted HDPE and fine reed fibers without coupling agent are obtained using a single screw extruder. In case of thermoplastic matrices that feature processing temperatures above 200 °C use of natural fibers may be inadequate as most natural fibers have low degradation temperatures (≃200 °C) [29].

In the manufacturing process of composites with well-balanced mechanical properties, the following steps should be controlled:

- Homogeneous dispersion of the fibers in the matrix;
- Well-balanced interaction between the matrix and the fibers to allow fiber pull-out;
- Low porosity of the matrix;
- Optimized percentage of fibers: enough to reinforce the material while allowing a continuity of the matrix [8].

2.6 Factors influencing the performance of composite materials

Natural fibers have many advantages compared to synthetic fibers such as low cost, availability, biodegradability, low density, minimal health hazards, improved surface finish of molded parts composites, less damage to processing equipment and satisfactory mechanical properties [5, 8].

On the other hand, there are some disadvantages associated with the use of natural fibers as reinforcement in polymer composites. These are fiber degradability, incompatibility between fibers and polymer matrices, inferior fire resistance, poor moisture resistance, limited processing temperatures and others. These issues may lead to degradation of mechanical properties of natural fiber polymer composites. High moisture absorption leads to poor processability and low mechanical performance of composites. The incompatibility between natural fibers and polymer matrices leads to low interface strength as compared to glass or carbon fiber composites. And low degradation temperatures of natural fibers limit the choice of thermoplastics for composite matrix [30].

To prevent some fibers disadvantages additional pre-treatment processes may be carried out. Interfacial treatment can help to overcome limited processing temperatures drawback. In conditions of high humidity, it is worth choosing appropriate fibers with lower content of hemicelluloses which are responsible for moisture absorption [30]. Atiqah et al. [3] found that the water absorption and thickness swelling increases with fiber content which advises to select the optimal content of natural filler in the composite material.

The ability of lignocellulosic fiber composites to absorb water is a key feature that determines their end-use applications. Abou-Zeid et al. [16] investigated that water absorption of reed fiber reinforced composites is reduced significantly compared to untreated reed fiber in all composites, but still higher than pure polymer composites. It was due to benzylation of reed fiber which lowers the hydroxyl groups in the cell wall of reed fiber molecules.

The stability of fiber reinforced polymer composites for thermal and hydrothermal ageing is well known to prevent catastrophic deterioration in an aquatic environment. Since one of the most major factors affecting the strength and stiffness of fiber reinforced polymer materials is temperature. The polymer-based materials' elastic modulus and strength decrease with rising temperature under continuous operating conditions due to thermal softening [13].

Natural fiber composites exposed outdoor with direct sunlight are subjected to ultraviolet radiation. Under these conditions they undergo two competing redox reactions. First reaction is formation of paraquinone chromophoric structures due to the oxidation of lignin. It causes yellowing of WPCs. Second reaction is reduction of these structures to hydroquinones, which results in photobleaching [30].

For faster ageing testing, an accelerated weathering process is used, which is carried out in ageing chambers. In these chambers, test specimens are subjected to controlled exposure of ultraviolet radiation, moisture, and heat. NFPC materials subjected to this process change both the polymer matrix and natural fibers within the matrix resulting in color fading due to lignin and water-soluble products leaching from the samples and partial shrinkage causing bending of samples [30].

Plastics that are exposed to sunlight may age, and natural fibers may degrade if they are exposed to water or a humid atmosphere. Both these factors reduce the composites' efficiency. WPCs suffer performance degradation and internal structural damage, such as matrix plasticization and surface blistering, when exposed to the outdoors and degradative medium [31].

When exposed to sunlight for a prolonged period of time, the mechanical properties of wood polymer composites (WPC) deteriorate, and the appearance fades due to photooxidation and photodegradation. In outdoor applications, solar radiation has a major impact on the service life of WPCs. The output of WPCs is also affected by humidity or aqueous conditions such as rivers or oceans. The aim of [31] was to investigate the performance of four different plant fiber reinforced polyvinyl chloride (PVC) composites in two different degradation environments: the first was immersion in simulated seawater plus xenon lamp aging, and the second was deionized water spraying plus xenon lamp aging. The study of the deterioration and aging mechanisms of four different forms of WPCs would help to encourage their use in the marine and commercial fields. The simulated seawater degradation using a xenon lamp results in a decrease in two-phase mass and an increase in crack. The plant fibers swell, exposing the fibers to the surface without being PVC coated, increasing the distance between the fibers and polymer and increasing the amount. After soaking the wood-plastic composite material in simulated seawater, sections of exposed plant fibers are fully stripped away, and color is deepened [31].

The effects of accelerated weathering on the properties of high-density polyethylene composites reinforced with fire retardants and microcrystalline cellulose were investigated in the [32] report. According to the results of the study, all the samples lost their initial gloss during the weathering process. Weathering results in microscopically rough and uneven degradation, resulting in gloss loss and roughness increase. Photoactive ion on the wood surface was also thought to cause glossiness loss. During the weathering phase, all samples were light in color, and the lightning effect continued for several samples until the end of the test. The composites containing microcrystalline cellulose had higher values of lightness difference than composites without it. This was most likely due to microcrystalline cellulose's UV absorption capability.

Regarding surface chemistry results, the drop in cellulose peak intensity may indicate that some cellulose degradation occurred during weathering. As the number of carbonyl groups increases after exposure, so does the number of chain scissions, resulting in more oxidation in high density polyethylene (HDPE) [32].

The article [33] studied the effects of outside and accelerated (xenon-arc and UVA) weathering on the visual appearance and chemical changes of wood plastic composite based on high density polyethylene and polypropylene. Colorimetry, scanning electron microscopy, Fourier transform infrared spectroscopy (FT-IR), and pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS) techniques were used to investigate visual and chemical changes.

Weathering of WPC resulted in a definite color change, mostly surface lightening, because of continued exposure time, according to the [33] report. Crazing and wood degradation were discovered after prolonged exposure period on weathered HDPE and PP-based WPC surfaces. In this analysis, three stages of degradation were identified. The surface layer of weathered WPC was first eroded, resulting in some cavities. Second, during both accelerated and external weathering, the extent and scale of the cavities increased with increased exposure time. The second stage was accompanied by the appearance of minor cracks on the weathered surface of WPC.

The relationship between chemical and color changes that occurred during exterior weathering of HDPE-based WPC was developed as a result of [33] research. Lightness was found to have a good association with wood lignin degradation ($r = 0.94$), carboxylic acid concentration ($r = 0.93$), and esterification ($r = 0.87$). As a result of deligninification and oxidation, exterior-weathered HDPE-based WPC becomes lighter.

The effect of UV radiation on fiber reinforced composites under accelerated ageing conditions and the prediction of lifetime performance are critical as mentioned in [13]. Figure 2.5 depicts the detailed information on processes and changes in the external look of fiber reinforced polymer composite structure that occur under UV radiation.

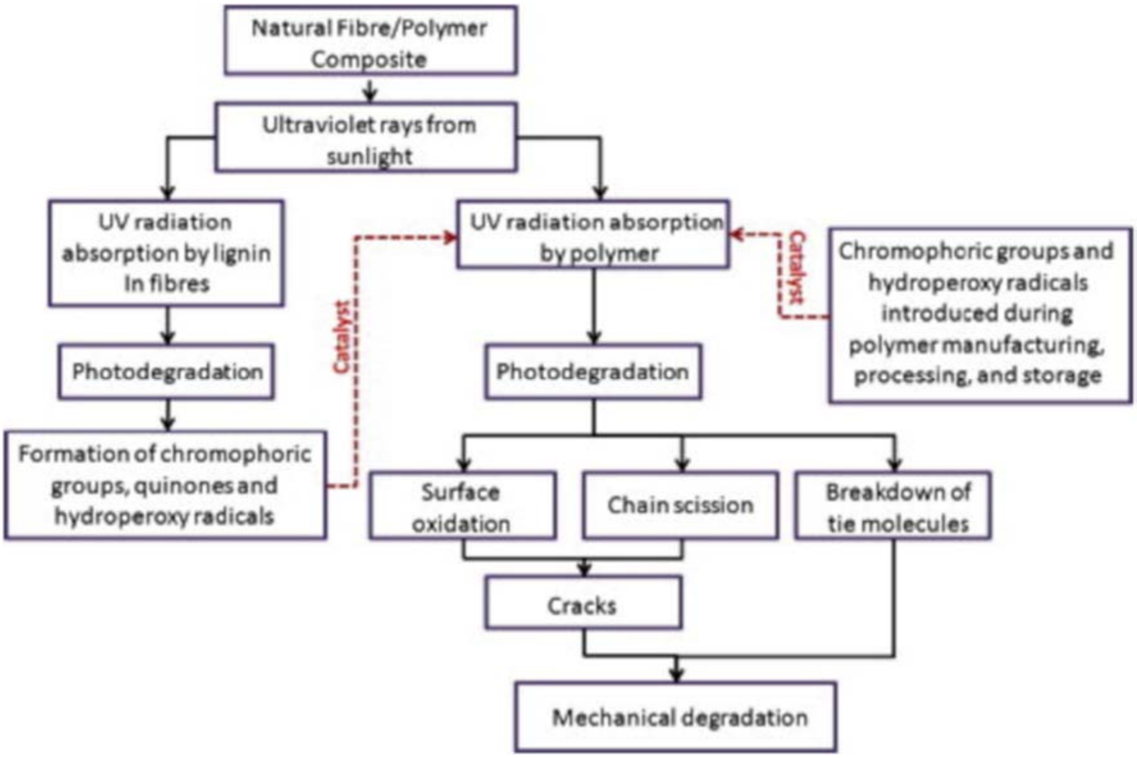


Figure 2.5 Degradation process on natural fiber-based polymer composites due to penetration of UV radiation [13]

2.7 Application of reed composites

The composite containing reed stalk and thermoplastic polymer can have excellent bonding strength and high density, and excellent strength (tensile strength, bending strength, impact strength, and flexibility). It can be used for building material including interior material (flooring material, internal material, furniture material, noise barrier and doors and windows), landscaping material (railing, fence, louver, and post) and exterior material which is installed on the outer wall of a building [34].

The aim in the [28] article was to show the technological potential of fully bio-based, binder-free composites made from the reed-like plant Typha sp. In spite of the coarse nature and texture of the raw fiber material and typha based fiber mats, panels demonstrated excellent surface smoothness and good heat insulation characteristic due to reeds porosity, making this innovative composite material highly appealing for light-weight applications requiring high surface performance criteria, such as powder-coated elements for the automotive and furniture industries.

The flexural properties of reed fibers reinforced natural hydraulic lime mortars were studied in the [35] article. The results of this study are important in understanding their flexural behaviour and providing scientific proof of the effectiveness of giant reed fibers in the production of green building masonry application materials such as bricks and laying mortars.

3. MATERIALS AND METHODS

3.1 Materials

Polymer matrix. Two types of polymers were used as a matrix in the composites. Polypropylene PPH 11012 Total Petrochemicals production in the form of granules with a melt flow index of 55 g/10 min and density of 0.905 g/cm^3. And polylactide-based biodegradable polymer compound Bio-Flex® S 7514 FKuR Kunststoff GmbH production in the form of granules with a melt flow index of 24 g/10 min and density of 1.37 g/cm^3.

Reed used as a filler was provided by Sutu OÜ. It was obtained in October-November 2019 from Saaremaa island. Reed powder size was less than 0.3 mm.

Pigments of black and blue colors were used for reed dying from the supplier Majatohter.

3.2 Methods

The composite materials were tested on durability. For that, the pure PP and PLA and their composites with reed (untreated and colored) were immersed in different liquids (water at temperatures of 25 °C and 70 °C and ethanol (70% concentration) to determine swelling in thickness and liquid absorption. Additionally, some samples of the pure PP and its composites were aged in the UV chamber and subsequently immersed in the liquids to observe the effect of UV degradation on the composites. The Color and gloss change for all the specimens was observed during the UV test and before and after immersion in the liquids. Due to time constraint, only the PP-based composites were subjected to UV ageing. For effective analysis of the results, the polymer boards and composite densities were also measured.

3.2.1 Fabrication of the composite materials

The composite preparation process consists of the following steps. The blend of polymer and reed were made in three colors – natural, blue and black, and with proportions of 50 wt.% of matrix and 50 wt.% of filler. Initially the reed powder was dried at 80 °C to constant weight. After drying, a batch of the powder was treated with blue and black color pigments. For this treatment, 3.4 l of water and 400 g of each pigment were used per 1 kilogram of reed. All components were mixed to a homogeneous mass and dried at 80 °C to a constant mass. The dried colored reed powder was crushed in a mortar and sieved (mesh size 315 µm).

The neat and colored reed powder was mixed with the polymers (PP/PLA), dried to a constant mass, and then pelletized in the Plasti-Corder PLE 651 extruder. Pellets were milled into small particles using cutting mill Retsch SM 100. The resulting mixture was dried at 80 °C for 24 h. Then approximately 35 g of PP-based composite mixture and 45 g of PLA-based composite mixture were transferred to the pressing frame with dimensions of 130*130*2 mm and pressed with CARVER hotpress. At first, mixture was melted at 180 °C for 5 minutes, then a pressure of 1.32 MPa was applied for 10 minutes, and finally the composite boards were cooled. The composite fabrication process is shown in Figure 3.1.

Figure 3.1 The scheme of preparation process

Nomenclature of samples used in the study is presented in Table 3.1.

Table 3.1 Nomenclature of samples

Type of samples	Abbreviation
Pure Polypropylene	Pure PP
Neat Reed + PP	R+PP
Black Reed + PP	RB+PP
Blue Reed + PP	RBL+PP
Pure Polylactide	Pure PLA
Neat Reed + PLA	R+PLA
Black Reed + PLA	RB+PLA
Blue Reed + PLA	RBL+PLA

3.2.2 Density determination

Density test was carried out according to ISO 1183-1 standard by immersion method using METTLER TOLEDO AX and MX/UMX Balances. Five (5) replicas with dimensions of 25*25 mm were measured for each of the composite type. The test pieces were weighted in the air to the nearest 0.1 mg and then weighted in distilled water at 23 °C.

The density, ρ_S, in grams per cubic centimeter, of the specimens, was calculated using the following equation 3.1.

$$\rho_S = \frac{m_{S,A} * \rho_{IL}}{m_{S,A} - m_{S,IL}}, \qquad (3.1)$$

where $m_{S,A}$ – the apparent mass of the specimen in air, g,

$m_{S,IL}$ – the apparent mass of the specimen in the immersion liquid, g,

ρ_{IL} – the density of the immersion liquid at 23 °C, g/cm^3.

Knowing the measured densities of polymers and composite materials based on these polymers, and that the proportion of the components of the composites is one-to-one, it is possible to calculate the density of reed from the following equation 3.2 derived in this study (see Appendix 1):

$$\rho_f = \frac{\rho_{cm} * \rho_m}{2\rho_m - \rho_{cm}} \qquad (3.2)$$

where ρ_f – the density of filler, g/cm^3,

ρ_{cm} – the density of composite material, g/cm^3,

ρ_m – the density of matrix, g/cm^3.

3.2.3 Swelling in thickness and water absorption

Swelling tests were carried out with water at the temperature of 25 °C and 70 °C and 70% solution of ethanol in water according to EN 317:1993 standard. Eight (8) replicas with dimensions of 25*80 mm were used for each type of liquid. Thickness and weight of test pieces were measured before test using SCHMIDT DMD-3-1C0958 digital indicator and METTLER TOLEDO AB204-S/FACT balance. Then test pieces were immersed in the water and ethanol at room temperature (25 °C) for 24 hours, and hot water (70 °C) for 2 hours. Following the liquid immersion, test pieces were taken out of the liquids, excess liquid was removed, and thickness and weight of each test piece were measured.

The swelling in thickness, G_t, and liquid absorption, G_w, of each test piece expressed as a percentage of the original thickness and weight, were calculated according to equation 3.3 and 3.4.

$$G_t = \frac{t_2 - t_1}{t_1} \cdot 100, \tag{3.3}$$

where G_t – swelling in thickness, %,

t_1 – the thickness before immersion, mm,

t_2 – the thickness after immersion, mm.

$$G_w = \frac{w_2 - w_1}{w_1} \cdot 100, \tag{3.4}$$

where G_w – liquid absorption, %,

w_1 – the weight before immersion, mm,

w_2 – the weight after immersion, mm.

3.2.4 Color and gloss measurements

Color and gloss change tests were carried out according to ISO 11664-4 and ISO 2813. 8 test pieces with dimensions of 25*80 mm were used. Color and gloss of test pieces were measured before and after immersion in liquids and every week in case with UV ageing test. The surface gloss at 60° geometry (based on EVS-EN 15534-1) was measured with 3NH tri-angle gloss meter HG268. The surface color was measured with 3NH high-quality colorimeter NR60CP. Surface gloss was measured in three parallels for each test piece and surface color was measured on three different points of each test piece.

The color difference (ΔE), of the specimens was calculated according to the equation 3.5.

$$\Delta E = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2}, \tag{3.5}$$

where ΔE – discoloration,

L_1 – the lightness before immersion,
L_2 – the lightness after immersion,
a_1 – the a coordinate before immersion,
a_2 – a coordinate after immersion,
b_1 – the b coordinate before immersion,
b_2 – the b coordinate after immersion.

Lightness ranges from 0 to 100 (the higher the value, the lighter the sample), while positive value of a parameter shows redness, negative – greenness and positive value of b parameter shows yellowness, negative – blueness. This can be represented in Figure 3.2.

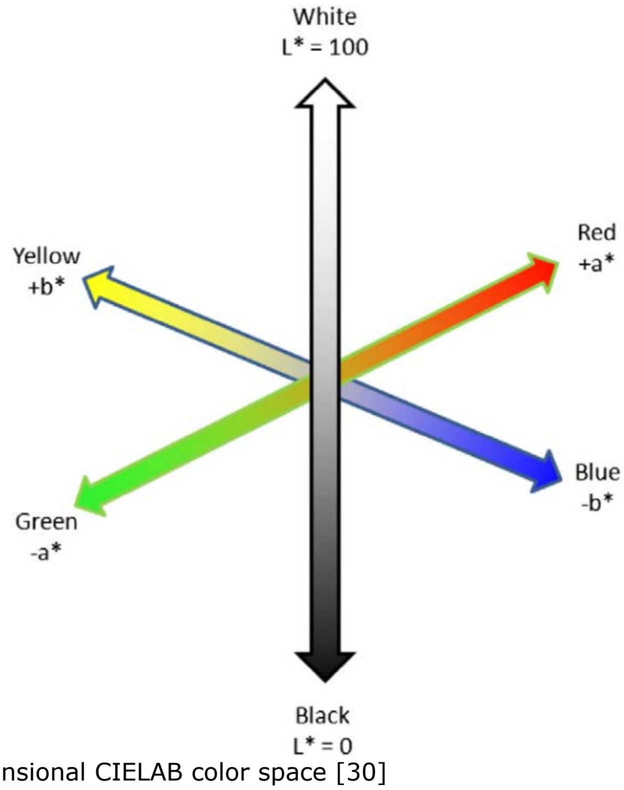


Figure 3.2 Three-dimensional CIELAB color space [30]

3.2.5 Ultraviolet radiation test

Ultraviolet radiation ageing test was conducted according to EN 927-6 standard. Pure PP and PP-based composites with reed samples were placed in the ultraviolet chamber with fluorescent UV-A 351 TL-D 36W BLB 1SL/25 lamps for 12 weeks. Surface color and gloss of test pieces were measured before test. Color and gloss of test pieces surface were measured after 24 hours exposure to the UV and every week afterwards. Test pieces placed in the UV chamber are presented in Figure 3.3.

Figure 3.3 Pure PP and PP with reed test pieces placed to the UV chamber

4. RESULTS AND DISCUSSION

Data obtained during the experiments and used for plotting the graphs are presented in Appendix 1.

4.1 Swelling in thickness and liquid absorption

4.1.1 Composite material samples without exposure to UV

Results for color and gloss change tests after immersion into water at 25 °C, at 70 °C, and ethanol f pure PP, PLA and their composites with reed (untreated and pigmented) without exposure to UV radiation are presented in Figures 4.1 and 4.2.

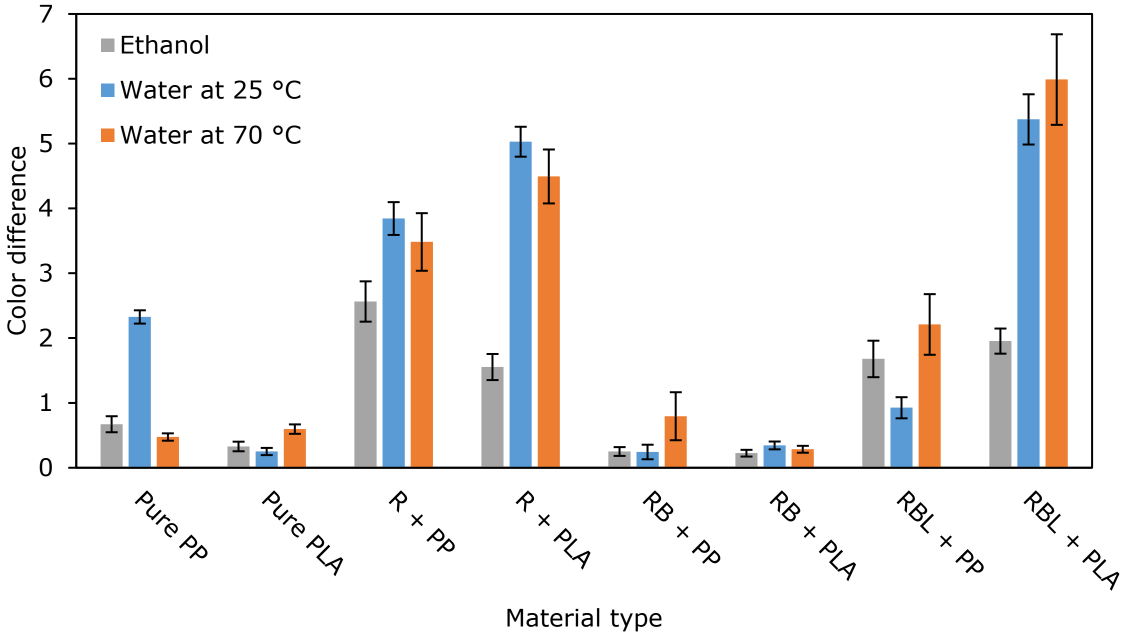


Figure 4.1 Color difference results for non-UV exposed pure PP, PLA and their composites after immersion in liquids

Discoloration of all the samples changed mostly due to change of lightness L. This means that all the samples became either brighter or darker after immersion to liquids. Composite materials experienced greater color change than pure polymer materials. Black colored reed composites among other materials showed best results in color change, which could be due to insolubility of black pigment as its content is Iron (III) oxide insoluble in water and ethanol.

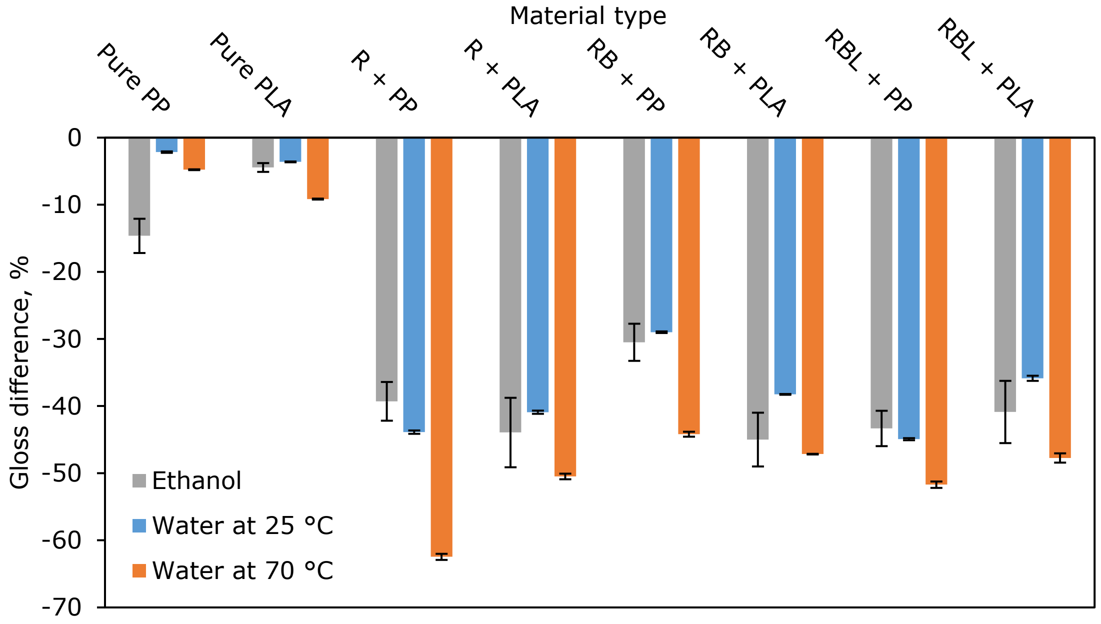


Figure 4.2 Gloss change results for non-UV exposed pure PP, PLA and their composites after immersion in liquids

Gloss of all the samples decreased, which means that they became more matte after immersion in liquids. Pure polypropylene samples gloss change degree is lower after immersion into water at different temperatures compared to polylactide, which may indicate polylactide as a less stable polymer in terms of gloss. Pure polymers showed little change in gloss compared to composite materials, suggesting that reed strongly influences gloss of material when exposed to liquids. The average percentage difference in gloss for pure polymers is -6.5% while for composite materials is -43.3%.

Gloss difference of neat reed composites after immersion in hot water was higher than that of black and blue colored reed composites. Regarding water at 25 °C, the neat reed composite samples showed slightly higher decrease of gloss except reed/PP and blue reed/PP composites as single factor ANOVA analysis performed in MS Excel (α=0.05) showed no significant difference between those parameters (see Appendix 1, Table 1.6). Overall, it can be concluded that colored reed composites gloss decreased less than neat reed composite after immersion into water. In case with ethanol this trend is not proved as according to single factor ANOVA analysis there is no significant difference between colored and neat reed PLA composites (see Appendix 1, Table 1.7).

Swelling in thickness and liquid absorption results after immersion into water at 25 °C and at 70 °C and ethanol of pure PP, PLA and PP-based and PLA-based composite materials with reed samples without exposure to UV radiation are presented in Figures 4.3 and 4.4.

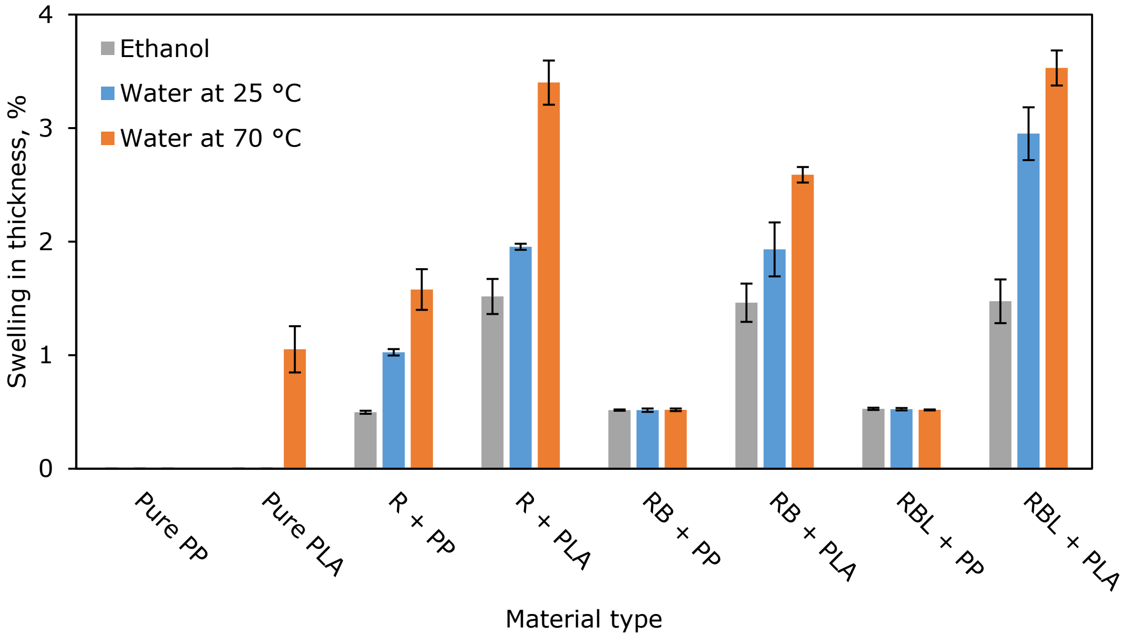


Figure 4.3 Swelling in thickness results for non-UV exposed pure PP, PLA and their composites after immersion in liquids

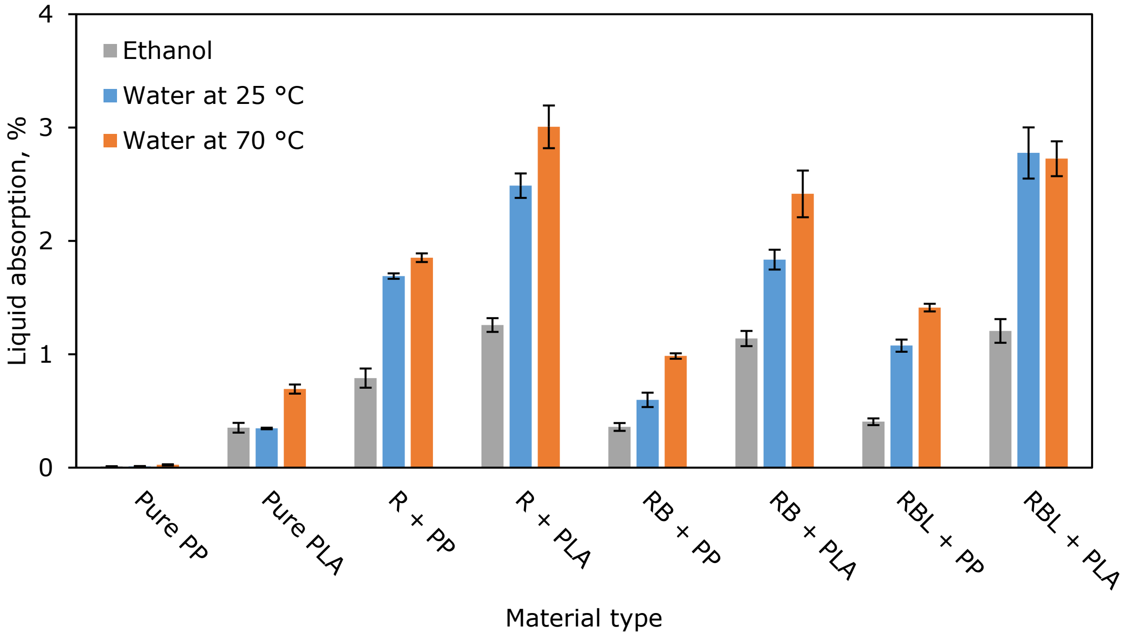


Figure 4.4 Liquid absorption results for non-UV exposed pure PP, PLA and their composites after immersion in liquids

It can be seen from the results that composite materials are more resistant to water at room temperature than to hot water. Pure PLA samples and composite materials samples with PLA as matrix absorbed more liquid and swelled in thickness to a greater extent compared to samples with PP as the matrix. This indicates that PLA is less resistant to moisture than PP, which is not unusual, considering that PP is hydrophobic in nature [36].

Samples made from pure polymers showed significantly better results in **swelling in thickness** than samples containing reed due to fillers hydrophilic nature (pure PP did not swell and pure PLA swelled only after immersion in hot water). Colored reed/PP composites swelled less than neat reed PP composites. While PLA composites do not have the same trend – in different liquids PLA composite samples behave differently. Single factor ANOVA analysis showed that there is no significant difference in swelling in thickness results in ethanol for composites with the same matrix (see Appendix 1, Table 1.8), these results did not exceed 1.52±0.15%. While the highest results were for PLA-based composites after immersion in hot water. PLA composites swelled twice more than PP composites. On average, polylactide-based composites swelled on 1.62% more than polypropylene-based composites.

As in the case with swelling in thickness, **liquid absorption** results of samples made from pure polymers much less than of samples containing reed for the same reasons. Colored reed composite samples absorbed lees liquid than neat reed composites, except for the case with blue reed/PLA composite which slightly absorbed more water at 25 °C based on single factor ANOVA analysis (see Appendix 1, Table 1.9). Liquid absorption of PLA/reed composites was on average 1.08% more than PP/reed composites.

As a result of the test with water at 70 °C most of the samples deformed, acquiring the shape of a bow which can be seen in Figure 4.5.

Figure 4.5 Deformation of PP samples after immersion to water at 70 °C

Abou-Zeid et al. [16] studied composites of polypropylene and reed. Untreated and benzylated reed fibers were used as a filler with 30% and 40% content of each type of the reed. The obtained composites were characterized through mechanical and physical properties including water absorption. Those results are comparable to the results obtained in this work. Research in the article showed that water absorption of pure polypropylene was approximately 0.15%, of untreated reed fiber composites with 40% content – 1.2% and for benzylated reed fiber composites – 0.8%. Water absorption of untreated reed composites from the article is lower than of no color reed composites considered in this work possibly due to lower content of filler, moreover, temperature of water is not mentioned in that research.

Colored composite material with 50 wt.% of reed showed much better resistance in water absorption and swelling in thickness compared to composite material with no color reed.-It might be due to the same reasons as in case with reduction in water absorption of benzylated reed composites in the article [16]. Colored reed probably has less hydroxyl groups in the cell wall of reed fiber what reduces water absorption of fibers.

4.1.2 Composite material samples exposed to UV radiation

Results for color and gloss change tests after immersion into water at 25 °C and at 70 °C and ethanol of pure PP and PP with reed composite materials samples exposed to UV radiation are presented in Figures 4.6 and 4.7.

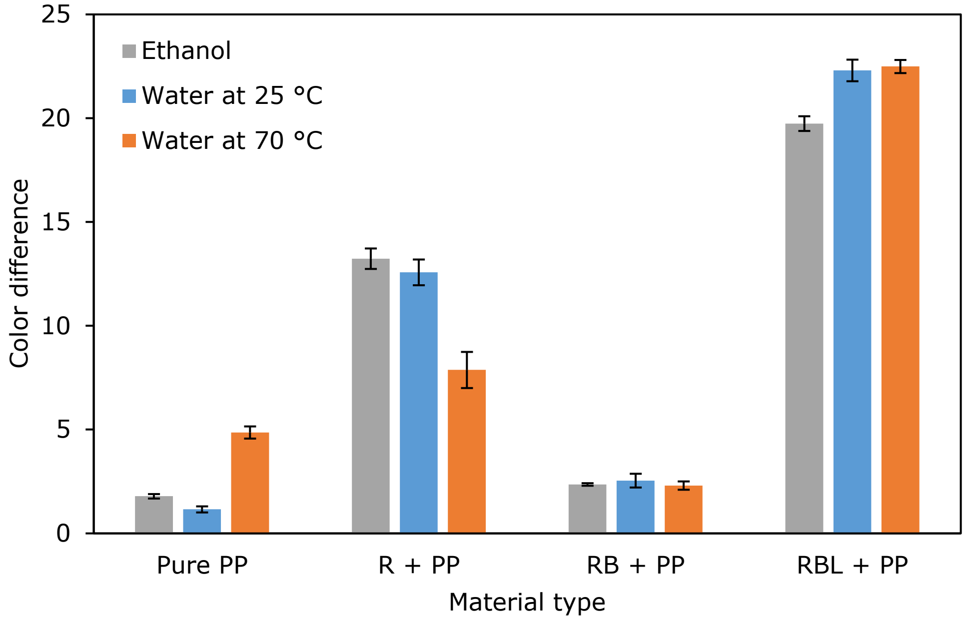


Figure 4.6 Color difference results for UV exposed pure PP and its composites after immersion in liquids

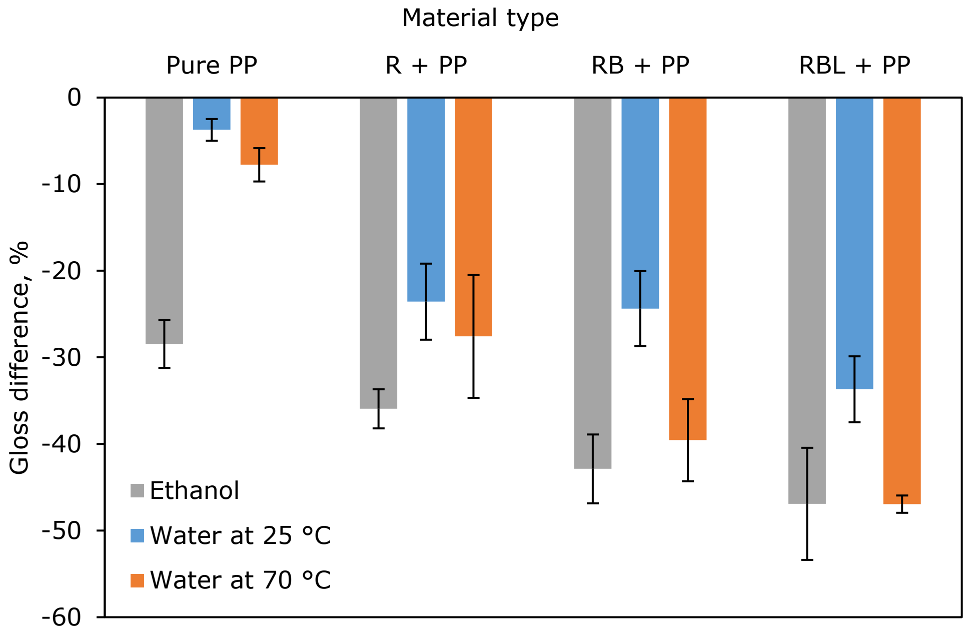


Figure 4.7 Gloss change results for UV exposed pure PP and its composites after immersion in liquids

Liquid absorption and swelling in thickness results after immersion in water at 25 °C and at 70 °C and ethanol of pure PP and PP with reed composite materials samples exposed to UV radiation are presented in Figures 4.8 and 4.9.

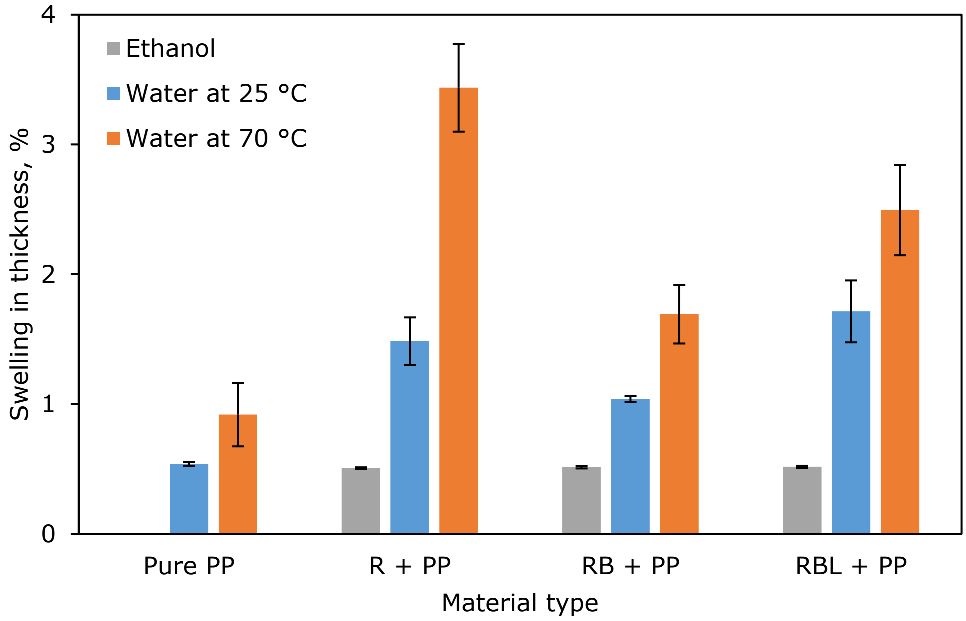


Figure 4.8 Swelling in thickness results for UV exposed pure PP and its composites after immersion in liquids

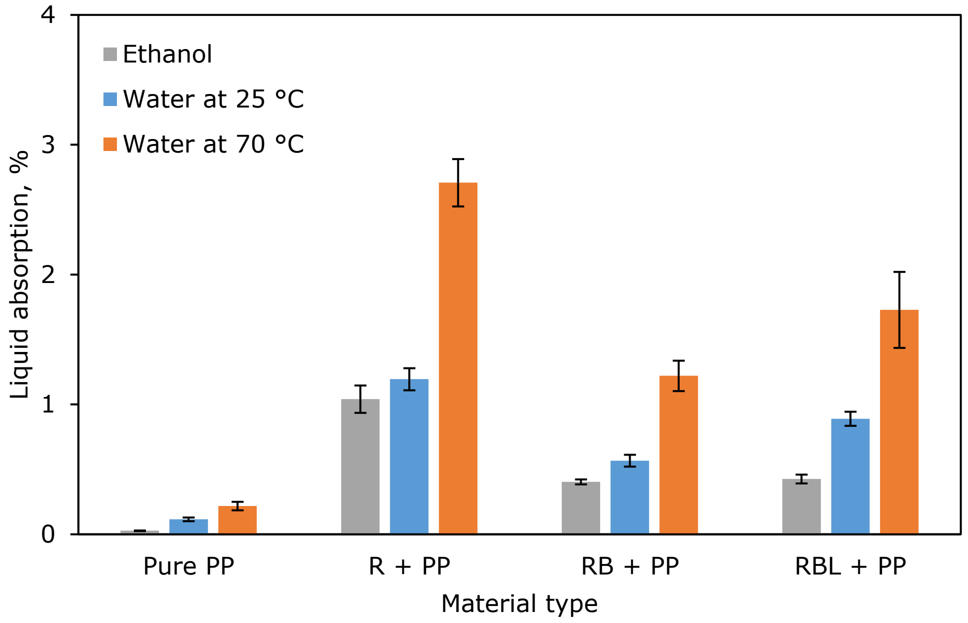


Figure 4.9 Liquid absorption results for UV exposed pure PP and its composites after immersion in liquids

Photos of test pieces before and after exposure to the UV radiation are presented in Figure 4.10.

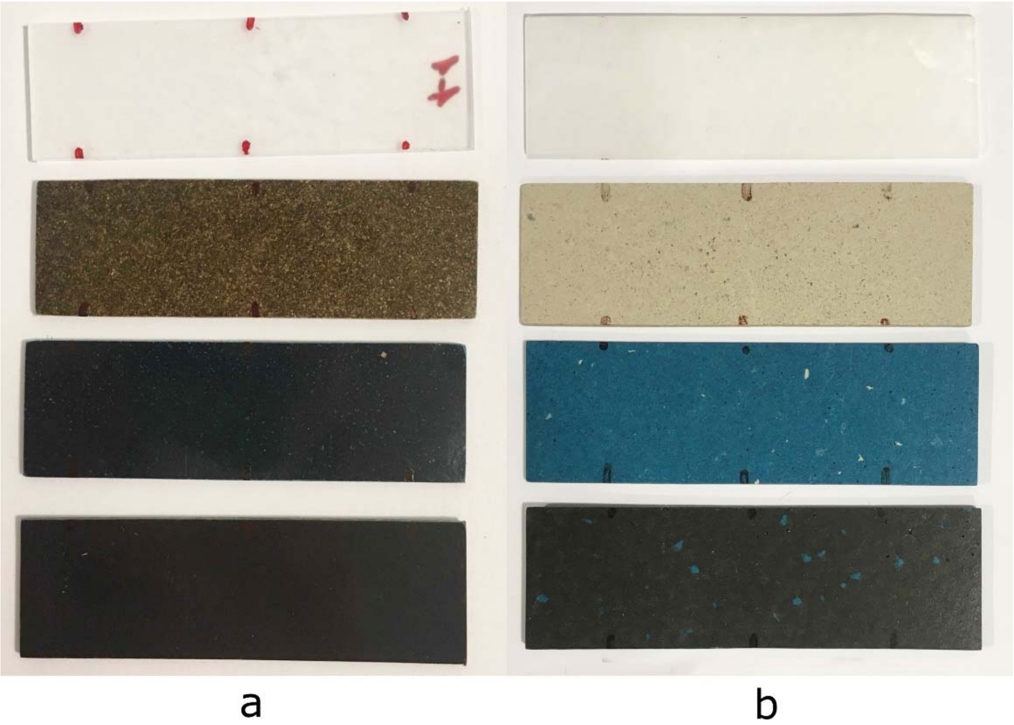


Figure 4.10 Pure PP and PP with reed composite samples before exposure to the UV radiation (a), samples after 12 weeks of UV radiation (b)

The general trend of behavior is the same as for the samples which were not exposed to UV radiation. Pure polypropylene showed the lowest results in terms of parameters, the highest results were for composite material with neat reed.

After the influence of ultraviolet radiation, swelling in thickness and liquid absorption parameters increased in most of the samples. This might be due to destruction of bonds in the cell walls. Therefore, more hydroxyl groups are formed, which increases water absorption of materials.

Pure PP became more matte after exposure to UV as gloss decreased more than in case with PP that was not exposed to the UV radiation. Reasons for that might be the cracks that occurred on the surface of the materials due to changes in crystallinity of the surface as mentioned in the [32] article.

4.1.3 Comparison of results for samples with and without UV exposure

Comparing PP samples with and without exposure to the UV radiation swelling in thickness of all the samples increased except test with ethanol (see Figure 4.11). Swelling in thickness of composites after UV radiation after immersion in water at 25 °C increased on 0.72% averagely comparing to composites without exposure to UV, and after immersion in hot water increased on 1.67% averagely. Increase of this parameter can be explained by possible crazing of the surface which had been revealed in the [33] article.

Lower results of swelling in thickness for ethanol test may be due to size of ethanol molecules which are bigger than of water, so they cannot get into samples so easily. Also ethanol molecules are less polar than molecules of water which leads to weaker hydrogen bonds between ethanol and reed [37]. As in the case with other samples previously, color change was better for black colored reed composites, among other materials, which may be attributed to the insolubility of black pigment (Iron(III) oxide).

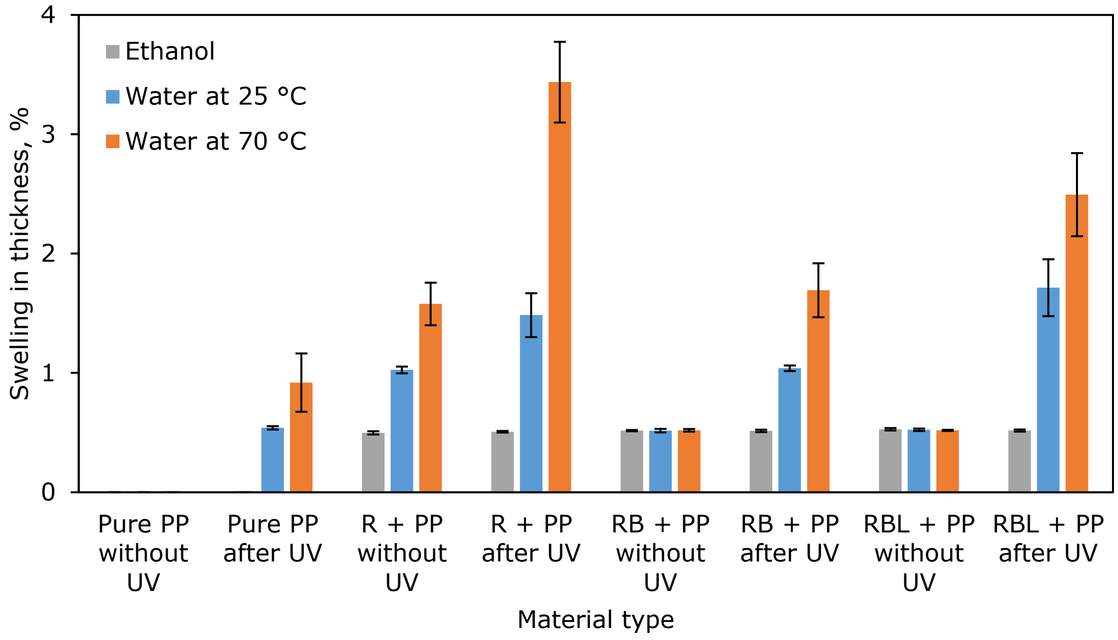


Figure 4.11 Swelling in thickness results for pure PP and PP/reed composites samples with and without exposure to UV

The same trend was observed for color change of the samples. This parameter increased mostly because of increase of lightness. Results can be seen in Figure 4.12. Blue reed/PP composites changed color the most with average increase of 19.9. Blue pigment possibly degraded to soluble products under the influence of ultraviolet radiation, and after immersion in liquids blue pigment washed out.

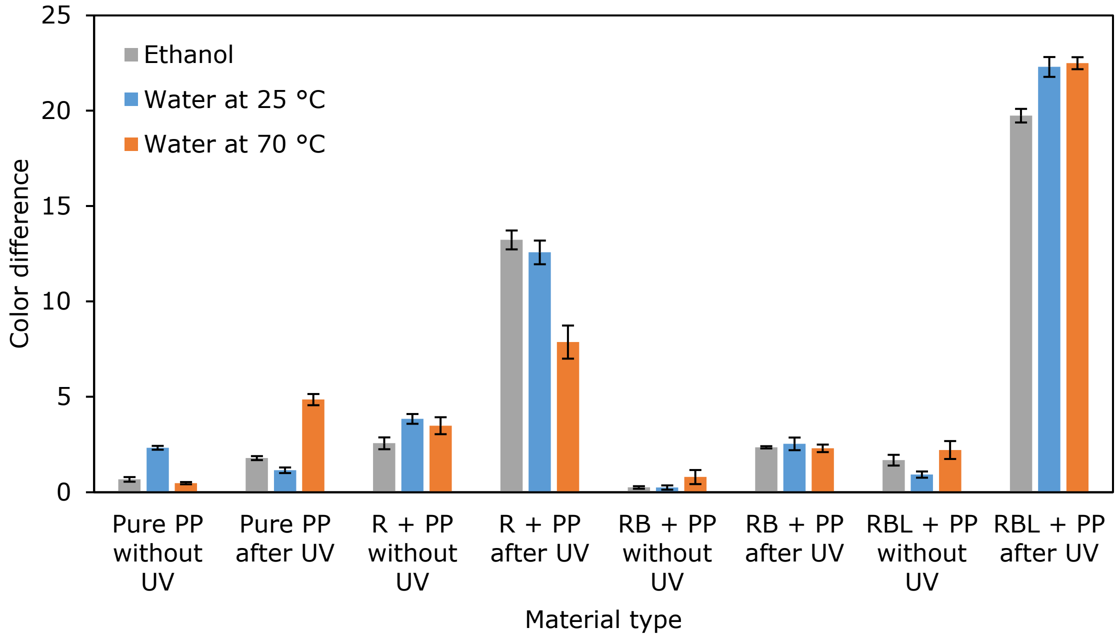


Figure 4.12 Color difference results for pure PP and PP/reed composites samples with and without exposure to UV

4.2 Ultraviolet radiation ageing

Regarding ultraviolet radiation test results for twelve weeks are gained. Composite material samples with neat reed increased **lightness** a lot and blue colored reed showed slight increase in lightness through time, while pure polypropylene and composite material with black colored reed remains almost unchanged in lightness. This may indicate that the black pigment is more stable in comparison with the blue pigment, at the same time neat reed and blue colored reed faded under UV radiation. Lightness results after UV degradation can be seen in Figure 4.13.

Fabiyi et al. investigated a strong correlation between lightness and wood lignin degradation, lightness and carboxylic acid concentration, and lightness and esterification. This proved that delignification and oxidation lead to an increased lightness of exterior-weathered HDPE-based WPC [33].

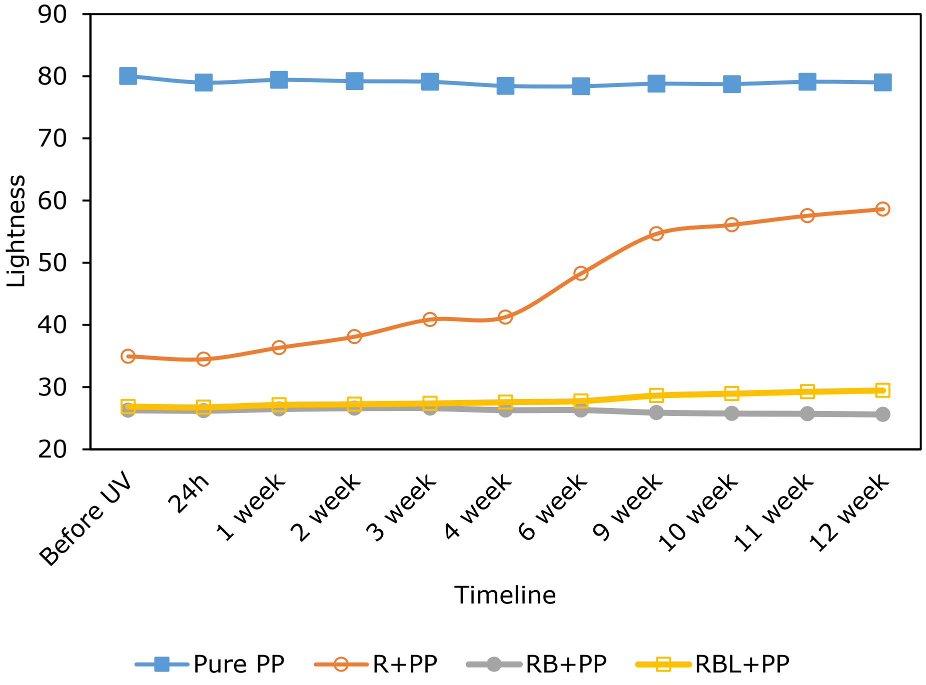


Figure 4.13 Lightness results

Gloss change results after UV degradation are presented in Figure 4.14. Gloss of all the samples did not change a lot in the beginning of the ageing experiment. In the middle of the experiment timeline this parameter values began to decrease. The probable reasons for this phenomenon are the cracks which occurred on the surface of test pieces under influence of UV radiation.

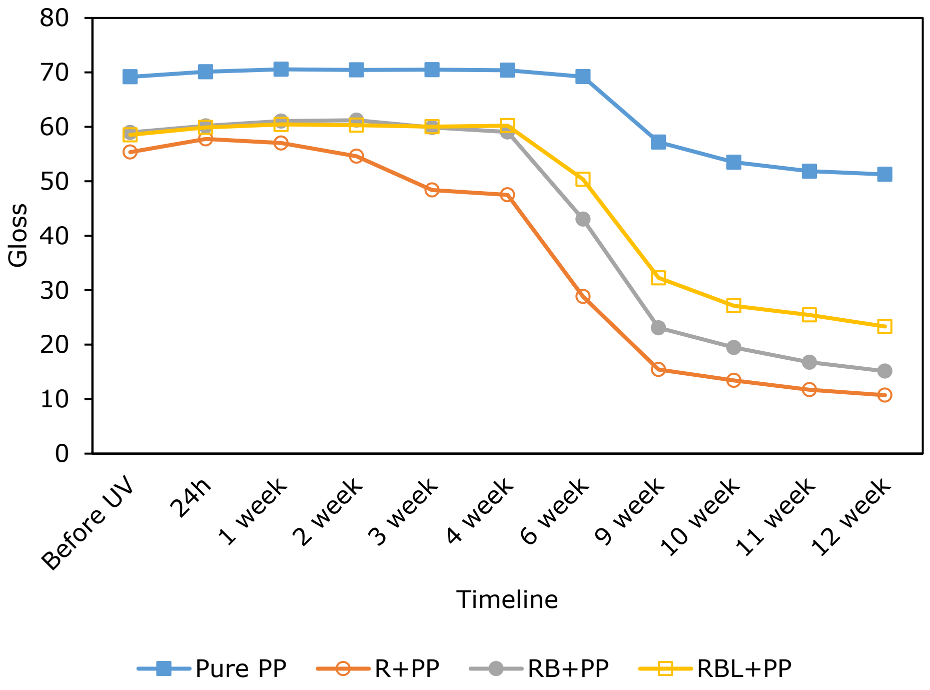


Figure 4.14 Gloss results

Results for the **color difference** ΔE are presented in Figure 4.15. Discoloration of neat reed/PP and blue reed/PP composite materials increases with time while pure polypropylene and black reed/PP composite samples changed color in the beginning of the experiment and behaved stable afterwards. It shows that reed effects color change, neat reed composite samples discolored to a greater extend comparing to colored reed composite samples. It can be said that color pigments protect composite materials from UV degradation. Discoloration of neat reed/PP and blue reed/PP composite materials is mostly due to their change in lightness throughout the ageing test. It was observed in the [33] article that wood polymer composites weathering resulted in a strong color change, mostly surface lightening, because of prolonged exposure time to UV radiation.

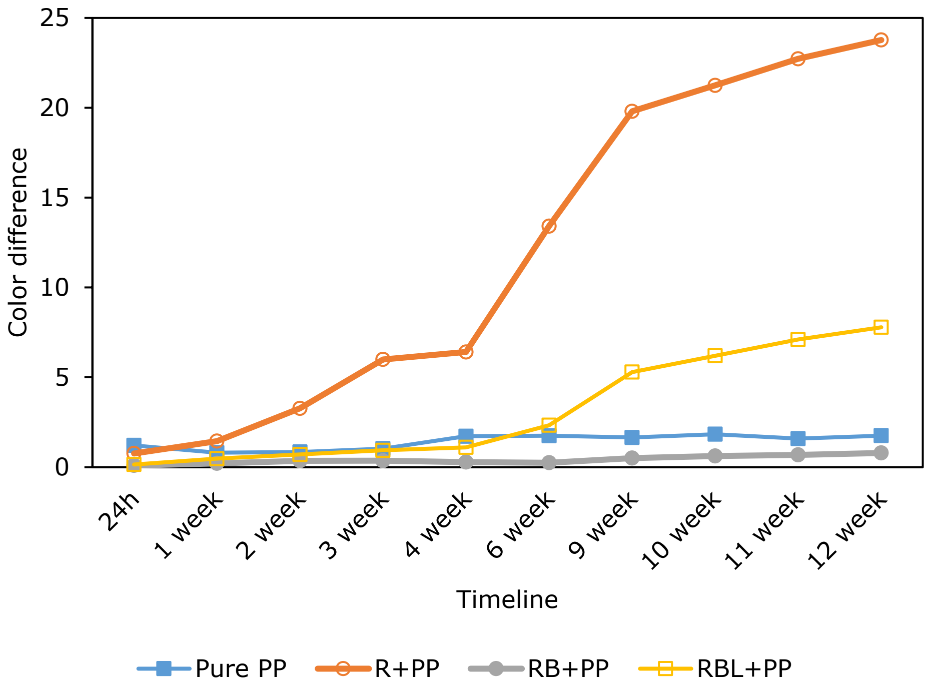


Figure 4.15 Discoloration results

4.3 Density

Results for the density test are presented in Table 4.1.

Table 4.1. Density of samples

Type of material	Density, g/cm3	STD
Pure PP	0.902	0.003
R+PP	1.091	0.007
RB+PP	1.142	0.008
RBl+PP	1.089	0.023
Pure PLA	1.353	0.001
R+PLA	1.386	0.003
RB+PLA	1.463	0.005
RBl+PLA	1.514	0.003

The density values for polypropylene and polylactide declared in the technical specification are 0.905 and 1.37 g/cm^3, respectively, which correlate with the measured in this test.

The density of reed powder from PP-based composite material is 1.380 g/cm^3, and from PLA-based composite – 1.421 g/cm^3. The difference in the obtained values can be explained by the inhomogeneity of the distribution of reed in composite materials. For more accurate results more experiments should be done.

Relatively low density of natural fibers (1.3 – 1.5 g/cm^3) is considered as one of their advantages, on the one hand [35], as a result of their use in conjunction with matrices of much higher density, lighter composites are obtained, which can have a positive effect on their transportation, for example. On the other hand, as the density of the material increases, the mechanical properties of the material generally improve [10]. In this case, the density of the polymers used in the composite materials is slightly lower than the density results of the obtained composites, which can probably have a positive effect on their mechanical properties.

5. CONCLUSION

In this project, two composite types were fabricated from polypropylene and polylactide using reed as the filler. The composites were incorporated with pigmented (black iron oxide and ultramarine blue) and unpigmented reed powder at 50 wt.% loading. Following the composite fabrication, durability tests with liquids (water and ethanol) and UV ageing were conducted.

Based on the obtained results, the addition of reed as a filler in the fabrication of composites results in a slight increase in thickness swelling (on 1.62% averagely) and liquid absorption (on 1.08% averagely) compared to the neat polymers. It is observed that the performance of the PLA-based composites was more impacted compared to that of PP. This could be explained by the fact that PLA is biobased, which makes it more susceptible to environmental conditions than PP. However, the overall performance of the composites was not meaningfully impacted by the addition of reed powder, making reed a suitable alternative filler material.

The use of reed in polypropylene-based composites reduces the consumption of synthetic, petroleum-based materials. On the other hand, the combination of reed and PLA creates more sustainable products using fully biobased materials. Though, further treatments may be required to improve product service durability, while the cost of PLA may offer a disadvantage. For better durability of composite materials from natural products, it is possible to incorporate additives, as seen by the improvement obtained with the color pigment treatment.

To conclude, reed powder, a plant-based material, can be suitably applied in the production of polymer composites and offer a positive alternative in material utilization for enhancing environmental sustainability.

SUMMARY

This master thesis investigated composite materials incorporated with reed powder as the filler. Three variants of reed powder were used: untreated and pigmented (black and blue). The reed performance was examined using a synthetic polymer (polypropylene) and a biobased polymer (polylactide). The performance of the composites vis-à-vis the reed treatment and polymer matrix was then characterized in terms of resistance to liquid absorption and swelling, as well as ageing with ultraviolet radiation for a period of 3 months.

Regarding the liquid resistance test, the results indicated that treating the reed with the color pigments decreased the composite water absorption and swelling. Furthermore, the composite materials with reed became more matte than pure polypropylene material as reed strongly influences gloss of material. Overall, polypropylene composites produced superior outcome to the PLA composites, though the neat polymer properties also indicated that PP was more stable to UV and liquid degradation. The photodegradation of the surface of the samples under the influence of ultraviolet radiation leads to a decrease in the gloss of the surface, as well as fading of the colored samples. This also leads to the increase of swelling in thickness.

Based on the data obtained, we can conclude that the resulting material showed adequate results in durability parameters, and any type of developed composites can be successfully used.

KOKKUVÕTE

Selles magistritöös uuriti komposiitmaterjale, milles kasutatakse täiteainena pilliroojahu. Töös kasutati kolme erinevalt töödeldud pilliroojahu: töötlemata, musta pigmendiga töödeldud ja sinise pigmendiga töödeldu. Pilliroo käitumist komposiidis uuriti sünteetilise polümeeri (poplüpropüleen) ja biopõhise polümeeri (polülaktiid) abil. Pilliroo komposiitide vastupidavusomadused määrati vedelike imavuse katsega ja 3 kuulise ultraviolettkiirgusega vananemise katsega.

Vedelikukindluse katse näitas, et pilliroo töötlemine värvipigmentidega vähendas komposiitide vedelike imendumist ja pundumist. Peale vedelikes leotuse katset muutusid pilliroogkomposiitmaterjalide pinnad matimaks kui puhta polümeeri pind. Tulemused näitasid, et PP komposiidid andsid üldiselt paremaid tulemusi kõikides katsetes kui PLA baasil komposiidid. Ka puhaste polümeeride võrdluses olid PP tulemused stabiilsemad peale vedelike leotuse ja UV vanandamise katset. Pilliroogkomposiitide pinna fotodegradatsioon ultraviolettkiirguse mõjul viib pinna läike vähenemiseni, samuti värviliste proovide tuhmumiseni. Seetõttu suureneb ka komposiitide veeimavus ja pundumine.

Saadud andmete põhjal võime järeldada, et töös valmistatud komposiitmaterjal näitas vastupidavuses piisavaid tulemusi ja neid oleks võimalik edukalt kasutada erinevates toodetes.

LIST OF REFERENCES

[1] O. V. Ershova, S. K. Ivanovskij, L. V. Chuprova and A. N. Bahaeva, Modern compositematerials on the basis of the polymeric matrix, International journal of applied and fundamental research, 2015.

[2] T. L. ALPÁR, M. SCHLOSSER, I. HAJDU and L. BEJÓ, "International Scientific Conference on Sustainable Development & Ecological Footprint," in *Developing Building Materials from Cement-bonded Reed Composite Based on Waste Materials*, 2012.

[3] A. Atiqah, M. Jawaid, M. R. Ishak and S. M. Sapuan, "Moisture Absorption and Thickness Swelling Behaviour of Sugar Palm Fibre Reinforced Thermoplastic Polyurethane," *Procedia Engineering,* 2017.

[4] S. C. Dubey, V. Mishra and A. Sharma, "A review on polymer composite with waste material as reinforcement," *Materials Today: Proceedings,* 2021.

[5] R. A. Ilyas and S. M. Sapuan, The Preparation Methods and Processing of Natural Fibre Bio-polymer Composites, Current Organic Synthesis, 2019.

[6] M. Sharma, R. Sharma and S. C. Sharma, "A review on fibres and fillers on improving the mechanical behaviour of fibre reinforces polymer composites," *Materials Today: Proceedings,* 2021.

[7] G. Rajeshkumar, S. Arvindh Seshadri, G. L. Devnani, M. R. Sanjay, S. Siengchin, J. Prakash Maran, N. A. Al-Dhabi, P. Karuppiah, V. A. Mariadhas, N. Sivarajasekar and R. A. Anuf, "Environment friendly, renewable and sustainable poly lactic acid (PLA) based natural fiber reinforced composites – A comprehensive review," *Journal of Cleaner Production,* 2021.

[8] M. Ramesh, K. Palanikumar and K. Hemachandra Reddy, Plant fibre based bio-composites: Sustainable and renewable green, Elsevier Ltd., 2017.

[9] C.-S. Shon, T. Mukashev, D. Lee, D. Zhang and J. R. Kim, Can Common Reed Fiber Become an Effective Construction Material? Physical, Mechanical, and Thermal Properties of Mortar Mixture Containing Common Reed Fiber, Sustainability, 2019.

[10] E. Keijsers, M. Oever, J. Dam, A. Lansbergen, C. Koning and H. Akker, The development of reed composite fiber boards using partially bio-based, formaldehyde- and monomeric isocyanate-free resins, Elsevier Ltd., 2019.

[11] K. P. Tian, C. Shen, B. Zhang, X. W. Li, J. C. Huang and Q. M. Chen, "IOP Conference Series: Earth and Environmental Science," in *Experimental study on mechanical properties of reed stalk*, 2019.

[12] A. Nourbakhsh and A. Ashori, "Wood plastic composites from agro-waste materials: Analysis of mechanical properties," *Bioresource Technology,* 2009.

[13] K. Mayandi, N. Rajini, N. Ayrilmis, M. I. Devi, S. Siengchin, F. Mohammad and H. A. Al-Lohedan, "An overview of endurance and ageing performance under various environmental conditions of hybrid polymer composites.," *JMR&T Journal of Materials Research and Technology,* 2020.

[14] V. G. Jiryakov, Organic chemistry, 1978.

[15] Z. Pu, Polymer Data Handbook, Oxford University Press, 1999.

[16] R. E. Abou-Zeid, N. A. EL-Wakil and Y. Fahmy, "Thermoplastic Composites from Natural Reed Fibers," *Egyptian Journal of Chemistry,* 2015.

[17] A. Bartos, B. P. Utomo, B. Kanyar, J. Anggono, F. E. Soetaredjo, J. M´ocz´o and B. Puk´anszky, "Reinforcement of polypropylene with alkali-treated sugarcane bagasse fibers: Mechanism and consequences," *Composites Science and Technology,* 2020.

[18] T. Yu, J. Ren, S. Li, H. Yuan and Y. Li, "Effect of fiber surface-treatments on the properties of poly(lactic acid)/ramie composites," *Composites Part A: Applied Science and Manufacturing,* 2010.

[19] K. Oksman, M. Skrifvars and J.-F. Selin, "Natural fibres as reinforcement in polylactic acid (PLA) composites," *Composites Science and Technology,* 2003.

[20] A. Bartos, K. Nagy, J. Anggono, H. Purwaningsih, J. M´ocz´ and B. Puk´anszky, "Biobased PLA/sugarcane bagasse fiber composites: Effect of fiber characteristics and interfacial adhesion on properties," *Composites,* 2021.

[21] E. Petinakis, L. Yu, G. Simon and K. Dean, Natural Fibre Bio-Composites Incorporating Poly(Lactic Acid), Petinakis et al., 2013.

[22] E. Rudnik, Compostable Polymer Materials, 2019.

[23] A. Buthainah, A. B. Dayang Radiah, W. Alnuami, Y. S. Ethar and A. J. Mohammed, Gasoline Diffusivity of Polypropylene-Polycarbonate Composites, IJITEE, 2014.

[24] V. K. Rastogi and P. Samyn, "CIWC-2," in *Compression Molding of Polyhydroxybutyrate Nano-composite Films as Coating on Paper Substrates*, 2020.

[25] M. N. Hosokawa, A. B. Darros, V. A. Silva Moris and J. M. Faulstich de Paiva, "Polyhydroxybutyrate Composites with Random Mats of Sisal and Coconut Fibers," *Materials Research,* 2017.

[26] N. M. Barkoula, S. K. Garkhail and T. Peijs, "Biodegradable composites based on flax/polyhydroxybutyrate and its copolymer with hydroxyvalerate," *Industrial Crops and Products,* 2010.

[27] T. H. Mokhothu and M. J. John, "Bio-based Fillers for Environmentally Friendly Composites," in *Handbook of Composites from Renewable Materials*, 2017.

[28] G. Wuzellaa, A. R. Mahendrana, T. Bätgeb, S. Jurya and A. Kandelbauer, Novel, binder-free fiber reinforced composites based on a renewable resource from the reed-like plant Typha sp., Elsevier B.V., 2011.

[29] D. Kraiem, S. Pimbert, A. Ayadi and C. Bradai, Effect of low content reed (Phragmite australis) fibers on the mechanical properties of recycled HDPE composites, Elsevier Ltd., 2012.

[30] Z. N. Azwa, B. F. Yousif, A. C. Manalo and W. Karunasena, A review on the degradability of polymeric composites based on natural fibres, Elsevier Ltd., 2012.

[31] X. Zhong, Y. Zhu, J. Fu, H. Lin and C. He, "Performance Analysis of Four Plant Fiber/Polyvinyl Chloride Composites under Two Degradation Conditions with Water or Seawater with Xenon Lamp," *BioResources,* 2020.

[32] A. Çavdar, E. Tomak, S. B. Torun and S. Arpaci, "Accelerated weathering resistance of high-density polyethylene composites reinforced with microcrystalline cellulose and fire retardants," *Journal of Building Engineering,* 2021.

[33] J. S. Fabiyi, A. G. McDonald, M. P. Wolcott and P. R. Griffiths, "Wood plastic composites weathering: Visual appearance and chemical changes," *Polymer Degradation and Stability,* 2008.

[34] H. L. Ryu, "REED COMPOSITE, MANUFACTURING METHOD THEREOF AND BUILDING MATERIAL USING THE SAME". Patent US 8,716,371 B2, 6 May 2014.

[35] D. Badagliacco, B. Megna and A. Valenza, "Induced Modification of Flexural Toughness of Natural Hydraulic Lime Based Mortars by Addition of Giant Reed Fibers," *Case Studies in Construction Materials,* 2020.

[36] N. Tang, Q. Jia, H. Zhang, J. Li and S. Cao, "Preparation and morphological characterization of narrow pore size distributed polypropylene hydrophobic membranes for vacuum membrane distillation via thermally induced phase separation," *Desalination,* 2010.

[37] P. Shao and R. Huang, "Polymeric membrane pervaporation," *Journal of Membrane Science,* 2007.

APPENDIX 1

Table 1.1 Weight, thickness, color, gloss measurements for pure PLA and PLA-based composites

Samples	Liquid	Before immersion to liquid						After immersion to liquid					
		Weight, g	Thickness, mm	Color			Gloss, 60°, GU	Weight, g	Thickness, mm	Color			Gloss, 60°, GU
				L_1	a_1	b_1				L_2	a_2	b_2	
Pure PLA	Water at 25 °C	4.8338	1.79	74.98	-0.73	3.39	64.7	4.8505	1.79	74.76	-0.69	3.33	62.3
R + PLA		5.4938	2.05	34.69	5.49	9.15	53.8	5.6305	2.09	39.63	5.17	9.99	31.8
RB + PLA		5.7675	1.94	25.90	1.45	1.00	55.8	5.8733	1.98	26.21	1.39	0.87	34.5
RBl + PLA		5.5954	1.95	27.61	-1.32	-5.35	48.7	5.7507	2.01	30.13	-4.80	-8.57	31.2
Pure PLA	Water at 70 °C	4.8196	1.80	75.44	-0.59	3.46	63.0	4.8530	1.82	74.91	-0.58	3.61	57.3
R + PLA		5.5241	2.03	34.44	5.43	8.93	50.3	5.6900	2.09	38.73	4.73	9.39	25.4
RB + PLA		5.7430	1.93	25.99	1.42	0.88	55.2	5.8824	1.98	26.14	1.41	0.74	29.4
RBl + PLA		5.6135	1.94	27.66	-1.44	-5.64	49.6	5.7691	2.01	30.52	-5.60	-8.84	26.4
Pure PLA	Ethanol 70%	4.7358	1.79	75.16	-0.75	3.19	57.5	4.7540	1.79	74.91	-0.86	3.06	54.8
R + PLA		5.5494	2.04	35.00	5.41	8.99	51.1	5.6190	2.07	36.17	4.86	8.35	27.9
RB + PLA		5.7812	1.96	25.81	1.44	0.91	46.9	5.8486	1.99	25.58	1.43	0.81	25.4
RBL + PLA		5.6647	1.98	27.63	-1.67	-5.74	43.2	5.7335	2.01	28.25	-3.08	-6.93	25.3

Table 1.2 Weight, thickness, color, gloss measurement for pure PP and PP-based composites without exposure to UV radiation

Samples	Liquid	Before immersion to liquid						After immersion to liquid					
		Weight, g	Thickness, mm	Color			Gloss, 60°, GU	Weight, g	Thickness, mm	Color			Gloss, 60°, GU
				L_1	a_1	b_1				L_2	a_2	b_2	
Pure PP	Water at 25 °C	3.2415	1.85	80.26	2.09	2.95	73.0	3.2418	1.85	79.10	2.03	0.80	72.4
R + PP		4.1065	1.95	33.94	5.67	9.99	51.2	4.1754	1.97	32.07	4.61	6.73	28.3
RB + PP		4.2045	1.90	26.24	1.59	1.06	55.4	4.2310	1.91	26.10	1.66	1.07	40.6
RBL + PP		4.2031	1.90	26.56	-0.12	-2.34	55.0	4.2495	1.91	27.00	-0.64	-3.11	30.5
Pure PP	Water at 70 °C	3.1924	1.80	80.25	1.97	3.00	74.5	3.1932	1.80	79.99	2.11	3.40	71.6
R + PP		4.1954	1.97	34.28	5.71	10.22	50.8	4.2731	2.01	32.75	4.47	7.37	18.5
RB + PP		4.3099	1.92	26.29	1.58	1.04	57.0	4.3524	1.93	25.53	1.74	1.07	33.5
RBL + PP		4.3088	1.93	26.73	-0.08	-2.36	56.7	4.3697	1.94	27.13	-1.96	-3.74	27.0
Pure PP	Ethanol 70%	3.2131	1.83	79.82	2.17	2.83	72.6	3.2134	1.83	79.10	1.80	2.83	61.9
R + PP		4.1491	2.00	35.72	5.78	10.84	52.3	4.1897	2.02	35.22	5.01	8.59	32.5
RB + PP		4.2453	1.94	26.38	1.56	1.11	58.3	4.2605	1.94	26.48	1.55	1.10	42.7
RBL + PP		4.2311	1.90	26.93	0.42	-2.29	63.6	4.2484	1.91	35.37	-0.88	-3.08	36.1

Table 1.3 Weight, thickness, color, gloss measurement for pure PP and PP-based composites after exposure to UV radiation

Samples	Liquid	Before immersion to liquid						After immersion to liquid					
		Weight, g	Thickness, mm	Color			Gloss, 60˚, GU	Weight, g	Thickness, mm	Color			Gloss, 60˚, GU
				L_1	a_1	b_1				L_2	a_2	b_2	
Pure PP	Water at 25 °C	3.1990	1.86	78.74	1.60	1.79	51.9	3.2027	1.87	77.77	1.17	2.23	50.5
R + PP		4.0950	1.94	57.80	3.63	10.66	11.4	4.1440	1.97	70.24	2.60	9.09	8.7
RB + PP		4.2376	1.93	25.67	1.78	1.28	15.1	4.2616	1.95	28.16	1.46	1.38	11.5
RBl + PP		4.1764	1.90	29.59	-4.62	-8.07	23.1	4.2136	1.93	43.87	-18.14	-18.59	15.3
Pure PP	Water at 70 °C	3.1721	1.85	79.04	1.50	1.77	50.6	3.1790	1.87	75.86	-0.38	4.90	47.0
R + PP		4.1302	1.93	58.83	3.67	10.80	10.2	4.2419	2.00	66.70	3.54	10.86	7.4
RB + PP		4.2000	1.92	25.50	1.88	1.37	14.8	4.2513	1.95	27.73	1.63	1.75	8.9
RBl + PP		4.1911	1.90	29.34	-4.29	-7.99	23.4	4.2635	1.95	43.02	-19.35	-17.56	12.4
Pure PP	Ethanol 70%	3.1084	1.79	79.17	1.05	2.06	52.0	3.1093	1.79	77.48	0.49	1.98	37.1
R + PP		4.1442	1.98	59.08	3.64	10.66	10.5	4.1873	1.99	72.15	2.41	8.99	6.7
RB + PP		4.2695	1.95	25.81	1.82	1.43	16.7	4.2868	1.96	28.15	1.62	1.58	9.5
RBL + PP		4.2644	1.94	29.50	-4.54	-8.10	23.8	4.2826	1.95	41.58	-17.08	-17.39	12.6

Table 1.4 Calculated density results for pure PP and PP-based composites

	Sample	Mass in the air, g	Mass in the water, g	Density, g/cm3
Pure PP	1	1.019	-0.105	0.904
	2	1.052	-0.113	0.900
	3	1.087	-0.119	0.899
	4	1.027	-0.109	0.901
	5	1.052	-0.104	0.907
	Mean			0.902
	St.dev.			0.003
Neat Reed + PP	1	1.255	0.112	1.095
	2	1.273	0.096	1.078
	3	1.32	0.115	1.092
	4	1.297	0.116	1.095
	5	1.241	0.111	1.095
	Mean			1.091
	St.dev.			0.007
Blue Reed + PP	1	1.263	0.155	1.136
	2	1.345	0.176	1.147
	3	1.259	0.151	1.133
	4	1.341	0.182	1.154
	5	1.178	0.15	1.142
	Mean			1.142
	St.dev.			0.008
Black Reed + PP	1	1.245	0.086	1.071
	2	1.339	0.125	1.100
	3	1.336	0.087	1.066
	4	1.292	0.146	1.124
	5	1.287	0.104	1.085
	Mean			1.089
	St.dev.			0.023

Table 1.5 Calculated density results for pure PLA and PLA-based composites

	Sample	m in the air, g	m in the water, g	Density, g/cm3
Pure PLA	1	1.5387	0.4042	1.353
	2	1.503	0.3947	1.353
	3	1.4577	0.3825	1.353
	4	1.5106	0.3955	1.352
	5	1.5591	0.4085	1.352
	Mean			1.353
	St.dev.			0.001
Neat Reed + PLA	1	1.6792	0.47	1.386
	2	1.6611	0.4617	1.382
	3	1.6874	0.4754	1.389
	4	1.6793	0.4693	1.385
	5	1.7273	0.4857	1.388
	Mean			1.386
	St.dev.			0.003
Blue Reed + PLA	1	1.7062	0.5458	1.467
	2	1.6883	0.5397	1.467
	3	1.6675	0.528	1.460
	4	1.7481	0.5571	1.465
	5	1.7622	0.555	1.457
	Mean			1.463
	St.dev.			0.005
Black Reed + PLA	1	1.7881	0.6093	1.514
	2	1.7611	0.5982	1.511
	3	1.734	0.5892	1.511
	4	1.745	0.5967	1.516
	5	1.7088	0.5855	1.518
	Mean			1.514
	St.dev.			0.003

Table 1.6 ANOVA: Single Factor for gloss results for neat reed/PP and blue reed/PP composites after water at 25 °C

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
R+PP	8	-351.06	-43.88	3.07
RBL+PP	8	-359.43	-44.93	6.00

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-Value*	*F crit*
Between Groups	4.37	1	4.37	0.96	0.34	4.60
Within Groups	63.55	14	4.54			
Total	67.92	15				

Table 1.7 ANOVA: Single Factor for gloss results for reed/PP composites after ethanol

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
R + PLA	8	-351.42	-43.93	26.77
RB + PLA	8	-359.89	-44.99	16.12
RBL + PLA	8	-326.97	-40.87	21.51

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-Value*	*F crit*
Between Groups	73.03	2	36.51	1.70	0.21	3.47
Within Groups	450.81	21	21.47			
Total	523.84	23				

Table 1.8 ANOVA: Single Factor for swelling in thickness results for PLA/reed composites after ethanol

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
R + PLA	8	12.14	1.52	0.02
RB + PLA	8	11.70	1.46	0.03
RBL + PLA	8	11.80	1.48	0.04

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-Value*	*F crit*
Between Groups	0.01	2	0.01	0.22	0.80	3.47
Within Groups	0.62	21	0.03			
Total	0.64	23				

Table 1.9 ANOVA: Single Factor for liquid absorption results for neat reed/PLA and blue reed/PLA composites after water at 25 °C

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
R + PLA	8	19.90	2.49	0.01
RBL + PLA	8	22.21	2.78	0.05

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-Value*	*F crit*
Between Groups	0.33	1	0.33	10.64	0.01	4.60
Within Groups	0.44	14	0.03			
Total	0.77	15				

Derivation step of density of reed equation:

$$\rho_f = \frac{m_f}{V_f};$$

$$\rho_f = \frac{\frac{1}{2} m_{cm}}{V_{cm} - V_m};$$

$$\rho_f = \frac{m_{cm}}{\frac{2m_{cm}}{\rho_{cm}} - \frac{2m_m}{\rho_m}};$$

$$\rho_f = \frac{m_{cm} * \rho_{cm} * \rho_m}{2m_{cm} * \rho_m - m_{cm} * \rho_{cm}};$$

$$\rho_f = \frac{\rho_{cm} * \rho_m}{2\rho_m - \rho_{cm}} \qquad (3.2)$$

where V_m – the volume of matrix, cm^3,

V_f – the volume of filler, cm^3,

V_{cm} – the volume of composite material, cm^3,

m_{cm} – the mass of composite material, g,

m_m – the mass of matrix, g,

m_f – the mass of filler, g,

ρ_f – the density of filler, g/cm^3,

ρ_{cm} – the density of composite material, g/cm^3,

ρ_m – the density of matrix, g/cm^3.