Kaunas University of Technology

Faculty of Mechanical Engineering and Design

Evaluation of Properties of Microcrystalline Cellulose Modified Polylactic Acid Films

Master's Final Degree Project

Ingrida Bernatonytė

Project author

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Consultant

Kaunas, 2024

Kaunas University of Technology

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Industrial Engineering and Management (6211EX018)

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Task of the Master's Final Degree Project

Given to the student – Ingrida Bernatonytė

1. Title of the Project

Evaluation of Properties of Microcrystalline Cellulose Modified Polylactic Acid Films

(In English)

Mikrokristaline celiulioze modifikuotų poli-pieno rūgšties plėvelių savybių vertinimas

(In Lithuanian)

2. Aim and Tasks of the Project

Aim: to compare and evaluate mechanical and physical properties, as well as hydrolytic degradability of MCC modified PLA compositions.

Tasks:

1. to evaluate the influence of MCC content on the tension properties of PLA films;
2. to evaluate hydrolytic degradability of PLA films vs MCC content;
3. to evaluate structural changes of MCC modified PLA films after hydrolytic degradation;
4. to apply statistical quality control methods for properties comparison.

3. Main Requirements and Conditions

The working length for tensile testing cannot be different between samples. One type of film must be tested at least 5 times.

4. Additional Requirements for the Project, Report and its Annexes

Not applicable.

Project author	Ingrida Bernatonytė		04-03-2024
	(Name, Surname)	*(Signature)*	*(Date)*
Supervisor	Eglė Fataraitė-Urbonienė		04-03-2024
	(Name, Surname)	*(Signature)*	*(Date)*
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	(Name, Surname)	*(Signature)*	*(Date)*

Bernatonytė Ingrida. Evaluation of Properties of Microcrystalline Cellulose Modified Polylactic Acid Films. Master's Final Degree Project, supervisor Assoc. Prof. dr. Eglė Fataraitė-Urbonienė; Faculty of Mechanical Engineering and Design, Kaunas University of Technology.

Study field and area (study field group): Production and Manufacturing Engineering (E10), Engineering Sciences (E).

Keywords: polylactic acid; microcrystalline cellulose; composite; tensile strength; biodegradability.

Kaunas, 2024. 56 p.

Summary

The aim of investigation was to compare and evaluate mechanical and physical properties, as well as hydrolytic degradability of MCC modified PLA films. Mechanical properties were evaluated according to the results of uniaxial tensile tests. Tests on PLA films reinforced with different wt. percentages of MCC as filler were executed and statistical analysis of the results was performed. It was found that most effective method for PLA film formation by compression method is 190 ^{o}C. It was shown that when MCC is used as a filler in PLA films in low amounts there is a trend of their stress at break decreasing with the increase amount of MCC, while ductility of tested samples increases. MCC filler content influence on the hydrolytic degradation of PLA was determined by weight loss testing and tensile testing of samples that have been immersed in a NaOH solution. Both the weight loss and tensile test results indicate that MCC content influences the intensity of hydrolytic degradation of PLA. The most intensive degradation was observed in PLA/MCC 0.5 wt. % film, with the PLA/MCC 1 wt. % film, however, hydrolytic degradation process was much slower and not as prominent. The PLA/MCC films surface structure before and after hydrolytic degradation was evaluated by comparing optical microscopy images. The optical microscope pictures showed roughened surface in all the films, which is presumed to be caused by the uneven surface of the hot – press. One can also see the uneven distribution of MCC particles in the PLA matrix and how some cracks and vacancies appear in the film after 120 h of hydrolytic degradation. ANOVA/Single factor software was utilized as a statistical quality control tool to determine the significance of the results difference between tested groups. This tool was found useful for evaluation and comparison mechanical and physical PLA film properties changes vs MCC filler content and degradation duration.

Bernatonytė Ingrida. Mikrokristaline celiulioze modifikuotų poli-pieno rūgšties plėvelių savybių vertinimas. Magistro baigiamasis projektas, vadovė doc. dr. Eglė Fataraitė-Urbonienė; Kauno technologijos universitetas, Mechanikos inžinerijos ir dizaino fakultetas.

Studijų kryptis ir sritis (studijų krypčių grupė): Gamybos inžinerija (E10), Inžinerijos mokslai (E).

Reikšminiai žodžiai: poli-pieno rūgštis; mikrokristalinė celiuliozė; kompozitas; savybės tempiant; bioskaidumas.

Kaunas, 2024. 56 p.

Santrauka

Tyrimo tikslas – palyginti ir įvertinti fizines, mechanines ir hidrolitinio skaidumo savybes PLA plėvelių, modifikuotų skirtingais kiekiais MCC užpildo. Atlikti tempimo bandymai, svorio netekimo analizė bei statistinė rezultatų analizė. Efektyviausia temperatūra plėvelių gamybai nustatyta 190 ℃. Taip pat, pastebėta tendencija, kad naudojant MCC kaip užpildą PLA plėvelėse, nedideliais kiekiais, didėjant MCC kiekiui mažėja jų įtempiai trūkimo metu, o tirtų mėginių tamprumas didėja. MCC užpildo kiekio įtaka PLA hidroliziniam skilimui buvo nustatyta atliekant bandinių, kurie buvo palikti NaOH tirpale, svorio netekimo ir tempimo bandymus. Tiek svorio netekimo, tiek tempimo bandymų rezultatai rodo, kad MCC kiekis turi įtakos PLA hidrolizinio skilimo greičiui, bet nebūtinai jį pagreitina. Sparčiausias skilimas buvo pastebėtas PLA/MCC 0,5 m. % plėvelės ir grynos PLA plėvelės bandiniuose, o PLA/MCC 1 m. % plėvelės hidrolizinio skilimo procesas buvo daug lėtesnis ir ne toks ryškus. PLA/MCC plėvelių paviršiaus struktūra prieš ir po hidrolizinio skilimo buvo įvertinta lyginant optinės mikroskopijos vaizdus. Optinio mikroskopo nuotraukose buvo matyti nelygus plėvelių paviršius, kuris, kaip manoma, atsirado dėl nelygaus karšto preso paviršiaus. Taip pat, galima pamatyti ir netolygų MCC dalelių pasiskirstymą PLA matricoje bei tai, kaip plėvelėje atsiranda įtrūkimai ir plyšiai po 120 valandų hidrolizinio skilimo proceso. ANOVA/Single faktor programinė įranga buvo naudojama kaip statistinė kokybės kontrolės priemonė, siekiant nustatyti apytikslį tašką, kuriame skirtingų plėvelių mechaninės savybės ženkliai pasikeičia hidrolizinio skilimo metu.

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List of Abbreviations and Terms

Abbreviations:

PLA – polylactic acid

MCC – microcrystalline cellulose

MPa – megapascals

σ – stress, MPa

ε - elongation, %

E – modulus of rupture, MPa

T – temperature, ^{O}C

Wt. % - weight percentage

Terms:

Tensile stress – the amount of external force per unit area of the body that causes the body to stretch in the direction of the applied force.

Elongation - observable ability of a substance to expand under stress.

Young’s modulus - a solid material's mechanical characteristic that assesses its compressive or tensile stiffness when force is applied lengthwise.

Introduction

Plastics have a big effect on our daily lives and our industries. Its global production surpassed 365 million metric tons in 2020 (15% originating from Europe) [1]. However, conventional plastic production relies heavily on non – renewable resources, which, in turn, results in substantial greenhouse gas emissions - around 5 t of CO_2 per ton of plastic (including emissions from its end-of-life treatment) [2]. Considering the recent global shift towards sustainability, bioplastics have gained more attention. They appear to be environmentally superior to conventional plastics because of their low carbon footprint, more sustainable sourcing, and the ability to fully deteriorate in the environment. In the past few years, various bioplastics, that are primarily derived from first-generation feedstocks, have entered the market – one of them is polylactic acid (PLA). Polylactic acid is a material that offers biodegradability, recyclability, and composability, which makes it suitable for a wide range of applications that include food containers, films, textiles, and packaging. In addition, its high biocompatibility has led to its application in biomedical fields like implant devices and tissue scaffolds [3]. Furthermore, PLA does not only present improved sustainability and versatile applications but also has a potential for significant market share growth in the upcoming few years, as there are predictions, indicating continuous increase in investments of PLA production [4].

A field of study that could potentially even further enhance PLA attractiveness across various industries is the creation of compositions with different additives and fillers in order to modify thermal, mechanical, physical or degradability properties of the finished product. The creation of "green" composites from combinations of natural fibers and biodegradable plastic materials as an alternative to conventional polymer composites is a topic worth discussing. The effectiveness of the final composition depends on the properties of the particular material used for reinforcement of PLA [5]. One such material is micro cellulose (MCC) – it is inexpensive, easily sourced and sustainable. When compared to other potential fillers like $CaCO_3$, it has a lower need for energy and impressive mechanical performance. From a production point of view, it is also non – abrasive which allows it to be used in higher dosages [6]. But how exactly does the addition of microcrystalline cellulose to polylactic acid at different percentages modifies its mechanical properties and affects degradability?

The purpose of this study is to compare and evaluate mechanical and physical properties, as well as hydrolytic degradability of MCC modified PLA. To achieve this goal, different PLA/MCC blends will be subjected to hydrolytic degradation for different duration and the collected samples will be further tested for changes in weight loss as well as mechanical properties during uniaxial tension. A statistical analysis will be performed on the results to determine their quality as well as a precision of the conclusions drawn from them.

Aim: to compare and evaluate mechanical and physical properties, as well as hydrolytic degradability of MCC modified PLA compositions.
Tasks:
1. to evaluate the influence of MCC content on the tension properties of PLA films;
2. to evaluate hydrolytic degradability of PLA films vs MCC content;
3. to evaluate structural changes of MCC modified PLA films after hydrolytic degradation;
4. to apply statistical quality control methods for properties comparison.

Hypothesis: The addition of microcrystalline cellulose to polylactic acid bioplastic can modify its mechanical properties during uni-axial tension as well as degradability.

1. PLA and PLA/MCC Composites – Properties, Processing, and Fields of Application

1.1. Polylactic Acid (PLA) Properties, Processing Methods, Fields of Application

Polylactic acid is one of the most promising and commonly used biopolymers in the biodegradable product industry. It has several advantages over other biopolymers – other than the fact that it is biodegradable, compostable, and potentially recyclable it is also produced from renewable sources, by fermentation of agricultural products (sugarcane, potatoes, rice etc.) and then applying a combination of oligomerization and cyclic dilactone processes. The resulting product can be applied to many fields that require biodegradability – mostly, that includes one – time – use products like disposable utensils and tableware, throwaway plastic bags and various packaging materials [5,7,8].

The physical properties of PLA determine its applicability in various industrial applications. The polymer is transparent, shiny, is not significantly permeable with water and oxygen, has high stability at low temperatures and high resistance of oils and grease. Because of these properties it is suitable to be utilized in the packaging sector for manufacturing films and bottles, as well as cups and trays. However, PLA physical properties, as shown in Table 1., vary depending on the molecular weight and crystallinity. The increase of molecular weight decreases crystallinity because of a formation of a longer polymer chain. When this happens viscosity and tensile strength increases. The ability to create different chemical structures can be utilized in PLA production, creating products with different properties, expanding the range of its possible applications. This is also considered an advantage of PLA over conventional petroleum – based polymers. Besides physical properties the mechanical properties and biodegradability also vary depending on the chemical structure of the polymer [7].

Table 1. Physical properties of PLA [7]

Property	**Values**
Specific Gravity	1–1.5
Surface Energy (dynes)	36–40
Melting Temperature (°C)	140–210
Molecular Weight (Daltons)	Approx. 1.6×10^5
Melt Flow Index (g/10 min)	4–22
Crystallinity (%)	5–35
Glass Transition Temperature (°C)	50–75
Solubility Parameters ($J^{0.5}/cm^{1.5}$)	21

When evaluating the mechanical properties of PLA, it is compared to its petroleum – based alternatives, as shown in Table 2. This type of comparison highlights that polylactic acid's tensile modulus is higher than that of polypropylene, poly – vinyl chloride or nylon. However, the flexural strength is lower than most of these polymers, with the exception of PP. On the other hand, PLA has shown to have a great potential for modification of these properties by the use of different fillers and additives [7].

Table 2. Mechanical properties of PLA compared to other polymers [7]

Polymer	**Tensile Modulus (GPa)**	**Yield Strength (MPa)**	**Flexural Strength (MPa)**	**Elongation (%)**
Polylactic acid (PLA)	3.2	49	70	2.5
Polyvinyl chloride (PVC)	2.6	35	90	3.0
Polypropylene (PP)	1.4	35	49	10
Polystyrene (PS)	3.4	49	80	2.5
Nylon	2.9	71	95	5

One of the key properties of PLA is its biodegradability. It is a process that takes place naturally with the involvement of bacteria, fungi, algae etc. During this process PLA breaks down to water, carbon dioxide and other inorganic molecules (the mechanism of PLA biodegradation is displayed in Fig.1). However, biodegradability of PLA is only rapid and certain under special temperature, pressure, and humidity conditions. When these conditions are less than favorable, the biodegradation process will slow down, and the amount of residue will differ. PLA biodegradation takes place in two distinct phases – surface degradation and intramolecular. Generally, when a polymer degrades its bonds are broken either through the intersectional chain, main chain or side chain. In the case of PLA, this occurs with the release of ester bonds, making the long polymer chain break down into shorter oligomers or monomers and dimers – carboxylic acid and alcohol. Microorganisms can then safely metabolize these smaller compounds by the use of various enzymes naturally present [8]. PLA can degrade both in aerobic and anaerobic conditions, however, the studies show that the process is much faster with the presence of oxygen [7].

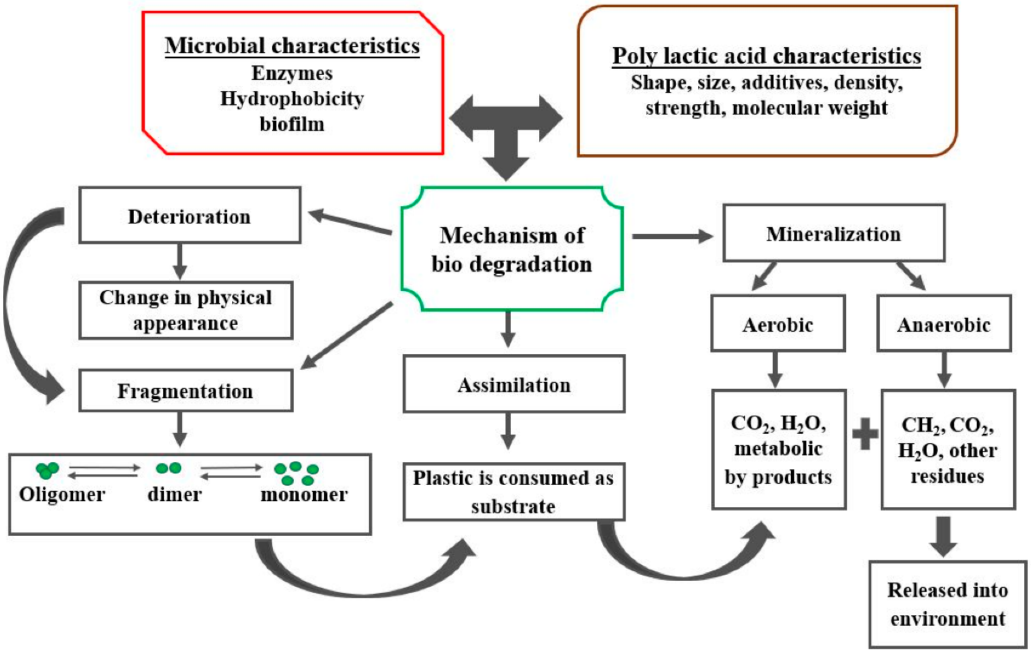


Fig. 1. Polylactic acid biodegradation process mechanism [7]

Other than environmental factors, this process also depends on certain PLA properties like melting and glass transition temperatures, surface area and molecular weight. Both higher melting point and molecular weight will result in slower biodegradation. Also, the structure of PLA has a great influence to this. PLA that is more crystalline will degrade slower than PLA that is more amorphous [7].

PLA is able to be processed using traditional polymer conversion methods that do not require large amounts of energy, giving PLA the advantage of being relatively inexpensive [7]. Technologies that are usually utilized in the processing of PLA are:

- Drying. In the presence of water and high temperatures the hydrolysis of PLA can occur which breaks down PLA molecules, reducing the molecular weight and therefore the quality of the finished product. Therefore, PLA needs to be dried to less than 0,01 wt.% water content before processing in high temperatures. Specific drying conditions can vary in between different systems but generally, drying temperature for amorphous PLA is 44 – 55 °C and 80 – 100 °C for crystalline PLA. The drying time is 2 – 4 hours [9].
- Extrusion. This is one of the most basic thermoplastic processing methods used to produce films, sheets, pipes, etc. The most popular extruders used in the polymer sector are screw extruders. They consist of a barrel that is heated by electric elements, a mixing and dosing unit for the polymer resin and additives, one or more screws that are rotated continuously by a motor and a nozzle through which the melted material is then extruded. The melting of the material is caused due to the heating elements and the friction generated by the rotating screw which also transports the melted material forward and through the nozzle. For PLA extrusion the heating temperature can range from 200 to 220 °C and the screw length to diameter ratio is recommended to be 24:1 – 30:1. Cast film extrusion is a suitable method to manufacture PLA film. It involves pulling and stretching the polymer in between two or more cooled rollers to obtain a needed thickness and orientation [9].
- Injection molding. A technology very similar to extrusion that is employed to produce a variety of mass – produced plastic parts like containers, preforms, bottle caps, toys etc. In this case, the screw not only rotates but also moves forward and back, injecting the melted material into a mold where it is then cooled and a solid part is made. Because PLA has a relatively low glass transition temperature, the cooling process in the mold can take longer than that of alternative petroleum – based polymers. Also, research has found that injection molded PLA products are likely to get brittle due to rapid physical aging after processing. Because of that, parts meant for further processing need to be kept in controlled environmental conditions. Another way to avoid this problem could be to employ more advanced technologies like shear controlled orientation injection molding [9].
- Blow molding. This is a secondary processing method that involves blowing air to form a heated thermoplastic preform into a desired shape, most commonly employed in the production of plastic bottles. For PLA, a specific technology called injection stretch blow molding is most commonly utilized. The preform used in this technology is relatively short and is first pre – stretched in the direction of the preforms axis before blowing it into a mold. This technology is made to preserve orientation, improve gas barrier and mechanical properties and result in a more transparent and glossier product [9].
- Thermoforming. Another secondary processing method that involves pressing a pre – extruded PLA sheet into desired shapes by using vacuum or air pressure. Cups, trays and containers can be made this way. Compared to other plastics, PLA sheets can be quite fragile and might require special handling to avoid breaking and cracking. However, systems created for PET rigid film processing can usually be utilized for PLA as well [9].

One of the most common fields where PLA can be utilized is the packaging sector or more specifically – food packaging. As the world is moving towards being more environmentally – friendly, people are more encouraged to use biodegradable materials instead of traditional polymers. Although PLA displays many positive traits like biocompatibility, high strength and easy processability it also has a few downsides like insufficient flexibility, poor barrier properties and crystallization behavior, which limit its potential uses. Because of that the attention has turned to employing various additives to create PLA mixtures and composites with improved physical, mechanical, optical and even antifungal and antibacterial properties. The resulting composited with their specific set of improved properties and applications are shown in Table 3 [10].

Table 3. Application fields of different PLA blends [10]

PLA/additive	**Properties improved**	**Application**
PLA/ZnO membranes	Mechanical properties, UV, visible light barrier performances.	Food packaging
PLA/Chitosan/Basil olive oil films	Tensile, barrier, and antioxidant properties.	Active food packaging
PLA/poly(butylene succinate)/cellulose fiber composite	Viscosity, Thermal properties, crystallinity, flexural modulus.	Hot cups or lids application
PLA/lignin films	Toughness, antioxidant performance, water vapor barrier properties, antioxidant, UV resistance behavior	Active food packaging
PLA/poly(vinyl alcohol)/poly(ethylene glycol) blends/thyme essential oil	Hydrophilicity, antibacterial properties	Antimicrobial packaging
PLA/chitin/cellulose nanofiber	Mechanical, thermal, and wettability properties	Green packaging
PLA/lycopene nanocomposite film	Mechanical properties, oxidative and color stability of margarine	Margarine packaging
PLA/selenium microparticles films	Water resistance, ultraviolet resistance, antibacterial and oxidation resistance	Food packaging
PLA/silica aerogel composite	Crystallinity, stretchability, elongation at break, high transparency	Food packaging
PLA/halloysite nanotubes bio nanocomposite	Thermal properties, mechanical properties (tensile strength, yield strength).	Food packaging
PLA/poly(butylene adipate-co-terephthalate) (PBAT) blends with incorporated trans-cinnamaldehyde	Antimicrobial properties, antifungal properties.	Bread packaging
PLA/cinnamaldehyde inclusions films	Antibacterial properties, tensile strength, water and oxygen resistance, life expectancy.	Fruit packaging
PLA/grape syrup films	UV absorption and light stability	Food packaging

Single - use plastic products have been one of the main environmental concerns, causing a large portion of waste in landfills. There are initiatives like Directive (EU) 2019/904 that strive to ban these types of products altogether. This is another field where PLA has a lot of growing potential. Already, single – use products like disposable plates, trays, and cutlery, as well as gloves and various types of bags are being produced using PLA as a base material [10]. For this reason, the synthesis of new materials from PLA is generating a lot of interest and making major advances in the field of research. For example, Delgado-Aguilar synthesized PLA blends with PCL using batch extrusion and injection molding equipment [11]. One of the key goals of PLA/PCL blends is to generate better toughness while maintaining the biodegradability of both components. Nevertheless, one of the main drawbacks of these blends is their mechanical performance at high temperatures. PCL's low melting temperature prevents it from being used in situations where extremely high temperatures are required. In other fields, however, this solution proves to be a great alternative for traditional petroleum – based materials.

Another field where PLA has a high potential to be utilized is the textile industry, replacing currently commonly used PET. PLA fibers have the clear advantage of biodegradability as well as being more natural, in between synthetic and natural fibers making it very suitable for applications like pharmaceutical and medical. However, the production of PLA fibers can be more challenging compared to PLA, due to its rapid thermal degradation and lack of resistance to alkaline. Currently PLA fibers a starting to be used in houseware textiles like bedding (duvets, pillows, mattresses), also, in single – use nonwoven products (wipes and tissues). They are also very suitable to use in the clothing industry, especially in activewear and underwear, as PLA fibers provide great moisture management and works well in blends with natural fibers like wool and cotton [11,13].

In agriculture, many developments have been made by the use of flexible films. Due to its poor waste management post – use it has had a negative impact on the environment. This is where biodegradable films could again prove useful, especially in areas where recycling after use is impossible, as it not only decomposes in soil but also shows no negative effects on its properties [11,14].

There are also various biomedical applications for PLA. For example, PLA material combined with recent advancements in 3D printing can be used in tissue engineering – to provide surfaces for the reconstruction and regeneration of various tissue [12]. Its biocompatibility and degradation properties make it a useful material for the fixation of bones, muscles, ligaments and even blow vessels and skin. It could also be used in drug delivery and tumor targeting [10].

One of the sectors that uses a lot of natural assets worldwide and, inevitably, has an adverse effect on the environment is the construction industry. As a result, greater effort has been initiated to develop sustainable building designs in an attempt to reduce the negative effects of construction which is why PLA has become more and more well-known as an alternative material for the building industry during the past few years. PLA composites are inexpensive, biodegradable, renewable, and work with most structural application production methods [10].

Electronic and Automotive industries have also been using PLA in various areas to reduce their carbon footprint. In addition to reducing the consumption of non - renewable material resources, the production of electronic goods made with renewable PLA material can save energy in small electronic applications. Therefore, even though PLA is already in high demand in China, the largest producer of electronics in the world, there are predictions for it to increase it even further over the next ten years [10].

1.2. Modification of PLA, Properties Evaluation Methods

As mentioned in the previous section, various drawbacks of pure PLA can be improved using various plant – based or inorganic fillers, additives, and even other polymers to make it suitable for a certain application as an alternative for petroleum – based plastic materials.

One of the greatest ways to toughen PLA is to blend it with flexible polymers. High elasticity polymers, including nitrile butadiene rubber and natural rubber, can significantly increase PLA's toughness, it removes the final material's ability to decompose naturally. To keep PLA tough and maintain its biodegradability, other biodegradable materials are combined with it, such as poly (butylene succinate) (PBS). PBS exhibits strong impact resistance and high elongation at brea - it toughens PLA while preserving its inherent strength and enhancing crystallization capability, making it the perfect material for PLA modification [13].

In a study done by Tao Zhao PBS was added to PLA in different percentages and the resulting blends were evaluated by mechanical and thermal properties, crystallization behavior. Thermal and crystallization properties were evaluated using Differential Scanning Calorimetry (DSC). The obtained values – glass transition temperature (T_g), cold crystallization temperature (T_{cc}), crystallization temperature (T_c), cold crystallization enthalpy (ΔH_{cc}), melt temperature (T_m), and melt enthalpy (ΔH_m), as shown in Table 4, indicate decreased thermal stability with the increase of PBS percentage, which is an important factor for processing parameter control [14].

Table 4. Thermal properties of different PLA/PBS blends [14]

PLA/PBS (w/w)	T_g, (°C)	T_{cc}, (°C)	ΔH_{cc}, (J/g)	T_m, (°C)	ΔH_m, (J/g)	T_c (°C)
100/0	61.9	109.5	35.4	170.2	39.6	120.3
90/10	60.9	103.2	26.2	169.6	38.6	113.4
80/20	59.8	101.9	22.8	169.3	37.7	110.6
70/30	59.3	101.6	21.7	169.1	38.5	90.1
60/40	58.6	99.1	19.4	168.9	34.9	87.8
50/50	58.2	100.6	16.4	168.9	31.3	86.9

Using the same technology, researchers also obtained cooling curves of pure PLA and PBS, as well as different blends. As shown in Fig. 2. pure PLA, as well as blends with less than 40 % of PBS do not exhibit signs of crystallization (no visible crystallization peak). However, a larger amount of PBS has been shown to increase the blend's crystallization capability [14].

To evaluate the mechanical performance of the blends, tensile testing is performed. The resulting stress – strain curve, shown in Fig. 3. shows that pure PLA has relatively high tensile strength of 70.5 MPa, but low elongation at break of 5.2%, which highlights typical PLA brittleness. The pure PBS, however, showed a high elongation at break of 16.1% and a low tensile strength of 33.5 MPa, suggesting a combination of good toughness and strength because of its flexible molecular chain structure. In the PLA/PBS blends, a change from brittle to ductile behavior is observed with the addition of PBS as little as 10 wt%, showing a significant increase in elongation at break from 5.2% to 13.2% [14].

Aside from improvement of these properties, it is important to access how blending PLA with PBS affects its ability to degrade. When investigating the hydrolytic degradation characteristics of PLA/PBS blends in a sodium hydroxide solution (pH=13) at 37 °C, it was observed that during the degradation process, the tensile properties of the blends deteriorated faster than both polymers would individually. This happens as a result of phase separation and the creation of numerous voids, increasing the contact area with the solution. Additionally, this phase separation increased the hydrophilicity of the blend, thereby accelerating the hydrolysis of the interface region between PLA and PBS in the blend [15].

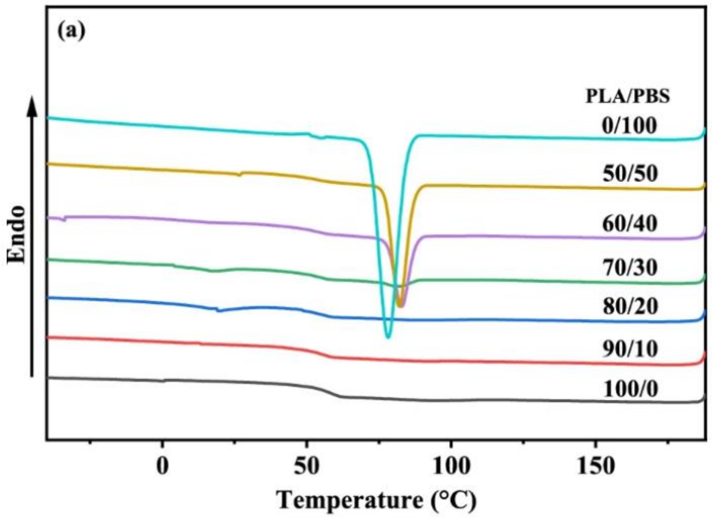


Fig. 2. Cooling curves of different PLA/PBS blends [14]

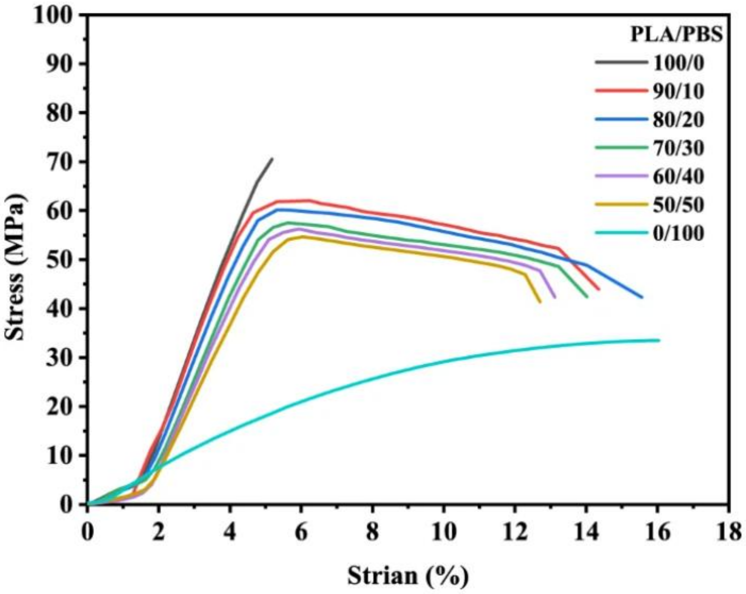


Fig. 3. Stress – strain curves of different PLA/PBS blends [14]

PLA is a suitable matrix for the use of various inorganic fillers. Some of the most popular ones include CaCO3, talc and glass – fiber. Calcium carbonate is widely used as a filler for PLA due to its affordability, availability, and compatibility with PLA matrix. It can improve stiffness, thermal stability, and barrier properties of PLA – based materials. In 2022, a study by Cristina Pavon [16] was performed in order to evaluate mechanical, thermal and degradation properties of $CaCO_3$ reinforced PLA samples produced using 3D printing technology.

In the study 2 different compositions of PLA/$CaCO_3$ were evaluated (3 and 5 wt.%) against pure PLA. Thermal properties of the reinforced PLA were determined using DSC technology. The results shown in Table 5 (glass transition temperature T_g and melt temperature T_m) as well as the obtained

DSC curves (Fig. 4) indicate that the addition of the filler does not alter PLA thermal properties drastically. Glass transition temperature remains exactly the same while the melt temperature fluctuates by the maximum of 6 °C [16].

Table 5. Thermal properties of $CaCO_3$ reinforced PLA [16]

PLA/CaCO3 (w/w)	**T_g (°C)**	**T_m (°C)**
100/0	60	158
97/3	60	152
95/5	60	157

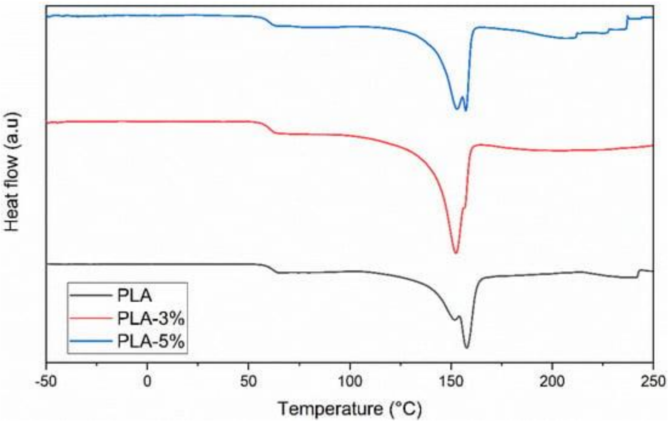


Fig. 4. DSC heat flow curves of various PLA/$CaCO_3$ combinations [16]

For the evaluation of mechanical properties, tensile and flexural tests were performed. The results that are presented in Table 6. show a decline in mechanical properties with an increase of filler.

Table 6. Tensile and flexural properties of $CaCO_3$ reinforced PLA [16]

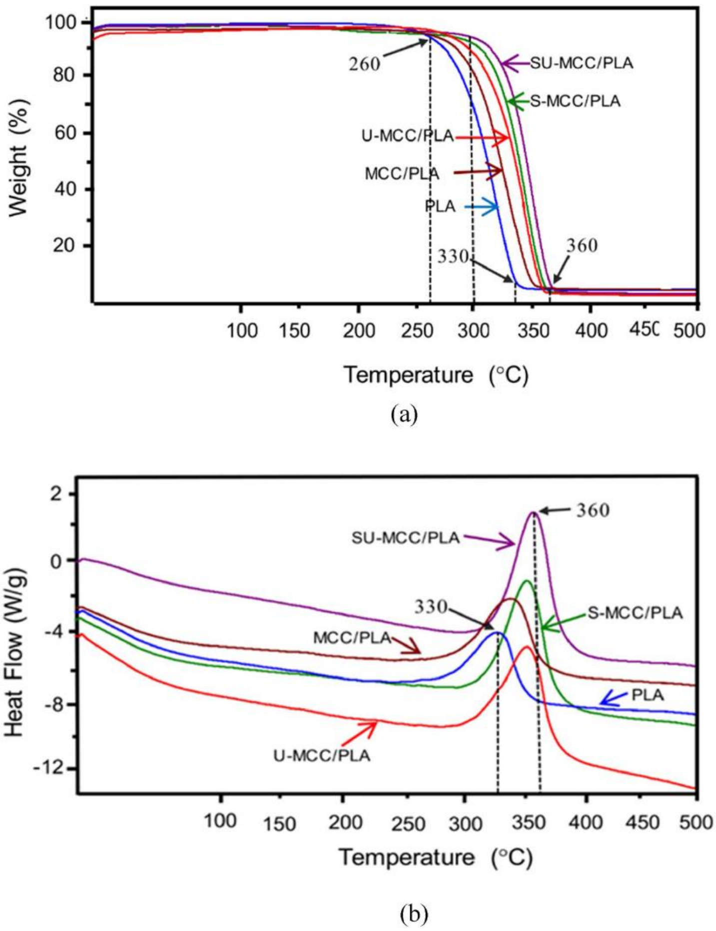
PLA/CaCO3 (w/w)	**Young's Modulus (MPa)**	**Tensile Strength (MPa)**	**Elongation at Break (%)**	**Young's Modulus in Flexure (MPa)**	**Flexural Strength (MPa)**
100/0	1201.2 ± 95.76	42.04 ± 1.98	9.79 ± 1.57	805.64 ± 10.113	45.53 ± 4.70
97/3	1534.6 ± 185.71	39.26 ± 2.98	4.26 ± 0.63	817.89 ±21.54	43.21 ± 5.65
95/5	1708.1 ± 43.22	31.22 ± 1.28	4.32 ± 0.45	823.43 ± 14.98	40.59 ± 6.67

When it comes to the biodegradation process of PLA reinforced with $CaCO_3$, studies show that the existence of this filler can accelerate it drastically, reaching 58 % biodegradation level in the first 30 days [17]. This phenomenon is due to the fact that the presence of calcium carbonate acts as a buffer in the composting medium by preventing the drop of pH levels when polylactic acid breaks down – which would normally inhibit the process.

Combining PLA and natural fibers is a promising field of research that has already led to a creation of various perspective materials with acceptable mechanical properties, and although these materials have some disadvantages like hydrophilic properties and low elasticity modulus, their most attractive quality is the ability to fully degrade in the environment, causing no harm to it. The main focus of this research is to find out how these materials can be applied to befit both the environment and the economy [18].

There are various possible sources of natural fibers that can be used to create these composites, but cellulose shows the most perspective, mostly due to its natural availability. This means that it fulfills important criteria like being cost – effective, accessible, and most importantly – sustainable and environmentally friendly. Compared to inorganic materials like the previously discussed calcium carbonate, it requires less energy and still exhibits impressive mechanical properties. Furthermore, because of its fibrous nature, it can align along the matrix axis, enhancing mechanical properties but not adding weight. Also, it is nonabrasive which simplifies processing, resulting in substantial cost savings [6].

There are studies already done on mechanical and thermal properties of PLA/MCC composite films. In a study done by Bo Zhao [19], the MCC was modified in 2 ways. First – by using ultrasound technology and second – with ultrasound technology and also by sulphonation of sulphuric acid. Thermal stability of these various PLA/MCC composite films was evaluated using DSC and TGA. Results shown in Fig. 5 reveal that composite films exceeds pure PLA in terms of thermal stability, especially with modified MCC versions [19].



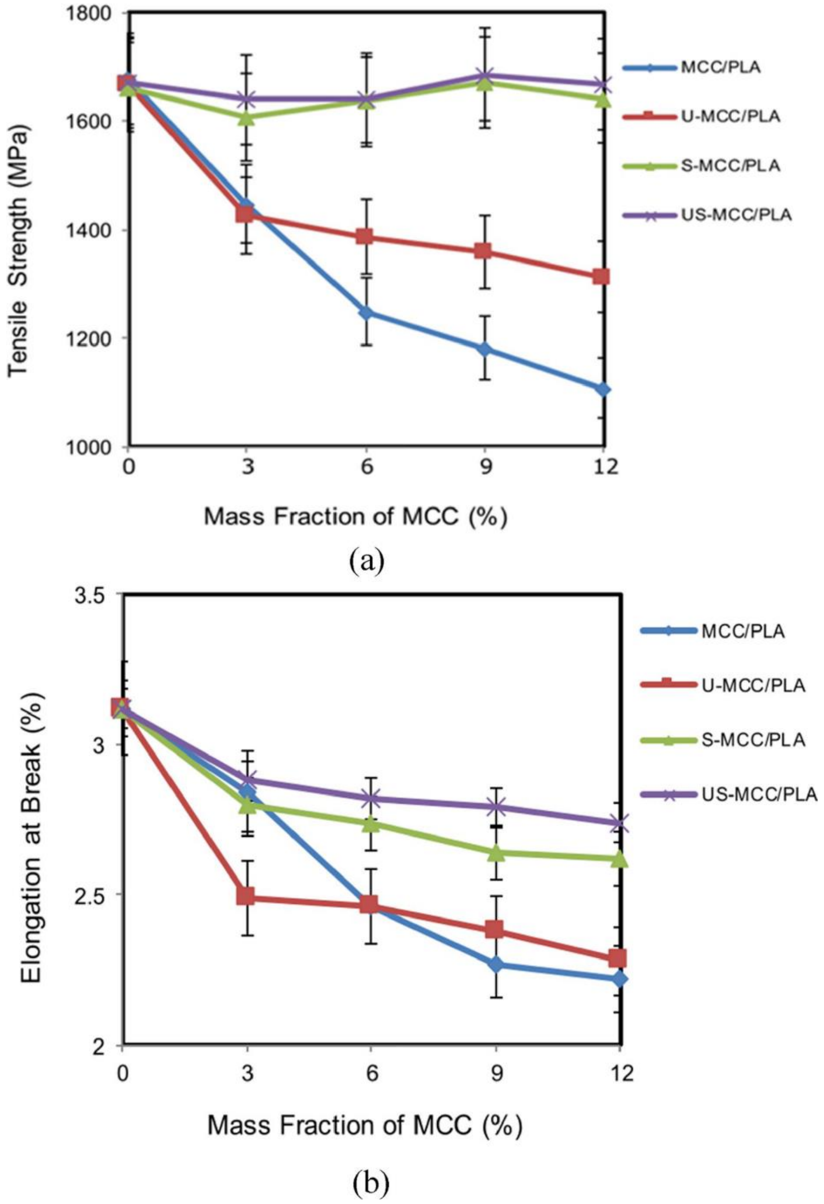
(a)

(b)

Fig. 5. Thermal graphs obtained by TGA (a) and DSC (b) [19]

In the same study, mechanical properties of the same variety of composite films were also evaluated using tensile testing. As displayed in the tensile graphs (Fig. 5.) the unmodified MCC/PLA composite films demonstrate worsening tensile properties as the MCC percentage increases. With modified MCC composites, the situation is not as consistent. At first the tensile strength increases and then decreases with the increased amount of MCC. Regarding elongation at break, different composite films exhibit worse behavior compared to pure PLA, and it shows a trend of declining further as the

MCC mass fraction increases. While the addition of MCC obviously affects the elongation at break of the composite films, this effect is less pronounced compared to unmodified MCC/PLA film [19].



(a)

(b)

Fig. 6. Mechanical properties of various compositions of PLA and MCC [19]

Studies show that due to the hydrophilic nature of micro cellulose, using it as filler accelerates the biodegradation process of PLA. In one particular biodegradability test, where the specimens were simply buried in the ground for 12 months, the weight loss was about 10 % higher with just 4 % addition of MCC. The difference was even more significant with the addition of 7 % MCC - 35 % higher weight loss compared to pure PLA, however, when 10 % of MCC was added, the difference dropped back to ~20 % [20].

1.3. Market tendencies of PLA usage and production

According to the most recent market report of European Bioplastics (2023), there is a steady increase in the bioplastics industry [4]. Global bioplastics production capacity is expected to rise from ~2.18 million tons in 2023 to ~7.43 million tons in 2028, as shown in Fig. 7.

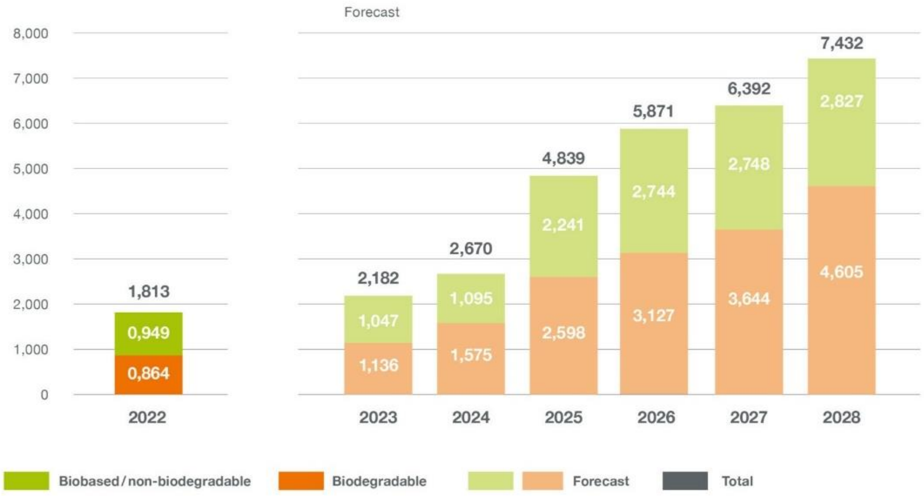


Fig. 7. Global production capacities of bioplastics [4]

Currently, biodegradable plastics represent about 52 % of the total global bioplastics production capacity and are expected to take up an even larger portion compared to bio-based and non-biodegradable plastics in the future. Among biodegradable plastics, PLA holds the largest market share (31 %) and it is forecasted to continue growing (up to 43.6 %) [4].

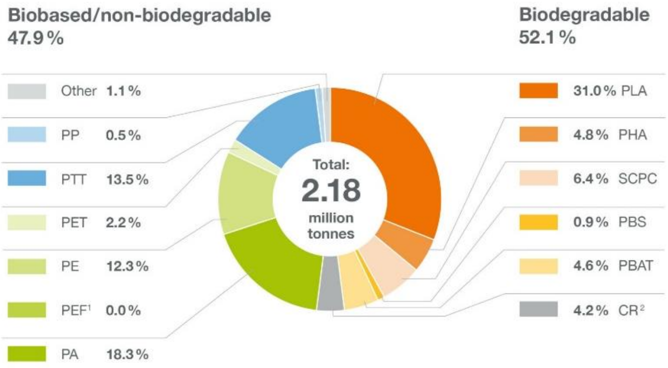


Fig. 8. Global production capacities of bioplastics 2023 [4]

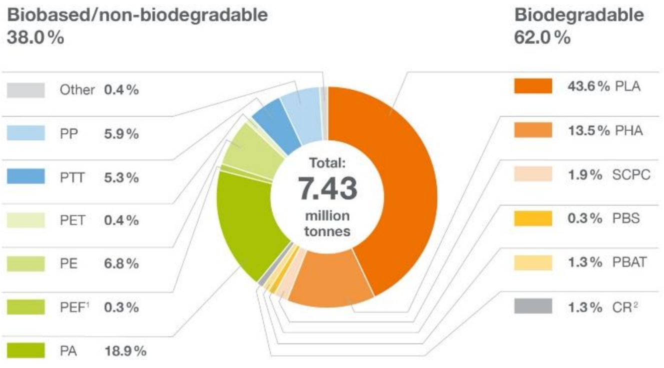


Fig. 9. Global production capacities of bioplastics 2028 [4]

Although PLA could compete with conventional plastics in terms of technical performance, its prices are still behind those of conventional plastics (see Fig. 10) That is mostly due to the fact that the production costs of PLA are notably higher. Typically, PLA production consists of these few steps: extraction of raw materials, glucose extraction, fermentation, and polymerization. The specific process routes vary based on the raw materials chosen for the production which in turn, also influences the cost structure. The choice of raw material can alter the costs in the first stage of production, as it consists of cultivating agricultural land: fertilizers, pesticides, energy for machinery etc. Moreover, the cost associated with extracting the product from the raw material can fluctuate, depending on the generated by – products and their value in the market [21].

Currently, corn and sugarcane are considered the primary plant sources for PLA production [22], but there's ongoing exploration into various innovative resources for lactic acid production. The reason for these efforts is to address environmental concerns related to land use and competition with food production coming from the current generation of feedstocks derived from food crops. Among these alternatives, utilizing residual plant material from cultivation (such as stover) and processing (like sugar cane bagasse) of these crops as cellulose-based feedstocks has been a topic of discussion for some time. The main advantage of these materials being obtained from by-products of other processes helps to alleviate the drawbacks associated with first-generation feedstocks. Additionally, in the recent years, there have been numerous proposals to completely dissociate PLA production from agricultural land use. For example, by leveraging by-products and waste from the food industry that typically hold small to no economic value [21].

For several reasons, financial considerations and resource limitations are regarded as important obstacles in the development of bioplastics supply chains and a bioeconomy. First, the cost differences between fossil-based and bio-based products are caused by the dissimilar stages of maturity of novel bio-based technologies and well-established fossil-based technologies. Bio-based technologies still need to go through a learning process and need large investments to be implemented effectively. Furthermore, because of the deeply rooted nature of fossil fuel-based technology, there are expensive changes that need to be implemented for the successful takeoff of the new technologies. Moreover, the costs of fossil-based plastics do not fairly reflect the significant negative environmental impacts associated with their manufacturing and consumption, such as the effects associated with greenhouse gas emissions [26,27].

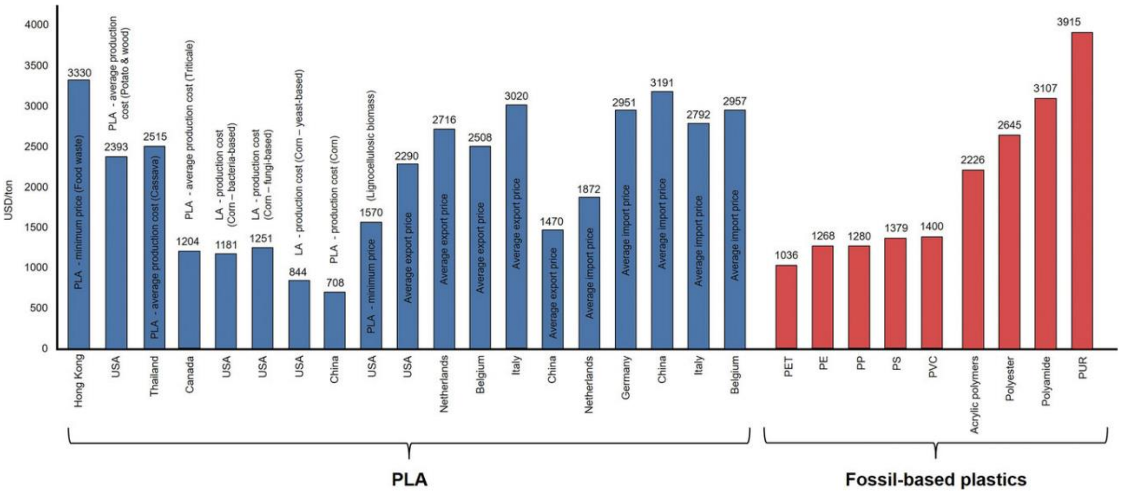


Fig. 10. PLA prices vs conventional plastic prices

Aside from the before mentioned challenges of PLA implementation in the market, it is also important to access the preference of final consumers. The adoption of these novel materials by consumers may be difficult for a number of reasons, especially if they come in contact with food. First of all, higher market prices that are a direct result of greater production costs, could make consumers more reluctant to sacrifice price convenience for sustainability. Furthermore, some consumers may even display neophobia when evaluating novelties and their preferences may be impacted by various opinions about the material's quality and safety. Furthermore, consumers' choices may be negatively affected by their lack of knowledge and experience with biopolymers. Considering these variables, customer behavior and preferences are vital in determining the market trends [23].

A study that evaluated barriers and enablers to buying biodegradable plastic products found that the main motivators for choosing biodegradable over conventional are the positive beliefs about the environmental impact. However, it is also important for consumers to have access to appropriate waste management facilities. On the other hand, when consumers lack of understanding of packaging terminology or even skepticism on these environmental claims contributes to negative attitudes to these products. Even so, the majority of respondents indicated that they would choose biodegradable products over non – biodegradable, given the chance [24].

All things considered, it appears that the only significant barrier in the fast emergence of PLA products is its cost of production and in turn, higher price. However, with the growing cost of fossil – based products it is likely that the situation may shift, and PLA will gain even more popularity in the coming years.

1.4. Chapter Summary

PLA offers numerous advantages such as biodegradability, composability and potential recyclability. Other than that it exhibits promising physical and mechanical properties which are also largely dependent on its degree of crystallinity. It can be processed easily using traditional polymer conversion methods like extrusion, injection molding, blow molding and thermoforming, however, just as PLA‘s fossil – based counterpart PET, it needs to be dried before processing to prevent degradation. This biodegradable material can be utilized in various industries - food packaging and single – use products being the most common, but also textiles, agriculture, biomedical, construction, electronics and automotive sectors.

There is also an option of modifying PLA using various additives and fillers to enhance its properties or make it more suitable for a specific application. Some examples include blending it with PBS which can improve toughness without changing biodegradability, using calcium carbonate to enhance stiffness, thermal stability and barrier properties or combining PLA with microcrystalline cellulose which not only modifies mechanical properties but might also speed up biodegradability.

The bioplastics industry is showing significant growth that are a result of growing environmental awareness and new regulations. Among other biodegradable polymers, PLA holds a significant market portion and is expected to grow further. However, its high cost still remains a challenge when competing with conventional plastic materials.

2. Materials and Methods

2.1. Materials

For the research, PLA films with different wt. percentages of MCC filler were used: 0 wt.%, 0.5 wt.%, 1 wt.% and 2 wt.%. The films were produced using PLA resin from Ingeo Biopolymer and MCC powder from SIAL Cellulose. For preparation of the solution for the hydrolytic degradability testing NaOH in granular form was used. The specifications of these raw materials are presented in Table 7.

Table 7. Specifications of MCC and PLA materials used during research

Material	Brand/ product name	Application	Specification	Value	Source
Microcrystalline cellulose (MCC)	SIAL Cellulose DFS0, microcrystalline	Suitable for thin layer chromatography	Color	White	[25]
			Form	Powder	
			Loss on drying	≤ 5.0 %	
			Residue on ignition	≤ 3.0 %	
			Infrared spectrum	Conforms to structure	
Polylactic Acid (PLA)	Ingeo Biopolymer 6202D	Fiberfill, nonwovens, agricultural woven and nonwoven fabrics, articles for household disposal	Specific Gravity	1.24	[26]
			Relative Viscosity	3.1	
			Melt Index, g/10 min (210°C)	15 - 30	
			Melt Density (230°C)	1.08	
			Glass Transition Temperature (°C)	55 - 60	
			Crystalline Melt Temperature (°C)	155 - 170	
Sodium hydroxide (NaOH)	SIAL Sodium hydroxide – puriss. p. a.	ACS reagent	Solubility	Water soluble	[27]
			Density (at 20 °C) (g/L)	1260	
			Carbonate Content	≤ 1 %	
			Appearance of solution	Complying	
			Assay	98 – 100,5 %	
			Heavy metal	≤ 0.002 %	
			Miscellaneous Assay	≤ 0.001 %	
			Aluminum	≤ 0.0005 %	
			Copper	0.0005 %	
			Irom	≤ 5 ppm	
			Mercury	≤ 0,05 ppm	
			Sulphate	≤ 30 ppm	
			Chloride	≤ 10 ppm	
			Total nitrogen	0.0003 %	
			Phosphate	0.0005 %	

2.2. Methods

2.2.1. Composition Preparation

The preparation of different PLA/MCC composition involved a few key steps. First, both materials were weighed accordingly for each desired filler content (0.5 wt. %, 1 wt. % and 2 wt. %) the mixture is then placed under a laboratory hot press Joos and film is formed by pressure and heat (see Fig. 11). During the process, the pressure force was 200 kN and the duration is 1 min. The sample was preheated for 2 min before the start of pressure application.

In order to determine the most effective temperature setting, at first, pure PLA film was produced at different temperature settings of 160 ℃, 170 ℃, 180 ℃ and 190 ℃. The mechanical properties of each film were evaluated under tension in order to select the temperature setting which resulted in a film with the best performance.

For obtained films testing pure PLA and PLA/MCC composite film was cut into 10 x 100 mm strip samples. Each sample was then categorized, numbered and prepared for the following testing.

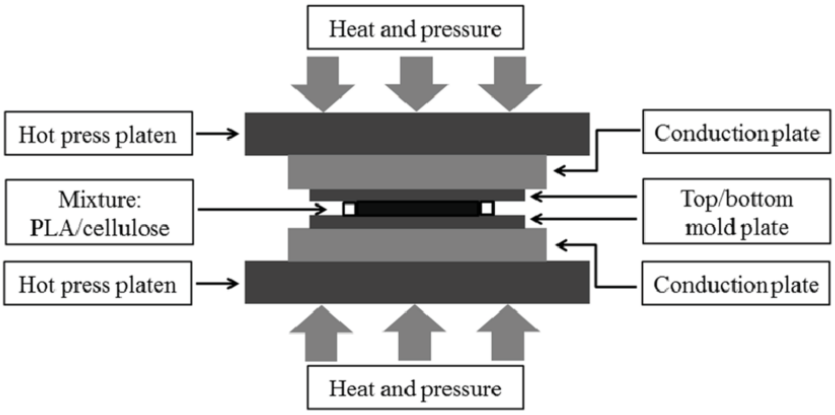


Fig. 11. Film production using hot pressing technique scheme [6]

2.2.2. Hydrolytic Degradation Procedure

The hydrolytic degradation test was performed in room temperature using a 0.4 % NaOH solution. The pH of the used solution was calculated using the following method:

1. The number of moles of NaOH in 1l of solution is calculated using the formula 2.1. Since NaOH dissociates into one mole of OH- ions per mole of NaOH (see equation 2.2), the resulting number equals to the concentration of hydroxide ions in the solution.

$$n = \frac{m}{M}; \tag{2.1}$$

n – number of moles (mol), m – mass of NaOH (g), M – molar mass of NaOH (g/mol).

$$NaOH + H_2O \; \rightarrow \; Na^+ + OH^- + H_2O; \tag{2.2}$$

2. The pOH is then calculated using formula 2.3 and from there, pH can be determined using the pOH and pH relationship formula 2.4.

$$pOH = -\log(OH^-)\,; \tag{2.3}$$

$$pH = 14 - pOH; \tag{2.4}$$

The weight of each sample was carefully measured before placing it in the solution. After a 24-hour hydrolysis period, 5 samples were taken out, rinsed and dried. Their weight was then measured again, and they were placed back into the solution for 24 more hours. Additional 5 samples are taken out, rinsed and dried for further testing of tensile properties. This process is repeated every 24 hours for a period of 5 days (120 hours). The relative weight loss of each sample is calculated using a provided equation:

$$w = \frac{w_0 - w_x}{w_0} \cdot 100\%; \tag{2.5}$$

Where w – relative weight loss (%), w_0 – sample weight prior degradation (g), w_x – sample weight after x hours of degradation (g).

2.2.3. Evaluation of Mechanical Properties Under Tension

A Tinius Olsen 25ST universal tensile testing machine was used to perform the tensile test. Upper head speed rate was 50 mm/min and the working length of the samples was 30 mm. The thickness of each sample was measured before testing using a thickness gauge TR25-100 with accuracy of 0.01 mm. As sample thickness average value of three measurements was assumed.

The results were generated as level of extension dependent on the force used. Using the collected data, it is possible to determine the relative elongation, % (formula 2.6), tensile stress σ, MPa (formula 2.7), and Modulus of Rupture modulus E (MPa) (Formula 2.8):

$$\varepsilon = \frac{\Delta l}{l} \cdot 100\% \qquad ; \tag{2.6}$$

Δl – difference in length (mm); l – original length (3 mm).

$$\sigma = \frac{F}{S} \qquad ; \tag{2.7}$$

F – applied force (N); S – cross – sectional area (mm^2).

$$E = \frac{\sigma_{max}}{\varepsilon_{break}} \qquad ; \tag{2.8}$$

σ_{max} – maximum tensile stress (MPa); ε_{break} – relative elongation at break (a).

2.2.4. Statistical analysis

For the statistical analysis of the results, the mean (formula 2.6), standard deviation (formula 2.7) and confidence interval (formula 2.8) of every sample stream was calculated:

$$\bar{x} = \frac{\sum x_i}{n} \quad ; \tag{2.9}$$

$$S = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}} \quad ; \tag{2.10}$$

$$CI = \bar{x} \mp t_\beta \left(\frac{S}{\sqrt{n}}\right); \tag{2.11}$$

t_β – coefficient dependent on confidence probability β and the number of degrees of freedom φ = n – 1, as presented in Table 8:

Table 8. Values of t_β according to the number of degrees of freedom

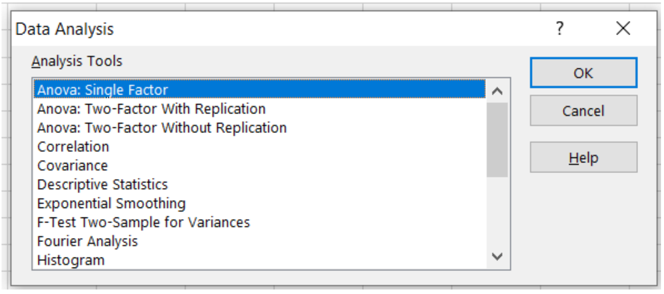
φ = n – 1	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
t_β	12.706	4.303	3.182	2.776	2.571	2.447	2.365	2.306	2.262

2.2.5. Evaluation of Structure of MCC Filled PLA Films

Optical microscopy images were acquired with Nikon Eclipse E200 POL Polarized light microscope equipped with 4x/0.1 eyepiece and Lumenera Infinity 1 high resolution microscopy camera.

2.2.6. Application ANOVA for Evaluation of Experimental Results

Tensile testing result consistency and quality is evaluated by calculating the Fischer’s criterium and comparing two sets of results. Calculations are carried out using a standard statistical analysis package in Microsoft Excel program ANOVA/Single Factor, as presented in Fig. 12.

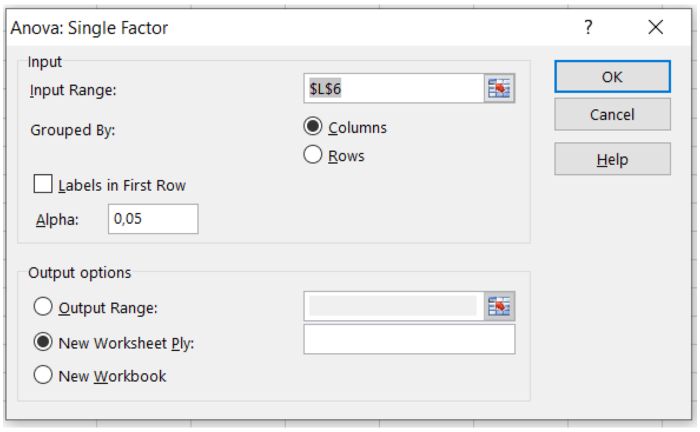

Data Analysis

Analysis Tools

Anova: Single Factor
Anova: Two-Factor With Replication
Anova: Two-Factor Without Replication
Correlation
Covariance
Descriptive Statistics
Exponential Smoothing
F-Test Two-Sample for Variances
Fourier Analysis
Histogram

Fig. 12. ANOVA package selection

The data range is inputted in the required field, as presented in Fig. 13:

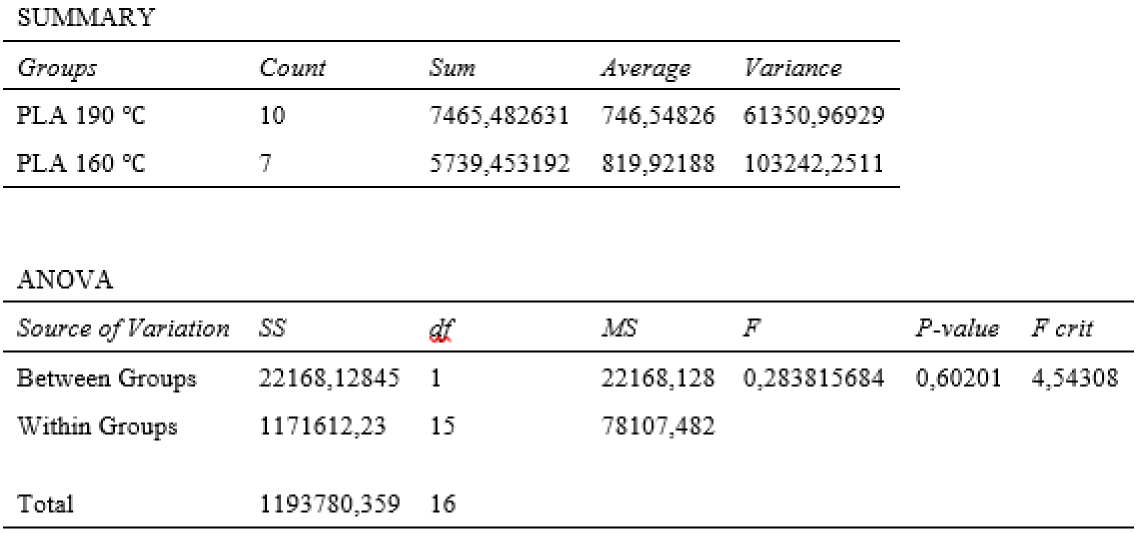

Anova: Single Factor

Input
Input Range: L6
Grouped By: ● Columns ○ Rows
☐ Labels in First Row
Alpha: 0,05

Output options
○ Output Range:
● New Worksheet Ply:
○ New Workbook

Fig. 13. Data input for ANOVA analysis

The results are required in a type of table, as presented in Fig. 14:



SUMMARY

Groups	Count	Sum	Average	Variance
PLA 190 °C	10	7465,482631	746,54826	61350,96929
PLA 160 °C	7	5739,453192	819,92188	103242,2511

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	22168,12845	1	22168,128	0,283815684	0,60201	4,54308
Within Groups	1171612,23	15	78107,482			
Total	1193780,359	16				

Fig. 14. An example of results acquired by ANOVA/Single factor analysis

The results are evaluated as follows:

- If $F < F_{crit}$, the variances can be considered without significant difference.
- If $F > F_{crit}$, the variances are different.

2.3. Chapter Summary

PLA/MCC composite films are produced using compression method at the temperature setting that was determined to be the most effective by initial testing of pure PLA films at different temperatures and then testing prepared rectangular samples behavior under tension.

Hydrolytic degradation was carried out in a 0,4 % NaOH water solution, by taking out 5 samples every 24 hours, rinsing, drying them, measuring their weight change, and then putting them back into the solution. The process took a total of 5 days (120 hours). Relative weight change is calculated.

Mechanical performance was tested under tension. From the collected data tensile stress, elongation at break and modulus was calculated.

Statistical analysis of both the degradation and tensile testing results was performed by calculating the mean, standard deviation and confidence interval.

Structure of the produced films before and after degradation was evaluated by looking at them under an optical microscope.

The standard ANOVA/Single Factor software was used to evaluate the quality and consistency of the results by comparing calculated Fisher's criteria F theoretical F_{crit} value.

3. Comparison of MCC Modified PLA Films Properties

3.1. Determination of the Effective Temperature Setting for the Preparation of the Composition

During the assessment of effective temperature for PLA film production, several elements were observed in the tensile curves (see Fig. 15), which helped to choose the most effective option. At a temperature of 160 °C (Fig. 15 – a), it is very obvious that the resulting film exhibits extreme brittleness, lacks ductility and withstands less than half of the load compared to samples produced at higher temperatures. With the increase of temperature to just 170 °C (see Fig. 15 – b), great improvement is seen in the tensile curve, demonstrating the highest average tensile strength and increased ductility. However, the results also display considerable inconsistency across the sample stream, with a standard deviation of 4.22 MPa. At 180 °C (see Fig. 15 – c), the resulting tensile curve is very similar to that at 170 °C regarding tensile strength and ductility but it exhibits very inconsistent elongation results among the sample stream. The tensile curve of film produced at 190 °C (see Fig. 15 – d) displays superior ductility and result consistency to other samples. The highest average tensile strength is seen in samples produced at 170 °C (see Table 9). However, the results also display considerable inconsistency across the sample stream, with a standard deviation of 4.22 MPa. Despite samples produced at 190 °C presenting slightly lower average maximum tensile stress compared to 170 °C, the standard deviation is reduced to approximately 3 MPa.

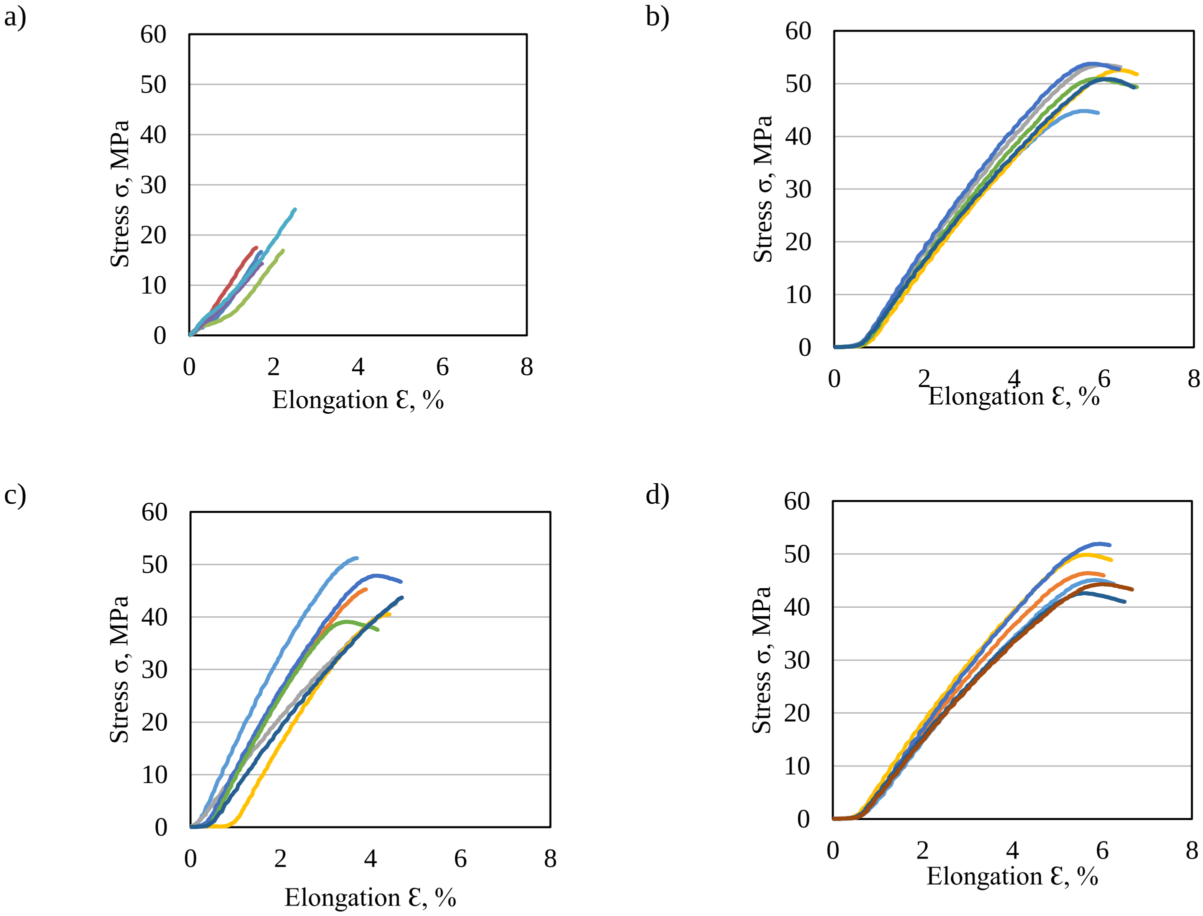


Fig. 15. Tensile curves of PLA films produced at different temperatures *T*, °C: a – 160, b – 170, c – 180, d – 190

Table 9. Statistical analysis of tensile testing results of PLA films, produced at different temperatures

Compression temperature, °C	**Sample no.**	**σ_{max}, MPa**	**ε_{break}, %**	***E*, MPa**
160	1	16.65	1.7	977.65
	2	17.48	1.59	1099.53
	3	16.91	2.22	761.81
	4	14.29	1.72	828.97
	5	25.1	2.51	1001.19
	Mean	18.09	1.95	933.83
	Standard deviation	4.1	0.4	136.47
	Confidence interval	(12.99; 23.18)	(0.01;0.02)	(764.41;1103.25)
170	1	44.8	5.46	820.51
	2	45	5.56	809.6
	3	53.53	5.89	909.4
	4	52.51	6.28	836.88
	5	53.76	5.65	950.86
	6	50.93	5.78	880.69
	7	50.86	5.98	849.98
	8	43.6	5.59	780.43
	Mean	49.37	5.77	854.79
	Standard deviation	4.22	0.27	56.03
	Confidence interval	(45.85;53.83)	(0.06;0.06)	(807.95;914.05)
180	1	51.19	4.89	1047.49
	2	45.25	5.19	872.43
	3	42.55	4.57	932.09
	4	40.50	5.82	695.88
	5	47.85	5.42	882.84
	6	39.08	5.72	683.67
	7	43.7	4.7	930.78
	Mean	44.3	5.18	863.6
	Standard deviation	4.2	0.49	131.64
	Confidence interval	(40.42;48.9)	(0.05;0.06)	(741.85;1007.65)
190	1	45.1	5.82	774.91
	2	46.4	5.65	820.75
	3	47.65	5.65	842.87
	4	49.85	5.59	892.3
	5	51.93	5.92	877.25
	6	47.25	5.45	866.44
	7	42.6	5.55	767.57
	8	44.3	5.95	744.54
	Mean	46.89	5.7	823.33

Compression temperature, °C	Sample no.	σ_{max}, MPa	ε_{break}, %	E, MPa
	Standard deviation	3.01	0.18	55.52
	Confidence interval	(44.37;50.07)	(0.06;0.06)	(776.91;882.05)

Judging from the observations gathered from the testing results and calculation, the temperature setting of 190 °C was selected for the production of composite films in further research.

3.2. Evaluation of Hydrolytic Degradation of PLA/MCC Films

Samples of all film compositions (0, 0.5, 1, 2 wt. %) were submerged in a NaOH solution to carry out the hydrolytic degradation procedure and evaluate the differences in its effect among the different films. The first observation that was made after a 24h hydrolytic degradation period in 0.4 % NaOH solution (pH 11) was the extremely rapid degradation of the composite containing 2 wt.% of MCC. All samples lost their shape completely after just 24 hours which, as a result, eliminated any chances of further testing for this particular composition. In Fig. 16 it is presented typical view of films after 24 hours.

Fig. 16. The appearance of PLA/MCC 2 wt.% composite samples after 24 hours

Other compositions kept their shape to an extent, through the entire 120-hour period. As seen in Table 10, pure PLA as well as PLA/MCC 1 wt. % composition kept their shape and did not have any breakage, only some surface deterioration was visible. PLA/MCC 0.5 wt.% composition started displaying breakage just after 24 hours of degradation and continued to deteriorate even further to the point where only 2 out of 5 samples have kept their original shape.

Table 10. Visual signs of hydrolytic degradation of different PLA/MCC compositions over 120 h period

Immersion duration *τ*, h	**PLA/MCC (wt. %)**		
	100/0	**99,5/0,5**	**99/1**
24 h			

Immersion duration τ, h	PLA/MCC (wt. %)		
	100/0	**99,5/0,5**	**99/1**
48 h			
72 h			
96 h			
120 h			

The same tendencies follow when evaluating the weight loss of the samples. The composition with 0.5 wt.% of MCC (Fig. 17 - b) displays the biggest relative weight loss average of 18.1 % after 120-hour hydrolytic degradation period. The results are very constant across the stream of samples in the first 48 hours and then start to vary gradually during the remaining time period. It’s weight loss trend progresses according to the equation y = 0.0016x – 0.0066, which indicates that the hydrolytic degradation slows down over time. In the meantime, pure PLA films (Fig. 17 - a) relative weight loss was on average 11.6 %. The results are relatively very consistent throughout the whole 120-hour testing period and the weight loss trend follows the equation y = 0.001x – 0.0012, which once again indicates slowing down of the degradation process. Composition with 1 wt.% of MCC (Fig. 17 – c) revealed similar resistance to hydrolytic degradation as pure PLA films with even a slight increase. It’s weight loss average after degrading for 120 hours was 10.9 %. The results are also relatively consistent, and the weight loss follows a trend according to the equation y = 0.0009x + 0.0004. In this case, the degradation seems to be speeding up slightly with the progression of time. The linear dependence determination coefficients that were calculated are valued close to 1, indicating that the chosen mathematical model is suitable for evaluation of hydrolytic degradation effects on PLA films.

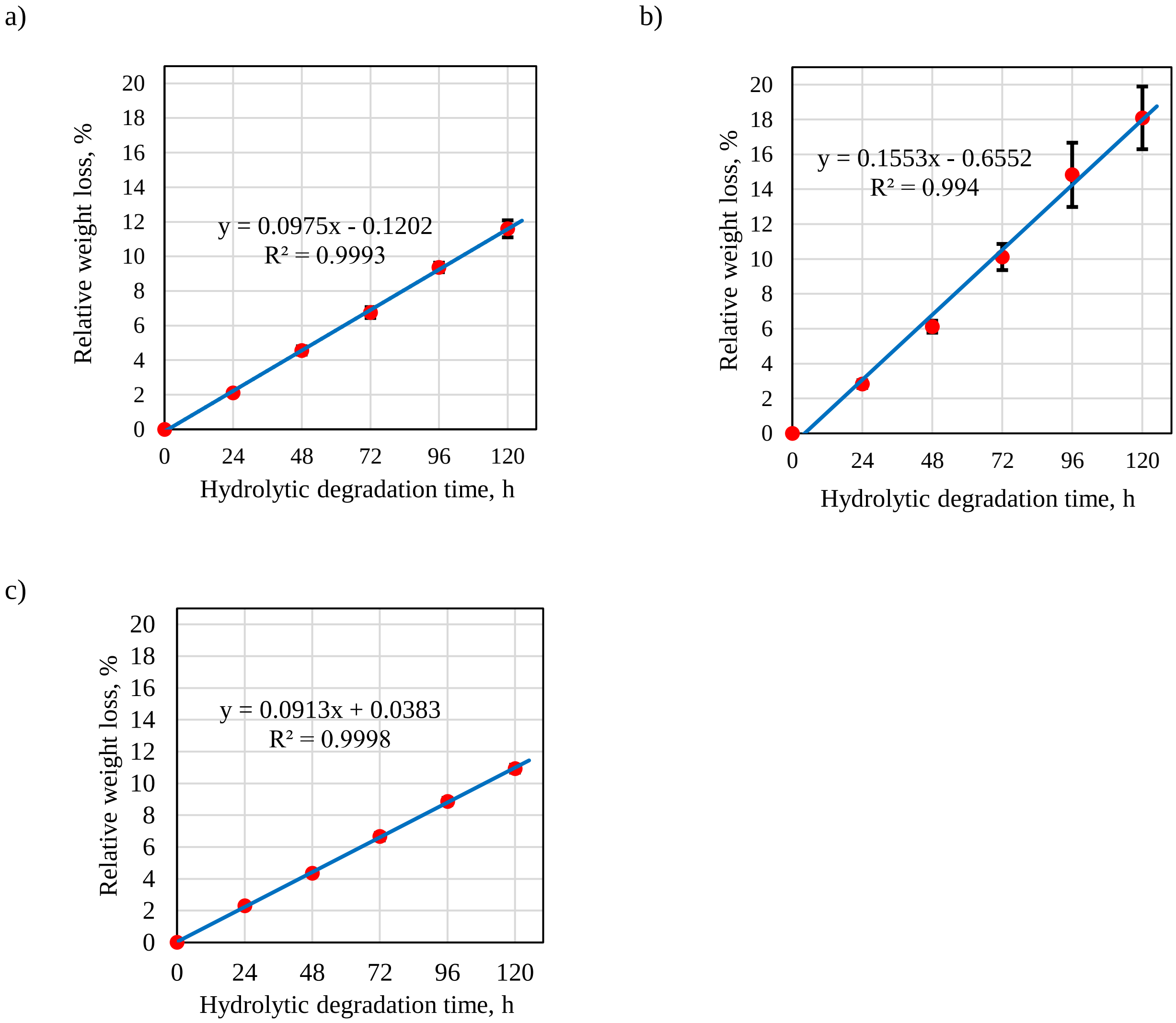


Fig. 17. Relative weight loss of PLA films vs /MCC content during period of 120 hour of hydrolytic degradation (a – 0 wt. % MCC, b – 0.5 wt. % MCC, c – 1 wt.% MCC)

Overall, this test shows that the addition of MCC to PLA film can alter its resistance to hydrolytic degradation in various ways, depending on the amount added. This inconsistency could attribute to the different dispersion of the filler in the PLA matrix, according to the amount added.

3.3. Evaluation of Tensile Properties After Hydrolytic Degradation

All PLA/MCC compositions were tested under tension to determine MCC filler content effect on the tensile properties of PLA. This test also allows to evaluate the hydrolytic degradation rate over time and compare tendencies among the films.

The first stream of samples to be analyzed is the pure PLA film and how it reacted to the hydrolytic degradation procedure over different periods of time. As a control group, 5 PLA samples that were not subjected to any hydrolytic degradation were tested. In the tensile curves, the control group (Fig. 18 – a) samples exhibit great strength, even slight elasticity and the results are very consistent among samples. Right next to it (Fig. 18 – b), the tensile test of samples that have been exposed to the NaOH solution for 24 hours is presented. There is a clear indication of the reduction in strength and almost complete loss of ductility. The material in general becomes more brittle. Throughout the rest of the test (Fig. 18 – c, d, e, f) some interesting changes in the curves can be noticed. Some samples begin to display ductile behavior and increased strength once again although it is never seen among the full sample set. This could be attributed to the inconsistencies among the sample structure, as it could have been more crystalline to begin with. However, one could argue, that by taking those few results out of the equation, the ductility and strength of PLA that has been degraded hydrolytically decreases over time.

Pure PLA film is known to be a stiff material, the calculated Modulus of Rupture (average of 794.15 MPa, see Table 11), as well as elongation at break (average of 5.76 %) both correspond to that knowledge. The material is, though, quite strong with stress at break average of 45.8 MPa. This data is consistent among the samples. Just after 24 hours of being exposed to the NaOH solution, there is already a clear decrease of the mechanical properties. The material becomes stiffer and more brittle with the increase of Modulus of Rupture to 880.72 MPa on average and stress at break reduction to 29.49 MPa. However, over time, there is no consistent change in these values, as the mechanical properties seem to be fluctuating and then settling to about 27 MPa stress at break and Modulus of Rupture of 890 MPa. The fluctuation could be explained by the inconsistencies in the sample structure, as just after 48 hours, there is a visible increase in deviation among each sample set which is clearly indicated by the increasing standard deviation and confidence intervals. Even so, it is inarguable that, judging from the change in the mechanical properties, shows an ability to degrade rapidly.

The tensile curves of PLA samples with the addition of 0.5 wt. % of MCC is presented in Fig. 19. In this case, there were once again some samples that fluctuate from the average behavior, displaying some elasticity and higher strength even after being in the NaOH solution. However, there is one very visible difference when comparing this composite film to the pure PLA film. The change in mechanical properties is even more rapid with the increasing hydrolytic degradation time. Cellulose should not have dissolved in a NaOH solution of this concentration. On the other hand, it could have caused the cellulose particles to swell, altering the existing composite structure and perhaps even increasing the contact area by creating vacancies (e.g. cracks) [28].

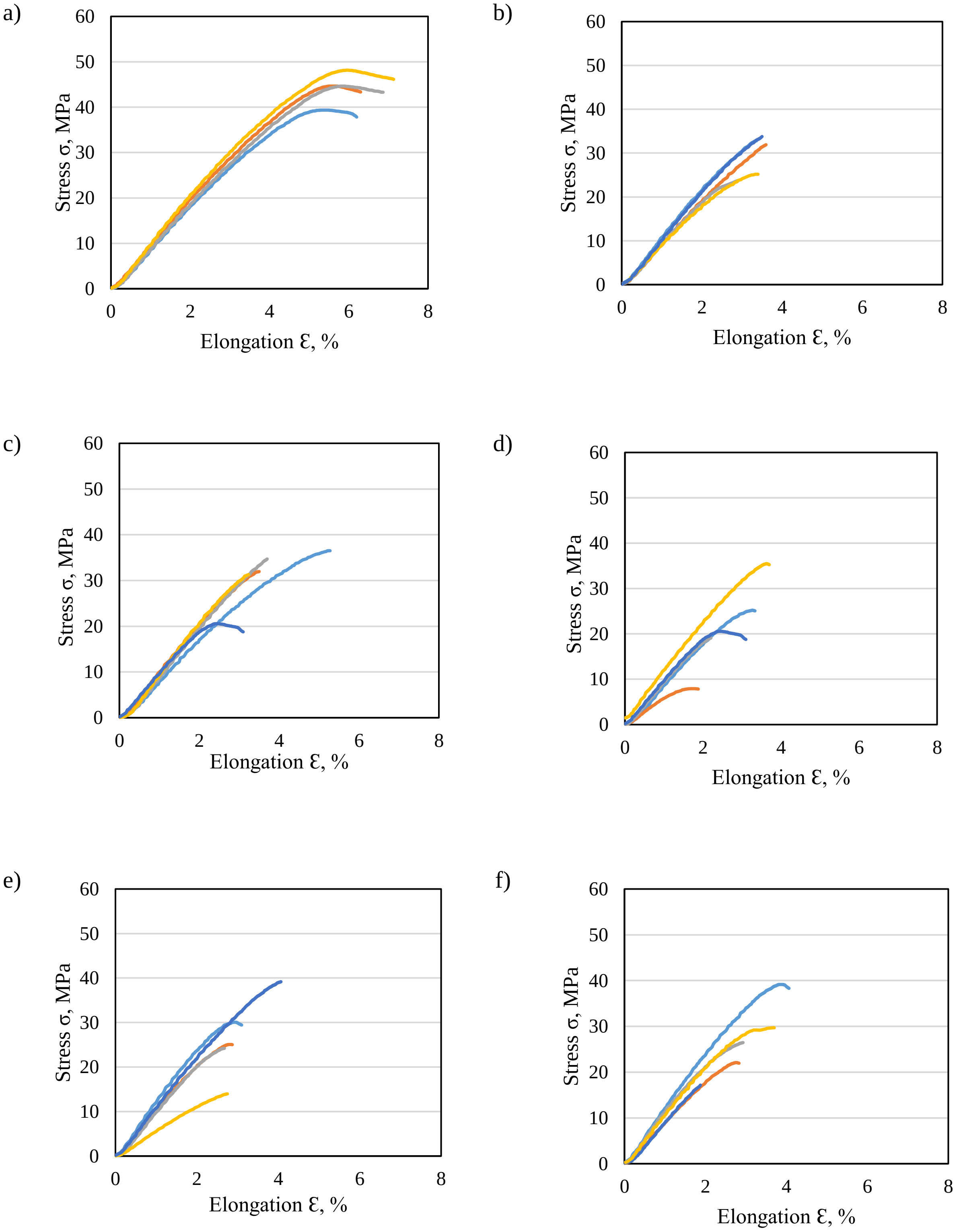


Fig. 18. Stress – strain curves of pure PLA film samples after various times of hydrolytic degradation: a – 0 h, b – 24 h, c – 48 h, d – 72 h, e – 96 h, f – 120h

Table 11. Stress at break, elongation at break and Modulus of Rupture of pure PLA film samples after different durations of hydrolytic degradation

Immersion duration τ, h	**Sample no.**	**σ_{max}, MPa**	**ε_{break}, %**	**E, MPa**
0	1	44.64	5.49%	813.57
	2	39.35	5.27%	747.19
	3	44.65	5.79%	770.88
	4	48.16	5.93%	812.75
	5	52.20	6.32%	826.39
	Mean	45.80	5.76%	794.15
	Standard deviation	4.76	0.41%	33.57
	Confidence interval	(39.88;51.71)	(0.05;0.06)	(752.47;835.84)
24	1	32.85	3.36%	977.01
	2	31.90	3.60%	886.20
	3	23.72	2.90%	817.97
	4	25.17	3.33%	757.09
	5	33.79	3.50%	965.31
	Mean	29.49	3.34%	880.72
	Standard deviation	4.68	0.27%	94.44
	Confidence interval	(23.68;35.29)	(0.03;0.04)	(763.47;997.96)
48	1	36.51	5.23%	698.84
	2	31.97	3.50%	914.39
	3	34.71	3.70%	938.06
	4	31.30	3.23%	968.00
	5	20.56	2.40%	858.17
	Mean	31.01	3.61%	875.49
	Standard deviation	6.21	1.03%	106.65
	Confidence interval	(23.3;38.72)	(0.02;0.05)	(743.1;1007.89)
72	1	25.23	3.26%	773.40
	2	7.92	1.67%	473.32
	3	19.09	2.20%	867.58
	4	35.50	3.63%	979.31
	5	14.74	1.74%	845.37
	Mean	20.50	2.50%	787.80
	Standard deviation	10.50	0.89%	190.70
	Confidence interval	(7.46;33.53)	(0.01;0.04)	(551.06;1024.54)
96	1	30.06	2.88%	1042.63
	2	25.07	2.78%	901.96
	3	24.20	2.66%	908.68
	4	13.97	2.75%	508.65
	5	39.17	4.06%	964.70

Immersion duration τ, h	**Sample no.**	**σ_{max}, MPa**	**ε_{break}, %**	**E, MPa**
	Mean	26.50	3.03%	865.32
	Standard deviation	9.18	0.58%	207.22
	Confidence interval	(15.09;37.9)	(0.02;0.04)	(608.07;1122.57)
120	1	39.15	3.82%	1024.92
	2	22.08	2.74%	805.73
	3	26.45	2.92%	904.93
	4	29.69	3.68%	807.95
	5	17.16	1.88%	914.55
	Mean	26.91	3.01%	891.62
	Standard deviation	8.31	0.78%	90.62
	Confidence interval	(16.59;37.22)	(0.02;0.04)	(779.11;1004.12)

When looking at the calculated values of PLA/MCC 0.5 wt. % sample stream there is no drastic change (see Table 12) in the maximum stress at break (average of 43.5 MPa), elongation at break (average of 5.09 %) and in turn Modulus of Rupture (average of 851.58 MPa) when comparing the two control groups that have not been exposed to the NaOH solution. However, just after 24 hours the maximum stress is already reduced to almost half of what it was, the ductility is clearly reduced and the same trends continues as time of test goes on. At the very end, after 120 hours of hydrolytic degradation the final maximum stress average is just 10.14 MPa, the elongation at break is 1.94 % and Modulus of Rupture is reduced to 485.99 MPa on average. The results are also quite consistent judging by the standard deviation and the confidence intervals. This behavior corresponds well to the previous parts of the study, where the composite film with the addition of 0.5 % of MCC showed the most sensitivity to hydrolytic degradation both when evaluating the samples visually and measuring weight loss.

Even still, the following test results of the PLA/MCC 1 wt. % film raise further questions, as the film displays similar behavior to pure PLA with even greater resistance to hydrolytic degradation. Some interesting observations can be made from the tensile curves presented in Fig. 20. With the control group (Fig. 20 – a) the results vary a little bit but all show almost no elasticity and slightly lower strength compared to pure PLA or even PLA/MCC 0.5 wt. % composite. The tensile curve that displays the testing results of samples that have been degraded hydrolytically for 24 hours (Fig. 20 – b) are visibly very variable. There are some samples in tensile curves presented in Fig. 20 – c, d, e that even display some ductility but no noticeable decrease in strength and also a slightly elevated inconsistency among the curves. In the final sample set (Fig. 20 – f) there seems to be no ductility left in any samples and the strength has decreased but not drastically from the start of the test.

The maximum stress is even lower than PLA/MCC 0.5 % composite at the average of 35.88 MPa (see Table 13), so is the elongation at break (average of 4.54 %) and Modulus of Rupture (average of 787.9 MPa), as could have been expected. It was not expected, however, for the resistance to hydrolytic degradation to not become even more rapid and it was even more surprising that it even seemed to reduce, compared to the pure PLA film. After 24 hours the average of maximum stress decreases to the average of 20.77 MPa, which, judging just from the average shows a quite rapid degradation.

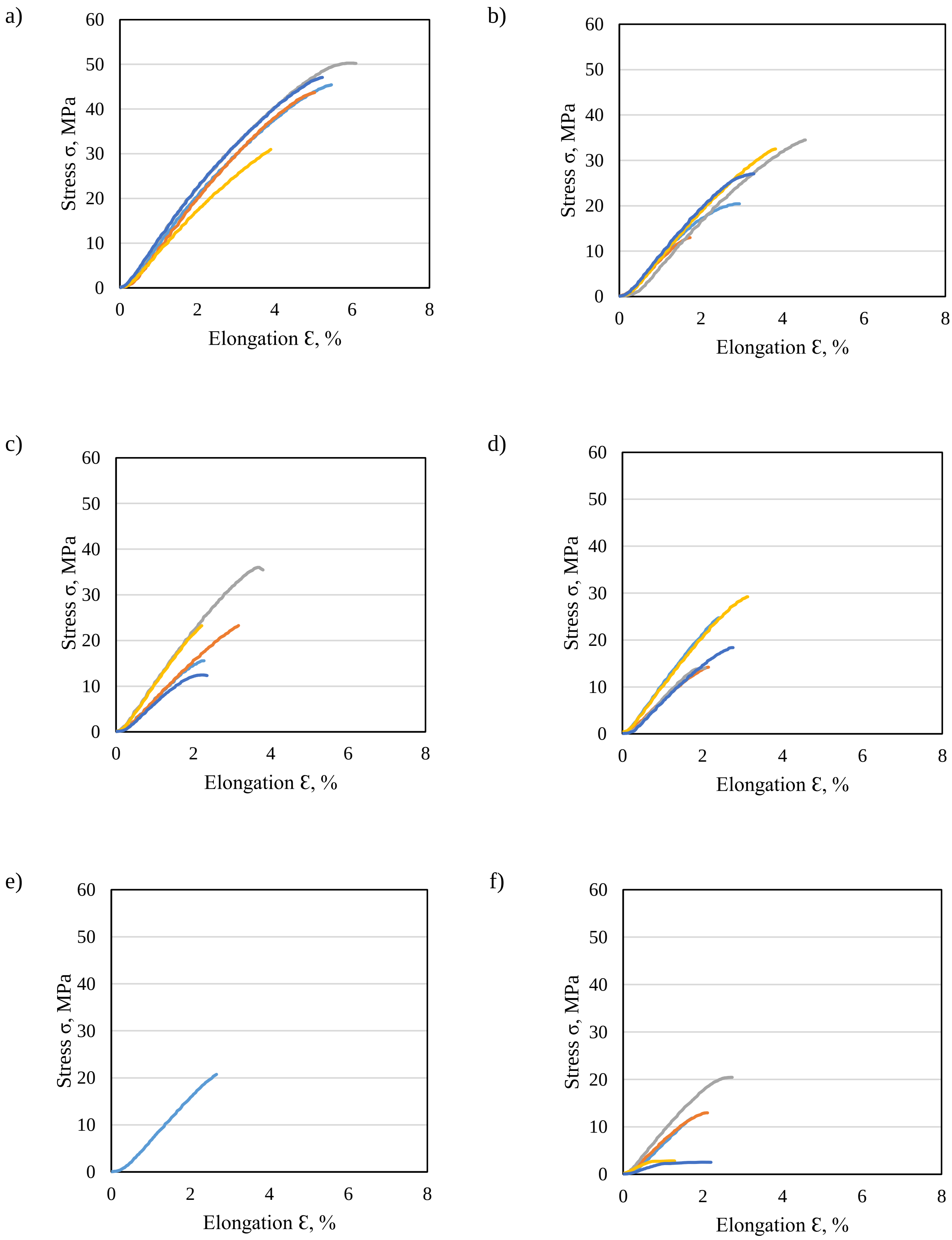


Fig. 19. Stress – strain curves of PLA film with 0.5 wt. % addition of MCC samples after various times of hydrolytic degradation: a – 0 h, b – 24 h, c – 48 h, d – 72 h, e – 96 h, f – 120h

Table 12. Stress at break, elongation at break and Modulus of Rupture of PLA film with 0.5 wt. % addition of MCC samples after different times of hydrolytic degradation

Immersion duration τ, h	**Sample no.**	**σ_{max}, MPa**	**ε_{break}, %**	**E, MPa**
0	1	45.43	5.46%	832.14
	2	43.70	5.02%	870.48
	3	50.28	5.85%	859.07
	4	30.98	3.90%	794.26
	5	47.08	5.22%	901.98
	Mean	43.50	5.09%	851.58
	Standard deviation	7.41	0.73%	40.67
	Confidence interval	(34.3;52.69)	(0.04;0.06)	(801.09;902.08)
24	1	20.43	2.85%	715.95
	2	12.98	1.73%	748.60
	3	34.49	4.55%	758.08
	4	32.51	3.83%	849.03
	5	27.03	3.29%	822.33
	Mean	25.49	3.25%	778.80
	Standard deviation	8.87	1.06%	55.04
	Confidence interval	(14.47;36.5)	(0.02;0.05)	(710.47;847.13)
48	1	15.57	2.28%	684.19
	2	23.28	3.17%	735.09
	3	36.02	3.66%	984.53
	4	23.25	2.22%	1048.69
	5	12.45	2.20%	565.97
	Mean	22.11	2.70%	803.69
	Standard deviation	9.11	0.67%	205.08
	Confidence interval	(10.8;33.43)	(0.02;0.04)	(549.1;1058.29)
72	1	24.73	2.41%	1026.00
	2	14.20	2.15%	660.55
	3	14.04	2.07%	679.28
	4	29.21	3.13%	934.79
	5	18.38	2.73%	672.26
	Mean	20.11	2.50%	794.58
	Standard deviation	6.69	0.44%	172.80
	Confidence interval	(11.81;28.41)	(0.02;0.03)	(580.06;1009.1)
96	1	20.74	2.66%	778.75
120	1	11.85	1.73%	686.07
	2	12.96	2.09%	621.01
	3	20.45	2.70%	757.38
	4	2.83	1.20%	236.16

Immersion duration τ, h	**Sample no.**	**σ_{max}, MPa**	**ε_{break}, %**	**E, MPa**
	5	2.55	1.97%	129.33
	Mean	10.13	1.94%	485.99
	Standard deviation	7.55	0.55%	283.52
	Confidence interval	(0.75;19.5)	(0.01;0.03)	(134.01;837.97)

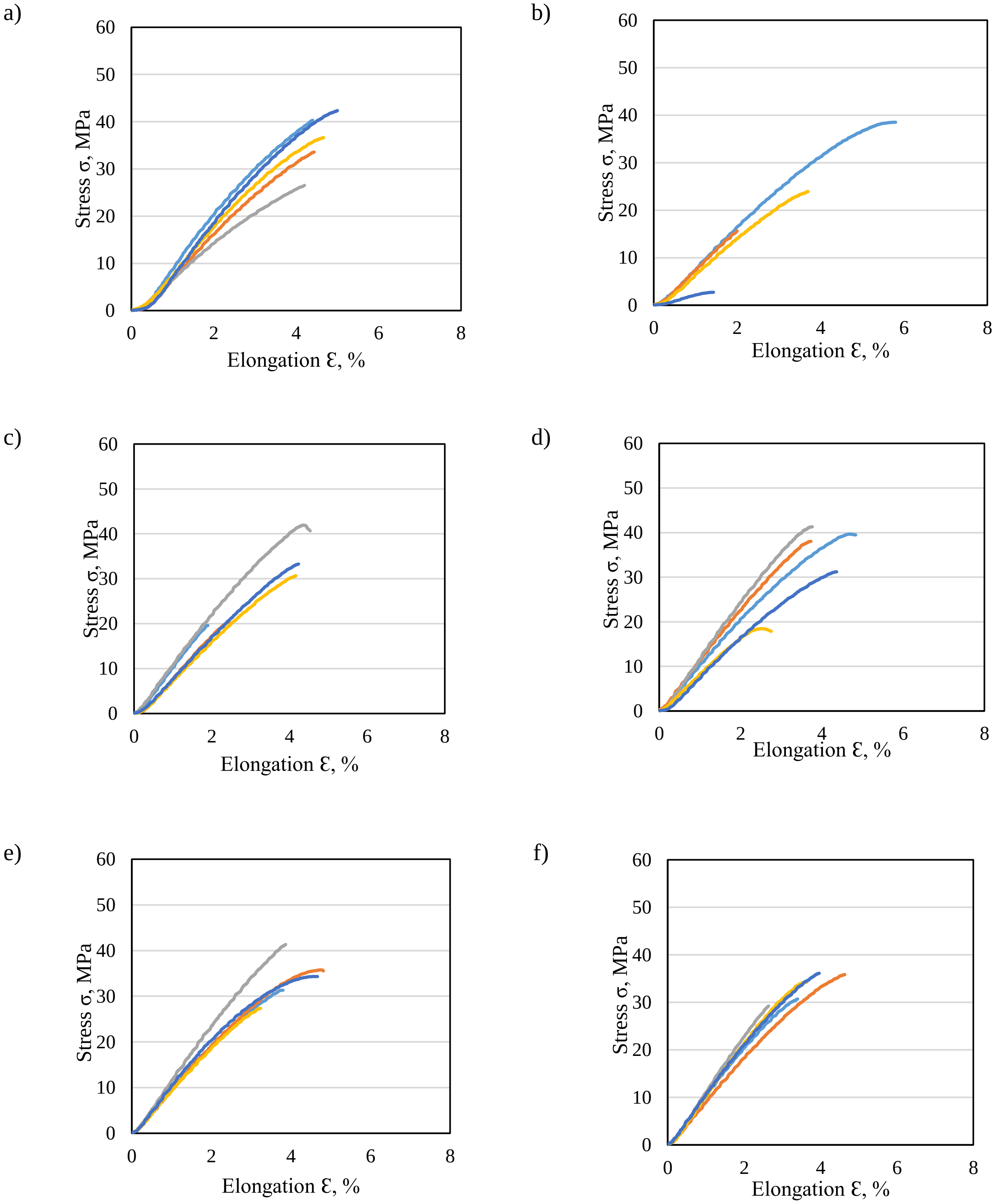


Fig. 20. Stress – strain curves of PLA film with 1 wt. % addition of MCC after various times of hydrolytic degradation: a – 0 h, b – 24 h, c – 48 h, d – 72 h, e – 96 h, f – 120h

On the other hand, these results have a very high confidence interval and that is mainly due to one result, of sample no. 5 that indicated an only 2.72 MPa maximum stress. That particular result could be evaluated as not valid, which in turn would increase the average drastically. This suggestion is also backed up by the further test results. After 48 hours the maximum stress increases to 29.17 MPa and the consistency is also better among the sample set. Just like with the pure PLA film, the results fluctuate a little bit as the degradation time goes on and, in the end, the maximum stress is 33.23 MPa, the elongation at break is 3.64 % and the Modulus of Rupture is 930.14 MPa. This shows that hydrolytic degradation for the PLA/MCC 1 wt. % film is extremely slow, compared to the other samples or even nonexistent, at least in the 120-h timeframe. The fluctuations, like mentioned before, could be due to the structural inconsistencies among samples.

Table 13. Stress at break, elongation at break and Modulus of Rupture of PLA film with 1 wt. % of MCC different duration of hydrolytic degradation

Immersion duration *τ*, h	**Sample no.**	**σ_{max}, MPa**	**ε_{break}, %**	**E, MPa**
0	1	40.29	4.40%	916.83
	2	33.57	4.43%	757.68
	3	26.52	4.20%	631.38
	4	36.64	4.66%	786.27
	5	42.37	5.00%	847.37
	Mean	35.88	4.54%	787.90
	Standard deviation	6.23	0.31%	106.74
	Confidence interval	(28.14;43.61)	(0.04;0.05)	(655.39;920.42)
24	1	38.51	5.72%	673.33
	2	15.63	2.00%	781.25
	3	23.04	3.17%	727.55
	4	23.93	3.70%	647.35
	5	2.72	1.43%	190.05
	Mean	20.77	3.20%	603.91
	Standard deviation	13.06	1.67%	237.03
	Confidence interval	(4.55;36.98)	(0.01;0.05)	(309.65;898.17)
48	1	19.61	1.90%	1033.70
	2	20.37	2.44%	834.69
	3	41.92	4.33%	968.12
	4	30.66	4.16%	737.06
	5	33.29	4.23%	786.90
	Mean	29.17	3.41%	872.09
	Standard deviation	9.36	1.15%	124.73
	Confidence interval	(17.54;40.79)	(0.02;0.05)	(717.25;1026.94)
72	1	39.66	4.67%	849.75
	2	38.04	3.72%	1023.38
	3	41.30	3.73%	1107.39
	4	18.46	2.52%	731.56

Immersion duration τ, h	**Sample no.**	**σ_{max}, MPa**	**ε_{break}, %**	**E, MPa**
	5	31.21	4.35%	717.57
	Mean	33.73	3.80%	885.93
	Standard deviation	9.36	0.82%	174.23
	Confidence interval	(22.11;45.35)	(0.03;0.05)	(669.63;1102.23)
96	1	31.31	3.77%	831.20
	2	35.76	4.72%	757.60
	3	41.32	3.87%	1068.61
	4	27.34	3.23%	846.53
	5	34.32	4.53%	756.98
	Mean	34.01	4.02%	852.18
	Standard deviation	5.20	0.61%	127.79
	Confidence interval	(27.55;40.47)	(0.03;0.05)	(693.54;1010.83)
120	1	30.71	3.40%	904.28
	2	35.85	4.63%	774.23
	3	29.23	2.64%	1107.32
	4	34.24	3.59%	953.32
	5	36.12	3.96%	911.55
	Mean	33.23	3.64%	930.14
	Standard deviation	3.10	0.73%	119.64
	Confidence interval	(29.38;37.08)	(0.03;0.05)	(781.61;1078.67)

The last sample stream to be tested was the PLA/MCC 2 wt. % composite. This composite unfortunately was not tested after being exposed to the NaOH solution, as the samples were not able to keep their shape even after 24 hours of degradation. This shows that the degradation rate of this composite was extremely rapid overall and that this composite is significantly more sensitive to hydrolytic degradation compared to other composites tested.

Putting the hydrolytic degradability aside, the mechanical properties of the control group can still be evaluated and compared to the composite films discussed above. The tensile curves for the PLA/MCC 0,4 % composite display very slight elasticity and very similar strength compared to all other sample streams (see Fig. 21). The tensile curves are not largely spread out through the graph except for one sample which displayed increased stiffness and less ductility.

The maximum stress average for this composite (see Table 14) stands at 32.64 MPa which is consistent with the previously seen tendencies of the maximum stress decreasing with the increase of MCC content. The elongation at break, however, is slightly higher with the average of 5.04 %. The Modulus of Rupture average is 669.32 MPa, which indicates that this composite has the least stiffness.

Overall, the addition of MCC to PLA films shows to decrease its strength with a larger amount of filler added but also has the potential to increase ductility. When it comes to hydrolytic degradability properties, the result flow is not as consistent but rather decreases and increases again depending on the percentage of MCC added.

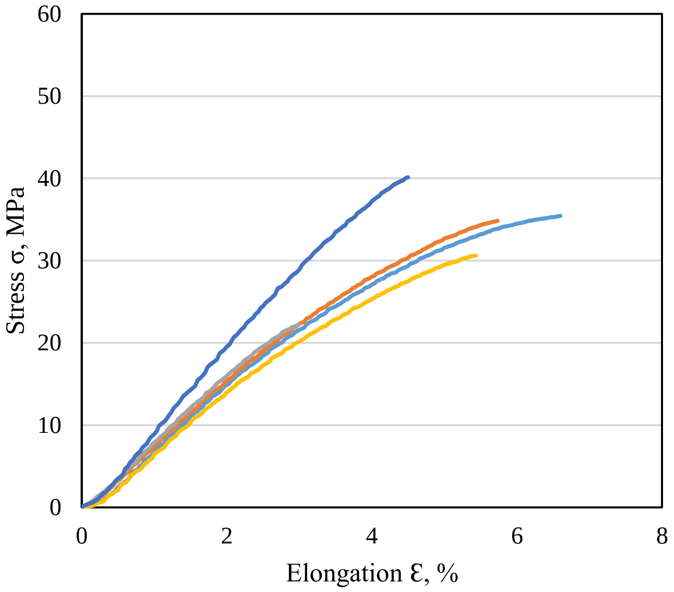


Fig. 21. Stress – strain curves of PLA film with 2 wt. % addition of MCC without hydrolytic degradation

Table 14. Stress at break, elongation at break and Modulus of Rupture of PLA film with 2 wt. % addition of MCC samples without hydrolytic degradation

Sample no.	**σ_{max}, MPa**	**ε_{break}, %**	**E, MPa**
1	35.44	6.59%	537.70
2	34.84	5.73%	608.45
3	22.19	2.99%	742.85
4	30.61	5.42%	564.71
5	40.14	4.50%	892.91
Mean	32.64	5.04%	669.32
Standard deviation	6.75	1.37%	147.79
Confidence interval	(29.69;35.6)	(0.04;0.06)	(604.56;734.08)

3.4. Evaluation Influence of MCC Content and Degradation Duration on the structure of PLA films

Optical microscopy images were taken to evaluate and note differences in surface structure changes between films produced at different temperatures, as well as films with different percentages of MCC before and after hydrolytic degradation.

When evaluating a good temperature for film production it was chosen to access not only the mechanical behavior but also the structural and surface properties of the resulting film. In Fig. 22 optical microscope images of PLA film produced at 160 °C (Fig. 22 – a) and PLA film produced at 180 °C (Fig. 22 – b) are presented. PLA film produced at 190 °C can also be seen in Fig 20 – a. What stands out in all of these images is the surface abrasion. All 3 films display uneven scratch – like patterns which are probably caused by the uneven surface of the hot – pressing equipment. The unevenness seems to be the most prominent in the film produced at 180 °C where larger vacancies that look like cracks can be seen. This phenomenon could also explain the large deviation of the tensile testing results that were acquired when testing this particular film. Although still quite uneven, film produced at 190 °C seems to have the least abrasion, once again confirming that 190 °C is indeed the effective temperature to produce film using this method.

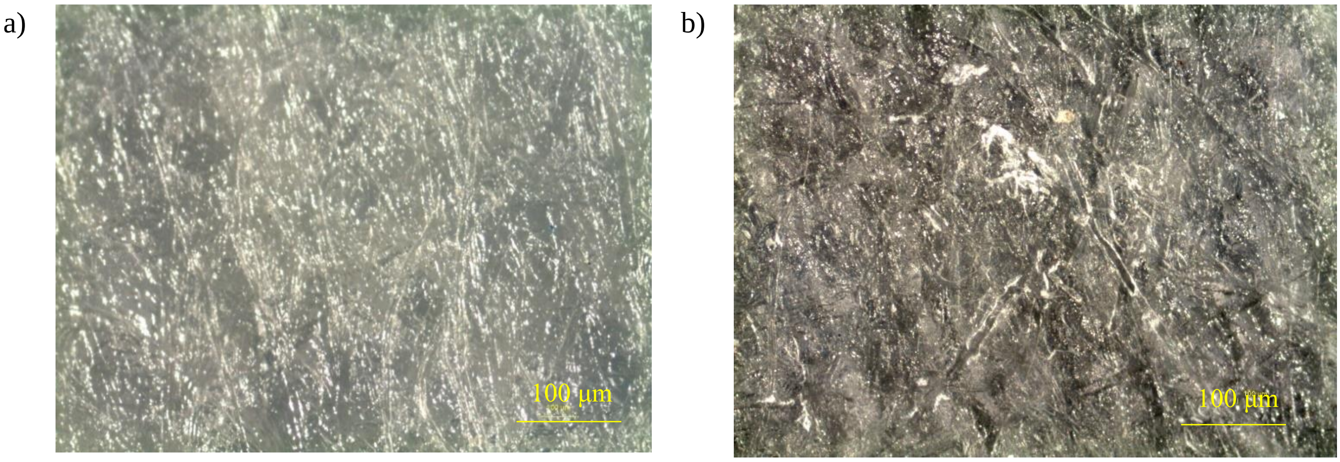


Fig. 22. Optical microscopy images of pure PLA films obtained at different temperatures T: a –160 °C, b – 180 °C

Pure PLA films before (Fig. 23 – a) and after 120 hours of hydrolytic degradation (Fig. 23 – b) are also compared. Because of the uneven surface area, it is not easy to indicate what exact damage to the surface area was caused by the NaOH solution. However, when looking closely there are a few distinct vacancies in the PLA film after 120 hours of hydrolytic degradation. These types of vacancies could cause both weight loss and the reduction of mechanical properties.

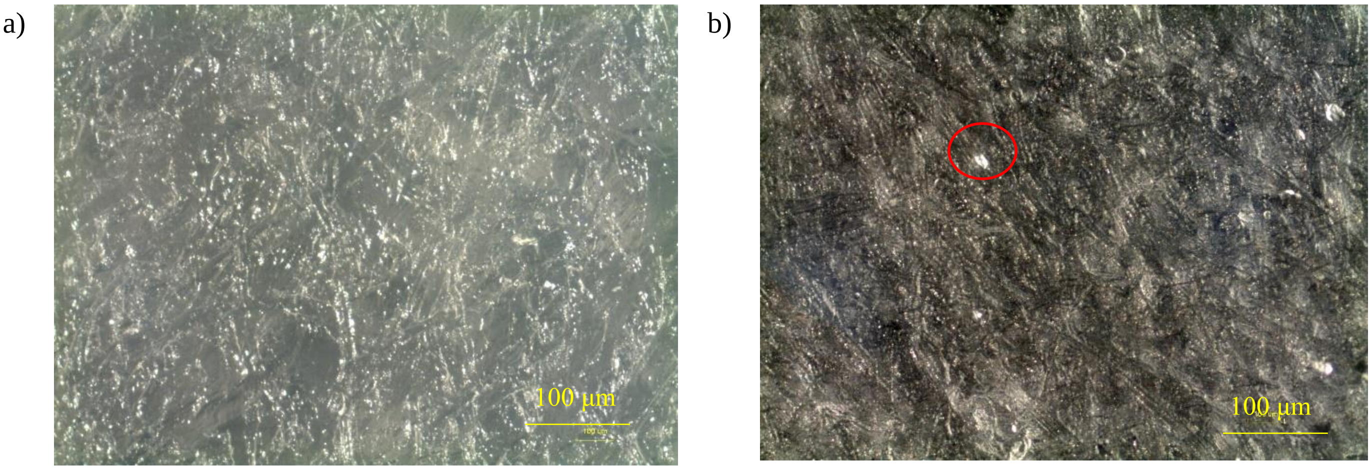


Fig. 23. Optical microscopy images of PLA film after hydrolytic degradation time τ: a – 0 h, b – 120 h

In Fig. 24 – 1 there is a picture of PLA/MCC 0.5 wt. % composite film before hydrolytic degradation. When comparing this picture to Fig. 23 – a, one can notice the MCC particle distribution in the PLA matrix. There seems to be no consistent orientation of the particles in the PLA matrix, which would also explain the inconsistencies among samples when testing the tensile properties. After 120 hours of hydrolytic degradation (Fig. 24 – b) there are very visible cracks and vacancies that are also a lot more prominent than in the pure PLA film (Fig. 23 – b) where they were barely noticeable. These vacancies increase the area of surface in the film making the contact area bigger and allowing for an exponentially more rapid hydrolytic degradation of PLA when exposed to a NaOH solution.

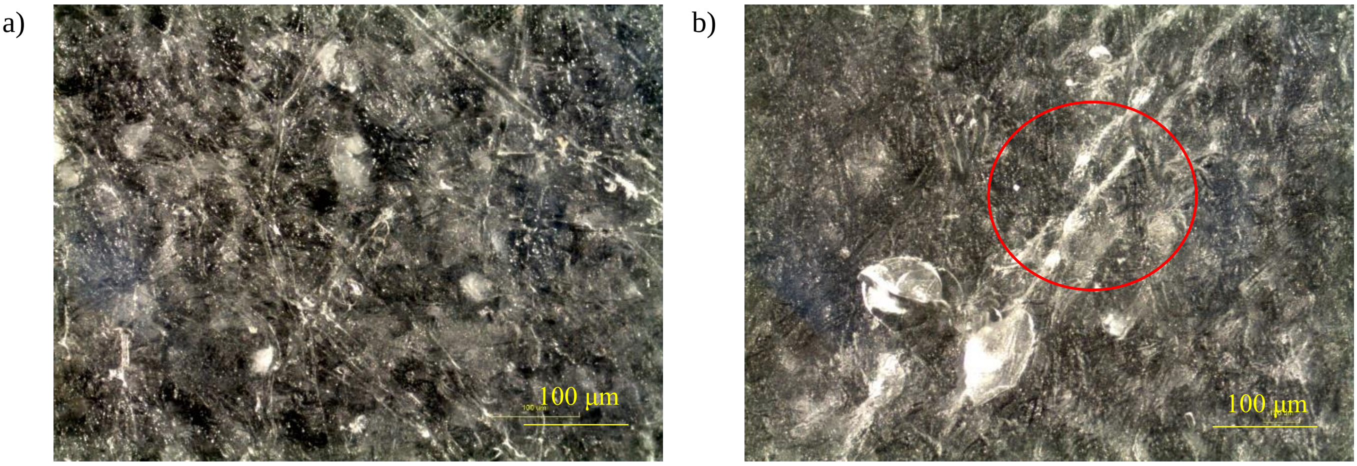


Fig. 24. Optical microscopy images of PLA/MCC 0.5 wt. % FILM after hydrolytic degradation time τ: a – 0 h, b – 120 h

Similarly, as in the picture above (Fig. 24 – a), when looking at the optical microscope picture of PLA/MCC 1 wt. % composite film presented in Fig 25 – a, one can see even more MCC fibers dispersed in the PLA matrix. Also, in the same way, the particles are not oriented neatly in the polymer matrix which in turn can cause inconsistencies in mechanical properties among samples. After 120 hours of hydrolytic degradation (Fig. 25 – b) there are small vacancies. Nonetheless, these vacancies are much less abundant compared to the PLA/MCC 0.5 wt. % composite film. This also considers and explains the previous weight loss and tensile testing results where this particular composite film exhibited results that indicated less rapid hydrolytic degradation compared to other sample streams.

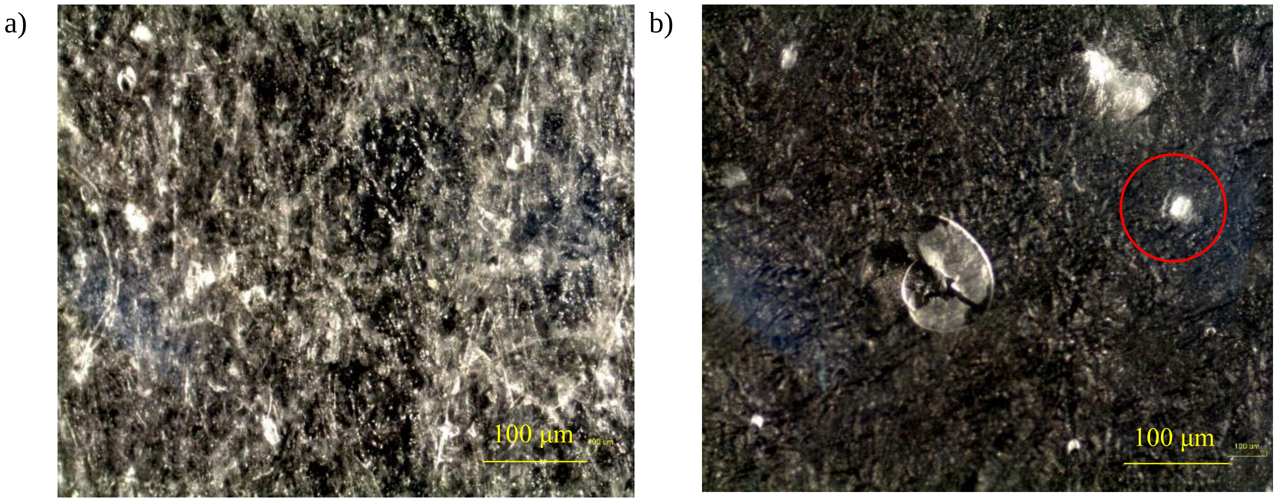


Fig. 25. Optical microscopy images of PLA/MCC 1 wt. % film after hydrolytic degradation time τ: a – 0 h, b – 120 h

In the case of PLA/MCC 2 wt. % composite film, only optical picture of it before hydrolytic degradation is available (Fig. 26). Just like in all the previous films, MCC fibers are visible. Their dispersion does not seem to differ compared to the other two composite films and there is no consistent distribution.

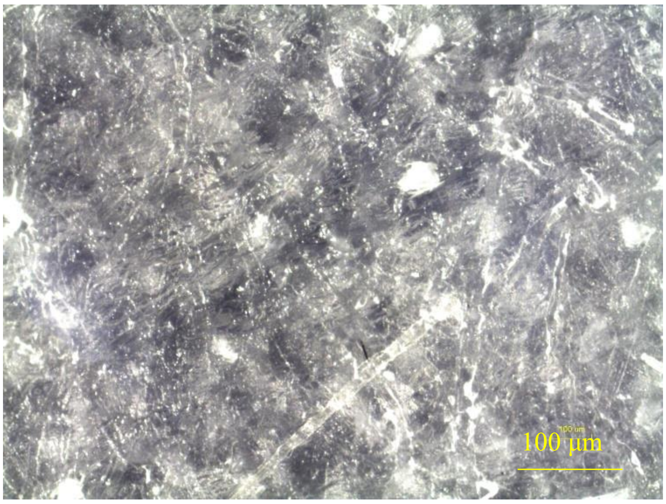


Fig. 26. Optical microscope picture PLA/MCC 0,4 % composite film without hydrolytic degradation

Overall, the optical microscopy images not only allow for visual comparison of films surfaces and structures before and after hydrolytic degradation but also corresponds well to most conclusions that were drawn from previous tests.

3.5. Chapter Summary

The first part of the experiment was to determine effective temperature for the production of PLA films by applying compression method. Taking into account both performance and the consistency of the results the temperature setting of 190 °C was selected.

PLA films with different amount of MCC (0,1 %, 0,2 %, 0,4 %) were exposed to hydrolytic degradation in the NaOH solution. PLA/MCC 0,4 % composite samples were not able to keep their shape even after 24 hours of degradation. As a results, no further testing could be carried out for this film. Other samples all displayed signs of degradation both in terms of weight loss and visually. The most rapid degradation was observed in PLA/MCC 0,1 % film.

The evaluation of mechanical properties represented the same tendencies as the weight loss testing in terms of degradability. PLA/MCC 0,1 % film displayed the most rapidly declining mechanical behavior with PLA/MCC 0,2 % film displaying very little to no reaction to the exposure to NaOH solution. Aside from degradability, there was also a trend of stress at break decreasing with the increase amount of MCC, while ductility of tested samples increased.

A visual analysis was performed to evaluate structural and surface changes in the different films before and after degradation, as well as how production temperature can influence film structure. The optical microscope pictures showed roughened surface in all the films, which is slightly less prominent in the film produced at 190 °C. One can also see the uneven distribution of MCC particles in the PLA matrix and how some cracks and vacancies appear in the film after 120 h of hydrolytic degradation.

4. Statistical Quality Control with Application ANOVA

4.1. Application of ANOVA/Single Factor for Degradability Data Analysis

Standard *ANOVA/Single factor* tool was applied in this research in order to determine the timeframe of hydrolytic degradation when the mechanical properties of PLA film reinforced with MCC filler start to drastically decrease. This tool is able to perform comparition betwwen two datasets and evaluate is difference between them significant or not. For this project, elongation at break was chosen as a value, which's changes are evaluated.

In the case of pure PLA film with no filler, as seen in Table 15, F is already larger than F_{crit}, just after 24 hours. From this one can make an assumption that somewhere in those 24 hours of hydrolytic degradation is a point where there is a significant change in the elongation at break of the material.

Table 15. ANOVA/Single factor analysis of PLA film before and after 24 h of hydrolytic degradation

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
PLA 0h	5	0,287866667	0,0575733	1,6404E-05
PLA 24h	5	0,166875	0,033375	7,1875E-06

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0,001463898	1	0,0014639	124,1040259	3,77E-06	5,317655
Within Groups	9,43659E-05	8	1,18E-05			
Total	0,001558264	9				

Similar trends are observed in the ANOVA analysis of PLA reinforced with 0,1 % MCC. Significant change in elongation at break is already noticed in the firs 24 hour degradation period, as seen in Table 16 ($F > F_{crit}$).

Table 16. ANOVA/Single factor analysis of PLA/MCC 0,1 % film before and after 24 h of hydrolytic degradation

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
PLA/MCC 0,1 % 0h	5	0,254533333	0,050906667	5,39369E-05
PLA/MCC 0,1 % 24h	5	0,162533333	0,032506667	0,000112112

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0,0008464	1	0,0008464	10,19461821	0,012747655	5,317655
Within Groups	0,000664194	8	8,30242E-05			
Total	0,001510594	9				

PLA film reinforced with 0,2 % MCC filler displays very different trends. As seen in the ANOVA analysis data provided bellow, *F* values are 3,09 after 24 hours (see Table 17), 4.46 after 48 hours (see Table 18), 3.,57 after 72 hours (see Table 19) and 2.87 after 96 hours (see Table 20) – all lower than the *Fcrit* value 5.32, indicating that there is no significant change in the elongation at break during the whole period of 4 days of immersion in the NaOH solution. However, after 120 hours of immersion, F value raises to 6,33 (see Table 21), finally showing a significant mechanical property change in the PLA/MCC 0,2 % film in-between 96 to 120 hours of immersion.

Table 17. ANOVA/Single factor analysis of PLA/MCC 0,2 % film before and after 24 h of hydrolytic degradation

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
PLA/MCC 0,2 % 0h	5	0,22685	0,04537	0,000009367
PLA/MCC 0,2 % 24h	5	0,160158333	0,0320317	0,000278961

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0,000444778	1	0,0004448	3,085225885	0,117072	5,317655
Within Groups	0,00115331	8	0,0001442			
Total	0,001598088	9				

Table 18. ANOVA/Single factor analysis of PLA/MCC 0,2 % film before and after 48 h of hydrolytic degradation

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
PLA/MCC 0,2 % 0h	5	0,22685	0,04537	0,000009367
PLA/MCC 0,2 % 48h	5	0,170566667	0,0341133	0,000132809

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0,000316781	1	0,0003168	4,456179186	0,067771	5,317655
Within Groups	0,000568705	8	7,109E-05			
Total	0,000885486	9				

Table 19. ANOVA/Single factor analysis of PLA/MCC 0,2 % film before and after 72 h of hydrolytic degradation

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
PLA/MCC 0,2 % 0h	5	0,22685	0,04537	0,000009367
PLA/MCC 0,2 % 72h	5	0,189858333	0,0379717	6,73853E-05

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0,000136838	1	0,0001368	3,565714764	0,095674	5,317655
Within Groups	0,000307009	8	3,838E-05			
Total	0,000443847	9				

Table 20. ANOVA/Single factor analysis of PLA/MCC 0,2 % film before and after 96 h of hydrolytic degradation

SUMMARY

Groups	**Count**	**Sum**	**Average**	**Variance**
PLA/MCC 0,2 % 0h	5	0,22685	0,04537	0,000009367
PLA/MCC 0,2 % 96h	5	0,201166667	0,0402333	3,66311E-05

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	6,59634E-05	1	6,596E-05	2,868089994	0,128805	5,317655
Within Groups	0,000183992	8	2,3E-05			
Total	0,000249956	9				

Table 21. ANOVA/Single factor analysis of PLA/MCC 0,2 % film before and after 120 h of hydrolytic degradation

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
PLA/MCC 0,2 % 0h	5	0,22685	0,04537	0,000009367
PLA/MCC 0,2 % 120h	5	0,1822	0,03644	5,36495E-05

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0,000199362	1	0,0001994	6,327303864	0,036066	5,317655
Within Groups	0,000252066	8	3,151E-05			
Total	0,000451428	9				

When comparing the PLA/MCC 0,2 % film with the 2 other previously tested films, it is inarguably obvious how much more resistible this film is to the NaOH, as it took around 4 times as much degradation time, to notice a guaranteed change.

4.2. Chapter Summary

ANOVA/Single factor package was used to determine the approximate point at which different films develop a significant change in mechanical properties during hydrolytic degradation while immersed in a 0,4 % NaOH solution. Results indicate that PLA film with 0,2 % MCC filler content has the highest resistance to the process, as the significant change is observed in the 96-to-120-hour period compared to other 2 films (pure PLA and PLA/MCC 0,1 %), where this change happens in the time period of the first 24 hours.

Conclusions

1. After performing tensile tests on PLA films reinforced with different wt. percentages of MCC (0.5, 1 and 2 wt. %) as filler and performing a statistical analysis of the results it was concluded that when MCC is used as a filler in PLA films in low amounts there is a tendency of stress at break decreasing with the increase amount of MCC – 45.8 MPa for pure PLA, 43.5 MPa for 0,5 % of filler, 35.88 MPa for 1 wt. % of filler and 32.64 MPa for 2 wt.% of filler.
2. influence of MCC filler content on the hydrolytic degradation of PLA was determined according to the weight loss and tensile test results of samples that have been immersed in 0.4 % NaOH solution every 24 hours for the total of 120 hours. Both the weight loss and tensile test results indicate that MCC content influences the intensity of hydrolytic degradation of PLA. The most rapid degradation was observed in PLA/MCC 0.5 wt. % film (~ 18 % loss of mass), with the PLA/MCC 1 wt. % film, however, hydrolytic degradation process was much slower and not as prominent (~ 11 % loss of mass).
3. The PLA/MCC films surface structure before and after hydrolytic degradation was evaluated by comparing optical microscopy images. The optical microscope pictures showed roughened surface in all the films, which is presumed to be caused by the uneven surface of the hot – press. One can also see the uneven distribution of MCC particles in the PLA matrix and how some cracks and vacancies appear in the film after 120 h of hydrolytic degradation.
4. ANOVA/Single factor software was utilized as a statistical quality control tool to determine the significance of the results difference between tested groups. This tool was found useful for evaluating and comparing mechanical PLA film properties changes during uniaxial tension vs MCC filler content and degradation duration. It was found that there was a significant change in mechanical properties of all tested samples in the 120 hour period of degradation.

Appendices

Appendix 1. Conference Certificate

11th International Young Researchers Conference

INDUSTRIAL ENGINEERING

from Zero to Hero

Certificate

This certificate confirms that

Ingrida Bernatonytė

attended in 11th International Young Researchers Conference
"Industrial Engineering 2024 – from Zero to Hero"
and published the article

Mechanical Properties of Microcrystalline Cellulose-Filled Polylactic Acid Films

in the conference proceedings

9 May 2024, Kaunas, Lithuania
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Dean of the Faculty of
Mechanical Engineering
and Design

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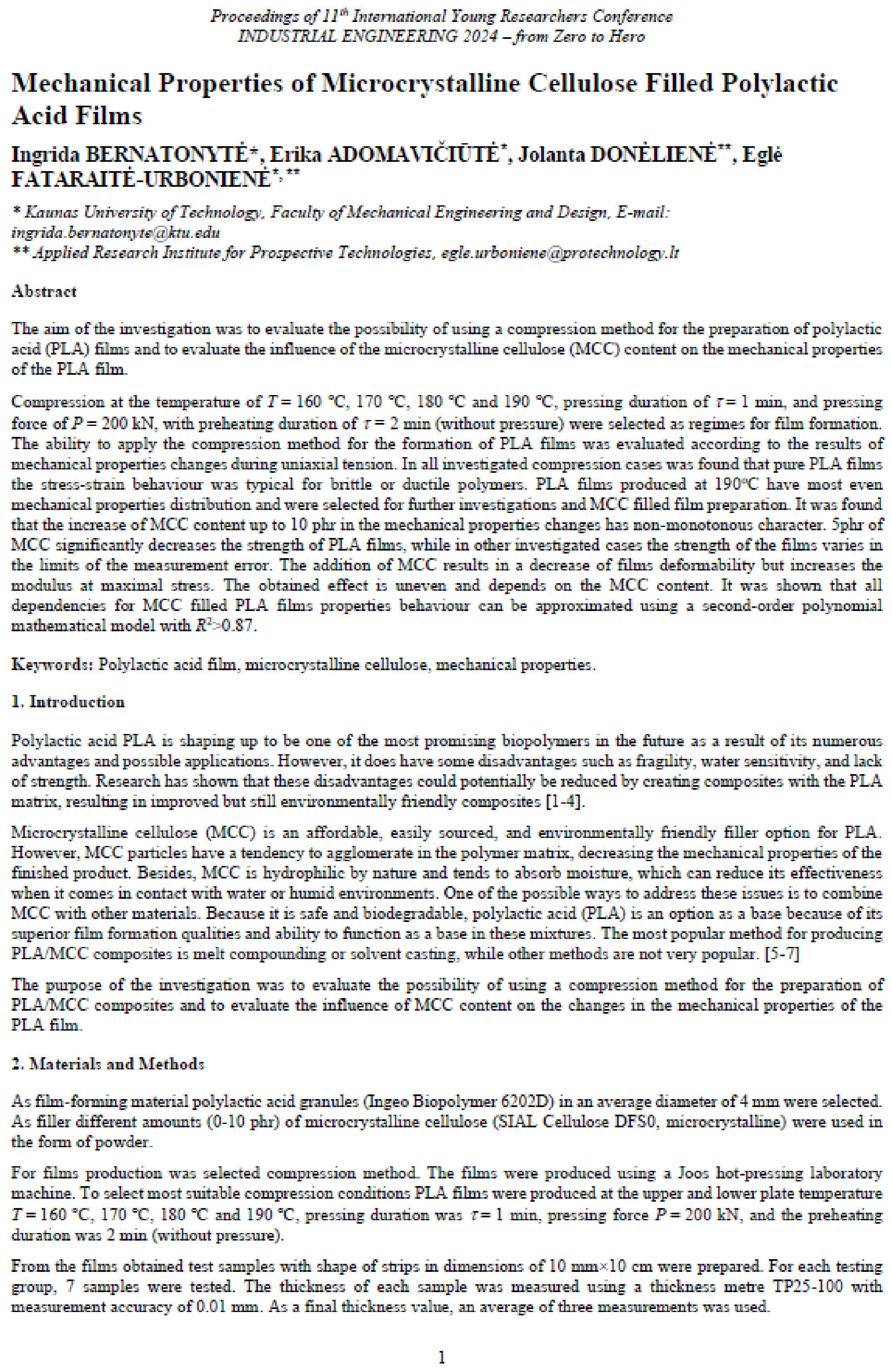
Appendix 2. Conference Publication Manuscript



Proceedings of 11th International Young Researchers Conference
INDUSTRIAL ENGINEERING 2024 – from Zero to Hero

Mechanical Properties of Microcrystalline Cellulose Filled Polylactic Acid Films

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Abstract

The aim of the investigation was to evaluate the possibility of using a compression method for the preparation of polylactic acid (PLA) films and to evaluate the influence of the microcrystalline cellulose (MCC) content on the mechanical properties of the PLA film.

Compression at the temperature of T = 160 °C, 170 °C, 180 °C and 190 °C, pressing duration of τ = 1 min, and pressing force of P = 200 kN, with preheating duration of τ = 2 min (without pressure) were selected as regimes for film formation. The ability to apply the compression method for the formation of PLA films was evaluated according to the results of mechanical properties changes during uniaxial tension. In all investigated compression cases was found that pure PLA films the stress-strain behaviour was typical for brittle or ductile polymers. PLA films produced at 190°C have most even mechanical properties distribution and were selected for further investigations and MCC filled film preparation. It was found that the increase of MCC content up to 10 phr in the mechanical properties changes has non-monotonous character. 5phr of MCC significantly decreases the strength of PLA films, while in other investigated cases the strength of the films varies in the limits of the measurement error. The addition of MCC results in a decrease of films deformability but increases the modulus at maximal stress. The obtained effect is uneven and depends on the MCC content. It was shown that all dependencies for MCC filled PLA films properties behaviour can be approximated using a second-order polynomial mathematical model with R^2>0.87.

Keywords: Polylactic acid film, microcrystalline cellulose, mechanical properties.

1. Introduction

Polylactic acid PLA is shaping up to be one of the most promising biopolymers in the future as a result of its numerous advantages and possible applications. However, it does have some disadvantages such as fragility, water sensitivity, and lack of strength. Research has shown that these disadvantages could potentially be reduced by creating composites with the PLA matrix, resulting in improved but still environmentally friendly composites [1-4].

Microcrystalline cellulose (MCC) is an affordable, easily sourced, and environmentally friendly filler option for PLA. However, MCC particles have a tendency to agglomerate in the polymer matrix, decreasing the mechanical properties of the finished product. Besides, MCC is hydrophilic by nature and tends to absorb moisture, which can reduce its effectiveness when it comes in contact with water or humid environments. One of the possible ways to address these issues is to combine MCC with other materials. Because it is safe and biodegradable, polylactic acid (PLA) is an option as a base because of its superior film formation qualities and ability to function as a base in these mixtures. The most popular method for producing PLA/MCC composites is melt compounding or solvent casting, while other methods are not very popular. [5-7]

The purpose of the investigation was to evaluate the possibility of using a compression method for the preparation of PLA/MCC composites and to evaluate the influence of MCC content on the changes in the mechanical properties of the PLA film.

2. Materials and Methods

As film-forming material polylactic acid granules (Ingeo Biopolymer 6202D) in an average diameter of 4 mm were selected. As filler different amounts (0-10 phr) of microcrystalline cellulose (SIAL Cellulose DF50, microcrystalline) were used in the form of powder.

For films production was selected compression method. The films were produced using a Joos hot-pressing laboratory machine. To select most suitable compression conditions PLA films were produced at the upper and lower plate temperature T = 160 °C, 170 °C, 180 °C and 190 °C, pressing duration was τ = 1 min, pressing force P = 200 kN, and the preheating duration was 2 min (without pressure).

From the films obtained test samples with shape of strips in dimensions of 10 mm×10 cm were prepared. For each testing group, 7 samples were tested. The thickness of each sample was measured using a thickness metre TP25-100 with measurement accuracy of 0.01 mm. As a final thickness value, an average of three measurements was used.

The mechanical properties of obtained films were evaluated during the uniaxial tensile test using a universal testing machine Tinius Olsen 25ST with an upper head speed rate 50 mm/min. From the obtained stress-strain curves elongation at break, ε (%), tensile stress σ (MPa), and modulus E (MPa) at maximal stress were calculated and compared.

For each testing group statistical parameters such as average, standard deviation, standard measurement error, and variation coefficient were calculated.

3. Results and discussion

In order to evaluate the ability to use the compression method for PLA film production, initial tests were performed to determine the most effective film formation temperature. Stress-strain curves for films obtained after compression at 160, 170, 180 and 190° C are presented in Fig. 1. It is clear that at all investigated cases obtained tension curves are typical for brittle or ductile polymer, but their deformability and strength at break are highly temperature dependent.

At a temperature of $T = 160$ °C obtained films were brittle, for them very low deformation values and stress at break values were found. The stress at break for the most of the tested samples did not reach 20 MPa (Fig. 1, *a*).

At temperature T = 170 °C (Fig. 1, b) the tensile curve shows a significant increase in strength, and the samples showed typical stress values for amorphous PLA, which vary in limits of 50-70 MPa [3].

At temperature $T = 180$ °C (Fig. 1, *c*) the results in tensile strength are very similar to those obtained at 170 ° C, but their value variation interval is significantly wider.

Stress-strain curves obtained at 190 °C (Fig. 1, d) indicate the narrowest results distribution between the tested group and tend to the conclusion about a more even structure of the film.

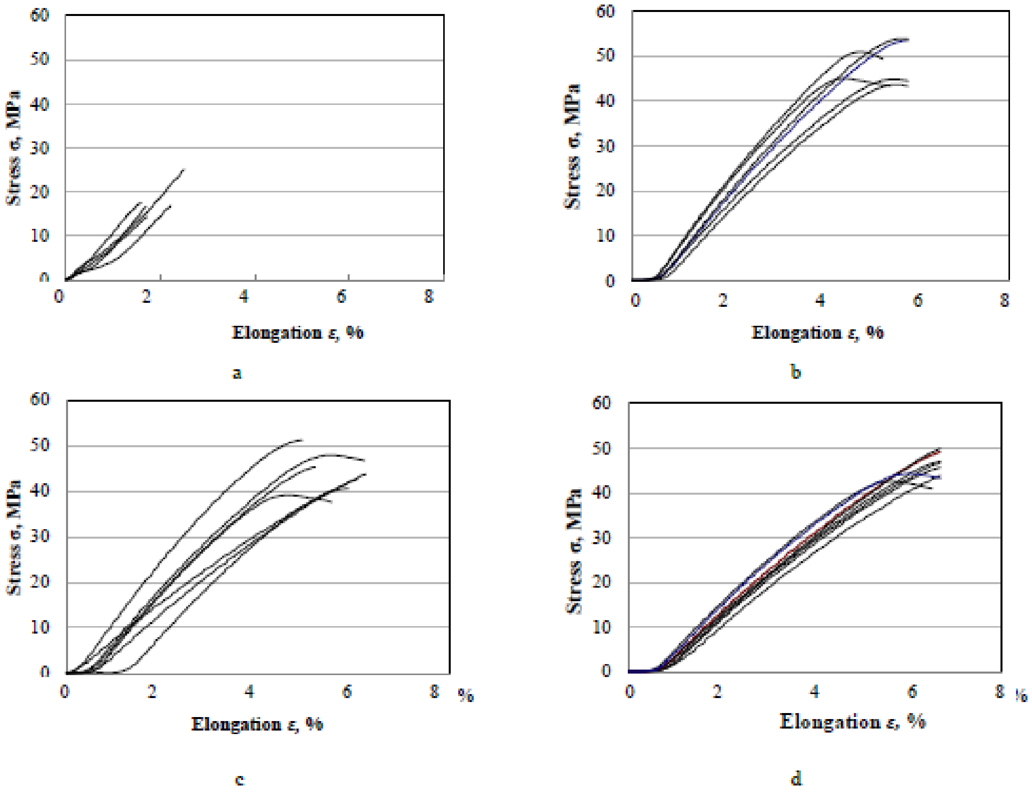


Fig. 1. Tensile curves of pure PLA *vs* film formation pressure temperature T, °C (a-160, b-170, c-180, d-190)

In the Table 1 for the more clear presentation and comparison of obtained results it is presented main statistical parameters of calculated stress and strain values for each tested group.

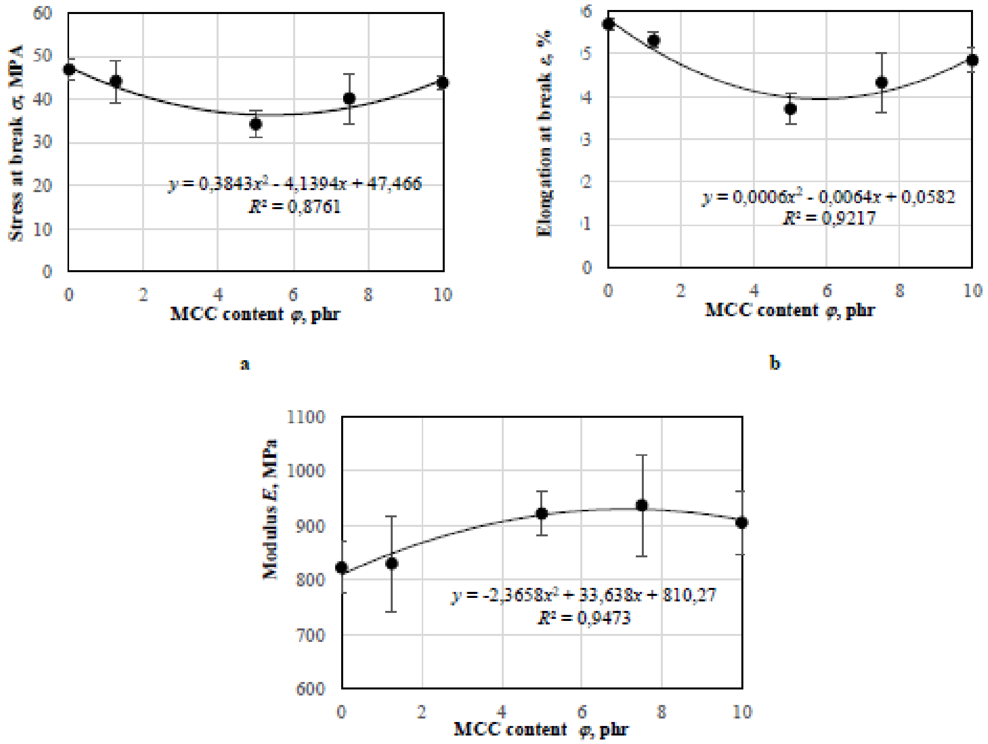
As it can be seen, the lowest standard measurement error and variation coefficient values were found for PLA films formed at $T = 190$ °C and statistically confirms narrow distribution of the results obtained. This also confirms presumption about suitability of PLA film production by a compression method, and most suitable compression temperature is 190°C. Due to this, T = 190 ° C was selected as an effective temperature for the following investigations.

Table 1. Main statistical parameters of the results of the stress strain test versus the temperature of PLA film formation

PLA film formation temperature, T ⁰C	**Parameter**	**Statistical parameters**			
		Average	**Standard deviation**	**Standard measurement error**	**Variation coefficient,%**
160	σ, MPa	18.09	4.10	5.70	22.69
	ε, %	1.95	0.4	0.01	20.28
170	σ, MPa	49	4.22	3.52	8.54
	ε, %	5.77	0.27	0.002	4.64
180	σ, MPa	44.30	4.20	3.89	9.49
	ε, %	5.18	0.49	0.005	9.5
190	σ, MPa	46.89	3.01	2.52	6.24
	ε, %	5.70	0.18	0.02	3.15

In Fig. 2 it is presented variation of PLA film strength at break (Fig. 2, a), deformability (Fig. 2, b), and modulus at maximal stress value (Fig. 2, c) in dependence on the MCC content. As can be seen, the addition of amounts up to 10 phr of MCC does not significantly worsen the strength of PLA film, in the exception case with 5 phr of MCC. This amount of MCC strength at break decreases from 46.89 down to 34.19 MPa, that is, more than 30%. In other cases, the variation of results is in the limits of the measurement error.

The dependence was approximated using the least square method. It was found that for approximation a second-order polynomial model with $R^2 = 0.8761$ can be used. The equation with regression coefficients of the mathematical model is presented in Fig. 2, *a*.



a

b

c

Fig. 2. Influence of MCC content on the tensile strength (a), elongation at break (b), and modulus (c) of PLA films

The changes of deformation properties are presented in Fig. 2, *b*. It is evident that at selected tensile speed rate (50 mm/min) all investigated films show a low deformability typical for PLA. The addition of MCC results in a decrease of films deformability, but this effect is uneven and depends on the MCC content. Reaching minimal elongation at break value at

5 phr of MCC, at larger amounts of MCC elongation at break values starts to increase but does not reaches deformability of unfilled PLA film. Mathematically this dependence also fits well the second-order polynomial mathematical model with R^2=0.9217.

Comparison of modulus *E* (Fig. 2, *c*) changes of MCC filled PLA films with stress and elongation dependencies indicates that, for previously discussed cases, dependencies have expressed minimum, while for modulus changes dependency has opposite character – obtained dependence has a maximum. An increase of PLA film modulus at amounts of 5-10 phr of MCC, while at 1.25 phr of MCC modulus it is the same as for unfilled films. It is interesting to state that the statistical distribution of the results obtained for pure PLA and filled with 1.25 phr of MCC average values are very similar, i.e. 823.3 MPa and 830.1 MPa for pure and 1.25phr MCC filled PLA film, respectively, but standard measurement error (confidence interval) for filled film is about two times higher (46.42 MPa and 87.61 MPa, respectively). This can be attributed to the structural unevenness of the film. On the other hand, the increase in modulus after addition of MCC is indicator of the increase of PLA film stiffness. Probably that is due to the development of some MCC network structure, but to confirm this statement structural investigations are required and will be performed in the nearest future. Approximation of obtained results also indicated the appropriateness of applying second-order polynomial mathematical model with R^2=0.9473.

4. Conclusions

1. The stress-strain behaviour of pure PLA films obtained by compression was typical for amorphous polymers. PLA films produced at 190°C have the most even distribution of mechanical properties.
2. The increase of MCC content up to 10 phr on the mechanical properties changes has a nonmonotonous character. 5phr of MCC significantly decreases the strength of PLA films, while in other investigated cases the strength of the films varies in the limits of the measurement error.
3. The addition of MCC results in a decrease of film deformability but increases the modulus at maximal stress. The obtained effect is uneven and depends on the MCC content.
4. All dependencies for MCC filled PLA film properties behaviour can be approximated using a second-order polynomial mathematical model.

References

1. ILYAS RA, SAPUAN SM, HARUSSANI MM, HAKIMI MYAY, HAZIQ MZM, ATIKAH MSN, ASYRAF MRM, ISHAK MR, RAZMAN MR, NURAZZI NM, NORRRAHIM MNF, ABRAL H, ASROFI M. Polylactic Acid (PLA) Biocomposite: Processing, Additive Manufacturing and Advanced Applications. Polymers (Basel). PDF: Online. 18 (2021), 13. Available from: https://pubmed.ncbi.nlm.nih.gov/33919530/. [viewed 20231004].
2. SURIANI, M.J., ET AL. Critical Review of Natural Fiber Reinforced Hybrid Composites: Processing, Properties, Applications and Cost. Polymers. PDF: Online. 13 (2021), 20. ISSN 20734360. Available from: //www.mdpi.com/20734360/14/1/202#metrics. [viewed 2023 0930].
3. FARAH S, ANDERSON DG, LANGER R. Physical and mechanical properties of PLA, and their functions in widespread applications A comprehensive review. Adv Drug Deliv Rev. PDF: Online. 2018. Available from: https://pubmed.ncbi.nlm.nih.gov/27356150/. [viewed 20231004].
4. ILYAS, R. A. AND ZUHRI, M. Y. M. AND AISYAH, H. A. AND ASYRAF, M. R. M. AND HASSAN, S. A. AND ZAINUDIN, E. S. AND SAPUAN, S. M. AND SHARMA, S. AND BANGAR, S. P. AND JUMAIDIN, R. AND NAWAB, Y. AND FAUDZI, A. A. M. AND ABRAL, H. AND ASROFI, M. AND SYAFRI, E. Natural Fiber Reinforced Polylactic Acid, Polylactic Acid Blends and Their Composites for Advanced Applications. Polymers. PDF: Online. 14 (2022), 14. ISSN 20734360. Available from: https://www.mdpi.com/20734360/14/1/202. [viewed 20230930].
5. DJALAL TRACHE, M. HAZWAN HUSSIN, CARYN TAN HUI CHUIN, SUMIYYAH SABAR, M.R. NURUL FAZITA, OWOLABI F.A. TAIWO, T.M. HASSAN, M.K. MOHAMAD HAAFIZ. Microcrystalline cellulose: Isolation, characterization and biocomposites application—A review. International Journal of Biological Macromolecules. PDF: Online. 93 (2016), A. m. ISSN 01418130. Available from: https://www.sciencedirect.com/science/article/pii/S0141813016310169. [viewed 2023 11 06].
6. HAIWEI REN, ZHIHANG XU, MING GAO, XUEYE XING, ZHE LING, LICHAO PAN, YAQIN TIAN, YI ZHENG, WENGUANG FAN, WEIXIA YANG. Preparation of microcrystalline cellulose from agricultural residues and their application as polylactic acid/microcrystalline cellulose composite films for the preservation of Lanzhou lily. International Journal of Biological Macromolecules. PDF: Online. 227 (2023) m. ISSN 01418130. Available from: https://www.sciencedirect.com/science/article/pii/S0141813022031099. [viewed 2023 11 07]
7. MARIUS MURARIU, PHILIPPE DUBOIS. PLA composites: From production to properties. Advanced Drug Delivery Reviews. PDF: Online. 107 (2016), 1746. ISSN 0169409X. Available from: https://www.sciencedirect.com/science/article/pii/S0169409X16301028. [viewed 2023 11 07].
8. DOGU, BERK IR KAYNAK, CEVDET. Behavior of polylactide/microcrystalline cellulose biocomposites: effects of filler content and interfacial compatibilization. Cellulose. PDF: Online. 23 (2016), 611 – 622. Available from: https://link.springer.com/article/10.1007/s1057001508390. [viewed 2023 11 07].

List of References

1. Plastics – the Facts 2021, An analysis of European plastics production, demand and waste data. PlasticsEurope. Online. (2021). Available from: https://plasticseurope.org/knowledge-hub/plastics-the-facts-2021/. [viewed 2024-04-14].
2. Industrial Transformation 2050 – Pathways to Net-Zero Emissions from EU Heavy Industry. Material Economics. Online. Available from: https://materialeconomics.com/publications/industrial-transformation-2050. [viewed 2024-04-14].
3. A. ABDELSHAFY, A. HERMANN, S. HERRES-PAWLIS, G. WALTHER. Opportunities and Challenges of Establishing a Regional Bio-based Polylactic Acid Supply Chain. Global Challenges. PDF: Online. 7 (2023), 7. Available from: org.ezproxy.ktu.edu/10.1002/gch2.202200218. [viewed: 2024-04-14].
4. Bioplastics Market Development Update 2023. European Bioplastics. Online. (2023). Available from: https://www.european-bioplastics.org/bioplastics-market-development-update-2023-2/. [viewed: 2024-04-14].
5. ILYAS, R. A. AND ZUHRI, M. Y. M. AND AISYAH, H. A. AND ASYRAF, M. R. M. AND HASSAN, S. A. AND ZAINUDIN, E. S. AND SAPUAN, S. M. AND SHARMA, S. AND BANGAR, S. P. AND JUMAIDIN, R. AND NAWAB, Y. AND FAUDZI, A. A. M. AND ABRAL, H. AND ASROFI, M. AND SYAFRI, E. Natural Fiber Reinforced Polylactic Acid, Polylactic Acid Blends and Their Composites for Advanced Applications. Polymers. PDF: Online. 14 (2022), 14. ISSN 20734360. Available from: https://www.mdpi.com/20734360/14/1/202. [viewed 2024-03-03].
6. HAIWEI REN, ZHIHANG XU, MING GAO, XUEYE XING, ZHE LING, LICHAO PAN, YAQIN TIAN, YI ZHENG, WENGUANG FAN, WEIXIA YANG. Preparation of microcrystalline cellulose from agricultural residues and their application as polylactic acid/microcrystalline cellulose composite films for the preservation of Lanzhou lily. International Journal of Biological Macromolecules. PDF: Online. 227 (2023). ISSN 0141-8130. Available from: https://www.sciencedirect.com/science/article/pii/S0141813022031099. [viewed 2024-04-14].
7. ILYAS RA, SAPUAN SM, HARUSSANI MM, HAKIMI MYAY, HAZIQ MZM, ATIKAH MSN, ASYRAF MRM, ISHAK MR, RAZMAN MR, NURAZZI NM, NORRRAHIM MNF, ABRAL H, ASROFI M. Polylactic Acid (PLA) Biocomposite: Processing, Additive Manufacturing and Advanced Applications. Polymers (Basel). PDF: Online. 18 (2021), 13. Available from: https://pubmed.ncbi.nlm.nih.gov/33919530/. [viewed 2024-03-03].
8. RANAKOTI, GANGIL, B., MISHRA, S. K., SINGH, T., SHARMA, S., ILYAS, R. A., & EL-KHATIB, S. Critical Review on Polylactic Acid: Properties, Structure, Processing, Biocomposites, and Nanocomposites. Materials. PDF: Online. 15 (2022), 12, 4312. ISSN: 1996-1944. Available from: https://www.mdpi.com/1996-1944/15/12/4312. [viewed 2024-03-03].
9. WANG J, PENG C, LI H, ZHANG P, LIU X. The impact of microplastic-microbe interactions on animal health and biogeochemical cycles: A mini-review. Sci Total Environ. PDF: Online. (2021). Available from: https://pubmed.ncbi.nlm.nih.gov/33940764/. [viewed 2024-03-03].
10. T. ANGELIN SWETHA, ABHISPA BORA, K. MOHANRASU, P. BALAJI, RATHINAM RAJA, KUMAR PONNUCHAMY, GOVARTHANAN MUTHUSAMY, A. ARUN. A comprehensive review on polylactic acid (PLA) – Synthesis, processing and application in food packaging. International Journal of Biological Macromolecules. PDF: Online. 234 (2023). ISSN

0141-8130. Available from: https://www.sciencedirect.com/science/article/pii/S0141813023006086. [viewed 2024-03-03].

11. BALLA, E., ET AL. Poly(lactic Acid): A Versatile Biobased Polymer for the Future with Multifunctional Properties—From Monomer Synthesis, Polymerization Techniques and Molecular Weight Increase to PLA Applications. Polymers. PDF: Online. 13 (2021), 11, 1822. Available from: https://www.mdpi.com/2073-4360/13/11/1822. [viewed 2024-03-03].
12. DELGADO-AGUILAR, MARC, RITA PUIG, ILIJA SAZDOVSKI, AND PERE FULLANA-I-PALMER. Substituting Single-Use Commodity Plastic Products. Materials. PDF: Online. 13 (2020), 11, 2655. Available from: https://www.mdpi.com/1996-1944/13/11/2655. [viewed 2024-03-16].
13. YANG Y, ZHANG M, JU Z. Poly(lactic acid) fibers, yarns and fabrics: Manufacturing, properties and applications. Textile Research Journal. PDF: Online. 91 (2021), 13-14. Available from: https://journals.sagepub.com/doi/abs/10.1177/0040517520984101. [viewed 2024-04-14].
14. SIMON KNOCH, FRANCINE PELLETIER, MIKAËL LAROSE, GÉRALD CHOUINARD, MARIE-JOSÉE DUMONT, JASON R. TAVARES. Surface modification of PLA nets intended for agricultural applications. Colloids and Surfaces A: Physicochemical and Engineering Aspects. PDF: Online. 598 (2020). ISSN 0927-7757. Available from: https://www.sciencedirect.com/science/article/pii/S0927775720303800. [viewed 2024-04-14].
15. MUNA M KAREEM, TOM HODGKINSON, MANUEL SALMERON SANCHEZ, MATTHEW J DALBY, K ELIZABETH TANNER. Hybrid core–shell scaffolds for bone tissue engineering. Biomedical Materials. PDF: Online. 14 (2019), 2. Available from: https://iopscience.iop.org/article/10.1088/1748-605X/aafbf1/meta. [viewed 2024-04-14].
16. ZHAO, ZHANG, D., YU, S., ZHOU, H., & PENG, S. Recent advances in compatibility and toughness of poly(lactic acid)/poly(butylene succinate) blends. e-Polymers. PDF: Online. 21 (2021), 1, 793-810. Available from: https://doi.org/10.1515/epoly-2021-0072. [viewed 2024-03-16].
17. ZHAO, T., YU, J., ZHANG. Thermal, crystallization, and mechanical properties of polylactic acid (PLA)/poly(butylene succinate) (PBS) blends. Polym. Bull. PDF: Online. 16 (2024), 81, 2481-2504. Available from: https://link-springer-com.ezproxy.ktu.edu/article/10.1007/s00289-023-04848-9#citeas. [viewed 2024-03-16].
18. ZHAO, XIPO, ZHANG, DIANFENG, YU, SONGTING, ZHOU, HONGYU AND PENG, SHAOXIAN. Recent advances in compatibility and toughness of poly(lactic acid)/poly(butylene succinate) blends. e-Polymers. PDF: Online. 21 (2021), 1, 793-810. Available from: https://doi.org/10.1515/epoly-2021-0072. [viewed 2024-03-16].
19. PAVON C, ALDAS M, SAMPER MD, MOTOC DL, FERRANDIZ S, LÓPEZ-MARTÍNEZ J. Mechanical, Dynamic-Mechanical, Thermal and Decomposition Behavior of 3D-Printed PLA Reinforced with CaCO3 Fillers from Natural Resources. Polymers. PDF: Online. 14 (2022), 13, 2646. Available from: https://www.mdpi.com/2073-4360/14/13/2646. [viewed: 2024-03-16].
20. BRDLÍK, P. Biodegradation of Poly(Lactic Acid) Biocomposites under Controlled Composting Conditions and Freshwater Biotope. Polymers. PDF: Online. 13 (2021), 4, 594. Available from: https://www.mdpi.com/2073-4360/13/4/594. [viewed 2024-03-18].
21. KADIER, A. Use of Industrial Wastes as Sustainable Nutrient Sources for Bacterial Cellulose (BC) Production: Mechanism, Advances, and Future Perspectives. Polymers. PDF: Online. 13 (2021). ISSN 2073-4360. Available from: https://www.mdpi.com/2073-4360/13/19/3365. [viewed 2024-03-18].

22. BO ZHAO, YI ZHANG, HAIWEI REN. Effects of microcrystalline cellulose surface modification on the mechanical and thermal properties of polylactic acid composite films. Taylor & Francis Group. PDF: Online. 49 (2020), 10, 450-455. Available from: https://doi.org/10.1080/14658011.2020.1801231. [viewed 2024-03-20].
23. MAHMOUD, BELHANCHE-BENSEMRA, N., & SAFIDINE, Z. Impact of microcrystalline cellulose extracted from walnut and apricots shells on the biodegradability of Poly (lactic acid). Frontiers in Materials. PDF: Online. 9 (2022). Available from: https://www.frontiersin.org/articles/10.3389/fmats.2022.1005387/full. [viewed 2024-03-26].
24. CLAUDIA WELLENREUTHER, ANDRÉ WOLF, NILS ZANDER. Cost competitiveness of sustainable bioplastic feedstocks – A Monte Carlo analysis for polylactic acid. Cleaner Engineering and Technology. PDF: Online. 6 (2022). ISSN 2666-7908. Available from: https://www-sciencedirect-com.ezproxy.ktu.edu/science/article/pii/S2666790822000167?via%3Dihub. [viewed 2024-04-01].
25. C. WELLENREUTHER, A. WOLF. Innovative Feedstocks in Biodegradable Bio-Based Plastics: a Literature Review. HWWI Research Papers. PDF: Online. 194 (2020). Available from: https://www-sciencedirect-com.ezproxy.ktu.edu/science/article/pii/S2666790822000167?via%3Dihub#cebib0010. [viewed 2024-04-01].
26. CORNAGO, E., P. BÖRKEY AND A. BROWN. Preventing single-use plastic waste: Implications of different policy approaches. OECD Environment Working Papers. PDF: Online. (2021). ISSN: 19970900. Available from: https://www.oecd-ilibrary.org/environment/preventing-single-use-plastic-waste_c62069e7-en. [viewed 2024 04 01].
27. M.S.S.R. TEJASWINI, PANKAJ PATHAK, SEERAM RAMKRISHNA, P. SANKAR GANESH. A comprehensive review on integrative approach for sustainable management of plastic waste and its associated externalities. Science of The Total Environment. PDF: Online. 825 (2022). ISSN 0048-9697. Available from: https://www.sciencedirect.com/science/article/abs/pii/S0048969722010658. [viewed 2024-04-01].
28. BUDTOVA, T., NAVARD, P. Cellulose in NaOH–water based solvents: a review. Cellulose. PDF: Online. 23 (2016), 5 – 55. Available from: https://doi-org.ezproxy.ktu.edu/10.1007/s10570-015-0779-8. [viewed 2024-05-07].
29. ELISA DE MARCHI, SILVIA PIGLIAFREDDO, ALESSANDRO BANTERLE, MARCO PAROLINI, ALESSIA CAVALIERE. Plastic packaging goes sustainable: An analysis of consumer preferences for plastic water bottles. Environmental Science & Policy. PDF: Online. 114 (2020), 305-311. ISSN 1462-9011. Available from: https://www-sciencedirect-com.ezproxy.ktu.edu/science/article/pii/S1462901120303300?via%3Dihub#bibl0005. [viewed 2024-04-01].
30. ALLISON, A.L. Barriers and Enablers to Buying Biodegradable and Compostable Plastic Packaging. Sustainability. PDF: Online. 13 (2022), 1463. Available from: https://www.mdpi.com/2071-1050/13/3/1463. [viewed 2024-04-01].
31. Specification Sheet Cellulose DFS-0. Sigma-Aldrich. Online. Available from: https://www.sigmaaldrich.com/LT/en/specification-sheet/SIAL/09906. [viewed 2024-04-14].

32. Ingeo™ Biopolymer 6202D Technical Data Sheet. Nature Works LLC. Online. Available from: https://www.natureworksllc.com/~/media/Technical_Resources/Technical_Data_Sheets/TechnicalDataSheet_6202D_fiber-melt-spinning_pdf.pdf. [viewed: 2024-04-14].
33. Specification Sheet Sodium hydroxide – puriss. p. a, ACS reagent. Sigma-Aldrich. Online. Available from: https://www.sigmaaldrich.com/specification-sheets/304/032/30620-BULK-M.pdf. [viewed 2024-04-27].