Kaunas University of Technology

Faculty of Mechanical Engineering and Design

Design of Starch-Based Biodegradable Films with Essential Oils for Sustainable Packaging

Master's Final Degree Project

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Supervisor

Kaunas, 2023

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 – Simona Kiškytė

1. Title of the Project

Design of Starch-Based Biodegradable Films with Essential Oils for Sustainable Packaging

(In English)

Bioskaidžių krakmolo plėvelių su eteriniais aliejais kūrimas tvarioms pakuotėms gaminti

(In Lithuanian)

2. Aim and Tasks of the Project

Aim: to develop starch-based biodegradable films containing essential oils to use as sustainable packaging

Tasks:

1. to prepare potato and tapioca starch based biodegradable films according to the established composition;
2. to analyze and compare mechanical properties of the films;
3. to analyze effect of essential oils to the properties of the films;
4. to investigate applicability of the developed films for practical purposes.

3. Main Requirements and Conditions

Environmental conditions: 21-22 °C, relative humidity: 45-55 %, distilled water, potato starch, tapioca starch, lentil flour, sorbitol, glycerol, vinegar, sheets of glass 150×150 mm, *Zwick Z005* tensile testing machine, *Dino light* microscope, *Lonis Schopper Leipzig* automatic micrometer.

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

Not applicable

Project author	Simona Kiškytė		2023-02-27
	(Name, Surname)	*(Signature)*	*(Date)*
Supervisor	Laura Gegeckienė		2023-02-27
	(Name, Surname)	*(Signature)*	*(Date)*
Head of study field programs	Regita Bendikienė		2023-02-27
	(Name, Surname)	*(Signature)*	*(Date)*

Simona Kiškytė. Design of Starch-Based Biodegradable Films with Essential Oils for Sustainable Packaging. Master's Final Degree Project, supervisor lect. Laura Gegeckienė; 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: starch; films; biodegradable; essential oils; plastic.

Kaunas, 2023. 56 p.

Summary

Oil-derived plastic consumption for daily and industrials needs is increasing every year, causing a lot of environmental and social issues. One of the biggest ones is generated waste and plastic pollution, as oil-derived plastics do not compose or biodegrade in the natural conditions and special waste management, transportation and recycling processes are needed in order to manage the generated plastic waste. Because of that, more sustainable alternatives to commonly used plastics are getting more and more attention. One of such are bio-based materials. Such biodegradable starch-based films were investigated in this study, to study their applicability in the industry. In order to improve properties of the films, samples, made with potato or tapioca starches, glycerol or sorbitol as plasticizers, lentil flour as a filler, were improved by adding peppermint or essential oil to the composition. 20 samples were made and compared by their appearance, mechanical properties, hydrophobicity and biodegradability, in order to investigate which composition is the most suitable for production of sustainable films and packaging. Essential oils were proven to have a slightly negative impact to the strength of the films but make them more resistant to water. In general, films made with starch as a base material are not as strong and resistant as oil-derived plastics but they are more environmentally-friendly and can decompose in the environment over time. The properties of the films with discussed composition need to be improved in order for them to be considered as an alternative to the widely-used man-made plastic materials.

Simona Kiškytė. Bioskaidžių krakmolo plėvelių su eteriniais aliejais kūrimas tvarioms pakuotėms gaminti. Magistro baigiamasis projektas, vadovė lekt. Laura Gegeckienė; Kauno technologijos universitetas, Mechanikos inžinerijos ir dizaino fakultetas.

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

Reikšminiai žodžiai: krakmolas; plėvelės; bioskaidžios; eteriniai aliejai; plastikas.

Kaunas, 2023. 56 p.

Santrauka

Iš naftos žaliavos pagamintų plastikų vartojimas kasdienėms ir industrinėms reikmėms auga kasmet, sukeldamas įvairias socialines ir aplinkosaugines problemas. Viena didžiausių yra sugeneruojamas atliekų kiekis ir aplinkos tarša plastiku, nes iš naftos pagaminti plastikai gamtoje natūraliomis sąlygomis nesuyra, tad reikalingi papildomi atliekų rinkimo, transportavimo bei apdorojimo ir perdirbimo procesai. Dėl šios priežasties, su įprastas plastikais lyginant tvaresnės alternatyvos sulaukia vis daugiau ir daugiau dėmesio. Vienos tokių yra iš biologinių žaliavų sukurtos medžiagos. Būtent tokios bioskaidžios krakmolo pagrindu pagamintos plėvelės ir yra aptariamos atliktame tyrime. Tam, kad būtų pagerintos jų savybės, plėvelių, paruoštų iš bulvių ar tapijokos krakmolo, taip pat glicerolio ar sorbitolio kaip plastifikatorių, bei raudonųjų lęšių miltų kaip užpildo, sudėtis buvo papildyta pipirmėčių ar arbatmedžio eteriniais aliejais. Iš viso buvo paruošta 20 plėvelių pavyzdžių, kurie buvo palyginti pagal savo išvaizdą, mechanines savybes, hidrofobiškumą bei bioskaidumą tam, kad būtų galima įvertinti tinkamiausia plėvelių sudėtį tolimesnei gamybai bei praktiniam panaudojimui. Eteriniai aliejai nežymiai pablogino mechanines plėvelių savybes ir turėjo neigiamą įtaką jų stiprumui, bet tuo pačiu pagerino jų atsparumą vandeniui. Įprastai krakmolo plėvelės yra ne tokios stiprios kaip įprastos plastikinės medžiagos, tačiau jos yra draugiškesnės aplinkai ir patekę į aplinką joje bėgant laikui suyra. Studijoje aptariamos plėvelės ir jų sudėtis turi būti tobulinama tam, kad jos galėtų būti alternatyva plačiai naudojamoms plastiko medžiagoms.

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Introduction

In various industries, from food to automotive, packaging is very important in the processes of the whole supply chain. Its main purpose is to ensure safety of the packed goods during the transportation and storage, so that the products would reach the customers safely and without damages. In order to do that, packaging must be of suitable mechanical properties – lightweight, flexible and strong, because not only does the packaging have a direct impact to the quality of the goods transported, it also affect business and their finances, since more packaging used means higher costs. However, in food industry, for example, packaging must not only ensure that the goods would not be damaged during the handling and would remain of representative look, it also needs to keep the products fresh for as long as possible. It means that the packaging must be durable and resistant to the changes of the surroundings. Because of such requirements, one of the most widely used packaging material is plastic – polyethylene, polypropylene and other similar materials, derived from oil. While they meet the requirements of various industries, are not only of suitable mechanical properties but also information can be easily printed on them (which helps to ensure traceability and meet legal requirements), plastics are not environmentally-friendly. As the materials are derivatives of oil and resistant to environment, they take hundreds of years to degrade in the nature. Because of this and quite low plastic recycling rates, plastic pollution on the Earth is increasing. In order to tackle this problem, politicians, scientists and businessmen are looking for more sustainable solutions, which would be suitable to replace plastics derived from oil. One of the discussed and researched options is packaging made from bio-based materials, without any unnatural additives. Such packaging is bio-degradable and does not leave a trace, thus not making a negative impact to our planet. However, even though such packaging materials are more environmentally-friendly, they are not suitable to be used very widely at the moment – conducted research shows, that at the moment they are not strong enough and do not have needed mechanical and other properties to be widely used as an alternative to traditional oil-derived plastics. Nonetheless, as people become more and more environmentally conscious, various legislative decisions are made and businesses get more and more focused on sustainability goals, it is very important to keep looking for solutions, which could have proper quality and needed to properties to become an alternative and substitution to oil-based plastics. In this work, starch-based films will be investigated as an alternative flexible packaging material to the commonly used plastics. As this is one of the most abundant organic materials in the planet and have quite good film-forming properties and can biodegrade, without leaving a trace in the environment, starch and starch-based films have a potential, with proper composition, to become an alternative to the plastic which are very widely used as packaging materials at the moment.

Aim: to develop starch-based biodegradable films containing essential oils to use as a sustainable packaging.

Tasks:
1. to develop potato and tapioca starch based biodegradable films;
2. to analyze and compare mechanical properties of the films;
3. to analyze effect of essential oils to the properties of the films;
4. to investigate applicability of the developed films for practical purposes.

Hypothesis: Essential oils have a positive effect to mechanical and other functional properties of biodegradable starch-based films.

1. Situation Analysis

1.1. Plastic Packaging Consumption and Pollution

As the world becomes more and more global each day and supply chains are getting more complex, it is very important to ensure safety of the packed goods during whole process – from the moment the product leaves the production line, to the reaching of their final destination thousands kilometers away from the manufacturing plant. In addition to that, food packaging must be not only durable, but also easy to be printed on, in order to ensure compliance with the legal requirements regarding information needed to be displayed on the packages, traceability data, etc., aesthetically pleasing for the purposes of marketing and for consumers to catch an eye on and many more. Thus, even though that at the end of its lifecycle packaging is considered as waste, it has a significant role during various processes of supply chains.

One of the most widely used packaging materials globally remains plastic. Bar chart from *statista* in Fig. 1 shows how packaging materials were distributed worldwide based on their demand in 2019. Flexible and rigid plastics combined take up to 44,3 % of global demand of packaging materials. Flexible packaging alone takes up more than quarter (25,5 %) of the global packaging demand [1].

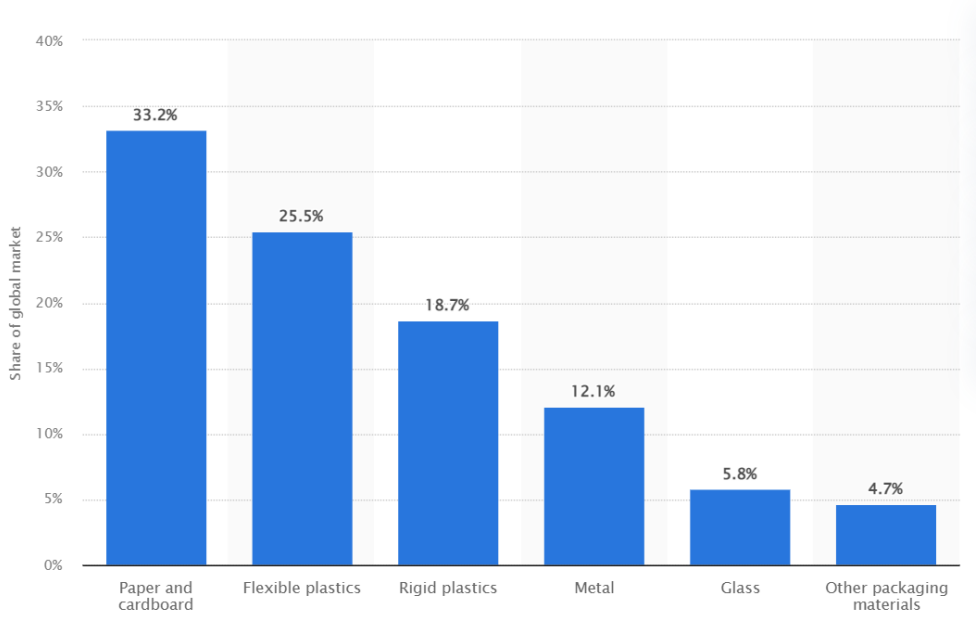

Fig. 1. Distribution of packaging demand worldwide in 2019, by material type [1]

As plastics are among the most popular packaging materials worldwide, it is no surprise that their production has increased significantly throughout the years. Fig. 2 displays data of global plastics production over the years from 1950 to 2019. Figures show, that in year 2019 more than 450 million tons of polymer resin and fiber were produced. That is more than double compared to the 200 million tons in year 2000. From year 1950, the growth of plastic production globally was exponential, which means that the plastic materials have become more and more important in various industries and their consumption, as well as the waster after the use of plastics, increased [2].

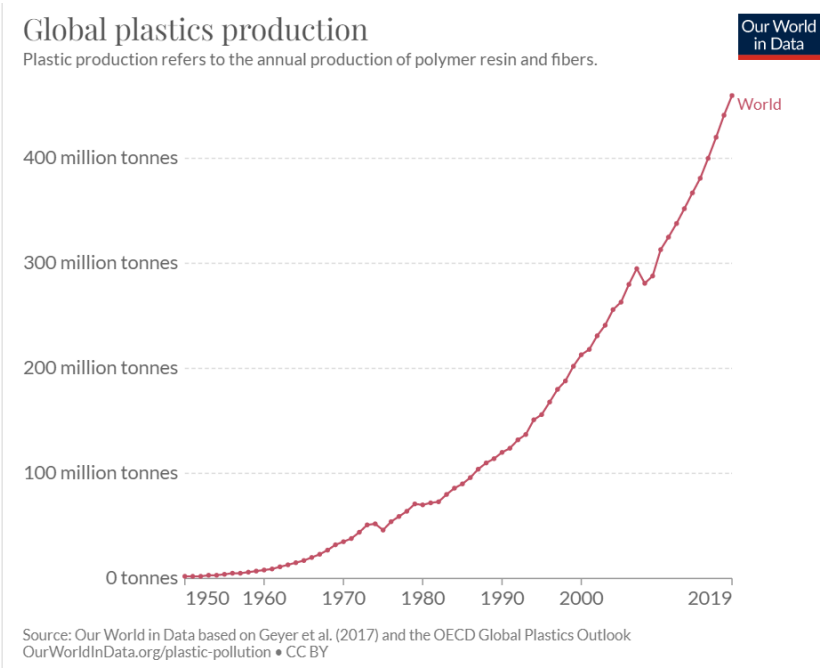

Fig. 2. Global plastics production, 1950-2019 [2]

Fig. 3 shows another graph from organization *Our World in Data*, which presents data of primary packaging production by industrial sector in year 2015. The leading industry was packaging, which was responsible for generating 149 million tons of plastic materials. Building and construction as well as textile industries, which took second and third places in the graph respectively, were responsible for less primary plastic production combined, compared to the industry of packaging. [3] Research made by C. Cimpan et al. helps to understand the situation even better – gathered data presented in Fig. 4 shows that the biggest part of packaging (almost 7000 kilotons) are used by and in the food sector. As food is usually consumed by people and used in their households, biggest share of plastic waste was generated (around 9000 kilotons) were generated by people in their homes. [4]

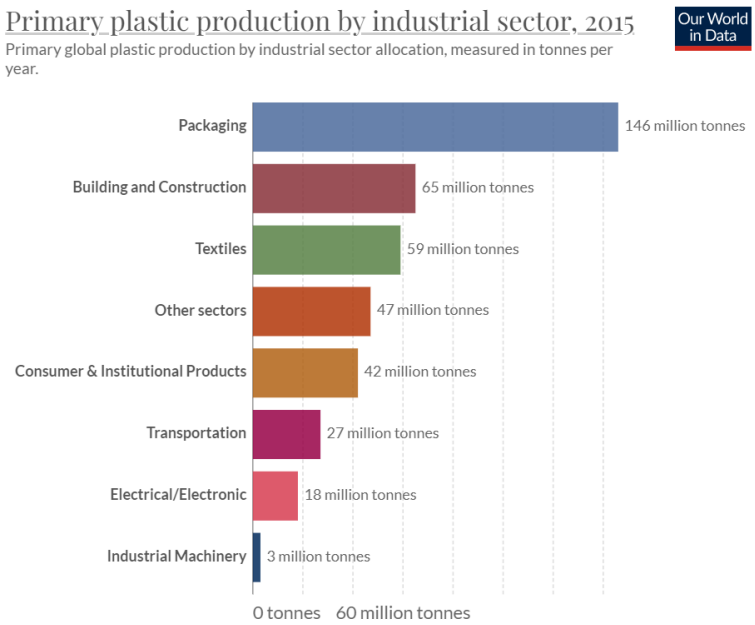

Fig. 3. Global primary plastic production by industrial sector in year 2015 [3]

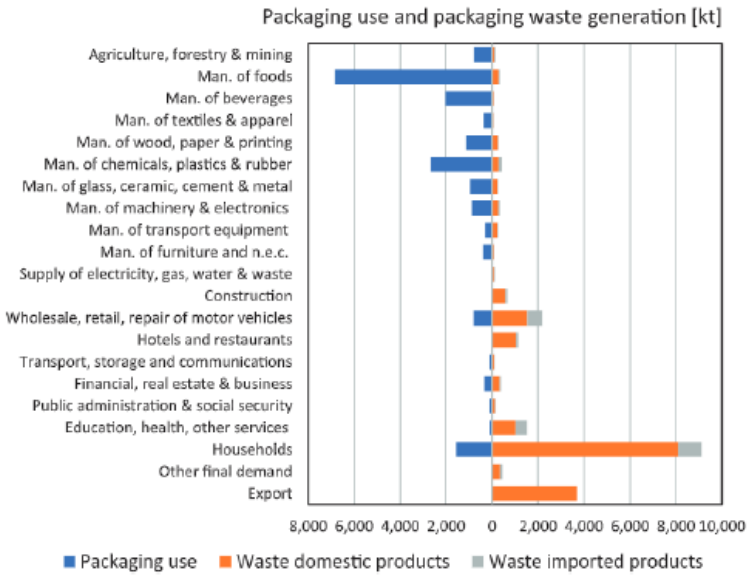

Fig. 4. Packaging use and packaging waste generation, kt [4]

Analysis made by Eurostat showed, that in European Union less than half of the plastic packaging materials, which were generated as waste, are being recycled. Gathered statistics show, that between years 2009 and 2019 generated amount of plastic waste increased from 27,5 kg per capita to 35 kg per capita. In the meantime, amount of recycled packaging has increased only from 10 kg per capita in 2009 to 15 kg per capita in 2019 – that means, 36,3 % of plastic waste were recycled in 2009 and during a decade of years recycled amount of waste slightly increased to 42,8 % in 2019. However, still less than half of plastic waste were recycled, remaining amount ended up in landfills as a waste [5]. Such mismanagement of plastic waste is contributing to the issue of environmental pollution significantly – because most popular and widely used packaging plastics as PET, PP, LDPE, HDPE, PVC [6] are derived from oil, under normal conditions they can still take hundreds of years to decompose. However, even in such way, they would leave micro-plastics behind, which would then could harm various living organisms by getting into the soil, water, animals and even humans. [7]

In order to cope with such problems and encourage people to deal with the waste they generate more responsibly, various initiatives were introduced by governments of some countries – for instance, some have started refund systems based on deposit of the packaging unit. However, effectiveness of such systems still has to be proved [8]. Thus, it is very important to have a holistic approach to issue and not only encourage people to be more responsible with their waste, but also to look for various ways, how the waste could be reduced in general. One of such options is further development of biodegradable materials, which degrade under the influence of various microorganisms, without damaging the planet and having much smaller negative effect to our environment. Especially keeping in mind that the industry of bioplastics is projected to triple over the next several years (from 2217 tonnes in year 2022 to more than 6000 tonnes in 2027, statistic presented in Fig. 5), majority of the produced bioplastics being used for the production of flexible packaging [9].

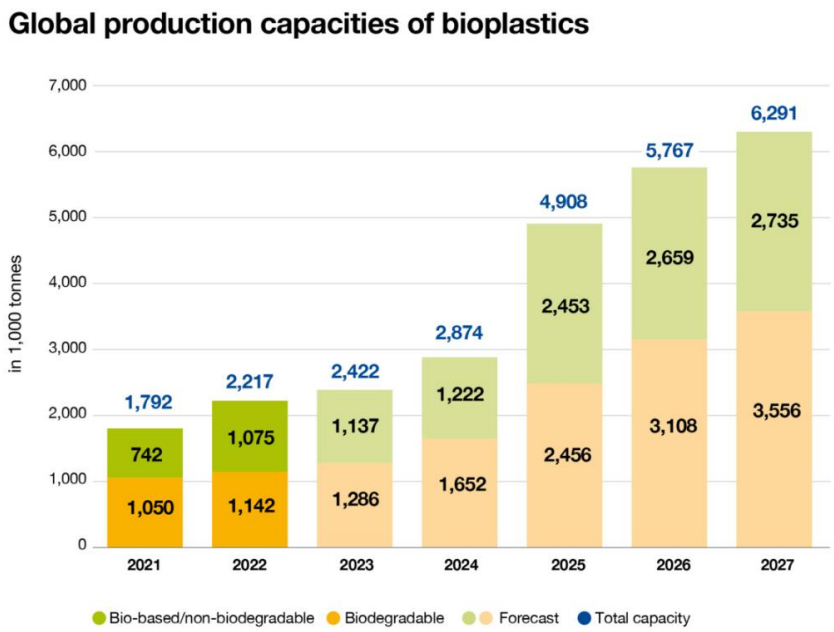

Fig. 5. Global production capacities of bioplastics – factual and projected [9]

1.2. Scientific Novelty of the Research

Starch, being one of the most abundant materials, is attractive for the scientists to be researched as a base material for the flexible film packaging. Because it is bio based and bio degradable, films, made with correct composition, can be both environmentally friendly and used as a substitution for plastic packaging.

Starch is not only a common biopolymer, it is also relatively inexpensive, easy to produce and properties of starch based materials can be manipulated by adding various adders to the mixture. Thus, it is easy to adjust and obtain a material with required properties. For instance, in order to improve flexibility of the films, plasticizers such as glycerol and sorbitol are added to the composition of the films. In some cases, vinegar can be used for such purposes as well, as acid weakens bonds between atoms in the starch polymer.

Not only do the additives to the starch have a direct impact to the properties of the films, the main matrix material can make an influence as well. As the starch can be obtained from different sources – such as potatoes, tapioca, rice, wheat, maize, etc. – it also differs in its chemical composition. Two main materials, which form the starches and their structures, are amylose and amylopectin, ant the ratio of these two structures based on the origin of the starch [10]. Amylose is responsible for the strength of the film – because of its linear structure (as seen in Fig. 6), it acts as a binder and thickener of the mixture and is mainly responsible for the strength of the starch films. Amylopectin, since it is a branched molecule, helps to thicken the films are responsible for the viscosity of starch-based films and the mixtures from which the films are made [11]. Differences between percentages of amylose and amylopectin in starches obtained from different sources are presented in table 1.

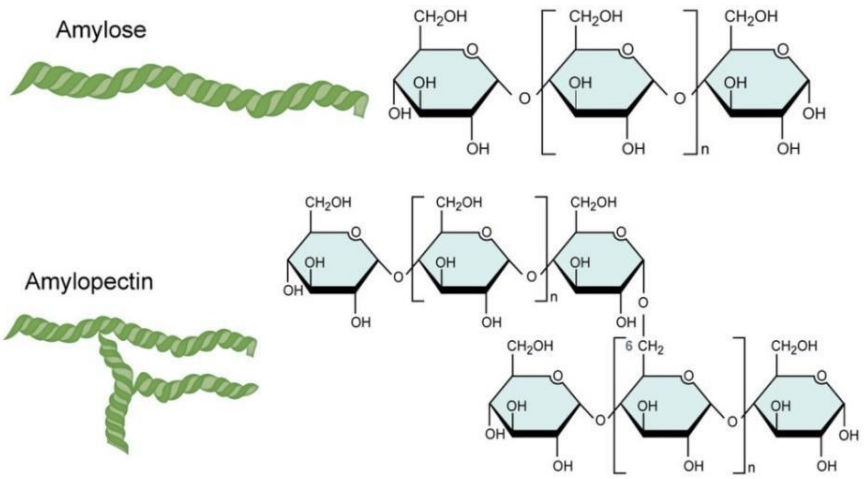

Fig. 6. Amylose and amylopectin molecules in starch [11]

Table 1. Percentages of amylose and amylopectin in starches from different origins [12,13]

Type of starch	**Amylose (%)**	**Amylopectin (%)**
Corn	17-25	75-83
Banana	17-24	76-83
Pea	20-30	70-80
Potato	17-24	76-83
Rice	15-35	65-85
Tapioca	19-22	78-81
Wheat	20-25	75-80
Yam	9-15	85-91
Waxy	< 1	> 99

In order to improve other properties of starch films, oils can be added. For instance, sunflower seed oil has been proven to be effective improving resistance of water of starch-based films [14], as well as PLA coating had a positive effect [15]. In order to make the films more suitable for food packaging and prolong shelf life of goods packed, various types of essential oils and their impact have been investigated [16]. Fillers, such as pea fibers, lentil flour, lignin, cellulose or oat bran, can be used to improve mechanical properties and thermal stability of the films [17,18]. However, further research is needed to obtain the most optimal composition of starch-based films in order to get the needed properties, which would be suitable for film application on a bigger scale.

1.3. Analysis of Similar Research

1.3.1. Mechanical Properties of Films

Some of the compositions of the bio-based films and their properties have already been investigated. In order to improve strength, tensile and other mechanical properties, various fillers have been considered. In the study of *Olle Resa, C. P., Jagus, R. J., Gerschenson, L. N.*, (2020) [18], fillers, such as oat bran, pumpkin peel and mesocarp, have been added to tapioca starch based films. It was found out that adding such materials to the film composition can improve the properties of the films

without making a negative impact to the antimicrobial properties. Results of the research, presented in table 2 show, that both of the added pumpkin fillers (pumpkin peel and mesocarp) have improved mechanical properties of the film. Also, positive effect has been noted for hydrophobicity and firmness of the films. The best effect was noted using pumpkin peel as a film filler (sample CB and NNB), since the firmness for CB sample was increased to 87,64 MPa and contact angle, indicating hydrophobicity, was improved 3 times, comparing to the sample without any fillers used (C, line one in table 2). [18]

Table 2. Mechanical properties and solubility parameters of tapioca starch based composite films, containing fillers (A – pumpkin mesocarp, B – pumpkin peel, C – oat bran) and with (NN) microbial as well as without (C) [18]

	Thickness (mm)	**Firmness (MPa)**	**Stress (MPa)**	**Strain**	**Solubility (%)**	**Contact angle (º)**
C	0,198 ± 0,003	2,360 ± 0,642	2,945 ± 0,613	1,316 ± 0,379	20,92 ± 10,75	11,96 ± 0,75
CA	0,315 ± 0,032	5,395 ± 1,308	2,683 ± 0,444	0,512 ± 0,089	25,35 ± 1,99	31,08 ± 7,98
CB	0,398 ± 0,076	87,64 ± 25,10	4,065 ± 0,596	0,053 ± 0,034	26,90 ± 4,81	48,29 ± 8,17
CC	0,216 ± 0,047	2,094 ± 0,578	2,659 ± 0,304	1,302 ± 0,374	27,68 ± 11,36	29,08 ± 7,98
NN	0,192 ± 0,001	0,249 ± 0,065	0,852 ± 0,253	3,453 ± 0,817	15,34 ± 9,20	47,74 ± 4,77
NNA	0,368 ± 0,095	2,223 ± 0,438	1,171 ± 0,184	0,540 ± 0,106	32,69 ± 4,87	38,50 ± 5,09
NNB	0,374 ± 0,080	3,558 ± 1,088	1,511 ± 0,323	0,441 ± 0,088	34,84 ± 10,33	60,00 ± 5,65
NNC	0,251 ± 0,041	0,411 ± 0,047	1,316 ± 0,231	3,202 ± 0,390	22,22 ± 9,62	51,50 ± 1,98

1.3.2. Additives to the main matrix

Fillers

In the study of *Ochoa-Yepes, O., Guz, L., Jaramillo, C. M. and Fama, L.*, (2018), lentil flour was researched as a filler to the tapioca starch based films. Matrix of the films consisted of tapioca starch (5 wt. %), distilled water (93,5 wt. %) and glycerol (1,5 wt. %) was added as a plasticizer, lentil flour (0,5 and 1 wt. %) was added as a filler. The results of the research have showed, that lentil flour can be considered as an additive to the starch-based films, as the positive impact to the values of Young's module, strength as well as the toughness of the films. Water vapor permeability was decreased by approximately 43 % (from 2,81 g $msPa^{-1} \cdot 10^{-10}$ to 1,61 g $msPa^{-1} \cdot 10^{-10}$) in the samples with lentil flour compared to the ones without the additive. Also, as the study has shown that films containing lentil flour are biodegradable, it was concluded that such type of materials could be used as a food packaging alternative [19].

Plasticizers

Study by *Bellesteros-Martinez, L., Perez-Cervera, C. and Andrade-Pizarro, R.* was performed in order to investigate the impact that two different plasticizers – sorbitol and glycerol – have to the starch-based films. Results, which can be seen in table 3, have showed that increasing percentage

both of sorbitol and glycerol can reduce puncture strength of the film; The glycerol, however, has a bigger negative impact compared to sorbitol and reduces the puncture strength up to 85 %, while sorbitol affects the film only by 49 %. Glycerol, on the other hand, had a more impact to the increase of elongation. Both sorbitol and glycerol increased water vapor permeability in the films [20].

The differences of the sorbitol and glycerol effect to the properties of the films can be attributed to the different chemical structures of the two components. Sorbitol has more hydroxyl groups (six) in comparison with glycerol (which has 3) [21] and its structure is also more similar to the structure of starch [22].

Table 3. Mechanical and other properties of sweet potato based starch films with different plasticizers [20]

Plasticizer	**Conc. w/w**	**WS, %**	**ΔE**	**PS, MPa**	**Eb, %**	**WVP, 10^{-10} g/m^{2}sPa**
Glycerol	10	23,21 ± 0,27	4,83 ± 0,12	9,78 ± 0,61	1,82 ± 0,09	4,44 ± 0,16
Glycerol	20	27,47 ± 0,93	4,50 ± 0,02	4,72 ± 0,18	2,38 ± 0,36	4,08 ± 0,15
Glycerol	30	31,32 ± 0,48	4,37 ± 0,06	4,02 ± 0,04	11,24 ± 0,96	6,34 ± 0,13
Glycerol	40	32,08 ± 0,76	4,20 ± 0,03	3,13 ± 0,11	13,24 ± 0,27	7,80 ± 0,14
Glycerol	50	33,37 ± 0,95	3,77 ± 0,06	1,76 ± 0,02	9,84 ± 0,12	9,59 ± 0,26
Sorbitol	10	18,15 ± 1,07	4,80 ± 0,10	9,37 ± 0,04	1,84 ± 0,05	3,70 ± 0,03
Sorbitol	20	24,44 ± 0,36	4,53 ± 0,15	8,94 ± 0,29	2,01 ± 0,04	4,10 ± 0,07
Sorbitol	30	29,68 ± 0,90	4,43 ± 0,12	6,49 ± 0,07	2,70 ± 0,20	4,73 ± 0,11
Sorbitol	40	36,70 ± 0,17	4,20 ± 0,06	5,92 ± 0,12	8,16 ± 0,16	5,93 ± 0,12
Sorbitol	50	37,51 ± 0,20	4,10 ± 0,08	4,95 ± 0,25	9,00 ± 0,05	6,95 ± 0,07
Control	0	14,25 ± 0,45	4,97 ± 0,09	10,95 ± 0,68	1,24 ± 0,12	4,65 ± 0,11

Essential oils

Essential oils are volatile, aromatic substances, usually obtained via extraction from various plants and their different parts. Even though that because of their chemical composition and volatility they research of the essential oils is not very easy, some researchers have already conducted several experiments in order to determine what kind of impact essential oils have to the films made from bio-based materials.

One of the main reasons, why essential oils are investigated as an additive to starch or chitosan-based films, which are then used for packaging, is their antimicrobial (inhibitory) properties. Because of the presence of hydrophilic and other functional groups, the essential oils can penetrate into the cells of microorganisms thus resulting antimicrobial, antifungal and other inhibitory properties [23, 24]. As it is presented in table 4, various essential oils can be used as additives in bio-based films used for food packaging and have a positive inhibitory effect on different types of foods.

Table 4. Effect of essential oils in bio-based films [25-27]

Essential oil	Film composition	Tested food	Observations
Rosemary	Chitosan	Fresh chicken	Increased shelf life, antimicrobial effect
Thyme	Chitosan	Meat	Antifungal effect – reduced yeast population
Tumeric EO	Chitosan	Marinated chicken	Antifungal effect
Citrus EO	Chitosan	Pacific mackerel	Antibacterial and antioxidant effect, increased shelf life
Cinnamon	carboxymethyl cellulose polyvinyl alcohol based films	Bread	Antioxidant and antifungal effect; increased shelf life
Bergamot EO	Polylactic acid	Mangoes	Extended shelf life, maintained quality longer
Thyme, oregano, tea tree and peppermint oil	Chitosan	Rice	Antifungal properties
Clove EO	Cassava starch	Banana	Antifungal properties, extended shelf life
Cinnamic aldehyde	Chotosan and corn starch film	Strawberry	Prolonged keeping of nutritional values, antimicrobial properties
Carvacrol essential oil	Corn starch	Not defined	Improved antimicrobial properties
Thymus kotschyanus essential oil	Corn starch and chitosan	Not defined	Improved antimicrobial properties, reduced oxidation of lipids

As for the essential oils as additives to the starch based films, different types of essential oils have different impact on the films and their properties. Study performed by Cai, C., Ma, R., Duan, M., Deng, Y., Liu, T. and Lu, D. showed, that essential oils can have not only positive effects to the properties of the starch films. In the study, impact of the thyme essential oil was investigated. Results have showed, that incorporating thyme essential oil to the film helped to improve preservation, increase tensile strength but at the same time reduce elongation and make the films more water-soluble (from 23,5 % in a control film without essential oils added to 36,5 % in a film with added thyme essential oil). [28] Study made by Song, X., Zuo, G. and Chen, F. investigated the effect of lemongrass essential oil to the corn and wheat starch based films. It was observed that the films containing lemongrass essential oil had lower solubility (e.g. 38,69 % compared to control sample 46,16 %) but at the same time lower tensile strength and bigger elongation at break [29]. Such differences are obtained because of different chemical structures of the used essential oils, hydroxyl groups present in the molecules, their interaction with starch and water molecules as well as hydrophilicity of the used essential oil.

The presented analysis suggests that in order to achieve the most optimal composition of starch-based films, various combinations of materials can be used. Both sorbitol and glycerol are suitable as plasticizers depending on the desired outcome. Essential oils also can positively contribute to the properties of film, depending on the intended usage of made material.

1.4. Methods That Are Used for Solving Similar Problems

1.4.1. Solutions Available in the Market

As the environmental issues and plastic pollution become more and wider discussed, some of the alternative biodegradable packaging solutions can already be found in the markets. However, their composition remains a trademark secret, information is not accessible to the public.

Biopak

Biopak is a company operating in Australia, New Zealand and United Kingdom, offering packaging materials which can biodegrade. The goods sold are made from sugarcane pulp, bioplastic (Ingeo™), paper and wood, which is FSC™ certified, as well as aqueous lining, used as a barrier coating [30].

Their products include, but are not limited to:

- Cups
- Lids and containers
- Plates and trays
- Bags
- Napkins
- Cutlery and straws

Paptic® Materials

These are plastic-free materials, made of wood fibers, which are approved as biodegradable under specific composting conditions. The materials can be fully recycled and no specific equipment is needed neither for manufacturing, nor for recycling processes – the same, as used for paper, is suitable for this material as well [31].

The company also offers different variations of the materials, each suitable for different applications (mostly packaging of fruits, vegetables or other dry products):

- Paptic Tringa® – used for pouches and gift bags, mailers; considered a premium packaging material
- Paptic Sterna® – suitable for production of big quantities, very durable, making it a great choice for e-commerce, bags and labeling.
- Paptic Apus® – good option for flexible packaging, as it is strong and light.

NTIC

The company owns several trademarks, such as Natur-Tec®, Natur-Bag®, and Natur-Ware®. They are stating that the materials they produce do not contain any traditional plastic materials, as they are not compatible with biodegradability, but meet almost the same properties, as, for instance, polyethylene.

In their manufacturing process, proprietary ReX Process is used in order to process the raw materials to the final products. Compostable resins are made from compostable and natural polymers, as well as various organic and inorganic materials, compatabilizers and modifiers. Products are made using injection molding, film or profile extrusion and extrusion coating [32].

ENVIPLAST®

ENVIPLAST® manufactures and provides materials, which are made from natural industrial starches, such as cassava and corn. Their produced bio-plastics can biodegrade in nature in several months, not leaving a trace of micro plastics which can be harmful [33].

They are offering two types of products:

- ENVIPLAST® WS – made from tapioca or corn starch with various additives, such as derivatives of vegetable oil. Suitable for making of bags and films (such as laundry, garbage, pet waste, etc.), is biodegradable and bio-based. However, they are stated to be affected by humidity, thus some specific storage conditions might be needed. Does not require specific facility of industrial composting.
- ENVIPLAST® WR – from this material eco-friendly films are produced. They are fully compostable but also resistant to water and humidity. Can also be composted at home, however, it does have biodegradable polyester (not bio-based material) in its composition.

Ecoflex®

Ecoflex® is a material manufactured and produced by one of the biggest chemical companies in the world BASF. It is stated to be biodegradable and is certified as compostable under industrial conditions by various standards (such as EN 13432, AS 4736, ASTM 6400 and others).

Raw materials used for the manufacturing of Ecoflex® products include but are not limited to polylactic acid (also known as PLA), starch, cellulose, lignin or PHAs. Because of their suitable mechanical properties (e.g. puncture resistance and stiffness) and various possible compositions, the Ecoflex® products can be used to produce flexible films to be used for packaging purposes [34].

As stated by the BASF, Ecoflex®, together with PLA, is commercialized and known under a name Ecovio®. This is a fully biodegradable material, which can be applied as a substitute to generally known and used plastics for manufacturing of bags (waste, shopping, etc.), coating for cardboards, other types of packaging [35].

1.4.2. Studies of Biodegradable Bags

In the study of Lopez, O. V., Lecot, C. J., Zaritzky, N. E., Garcia, M. A., heat sealing properties of corn starch films were investigated in order to determine if such films could be converted into bags and used further as a packaging alternatives to the ones existing in the market. Materials used for the film preparation were corn starch, water and glycerol was added as a plasticizing agent. As two different types of corn starch were used (native and acetylated), three different 5 % w/w suspensions were prepared and gelatinized at 90 ^{o}C temperature for 20 minutes. 30 g of glycerol for 100 g of used corn starch were added in order to gelatinize the suspension. The prepared suspensions then were casted on the Petri dishes and dried in the oven at 60 ^{o}C. Different measurements were made in order to determine the parameters of the films and their applicability as a packaging material [36].

Humidity of the film

The parameter was measured by drying samples at 105 ^{o}C and comparing the weights of the samples before and after. The results have showed that the composition of the films did not have a significant

impact to the humidity content of the film. The biggest difference was noted in the films which contained glycerol (samples with glycerol have reached 15,28-15.75 % humidity, while the samples without it had the humidity level of 8.43-9.08 %). This is because the added plasticizer is a hydrophilic agent with hydroxyl groups, which can adsorb water molecules. [36]

Thickness and morphology

The thickness of the samples was measured in ten different locations of the samples using digital thickness gauge and mean of the determined values was calculated. As it was determined, the composition of the films had an impact to the film thickness – the bigger was the concentration of acetylated starch, the thicker was the final film sample. Also, adding glycerol also attributed to the increased film thickness and increased it in average by 20 %. [36]

Morphology of the films was evaluated using scanning electron microscope (SEM). The obtained images, as seen in Fig. 7, have showed that films with plasticizers have much more even structure compared to the films only with starch blends – in the latter ones, multiple layers can be seen [36].

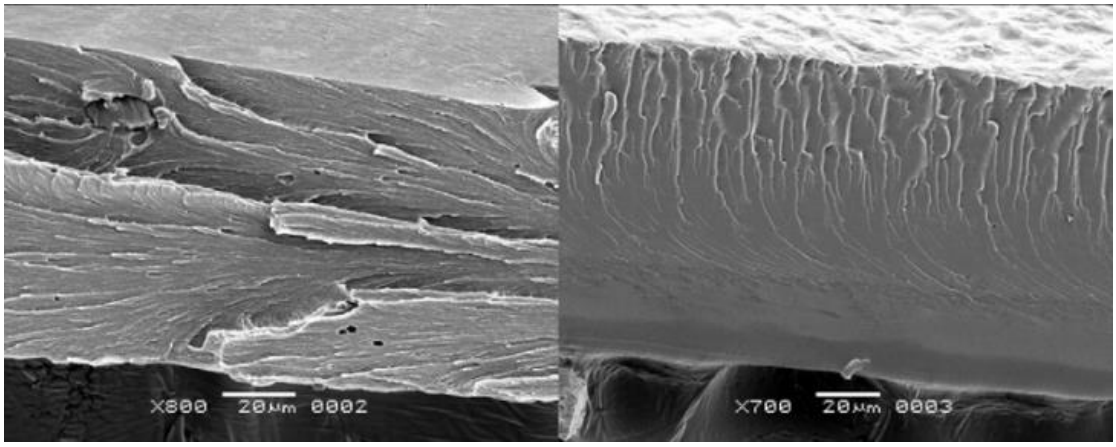

Fig. 7. SEM images of starch blend film without plasticizer (left) and with glycerol as plasticizer (right) [36]

Mechanical properties

In order to determine mechanical properties of samples, stress-strain curves at least 10 probes of 7x0,7 cm for each film sample were obtained using texturometer. Then tensile strength and elongation at break, as well as elasticity modulus were calculated using the information from the graphs.

The films without plasticizers have been more rigid and brittle, compared to the plasticized ones. Also, glycerol has enhanced the flexibility of the films and increased the deformation. The results both of the plasticized and non-plasticized samples could be explained by the formed structure of the films (as it was seen in the SEM images), polymer chains and interconnections between them. The brittleness of the films without plasticizers is a result of the layered film structure. The glycerol, on the other hand, acts as a lubricant between the starch chains, thus making the polymeric chains more slippery with each other. [36]

Heat sealing capacity

In order to measure heat sealing capacity of the films, the impulse sealing technique was used to seal the films. To consider the layers properly fused and formed zip to be of a good quality, after exposed to the heat, new homogenous layer should be formed.

The results of such measurement showed, that films with plasticizers showed failures related with the adhesion of the layers, while films without plasticizers were ruptured near the heat-formed zip. The failure modes of both variants (plasticized and non-plasticized films) can be seen in Fig. 8 [36].

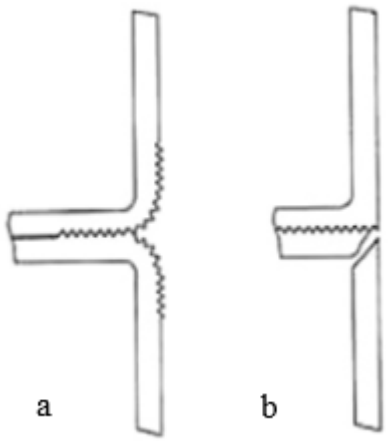

Fig. 8. Failure modes of (a) plasticized films and (b) non-plasticized starch films [36]

Thus, as the reviewed study has showed, plasticizing the films is needed in order to improve their mechanical properties and elongation as well as the flexibility of the films. However, the heat sealing conditions could be optimized in order to achieve better results.

1.5. Conclusions of Situation Analysis

Plastic consumption, especially as packaging materials, in increasing every year, causing environmental issues due to the plastic pollution. In order to tackle the problem, scientific studies have been started to look for more sustainable alternatives to oil-derived plastics. Due to the abundancy, low costs and other properties, starch has been getting more attention from scientific community and is being researched as a substitution for widely-used conventional plastic packaging. Various film compositions have already been studied, however, further research is still needed to have the most optimal alternative solution.

2. Methodological Part

In this part, the methodology used for further experimental part is described. As the aim is to develop starch based films and investigate their functional properties, films of different compositions are created based on the previously discussed literature.

During the study, the following stages are considered:

- Creating comparable starch based films of different compositions
- Measuring thickness of the films
- Measuring and comparing mechanical properties (tensile strength, Young's module)
- Measuring film contact angle with water
- Evaluating air residues in the film with the microscope
- Evaluating biodegradability of the films
- Evaluating antifungal and antimicrobial properties of the films

The mentioned research parts help to determine the most optimal composition of starch-based films as well as to analyze them as an alternative food packaging.

2.1. Materials Used

The following materials were used to make the films: potato starch, tapioca starch, red lentil flour, sorbitol (50 %), glycerol, vinegar (9 %), distilled water, peppermint (*Mentha piperta L*) essential oil and tea tree (*Melaleuca alternifolia*) essential oil.

Starch

Two different types of starches were used to make starch-based film samples. While the chemical composition of both selected starched (potato and tapioca) is the same, starches from different origin differ in the shape of granules, ratio of amylose and amylopectin, etc. The difference of the composition (amylose and amylopectin percentage) was already presented in table 1 – both potato and tapioca starches are in the very similar range and have almost the same amylose/amylopectin ratio.

The differences of the granule size and shape can be seen in Fig. 9. The granules of potato starch are of oval shape, more centered on one side of the granule; their size can vary between 14,3-53,6 μm. Tapioca starch granules are more spherical, they do not have one shape defined, but they are more centered. Tapioca starch granules are relatively smaller than potato starch ones, as their size varies between 7,1-25,0 μm [37].

In table 5 properties and parameters of the potato starches, such as pH, solubility in water, gelatinization temperature and other are compared. As it can be seen, tapioca starch has a lower pH value (4,8) than potato starch (7,15), meaning that it is more acidic. Potato starch has more moisture (9,37 %) than tapioca starch (7,54 %) but it is slightly less soluble in water than tapioca starch both in 20 ^{o}C and 70 ^{o}C temperatures. The gelatinization temperature of both starches is very similar – 67,15 ^{o}C for potato starch and 66,20 ^{o}C for tapioca starch [37]. Another study conducted by Ai, Y. and Jane, J. L., defined the gelatinization temperatures of both starches as 63,50 ^{o}C and 67,60 ^{o}C respectively, but the values still remain in almost the same temperature range [38]. Because of such properties, tapioca starch can have a high viscosity and be a suitable binder for other materials.

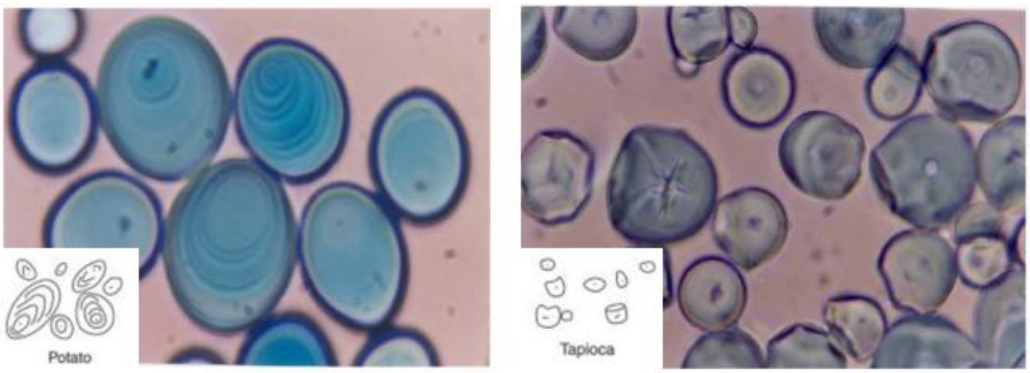

Fig. 9. Microscope pictures and shapes of granules of potato and tapioca starches [37,39]

Table 5. Comparison of potato and tapioca starch properties [37,38]

Parameter	**Potato starch**	**Tapioca starch**
pH at 20 ºC	7.15 ± 0.04	4.80 ± 0.03
Moisture, %	9.37 ± 0.18	7.54 ± 0.14
Solubility at 20 ºC, %	1,21	1,90
Solubility at 70 ºC, %	13,49	14,36
Gelatinization temperature, ºC	63,5-67,15	66,20-67,6

In this research, potato starch *Alojas* and *Sano* tapioca starch. Composition and parameters of potato starch are presented in table 6 and table 7. Information about tapioca starch can be found in table 8.

Table 6. Chemical composition of potato starch [40]

Compound	**Value, %**
Salt	0
Carbohydrates	80,0
Protein	0,1
Fat	0,1

Table 7. Parameters of potato starch [40]

Parameter	**Value**
Moisture content, %	18,00-20,00
pH	6,0
Solubility, %	Fully soluble after the mixture is boiled
Acetyl value, %	2,5 at most
Brabender viscosity, at 95°C, BU	200-500

Table 8. Chemical composition of tapioca starch [41]

Compound	**Value, %**
Salt	0,1
Carbohydrates	88,69
Protein	0,2
Fat	0,02
Fiber	0,9

Red lentil flour

In order to improve mechanical properties of the films, *Probio* red lentil flour was used. The flour acted as a filler and main aim with adding them was to make the film mechanically stronger. Composition of the used flour are presented in table 9.

Table 9. Chemical composition of red lentil flour [42]

Compound	**Value, %**
Salt	0,02
Carbohydrates	57,0
Fat	1,7
Fiber	10
Protein	24

Plasticizers

As plasticizers, to make the films more flexible, not as rigid and brittle, acetic acid and glycerol as well as sorbitol were used.

According to the study made by Olivato, J. B., Grossmann, M. V. E., Bilck, A. P. and Yamashita, F., organic acids have a positive effect to the mechanical properties of the starch films. This is because organic acids speed up the hydrolysis of starch molecules and initiate crosslinks between polymer chains. Thus, the films become more resistant [43]. It can also act as a plasticizer since destroying the bonds in linear polymer molecules make them more flexible within each other.

In this study, vinegar (also known as acetic acid) of 9 % concentration (producer was used in order to improve properties of the films.

As plasticizers, sorbitol and glycerol were also added. Chemical structures of all three used plasticizers (including acetic acid) can be seen in Fig. 10. They make the films more elastic, flexible and less brittle by increasing the moisture and humidity of the films. This is because all of the mentioned compounds have hydroxyl groups in their structure, which make hydrogenous bonds with water molecules. The pH of the compounds is as following: acetic acid – 4 (at 9 % concentration), glycerol and sorbitol – 7 [44-46].

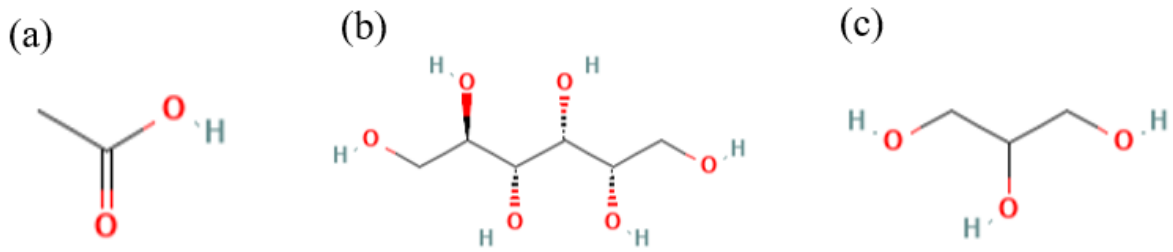

Fig. 10. Chemical structure of (a) acetic acid, (b) sorbitol, (c) glycerol [44-46]

For the purpose of this research, both sorbitol and glycerol were obtained from *Sapolita*. Parameters of both glycerol and sorbitol are presented in table 10 and table 11 respectively.

Table 10. Parameters of glycerol [47]

Parameter	**Value**
Glycerol, %	>99,5
Water, %	<0,05
Density, g/ml	1,26

Table 11. Parameters of sorbitol [48]

Parameter	**Value**
Sorbitol, %	~50
Water, %	~50
Density, g/ml	1,30

Essential oils

As it was discussed in the prior parts of this work, essential oils can have positive impact to the properties of the films, especially if they are added with the aim to improve antimicrobial, antibacterial and antifungal properties of them and, in case the films are developed with the aim to be used for food packaging, to prolong the shelf life of the products.

In this study, two essential oils were used as additives in the starch films – tea tree (*bot. Melaleuca alternifolia*) and peppermint (*bot. Mentha piperia L*), both of them were manufactured by "Kvapų namai".

According to the chromatograms provided by the manufacturer, these are the main chemical components found in the essential oils:

- In tea tree essential oil – terpinen-4-ol (42,16 %), terpinene gamma (19,30 %), terpinene alpha (9,68 %) [49]
- In peppermint oil – menthol (40,88 %), menthone (18,14 %) [50].

Already conducted research shows, that the main components of selected essential oils have antimicrobial, antibacterial and antifungal properties. Study by Saharkhiz, M. J., Motamedi, M.,

Zomorodian, K., Pakshir, K., Miri, R. and Hemyari, K. has showed antifungal activities against *Candida* species, as well as encapsulated *C. neoformance* yeast. [51].

Study performed by Chidi, F., Bouhoudan A. and Khaddor, M. has proven that tea tree essential oils and its main component terpinen-4-ol has proven to be efficient against *Penicillium* and its species [52]. Research by Felšöciová, S., Vukovic, N., Jeżowski, P, and Kačániová, M., has showed that peppermint oil is also one of the most efficient essential oils against the *Penicillium* microorganisms [53]. And as the mentioned microorganism genus can be found in food storage molds, further investigation of the essential oil applications should be conducted.

2.2. Methodological Part

2.2.1. Preparation of the Films

For the preparation of the films different compositions of starch, plasticizers and essential oils as well as red lentil flour were used. They are presented in table 12.

The following steps were taken in order to prepare the films:

- Starch, red lentil flour, water and plasticizers of calculated mass were added to the beaker and mixed at 25 ^{o}C for 20 min, until homogenous mixture was reached
- Then the heating was increased to 70 ^{o}C, so that the gelatinization could start and once the temperature was reached, mixture was heated for 7 min
- The temperature was reduced to 50 ^{o}C and essential oil was added; the mixture then stirred for 1,5 min
- After the essential oil was added, mixture was cooled down to 40 ^{o}C
- Using wide spatula, the formed gel was spread on a 15x15 cm glass plate
- Prepared sample was dried at 22-25 ^{o}C temperature for 96 hours and then carefully removed

In order to achieve accurate results, 5 samples of each composition were prepared.

Table 12. Composition of starch films

No. 1	**No. 2**	**No. 3**	**No. 4**
H_2O – 49 ml Potato starch – 9 g Lentil flour – 1,2 g Sorbitol – 22 g Vinegar – 6 ml	H_2O – 49 ml Potato starch – 9 g Lentil flour – 1,2 g Sorbitol – 22 g Vinegar – 6 ml Peppermint essential oil – 0,3 ml	H_2O – 49 ml Potato starch – 9 g Lentil flour – 1,2 g Sorbitol – 22 g Vinegar – 6 ml Peppermint essential oil – 0,5 ml	H_2O – 49 ml Potato starch – 9 g Lentil flour – 1,2 g Sorbitol – 22 g Vinegar – 6 ml Tea tree essential oil – 0,3 ml
No. 5	**No. 6**	**No. 7**	**No. 8**
H_2O – 49 ml Potato starch – 9 g Lentil flour – 1,2 g Sorbitol – 22 g Vinegar – 6 ml Tea tree essential oil – 0,5 ml	H_2O – 65 ml Potato starch – 9 g Lentil flour – 1,2 g Glycerol – 6 g Vinegar – 6 ml	H_2O – 65 ml Potato starch – 9 g Lentil flour – 1,2 g Glycerol – 6 g Vinegar – 6 ml Peppermint essential oil – 0,3 ml	H_2O – 65 ml Potato starch – 9 g Lentil flour – 1,2 g Glycerol – 6 g Vinegar – 6 ml Peppermint essential oil – 0,5 ml

No. 9	**No. 10**	**No. 11**	**No. 12**
H_2O – 65 ml Potato starch – 9 g Lentil flour – 1,2 g Glycerol – 6 g Vinegar – 6 ml Tea tree essential oil – 0,3 ml	H_2O – 49 ml Potato starch – 9 g Lentil flour – 1,2 g Glycerol – 22 g Vinegar – 6 ml Tea tree essential oil – 0,5 ml	H_2O – 49 ml Tapioca starch – 9 g Lentil flour – 1,2 g Sorbitol – 22 g Vinegar – 6 ml	H_2O – 49 ml Tapioca starch – 9 g Lentil flour – 1,2 g Sorbitol – 22 g Vinegar – 6 ml Peppermint essential oil – 0,3 ml
No. 13	**No. 14**	**No. 15**	**No. 16**
H_2O – 49 ml Tapioca starch – 9 g Lentil flour – 1,2 g Sorbitol – 22 g Vinegar – 6 ml Peppermint essential oil – 0,5 ml	H_2O – 49 ml Tapioca starch – 9 g Lentil flour – 1,2 g Sorbitol – 22 g Vinegar – 6 ml Tea tree essential oil – 0,3 ml	H_2O – 49 ml Tapioca starch – 9 g Lentil flour – 1,2 g Sorbitol – 22 g Vinegar – 6 ml Tea tree essential oil – 0,5 ml	H_2O – 65 ml Tapioca starch – 9 g Lentil flour – 1,2 g Glycerol – 6 g Vinegar – 6 ml
No. 17	**No. 18**	**No. 19**	**No. 20**
H_2O – 65 ml Tapioca starch – 9 g Lentil flour – 1,2 g Glycerol – 6 g Vinegar – 6 ml Peppermint essential oil – 0,3 ml	H_2O – 65 ml Tapioca starch – 9 g Lentil flour – 1,2 g Glycerol – 6 g Vinegar – 6 ml Peppermint essential oil – 0,5 ml	H_2O – 65 ml Tapioca starch – 9 g Lentil flour – 1,2 g Glycerol – 6 g Vinegar – 6 ml Tea tree essential oil – 0,3 ml	H_2O – 65 ml Tapioca starch – 9 g Lentil flour – 1,2 g Glycerol – 6 g Vinegar – 6 ml Tea tree essential oil – 0,5 ml

2.2.2. Methods of analysis

Visual evaluation

Visual evaluation is done to check, if film was properly formed and evaluate the initial appearance, if there are any damages, etc. The following points should be analyzed:

- Colour
- Rigidity
- Film transparency
- Presence of air bubbles
- Quality of the film surface
- Damages visible to the naked eye

Measurement of thickness

Measurement of thickness was performed using a *Lonis Schopper Leipzig* automatic micrometer (accuracy ± 0,01 mm). In order to do the measurement, samples of required size and from different locations of the films were placed in between two micrometer plates. The upper one was then pressed using a constant force and the thickness value in millimeters was indicated by the device. In order to obtain the most accurate results, measurements were done in 10 different places in the films.

Tensile strength

In order to calculate value of the maximum force, which can be withheld by the material, tensile strength test was performed. The test was done using *Zwick Z005* equipment, with 5 samples of dimensions 1,5 x 15 cm for each of the properly formed films. The prepared samples were placed between the two grippers set at 10 cm distance between each other, which were then moved in opposite directions at constant speed while increasing applied force until the sample broke. The load-elongation curve was plotted as well as the following values were provided by the used software: maximum applied force, elongation at maximum force, total elongation and force at breaking point.

The values in the obtained load-elongation curve were used to calculate tensile strength using formula (1):

$$\sigma = \frac{F}{A} \quad (1)$$

here σ – tensile strength, MPa; F – force, N; A – area, mm^2.

Area was calculated according to the formula (2)

$$A = h \cdot w \quad (2)$$

here A – area, mm^2, h – thickness of the samples, mm, w – width of the sample, mm.

Young's modulus

Young's modulus is used to evaluate elasticity of the material. It helps to define, whether material can be stretched and deformed easily, or not. The higher is the value of Young's modulus, the bigger force is required to reach same value of tension. That is, the lower the value the Young's module, the more flexible and elastic is the material.

Young's modulus is calculated using the (3) formula:

$$E = \frac{\sigma}{\varepsilon} \quad (3)$$

Here E – Young's modulus, MPa; σ – tensile strength, MPa; ε – longitudinal strain.

Young's modulus values of some widely used plastics [54]:

- Polypropylene (PP) – 1-1,4 GPa
- Polyethylene terephthalate (PET) – 2,8-3,5 GPa
- Low-density polyethylene (LDPE) – 0,11-0,45 GPa
- Polylactide (PLA) – 3,8 GPa
- Cellulose acetate (CA) – 0,6-2,8 GPa

Contact angle

Contact angle with water is measured in order to evaluate, whether the prepared film is more hydrophilic or hydrophobic. The bigger the angle, the more tested surface is hydrophobic. The measurement was done using BV S1008 method and results were evaluated according to the ASTM D5946 standard, presented in table 13.

Table 13. ASTM D5946 standard for the lever of polymer surface treatment [55]

Level of surface finishing	**Contact surface angle, °**
No processing or slight processing	> 90
Small	85-90
Medium	78-84
High	71-77
Very high	< 71

Morphology

DinoCapture 2.0 microscope was used to evaluate the morphology and surface of the films – to determine if there are any particles present, size of pores, air bubbles, how rough is the surface, etc. Such evaluation helps to better understand and evaluate film forming procedure as well as properties of the materials.

Biodegradablity

Biodegradability was tested as defined in the study by of Ochoa-Yepes, O., Guz, L., Jaramillo, C. M. and Fama, L. Samples of 2 x 2 cm size were buried 5 cm deep into plastic boxes with compost (composition and properties of the compost presented in table 14). In order to monitor the biodegradability progress, samples were taken out even 5 days. To keep the moisture level of the compost, water was sprayed on top every two days [19].

Table 14. Composition and properties of the compost

Conductivity, mS/cm	0,9-1,6
pH	5,6-6,8
Soluble nitrogen (N), mg/kg	200-350
Soluble phosphorus (P_2O_5), mg/kg	50-200
Potassium (K_2O), mg/kg	300-500
Humidity, %	Not more than 70
Fraction, mm	0-20

2.3. Methodological Part Conclusions

Properties of materials were reviewed and their selection for the study as well as their purpose were justified. Potato and tapioca starches were selected as matrix material for the film, red lentil flour was used as a reinforcement for the film. Glycerol and sorbitol, as well as acetic acid were used as plasticizers to increase flexibility of the films. Two types of essential oils – peppermint and tea tree- were chosen based on current studies and their antimicrobial properties to evaluate what kind of impact they would have to other properties of the films. Selected compositions of the films were presented and methods of analysis used for the research were presented. In order to determine film suitability for practical application, visual evaluation, tensile strength measurement as well as Young's modulus calculation, evaluation of hydrophobicity, morphology and biodegradability were selected to be performed.

3. Results of Research

In total films of 20 different compositions were prepared, as it was described in section 2.2.1. Then the measurements defined in section 2.2.2. were made and the results are presented in the following sections.

3.1. Visual Evaluation

After the samples were completely dry, they were taken off of the glass plates and their visual evaluation was performed. Description of the samples is presented in the table 15, photos of the films can be seen in Fig. 12. 4 films out of 20 were identified as not properly formed.

A slight red colour in some films was visible due to the red lentil flour added to the composition. All of the films, which were covered in white material after drying completely (approximately 1 week from making the samples; affected films were no. 1-5 and 11-15), had both sorbitol and acetic acid in their composition. Due to the suitable conditions for the chemical reaction to take place, fructose was formed from the sorbitol and acetic acid. Fructose are white crystals, soluble in water and of sweet taste. Fructose on the surface of the films could also have an impact to the stickiness of the film. The chemical reaction is presented in Fig. 11 [56]. Visual appearance of the film covered with fructose can be seen in fig. 13 – it becomes of matte surface, not clear anymore, feels more rigid.

Samples made with glycerol were softer and more flexible compared to the films made with sorbitol as a plasticizer. Samples made from tapioca starch as a base material had much smoother surface than films made with potato starch.

Table 15. Visual evaluation and description of the films

Sample	Description
No. 1	Soft, flexible, transparent, with visible air bubbles. After drying completely, surface became covered in white material, which could be easily removed by wiping it off with water. With coverage of white material, film became sturdier, not as flexible.
No. 2	Film not formed. Obtained pieces were of rough surface, brittle, felt slightly sticky. Parts of the pieces covered in white material. Has an aroma of menthol (from peppermint essential oil)
No. 3	Film not formed. Obtained pieces were of rough surface, brittle, felt slightly sticky. Parts of the pieces covered in white material. Has an aroma of menthol (from peppermint essential oil)
No. 4	Soft and flexible, slightly sturdier than sample no. 1, transparent with a soft shade of red, slightly visible air bubbles. After drying completely, surface became covered in white material, which could be easily removed by wiping it off with water. Has a soft aroma of tea tree essential oil. With coverage of white material, film became sturdier, not as flexible.
No. 5	Film not formed properly. Soft and flexible, but obtained pieces were of rough surface, brittle, felt slightly sticky, with a soft shade of red. After drying completely, surface became covered in white material, which could be easily removed by wiping it off with water. Has a soft aroma of tea tree essential oil. With coverage of white material, film became sturdier, not as flexible.
No. 6	Soft, flexible, parts of the film were slightly of rougher surface and sturdier, more rigid compared to other samples made with potato starch and glycerol as plasticizer; has a shade of light red colour, but the film still can be seen-through. Is odorless
No. 7	Soft, flexible, film has an even surface with some visible air bubbles; has a shade of light red colour but the film is transparent. Parts of film, which were thicker, did not for completely. Has a soft aroma of peppermint essential oil.

Sample	Description
No. 8	Soft, flexible, film has an even surface with some visible air bubbles; has a shade of light red colour but the film is transparent. Parts of film, which were thicker, did not for completely. Has a soft aroma of peppermint essential oil.
No. 9	Very soft and flexible, film has an even surface with some visible air bubbles; has a shade of light red colour but the film is transparent. Has a soft aroma of tea tree essential oil.
No. 10	Film not formed. Surface is rough, film is sturdier than sample 9; has a shade light yellow colour, has a soft aroma of tea tree essential oil.
No. 11	Soft, flexible, transparent, with visible air bubbles. After drying completely, surface became covered in white material, which could be easily removed by wiping it off with water. With coverage of white material, film became sturdier, not as flexible. Does not have an odor, can feel slightly sticky
No. 12	Soft, flexible, transparent, with visible air bubbles. After drying completely, surface became covered in white material, which could be easily removed by wiping it off with water. With coverage of white material, film became sturdier, not as flexible. Has a soft aroma of peppermint essential oil, can feel slightly sticky. Some parts of the film were damaged while taking the film off of the glass plate.
No. 13	Soft, flexible, transparent, with visible air bubbles. After drying completely, surface became covered in white material, which could be easily removed by wiping it off with water. With coverage of white material, film became sturdier, not as flexible. Has a soft aroma of peppermint essential oil, can feel slightly sticky. Some parts of the film were damaged while taking the film off of the glass plate.
No. 14	Soft, flexible, transparent, with visible air bubbles. After drying completely, surface became covered in white material, which could be easily removed by wiping it off with water. With coverage of white material, film became sturdier, not as flexible. Has a soft aroma of tea tree essential oil, can feel slightly sticky
No. 15	Soft, flexible, transparent, with visible air bubbles. After drying completely, surface became covered in white material, which could be easily removed by wiping it off with water. With coverage of white material, film became sturdier, not as flexible. Has a soft aroma of tea tree essential oil, can feel slightly sticky
No. 16	Very soft and flexible, film has an even surface with some visible air bubbles; has a shade of light red colour but the film is transparent; is odorless
No. 17	Very soft and flexible, film has an even surface with some visible air bubbles; has a shade of light red colour but the film is transparent. Has a soft aroma of peppermint essential oil.
No. 18	Very soft and flexible, film has an even surface with some visible air bubbles; has a shade of light red colour but the film is transparent. Has a soft aroma of peppermint essential oil.
No. 19	Very soft and flexible, film has an even surface with some visible air bubbles; has a shade of light yellow colour but the film is transparent. Has a soft aroma of tea tree essential oil.
No. 20	Very soft and flexible, film has an even surface with some visible air bubbles; has a shade of light yellow colour but the film is transparent. Has a soft aroma of tea tree essential oil.

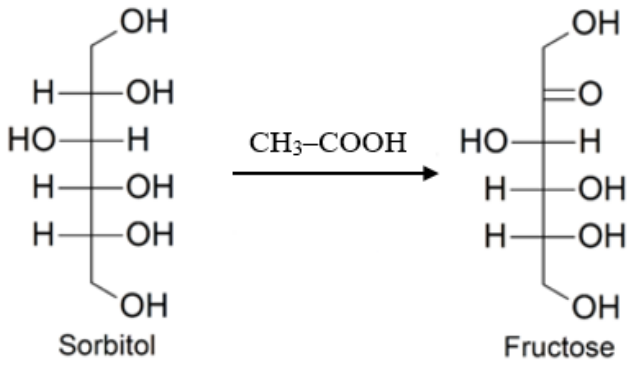

Fig. 11. Chemical reaction of sorbitol and acetic acid forming fructose

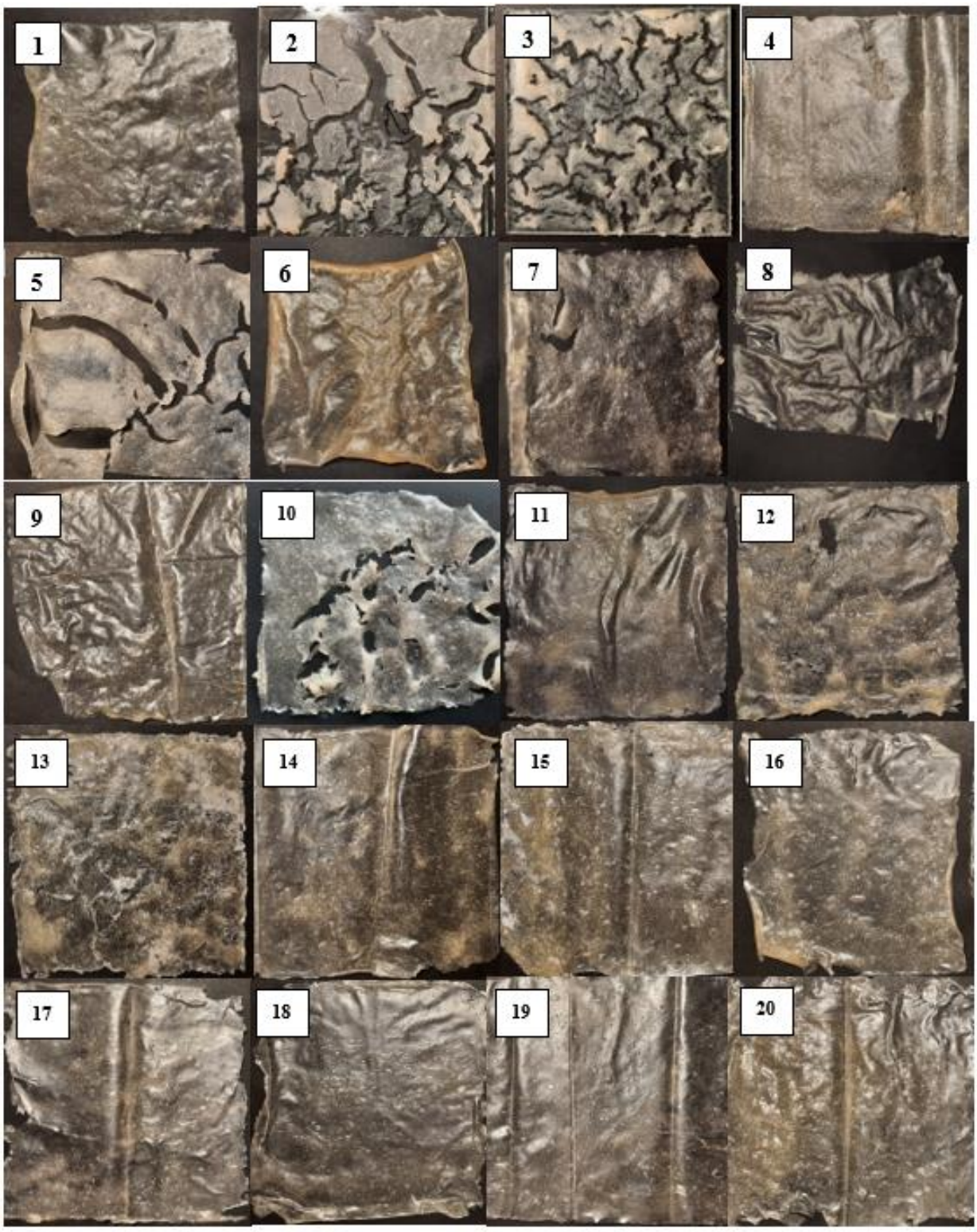

Fig. 12. Prepared film samples

Fig. 13. Sample of film no. 13 covered in white material (fructose crystals)

In general, appearances of the films did not differ much. The biggest differences were observed between samples made with glycerol and sorbitol, as the latter ones, when completely dried, were covered in white fructose crystals. Also, films made with potato starch seemed to be not as flexible and soft as the ones made with tapioca starch. Essential oils did not have an impact to the film appearance.

3.2. Film Thickness

Results of the thickness measurements are presented in Fig. 14. The obtained values vary because of the chosen casting method with a spatula (not possible to control the thickness) and because of different compositions of the films – films made from potato starch had slightly bigger thickness than samples made from tapioca starch. Also, samples made sorbitol were also significantly thicker than samples made with glycerol. In general, the average thickness of samples varies in the range of 0,16 mm and 0,58 mm. Also, as it was observed during visual evaluation, thicker films had a tendency not to form completely.

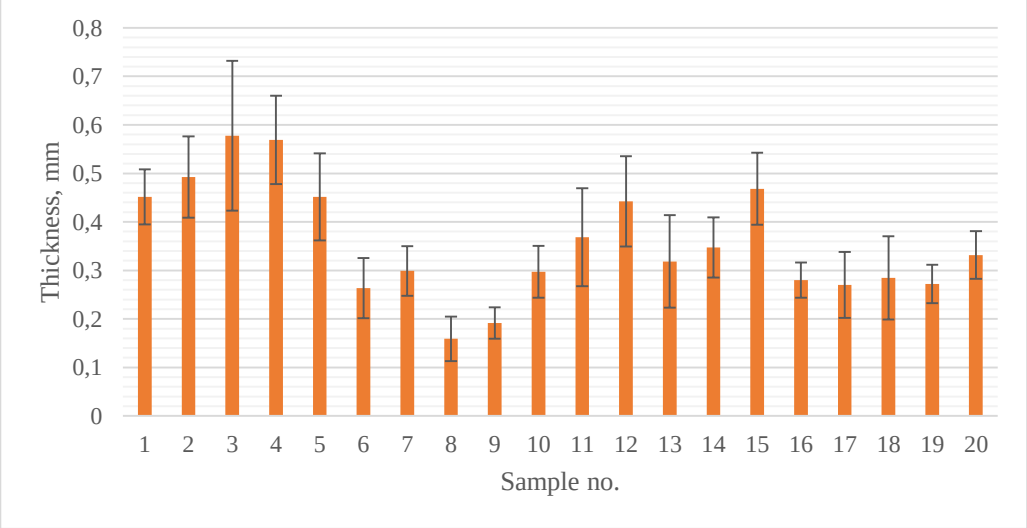

Fig. 14. Results of thickness measurements

Thickness of the films can have a significant impact to other properties of the films, such as strength, plasticity, rigidity, elasticity, etc. Thus, in order to be able to compare the measurement results more

accurately, film thickness should be similar and between samples vary as little as possible. For that, different film-making method could be chosen.

Also, too thick films are not desirable because of their limited applicability. While they might be more rigid, bigger thickness results in less flexibility and breaking easier. Usually, thickness of bio-based biodegradable films are much lower, some researchers have managed to obtained results as little as 0.099 to 0.1599 mm for films made with potato starch [57]. Therefore, the thickness of the produced sample for this research, should be much lower in order to apply the composition for practical application.

3.3. Film Strength

Film strength was measured for 16 samples – films no. 2, 3, 5 and 10 were not tested because they did not form properly and it was not possible to obtain the samples for testing of required size. Film number 8 was tested only with two samples, as more were not possible to obtain due to not fully formed film. The obtained load-elongation graphs can be seen in figures 15-17. Obtained results and graphs varied depending on the composition of the prepared samples.

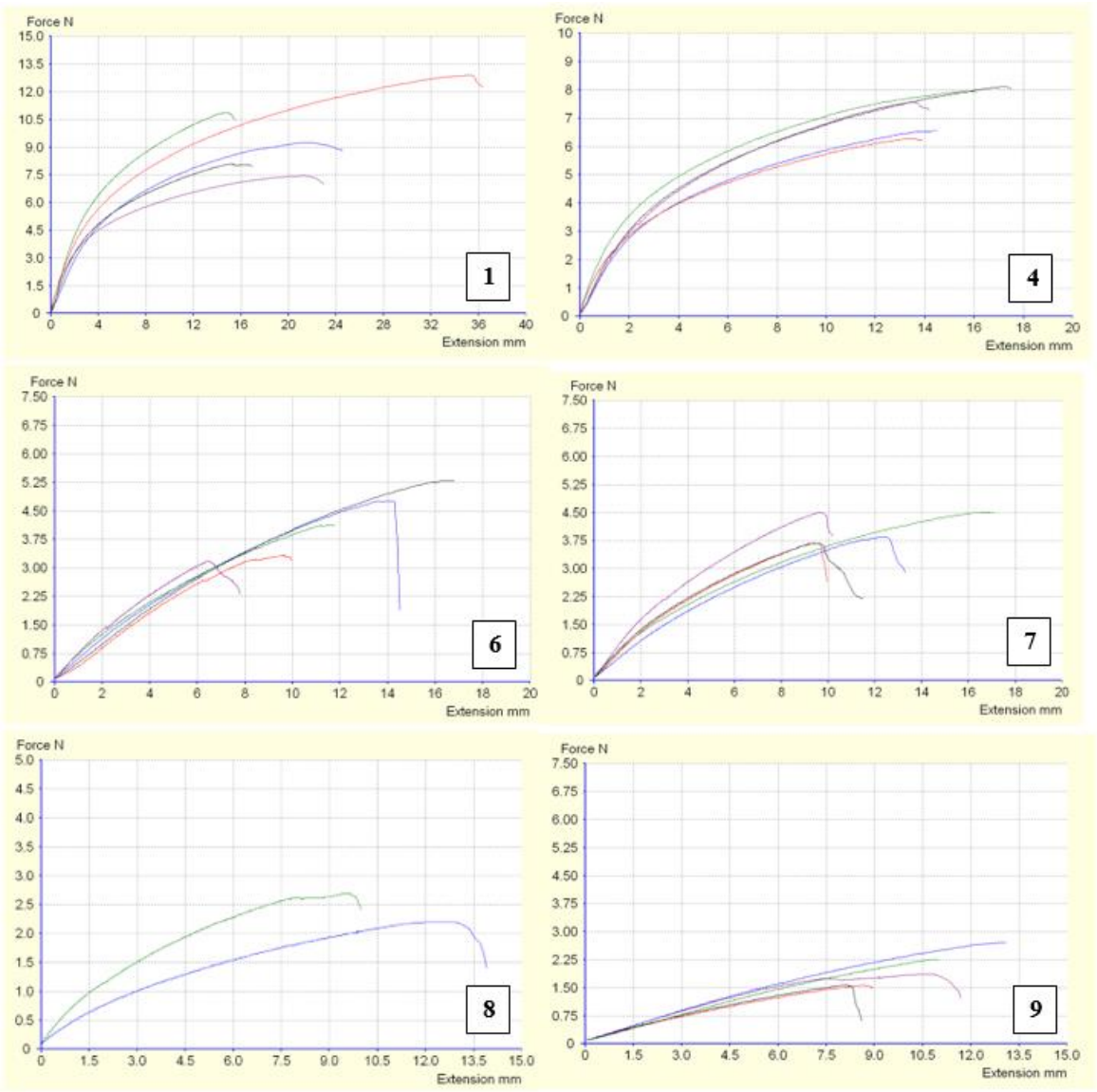

Fig. 15. Load-elongation curves of films no. 1, 4, 6-9; all made with potato starch

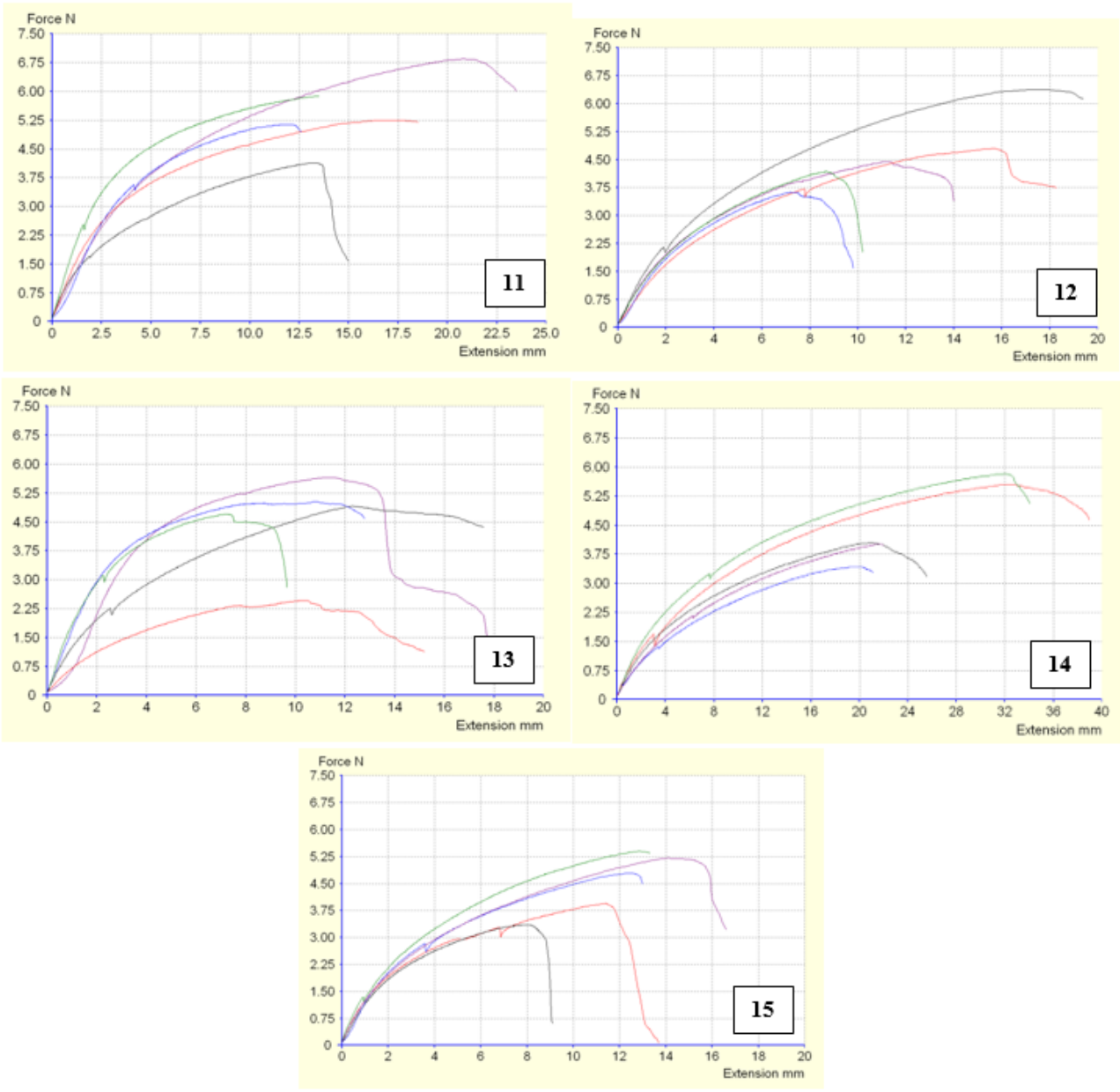

Fig. 16. Load-elongation curves of films no. 11-15; all made with tapioca starch and sorbitol as plasticizer

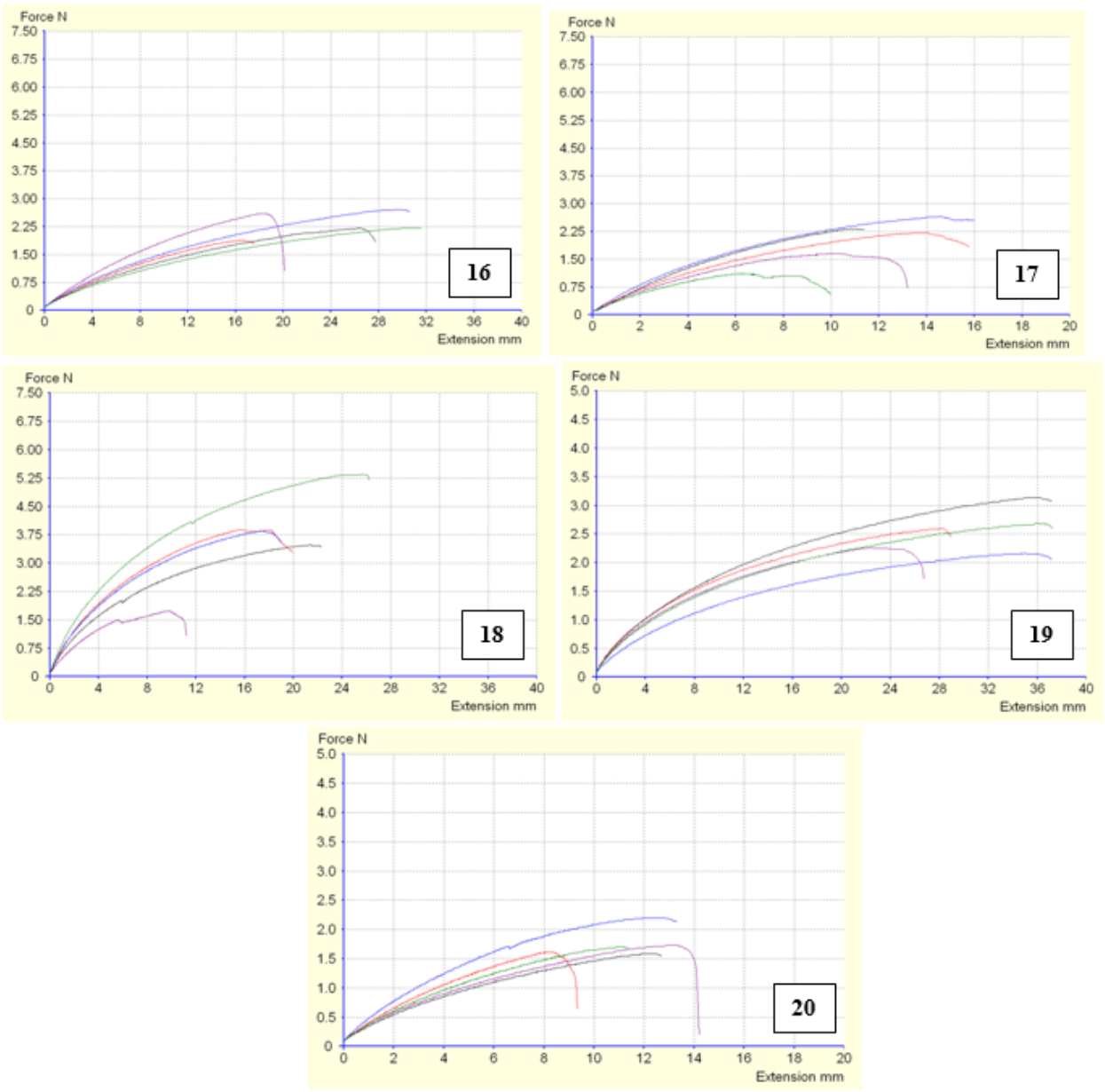

Fig. 17. Load-elongation curves of films no. 16-20; all made with tapioca starch and glycerol as plasticizer

Based on the load-elongation curves of each of the sample, average of all obtained maximum force values, elongations at it, total elongation and force values at break were calculated and results presented in table 16.

Table 16. Mechanical properties of the prepared films

Sample	**FH, N**	**εH, %**	**εB, %**	**FB, N,**	**σ, MPa**	**E_{mod}, MPa**
No. 1	9,710	21,340	23,300	9,290	2,151	10,078
No. 4	7,290	14,640	15,240	7,200	1,281	8,751
No. 6	4,141	11,490	12,180	3,353	1,572	13,677
No. 7	4,050	11,380	12,410	3,218	1,355	11,903
No. 8	2,450	10,760	11,940	1,908	1,541	14,320
No. 9	1,996	10,140	10,670	1,650	1,043	10,284
No. 11	5,450	14,950	16,620	4,716	1,480	9,901
No. 12	4,688	11,900	14,340	3,374	1,060	8,907
No. 13	4,549	10,280	14,930	2,814	1,428	13,894

Sample	FH, N	εH, %	εB, %	FB, N,	σ, MPa	E_{mod}, MPa
No. 14	4,567	24,910	28,360	4,024	1,314	5,275
No. 15	4,541	11,620	13,140	2,743	0,970	8,347
No. 16	2,326	23,940	25,540	1,907	0,830	3,469
No. 17	1,989	10,920	13,280	1,587	0,736	6,740
No. 18	4,143	19,925	21,875	3,864	1,456	7,308
No. 19	2,570	31,100	33,480	2,373	0,944	3,035
No. 20	1,767	11,140	12,190	1,241	0,533	4,785

Here FH – maximum force, N; εH – elongation at maximum force, %; εB – total elongation, %, FB – force at break, N; σ – tensile strength, MPa, E_{mod} – Young's module, MPa

Fig. 18 presents maximum applied force values for the tested samples. As it can be seen from the graph, films made with potato starch were the strongest ones and could withstand the highest force values. Also, samples made with sorbitol as plasticizer (samples no. 1, 4, 11-15) demonstrated bigger strength compared to the samples made with glycerol as plasticizer (samples no. 6-9, 16-20). In most of the cases, added essential oils to the composition resulted in lower tensile strength (except for samples 18). Also, as it is seen from the graph, maximum force values varied not only because of the composition of the films, but thickness of the films had an impact as well.

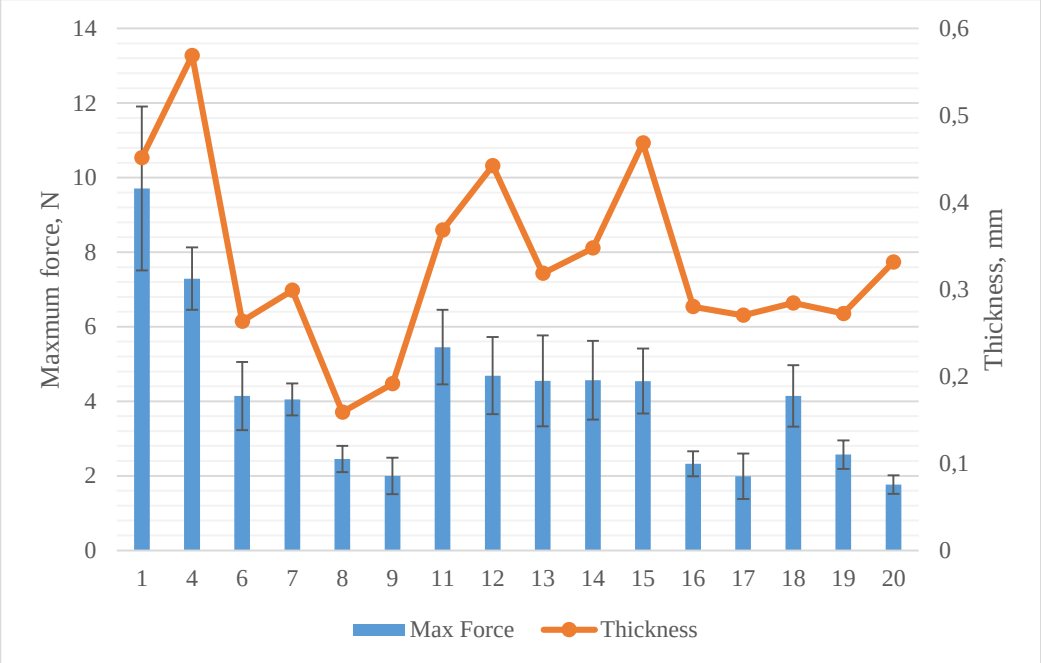

Fig. 18. Comparison of sample thickness and maximum tensile force

Comparing the calculated tensile strength values, presented in Fig. 19, it can be seen that the biggest tensile strength value (2,151 MPa) was obtained with the sample no. 1. In general, samples made with sorbitol demonstrated lower tensile strength values compared to the samples made with glycerol. The lowest strength (0,355-0,629 MPa) were calculated for the samples made with tapioca starch and glycerol as a plasticizer meaning that samples 16, 17, 19 and 20 were able to withheld lowest force. Also, samples with essential oils demonstrated lower tensile strength than films without them. In comparison, studies from other researchers have showed, that bio-based biodegradable films can reach tensile strength values up to 9,37-9,78 MPa [20]. Thus, tensile strength of the researched films needs to be improved by changing composition of the films and improving the film-making process.

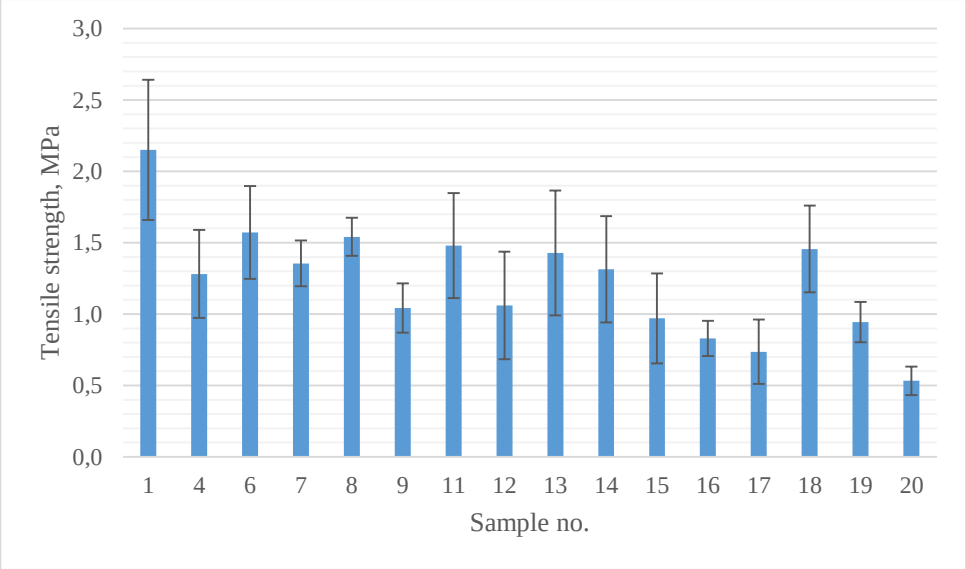

Fig. 19. Tensile strength of the samples

3.4. Young's Modulus

Values of Young's module are presented in Fig. 20. As it can be seen, samples made with potato starch and glycerol as plasticizer (samples no. 6-9) were the least elastic ones, as they had the biggest values of Young's modulus. Samples made with tapioca starch and glycerol (films no. 16-20) were the most flexible and elastic ones. Films made with potato starch and sorbitol were more elastic compared to the samples made with potato starch and glycerol. Films made with tapioca starch behaved in opposite – samples, which had sorbitol as plasticizer had in general slightly higher values of Young's modulus compared to the ones with glycerol, meaning that they were stiffer and not as elastic.

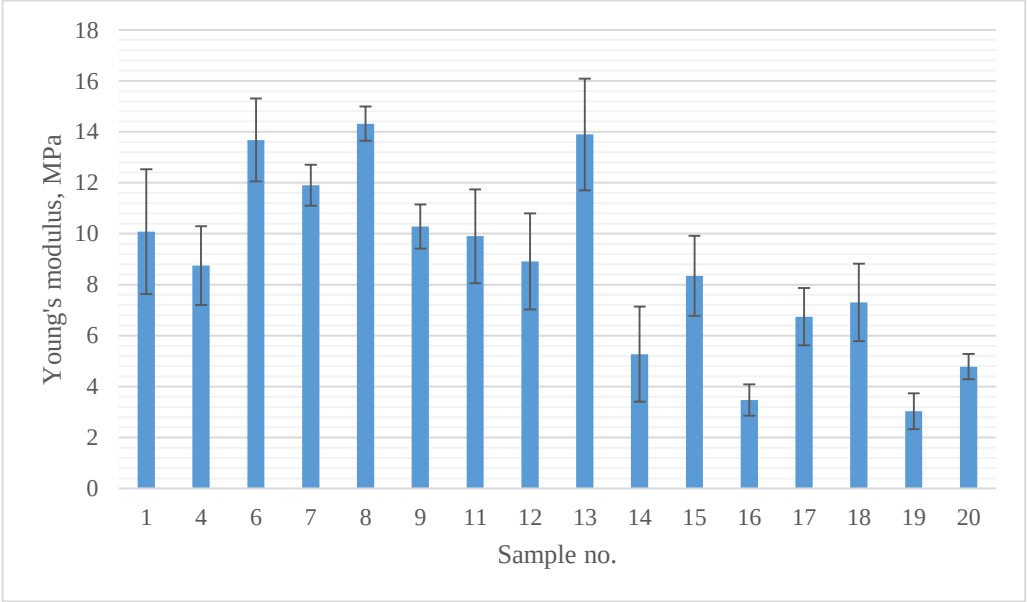

Fig. 20. Young's modulus of the samples

Results of the measured samples were much lower compared to the oil-derived plastics, meaning, that the practical applicability based on this value is limited. Nonetheless, the obtained results were similar to the ones presented in the study made by Tryznowska, Z. Z, and Kaluza, A. [58]:

- Maize – 14,2 MPa
- Potato – 14,5 MPa
- Oat – 1,8 MPa
- Rice – 9,6 MPa
- Tapioca – 0,8 MPa

As it can be seen, Young's modules values for films made with potato and tapioca starches were increased (to 14,320 MPa with samples no. 8 and 13,894 MPa with samples no. 13 respectively).

3.5. Contact Angle

Results of contact angle measurement are presented in Fig. 21. As it can be seen, samples made with potato starch (no. 1-9) were more hydrophilic compared to the samples made with tapioca starch (no. 11-20). However, for samples made with both types of starches, films with sorbitol as plasticizer were much more hydrophilic compared to the ones made with glycerol – samples no. 1, 4, 11 and 12 could not be measured as the drop of water was absorbed immediately, thus contact angle is considered as 0^o in the graph. Samples 7-9 showed only very little positive or even negative impact of essential oils to the contact angle measurement. Essential oils, on the other hand, had a positive impact to the samples made with tapioca starch. Films no. 13-15 have reached up to 30^o contact angle, when samples without (no. 11) and smaller amount of peppermint essential oil (no. 12) were very hydrophilic with full water absorption. Samples 17 and 18 were prepared with peppermint essential oil and it influenced contact angle more positively in comparison to the tea tree essential oil (samples 19 and 20) for the film with same tapioca starch and same glycerol plasticizer. Also, comparing samples 16-20, bigger amount of essential oils in the composition resulted in the bigger hydrophobicity. The most hydrophobic sample (contact angle $43,56^o$) was no. 18, made with tapioca starch, glycerol as plasticizer and 0,5 mm peppermint essential oil. However, according to the ASTM D5946, most of the tested films can be considered of having very high lever surface finishing.

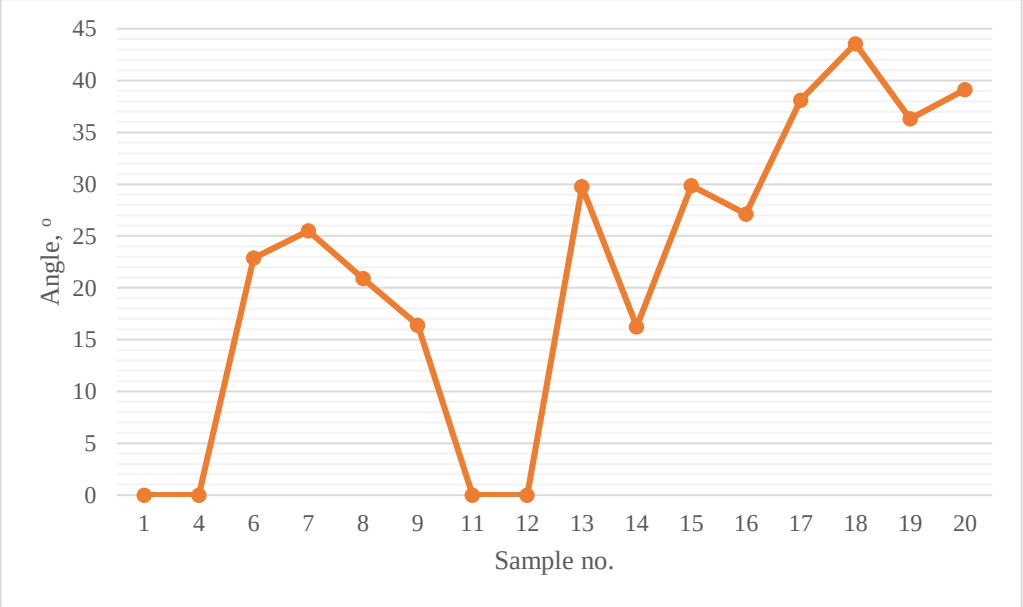

Fig. 21. Results of contact angle measurements

Nonetheless, hydrophobicity of the films could also be improved, as similar researches with different compositions of the films show contact angles up to $60\text{-}66^o$ for potato and tapioca starches [18, 58].

3.6. Morphology

During visual evaluation of the films, air bubbles in the structure were seen in most of the samples. The structure of the films was checked with a microscope as well and photos of the analysis are presented in figures 22-24. Air bubbles (as marked in Fig. 22 for sample no. 1 with blue arrows) were observed in all 20 samples of prepared films. Less and smaller bubbles formed in the films made with glycerol compared to the ones made with sorbitol. But they also seemed to have rougher surface (as can be seen in fig. 23, samples 6-10, as well as Fig. 24, samples 16-20). Such air gaps are not desirable in the films, since it can affect mechanical properties of the samples in a negative way as with the presence of such bubbles integrity of the films is damaged – meaning, that in the places of the bubbles film is much thinner, it is easier to tear it apart and films become weaker. Such air bubbles might have been one of the reasons of having relatively low tensile strength of the films, as it was discussed in previous sections. Also, small pieces of red lentil flour can be observed as well, meaning that flour of finer fraction should be used.

Air bubbles in films might appear due to the mechanical mixing during film making (homogenization, gelatinization) and because of the manual casting of the films as well as the relatively long drying time and other film-curing conditions. This issue could be prevented by reducing mixing speed, choosing different mixing method, degassing the obtained mixture before casting it and also choosing different film casting method as spreading the mixture with spatula might have affected integrity of the films, resulting in air bubble gaps on the surface and within the middle of the films.

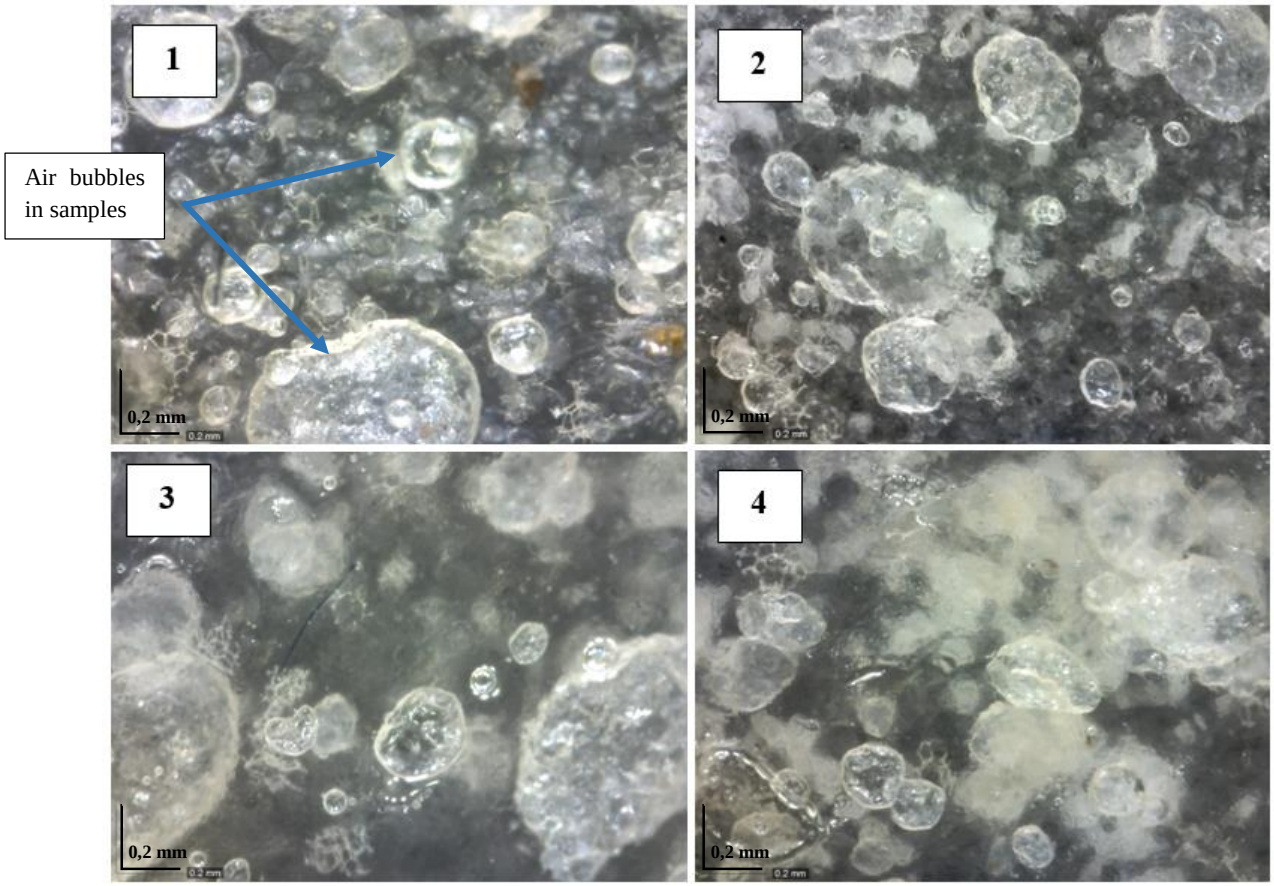

Fig. 22. Microscope images of films no. 1-4

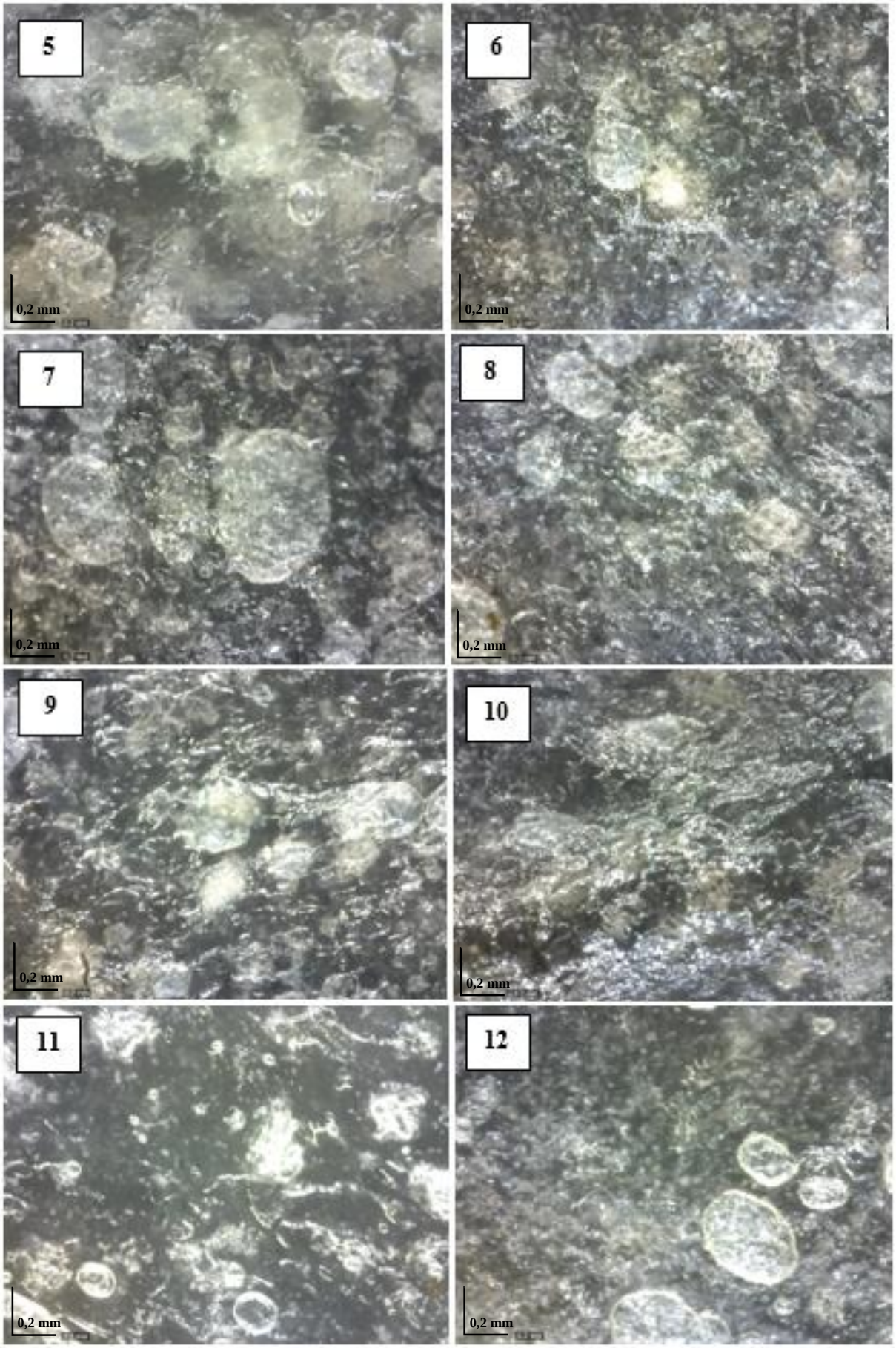

Fig. 23. Microscope images of films no. 5-12

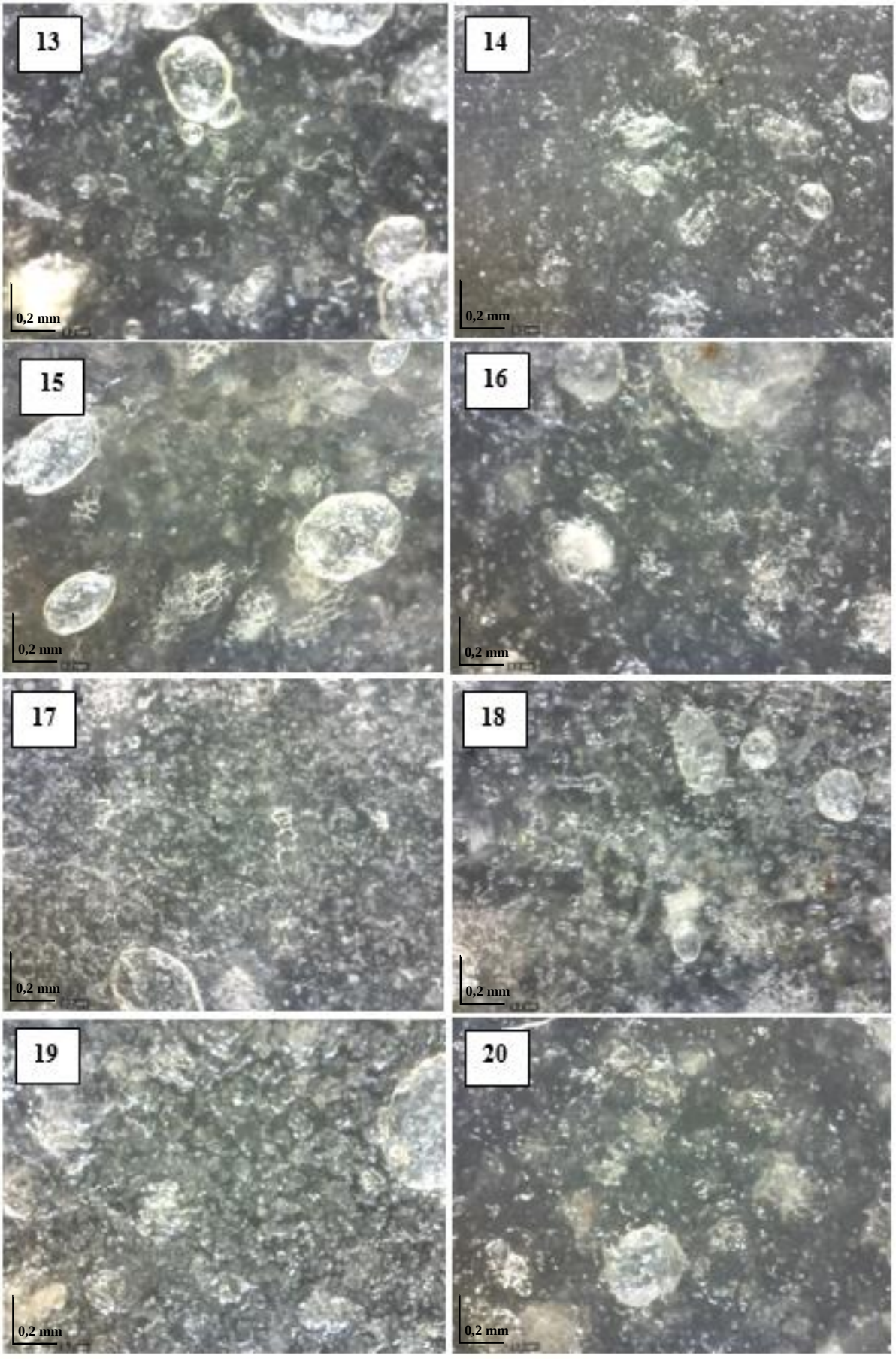

Fig. 24. Microscope images of films no. 13-20

Fig. 25 presents imaged of few films (samples 2, 4, 11, 13), which were covered in fructose crystals (as marked in Fig. 25 for sample no. 2 with red arrows) and resulted in white not clear matte films. As it can be seen fructose crystals differed in sizes and shapes, thus some of the films were covered slightly more than the others.

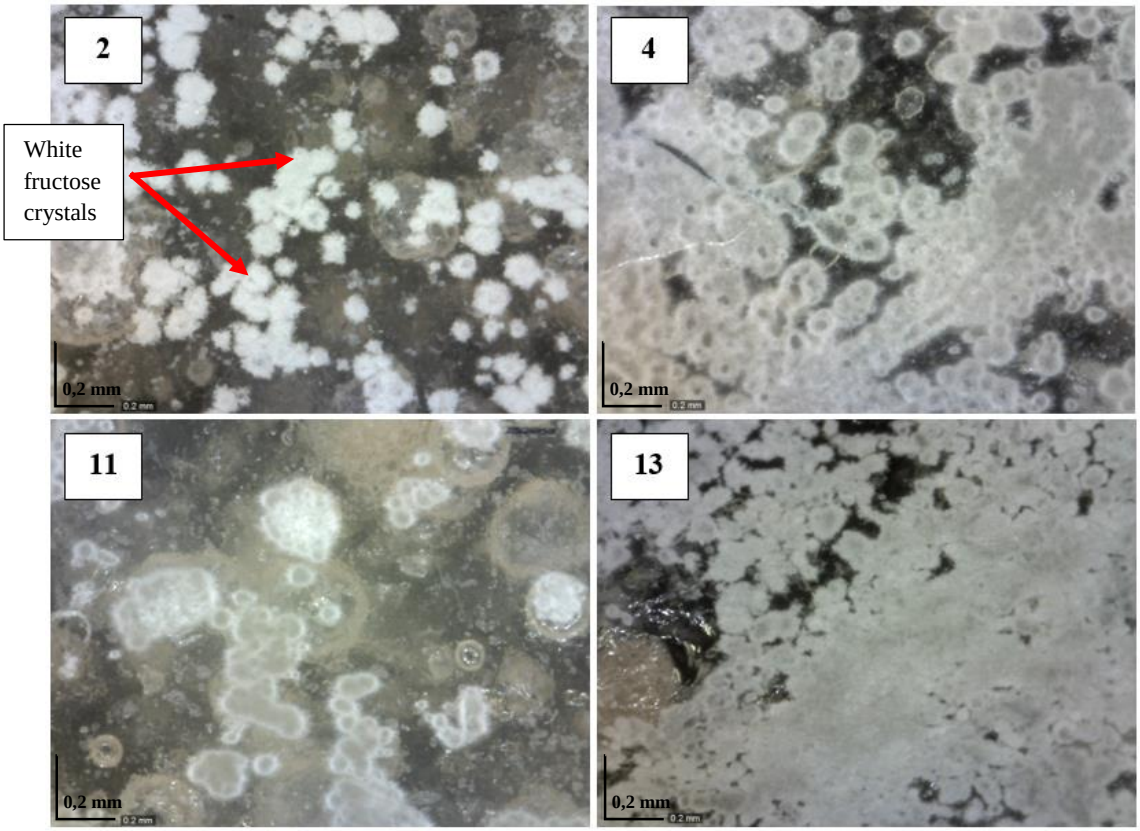

Fig. 25. Microscope images of films no. 2, 4, 11 and 13, 4 out of 10 samples, made with sorbitol, which were covered with fructose

Thus, as it can be seen from the figures 22-24 and Fig. 25, structure of the films is not completely integral and in most of the films it was disrupted by the air bubbles. As their appearance in the films was influenced by the mechanical stirring and manual casting, film-making process should be improved in order to prevent them. White crystals, which covered samples made with sorbitol as plasticizer, were also observed under the microscope. The coverage of the films was different, nonetheless, in all of the films with sorbitol, it could be seen not only when magnified, but also with a human eye.

3.7. Biodegradability

Figures 26 and 27 show the changes of the potato and tapioca starch-based films placed in a compost on day 0 and after 20 days. It is seen that after this time appearance of the films clearly changed, size and mass of the samples significantly decreased. Meaning, that the prepared films can biodegrade. It was also observed that samples containing essential oils and with higher hydrophobicity takes longer time to biodegrade and requires more special conditions for that. Also, thickness of the films had an impact to the level of degradation – the thicker the film, the more time it need to decompose.

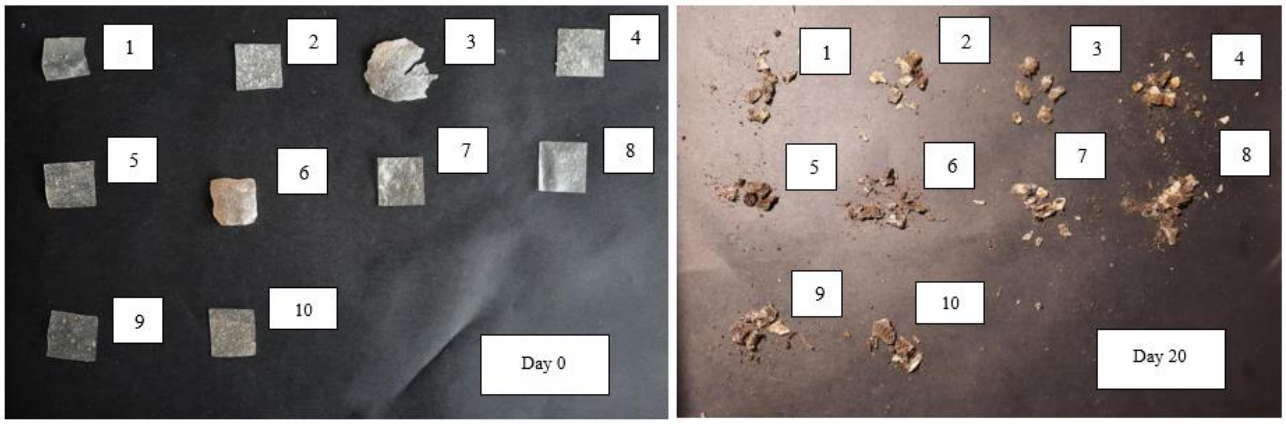

Fig. 26. Potato starch films on day 0 and day 20

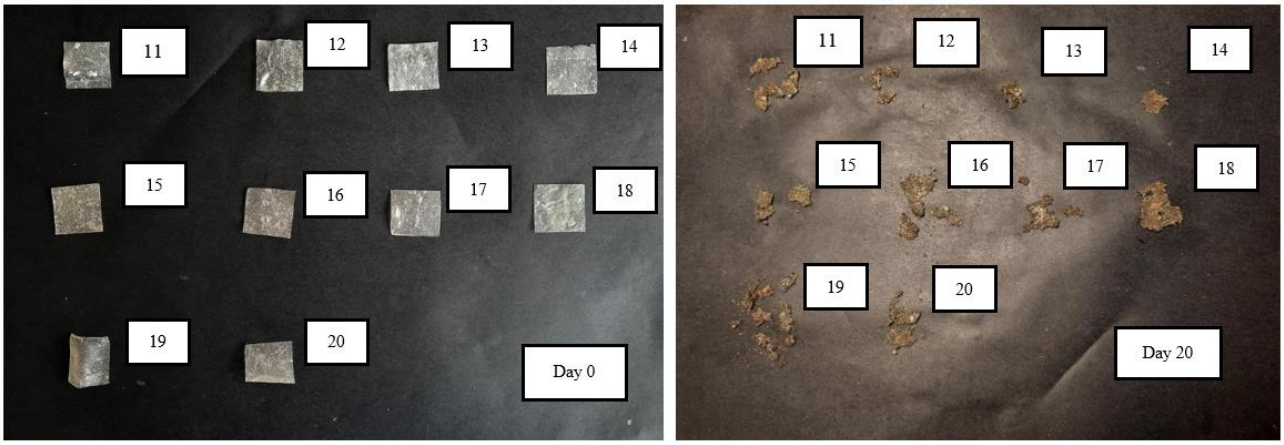

Fig. 27. Tapioca starch films on day 0 and day 20

Comparing the obtained results with the studies of other researchers, films made with similar composition can take up to 30 days to biodegrade [18]. Meaning, that the obtained biodegradability results of the composed films are valid, even with the observed influences of the essential oils.

3.8. Conclusions of the Experimental Part and Further Recommendations

During the experiment, properties of starch-based films with different compositions were investigated and compared. It was observed, that the films made from tapioca starch had a better tendency to form films, as all 10 samples were suitable for further analysis whereas 4 out of 10 films made with potato starch were considered as not properly formed. The thickest films were formed with sorbitol as a plasticizer, samples with glycerol were much thinner. However, samples with sorbitol proven to be stronger as their calculated tensile strength was slightly bigger. For all of the compositions, essential oils had a negative impact to the strength as the tensile strength was lower compared to the samples without essential oils. Obtained Young's modulus for the samples was higher compared to the values provided in other literature sources for starch-based films. However, the values for both tensile strength and Young's modulus were much lower compared to the widely-used plastics, meaning, that the applicability of the discussed films is very limited.

Essentials oils have proven to be effective in increasing hydrophobicity of the samples compared to the compositions without essential oils. This also has impacted biodegradability of the samples, as the samples which are more hydrophilic tend to biodegrade in a shorter amount of time. But higher

hydrophobicity for the films is desired as then the films can be applied to practical usage as packaging materials.

To further improve properties of the films in order to make them applicable for practical use, different film-making and casting process should be chosen. For instance, manufacturing of films using doctor blade in order to better control thickness and other parameters of the films. Also, other compositions of plasticizers as well as other reinforcement materials instead of red lentil flour (e.g. PLA) could be used to check their influence and synergy with essential oils. In order to better investigate impact of the used essential oils, antimicrobial properties of the films should be tested.

4. Managerial and Economical Part

In this section of the work, applicability of starch-based films is discussed based on the price of the materials, limitations of technological manufacturing processes and comparing the environmental impact of the bio-based biodegradable films with the currently used oil-derived plastics.

4.1. Raw Material Prices

In order to be commercially viable, starch-based films ideally should be cheaper or at least of a similar price compared to the other available alternatives. Bulk costs of raw materials, used in study (potato and tapioca starches, 50 % sorbitol, glycerol, red lentil flour, 9 % vinegar, distilled water, peppermint and tea tree essential oils), are presented in table 17.

Table 17. Raw material prices [60-63]

Material	**Price**
Potato starch	1725 EUR/1000 kg [59]
Tapioca starch	6000 EUR/1000 kg [59]
Red lentil flour	11000 EUR/1000 kg [60]
Sorbitol	5500 EUR/1000 kg [48]
Glycerol	3290 EUR/1000 kg [47]
Distilled water	320 EUR/1000 kg [61]
Vinegar	490 EUR/1000 kg [59]
Peppermint essential oil	48 EUR/l [62]
Tea tree essential oil	62,47 EUR/l [62]

Raw material costs, to manufacture 1000 kg of the film, can vary from approx. 834 eur to 2666 eur, based on the composition of the films. Most expensive film composition is with tapioca starch, sorbitol as plasticizer and tea tree essential oil. Films made with potato starch instead of tapioca starch and films made with glycerol instead of sorbitol should be generally cheaper. Also, films with essential oils are also generally more expensive. It is important to mention that labor, utility and other costs were not taken in consideration into this cost calculation. Also, companies buying material in bulk usually are able to purchase them in lower prices, meaning that the cost calculation is just a brief estimation of the possible price.

Comparing the cost of currently existing alternatives, prices for biodegradable packaging varies between 2-6 EUR / kg and 1-2 EUR / kg to make traditional plastics [63]. Meaning, that due to the limitations of manufacturing processes, prices of raw materials and comparably low costs of oil, biodegradable packaging remains more expensive than currently widely used oil-derived plastics.

4.2. Manufacturing Processes and Their Limitations

Manufacturing of biodegradable films can be classified into wet and dry processes. Casting of the films is considered a wet process and mainly used in scientific research as it is very suitable for making small quantities of films in laboratories. Casting is done by pouring prepared suspension onto some plate (e.g. Petri dish), drying the casted material and peeling it off. This method of film-making

has several disadvantages making it unsuitable for larger scale-production. First on all, it is nearly impossible to have full control of film thickness as this is done only by selecting specific amount of mass which is poured (casted) onto the plate. Thus, the variations of the film thickness cannot be avoided. Another disadvantage is long drying process of the films. Pouring suspension prepared with some type of solvent (in most cases, for biodegradable starch films, water is used as a solvent) results in a long drying time needed for the used solvent to evaporate and for the film to be completely dry – otherwise it is not suitable to be used. Therefore, such type of large-scale production would be very time-consuming and would require a lot of space or even separate equipment where the films could be dried. Wet film casting process in a small laboratory scale can be seen in Fig. 28. [64]

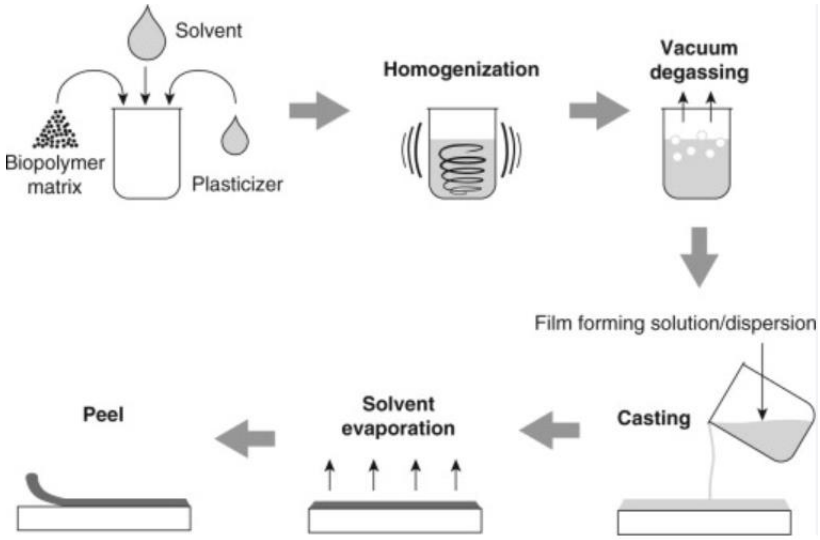

Fig. 28. Classic casting of the films manufacturing method [64]

Similar to the classic casting method is tape-casting. This type of film-making is made by pouring the suspension on a moving belt and thickness being controlled by a blade positioned above the casted suspension (illustration of the process can be seen in Fig. 29). The films are then removed by a knife at the end of a conveyer belt. However, studies for such type of manufacturing method for bioplastics are scarce, this method is more commonly applied in paper, ceramics and other manufacturing [65, 66].

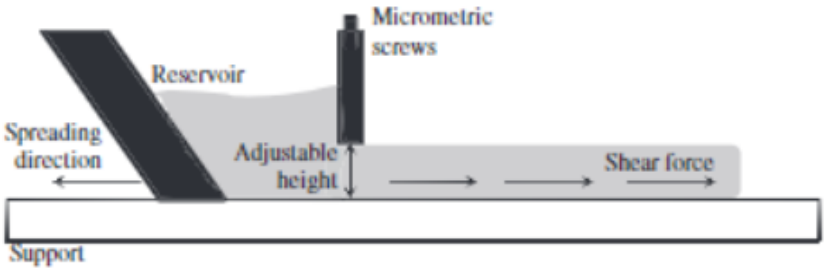

Fig. 29. Tape-casting manufacturing method [65]

Dry methods of film making include molding and extrusion of the films. These are more suitable for wider-scale application as they are already quite common in plastic manufacturing. Molding of the films include both compression and injection molding techniques. In both of the cases resin is pressured or injected into the prepared mold, allowing it to become of the desired shape when it is cooled down. In the process of extrusion, suspension is transported with the help of a screw, it is there

mixed, heated, melted, etc., until it reaches the end and is pressured through the extrusion nozzle (schematic view of extrusion process can be seen in Fig. 30).

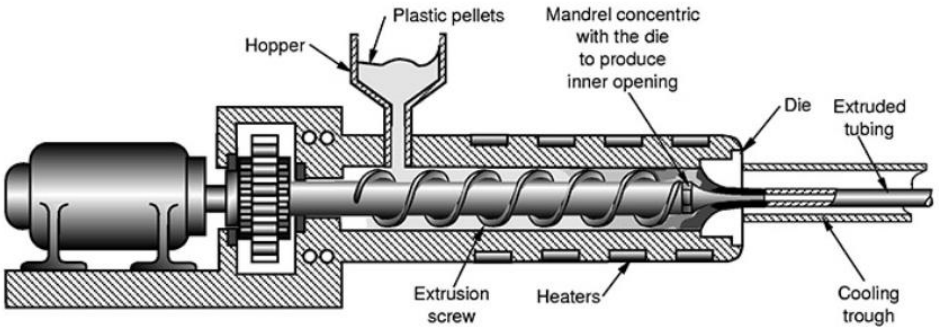

Fig. 30. Schematic view of extrusion process [67]

Both molding and extrusion of the films are widely used for the plastic manufacturing, meaning that the techniques are quite well developed. However, they are not the common for manufacturing of the bioplastics. Such methods are not very well researched as the equipment is expensive and for companies, which are already using these methods in their manufacturing processes, production of the starch-based films is not commercially attractive due to additional labor and utility costs, disruptions in manufacturing of the plastics with better properties. Also, as starch based suspensions are of high viscosity and humidity, commonly used equipment might not be able to properly to operate, if its properties and capabilities are not adjusted.

4.3. Socio-environmental Impact

Biodegradable and bio-based plastics are being researched and investigated as an alternative to currently used oil-derived plastics in order to achieve global and more local European Union sustainability and circular economy goals. However, even though that under specific conditions films made from biopolymers completely biodegrade without leaving a trace of micro plastics, it can still create some environmental and waste management issues in the long run, if end-of-life options are not considered and foreseen before wider applicability.

With the development of biodegradable films, it is expected that they will be able to contribute to solving issue of over-filled landfills and littering [68]. However, this might not be entirely possible as in most cases, biodegradable materials require specific conditions to biodegrade. Meaning, that depending on the main material, composition and other specifics, as well as the environment in which they are placed. In most of the cases, very specific conditions (anaerobic or aerobic ones, microorganisms, soil or compost, etc.) are required for a particular material. In case all of the needed conditions are not met, biodegradation might become a very slow process, not necessarily significantly contributing to solving the excessive waste issue.

Nonetheless, researchers suggest that the biodegradation should not be considered as an only and best alternative to the biodegradable starch based film management. As it is presented in Fig. 31, which shows typical lifecycle of a biodegradable polymer, materials of good quality first should be recycled before placing them for biodegradation or wasting in landfills, especially keeping in mind that such waste management processes are recommended by European Directives. Thus, managing the waste might result in additional handling costs.

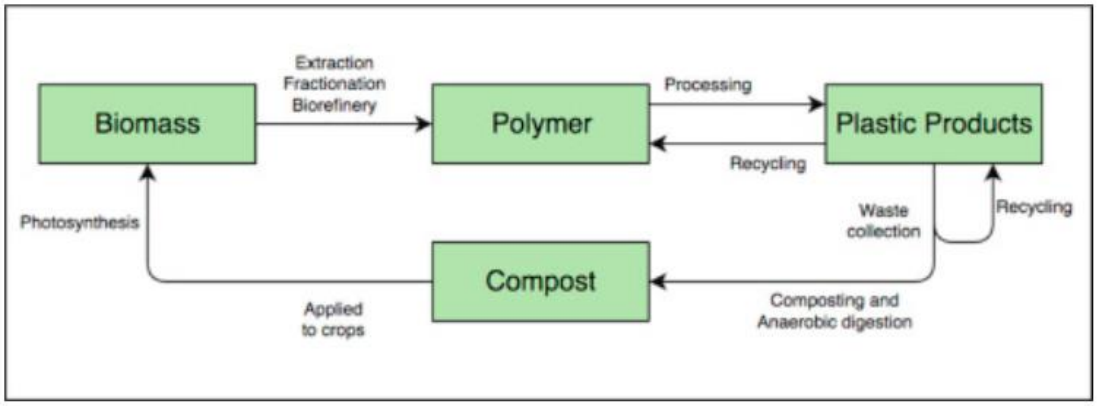

Fig. 31. Biodegradable polymer lifecycle and waste management scheme [69]

Waste management of the bio-based polymers include such practices as mechanical and chemical recycling, incineration, accumulating the materials in the landfills and composting in home and industrial conditions. Some researchers suggest that disposing such types of packaging in landfills can make even bigger negative impact to the environment and global warming as biodegradable materials, in order to be considered as such, must decompose to CO_2, water, biomass and methane, according to European (EN13432), international (ISO17088) and other standards. And since it is proposed that methane is contributing to the greenhouse gas effect than carbon dioxide, considering landfills as a suitable alternative to manage end of life of bio-based and biodegradable materials is not entirely best option. Mechanical recycling of starch-based polymers is possible and conducted studies show some prospects of managing starch-based polymer waste in such way. Chemical recycling of starch-based materials, on the other hand, is not studied so far. [69].

Similar issues have been raised by European Plastic Converters. They are stating that biodegradable materials require more material and resources in order to reach the same durability and general performance as conventional plastic materials. Also, consumers, when knowing that the material is biodegradable, might feel discouraged to dispose them properly, resulting in increased littering and waste in landfills [70].

Yet another thing limiting the applicability of the materials is their limited shelf-life, especially if they are used as food packaging. Exposing them to certain environmental conditions (high humidity, excessive heat or cold, etc.) might negatively affect properties of the biodegradable films, especially made from such biopolymers as starch, resulting in compromised packaging functions, while the main purpose of it is to protect the carries products.

4.4. Conclusions of the Managerial Part

Discussed costs, manufacturing technologies and socio-environmental situation have both advantages and disadvantages comparing bio-based biodegradable materials to conventional plastics. While they might be in general more expensive, requiring alterations in manufacturing technologies and end of life management still needs to improved and reviewed in order to reach sustainability targets, governmental and political decisions. Especially in the European Union, which targets to have climate neutral economies in the upcoming decades, encourages further development and research of biodegradable materials, as well as improving their properties for practical application purposes and other technological and managerial improvements.

Conclusions

1. Starch-based biodegradable films were prepared using potato and tapioca starches as a matrix material. Red lentil flour was used to reinforce the films, sorbitol and glycerol in combination with acetic acid were added as plasticizers in order to increase flexibility of the films. Essential oils with studied antimicrobial properties were added to the composition to investigate their impact for other film properties. 16 films out of 20 samples were formed and suitable for further investigation.
2. To measure mechanical properties of the films, tensile strength test was performed. Tensile strength and Young's modulus were calculated from the obtained load-elongation curves. Samples made with potato starch showed better resistance to load as they could withstand bigger force before breaking. Samples with sorbitol also were proven to be stronger than samples with glycerol as plasticizer. Same tendency was observed with elasticity of the films and values of Young's modulus. Majority of the samples (12 out of tested 16) had hydrophobic properties as well.
3. Added essential oils had negative effect to the strength of the films – tensile strength of samples with essential oils was lower compared to the films without them. In most of the studied cases, Young's modulus of samples with essential oils was at least slightly higher compared to the analogical samples without essential oils. Such additives to the composition proved to be effective when increasing hydrophobic properties of the films. Samples with higher essential oil concentration had bigger contact angle with water, thus meaning that they were not as hydrophilic as films without essential oils.
4. Manufacturing of the biodegradable starch-based films currently has limitations due to the costs of the raw materials, manufacturing and technological specifications as well as end of life and waste management. Also, discussed film composition showed poorer mechanical and other values compared to the ones obtained during studies of other researchers. Thus, in order for such types of films to be applied as a packaging alternative, further research and investigations on the composition is needed.

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