Biopolymers in Packaging Application

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Theses guidelines

With the advent of new legislation, there is pressure to develop new materials for packaging applications. In view of this fact, the thesis will deal with the study of biopolymeric materials in terms of their possible applications in the packaging industry. The thesis will first of all include a research on the topic under study. Subsequently, a series of samples based on biopolymer will be prepared. The prepared materials will be evaluated in terms of properties most important for packaging materials.

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1. Wu, Feng; Misra, Manjusri; Mohanty, Amar, K.: Challenges and new opportunities on barrier performance of biodegradable polymers for sustainable packaging, *Progress in Polymer Science*, 2021, 117, art. no. 101395.
2. Hamad, K., Kaseem, M., Ayyoob, M., Joo, J., Deri, F. Polylactic acid blends: The future of green, light and tough, *Progress in Polymer Science*, 2018, 85, pp. 83-127.
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4. Ebnesajjad, Sina. Handbook of Biopolymers and Biodegradable Plastics – Properties, Processing and Applications. London, UK: 2013, Elsevier, ISBN: 978-1-4557-2834-3.

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ABSTRACT

Polylactic acid (PLA) is an important biopolymer applied in the search for biodegradable packaging and the removal of pollution caused by commodity polymers. However, some parameters of PLA do not meet the requirements placed on the material in the application area. For these reasons, different types of additives are used. The presented work focused on the study of biopolymers from the point of view of their possible application in the packaging industry. Orotic acid and nanoclays were studied as modifying additives. As part of the presented study, samples were prepared, which were subsequently subjected to analysis. The testing was mainly focused on the barrier properties of the obtained materials.

Keyword: Biopolymer, Polylactic Acid (PLA), Orotic Acid (OA), Clay, Barrier Properties.

ABSTRAKT

Kyselina polymléčná (PLA) je důležitým biopolymerem uplatňujícím se při hledání biologicky odbouratelných obalů a odstranění znečištění způsobeného komoditními polymery. Některé parametry PLA však nevyhovují požadavkům kladeným na materiál v aplikační oblasti. Z těchto důvodů se využívají různé typy aditiv. Předložená práce se zaměřila na studium biopolymerů z pohledu jejich možné aplikace v obalovém průmyslu. Jako modifikující aditiva byla studována kyselina orotová a nanojíly. V rámci předložené studie byly připraveny vzorky, které byly následně podrobeny analýze. Testování bylo zaměřeno především na bariérové vlastnosti získaných materiálů.

Klíčové slovo: biopolymer, kyselina polymléčná (PLA), kyselina orotová (OA), jílová plniva, bariérové vlastnosti.

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I also appreciate the immense contribution through encouragement from my wife and family as I navigated through this journey of achieving academic excellence

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CONTENT

INTRODUCTION

With the advent of a very successful catalytic polymerization method over the past few decades, the synthesis of polymers has significantly advanced in technology. Due to their low production costs, commodity polymers such as polyethylene, polypropylene, polystyrene, and poly(vinyl chloride) (PVC) have been widely employed in the mass production of disposable packaging. Thus, polymer pollution has emerged as a significant problem on a global scale. It takes hundreds of years for these synthetic polymers made from petroleum to completely breakdown into safe soil constituents. This, together with declining crude oil supplies, is spurring research into the development of environmentally benign sources of polymer raw materials(1).

Nowadays, bioplastics comes into the picture. They must be utilized extensively if they are to be effective in combating polymer pollution or the usage of fossil fuels. The usage of bioplastics is still somewhat restricted, though, since they are more expensive to produce than traditional plastics (2).

Recently, research has been done extensively into the synthesis of bioplastic and biodegradable packaging alternatives, especially with reference to renewable substitutes for conventional plastics made from oil. The naturally existing polymers like starch and polysaccharides, chitosan, PLA and PHA are well known biopolymers. These natural polymers do not exhibit the same material characteristics as conventional plastics on their own, which restricts the technology's potential applications. Polylactic acid (PLA) and starch-based polymers are the two main categories of biodegradable plastics that are now being studied for possible entry into market in the near future [3]. These polymers are biodegradable, but complete degradability won't happen until the products produced from them are properly disposed of in a composting facility.

The most extensively produced biodegradable polymers are PVAL and PLA, while others, such polycaprolactone and polyhydroxylbutylarate, are only made in small quantities in labs or pilot plants. The biodegradable polymer PVAL, however, is of the petrochemical kind. PVAL is primarily used in coatings, adhesives, and sizing agents for textiles. Only a small quantity of PVAL is produced for packaging uses. This is mainly due to PVAL's hydrophilic characteristics. PVAL absorbs a lot of moisture after prolonged outdoor exposure. PVAL comes in both fully hydrolysed and forms with partial hydrolysis. Both kinds of PVAL are soluble in water, although hydrolyzed PVAL has a higher solubility temperature.

The presented work focused on the study of biopolymers from the point of view of their possible application in the packaging industry. PLA mixtures were prepared by mixing PLA (L175) with orotic acid and clay fillers (cloisite Na^+ , 10A and 20A). The mixtures with different percentage compositon of orotic acid and clay were prepared. Next, the testing was mainly focused on the barrier properties of the obtained materials.

I. THEORY

2. PACKAGING

Packaging refers to the preparation of items for preservation, storage, transit, and exhibition. Packaging must also fulfil the following requirements [4] the ability to preserve the item from physical and chemical damage, the ability to facilitate handling and transportation, and the ability to persuade buyers to purchase the goods. There are three categories of packaging: primary, secondary, and tertiary.

2.1 Primary Packaging

Primary packaging is the packaging which goes into contact directly with the consumable or essential commodity. Also known as sales or consumption packaging, this kind of packaging is used to transport goods. From the time the product is placed there until it is removed, it is responsible for maintaining it in top condition.

2.1.1 Types of Primary Packaging

Due to the variety of forms that primary packaging can take for a variety of items; it can be challenging to recognize. The primary packaging for FMCG (fast-moving consumer goods) is typically a jar, can, bottle, pouch, or foil bag. The primary packaging for white goods, electronics, and other related products is often a cardboard box. One could also argue that the plastic bags in which many electronic goods are packaged are the primary packaging, with the cardboard box serving as secondary packaging.

2.2 Secondary Packaging

It is the packaging that brings together all the primary packaging forms of a single product. It is also known as grouped packaging. Secondary packaging's purpose is to make it easier for products to be loaded in storage facilities and at points of sale. In addition to providing protection from the rigors of transportation over both short and long distances, they should also be simple to transport by hand.

2.3 Tertiary Packaging

Tertiary packaging is utilized to suit the product's storage and handling demands while also protecting it from damage and weather conditions during transit (4).

2.4 Package properties

A package must meet a number of specifications or performance characteristics depending on the package application area. They are principally concerned with mechanical, barrier, sealing, and adequate chemical resistance to the environment and the goods packed within it.

Mechanical properties include tensile strength, puncture resistance, tearing strength, stiffness, and other features.

The barrier properties are connected with low permeability of gases (air, O_2, CO_2, N_2, moisture, aroma, or fat). In same cases the package has to protect the good from light too. Every piece of packaging must be properly sealed in order to ensure that the seal integrity and strength are good enough for the predicted shelf life and handling method of the package.

Finally, chemical resistance is connected with the interactions between the packaging and the packaged content include chemical or physical reactions between the content, its packaging and the surrounding environment, which consequently affect the composition, quality and physical properties of both the packaged content and the packaging. The interactions between the packaging and the packaged content, especially in the case of food or cosmetics, represent a very broad complex of processes including all the principles of packaging protection.

The main task of the packaging is mainly ensured that the entire package will remain intact for the duration of its shelf life. A manufacturer must uphold not just the legal standards but also its obligation to its customers.

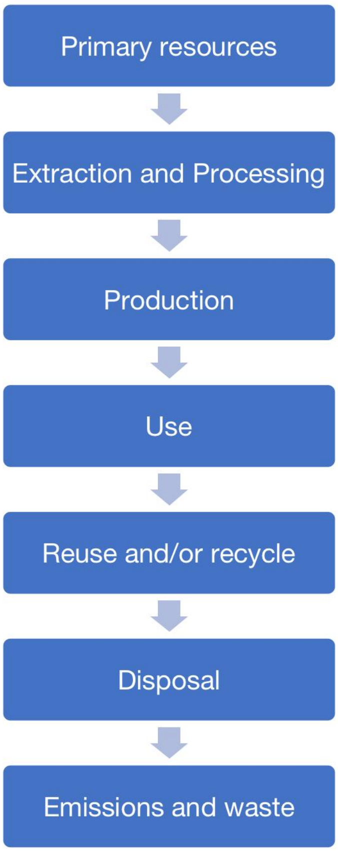


Figure 1. The Life cycle of Packaging

2.5 Choosing Packaging Materials

To choose right packaging material is connected with a lot of factors like type of material (special requirements for e.g. food packaging, cosmetic product), safety, practicality, durability, package weighs, final print effect, delivery requirements and standards, shipping restrictions and costs in the countries to which you are shipping. An increasing number of global packaging standards and rules are driving the present need for environmentally friendly packaging designs and materials. Packaging, according to the Sustainable Packaging Coalition, should be "sourced responsibly, designed to be effective and safe throughout its life cycle, made entirely of renewable energy, and once used, recycled efficiently to provide a valuable resource for subsequent generations of packaging"(5). Plastic packaging is frequently used once and then discarded, culminating in a perpetual waste stream. Furthermore, multilayer packaging is not possible to recycle. It is not possible to separate individual layers and sort them. In general, the main problems with plastic waste resulted from the long-life of synthetic polymers in the environment. In previous approaches, the ideas to decrease plastic waste in environment was based on the using natural fillers in non-biodegradable polymers to enhance the degradation process in environment (4). Nowadays, mainstream research is focused on biopolymers. In the case of biopolymer packaging, consumers will have another option: they can collect the materials to be degraded in controlled conditions.

3. BIOPOLYMERS

Biopolymers belong to the group of polymers made from renewable resources. . This section covers two types of biopolymers: those derived from living organisms and those that must be polymerized, but are derived from renewable resources. Polysacharide (starch, cellulose), protein (wheat gluten, soy protein, gelatin), and polyesters such as polyhydroxyalkanoates (PHAs) are examples of the first class of biopolymer. Polylactic acid (PLA) is the second kind of biopolymer.

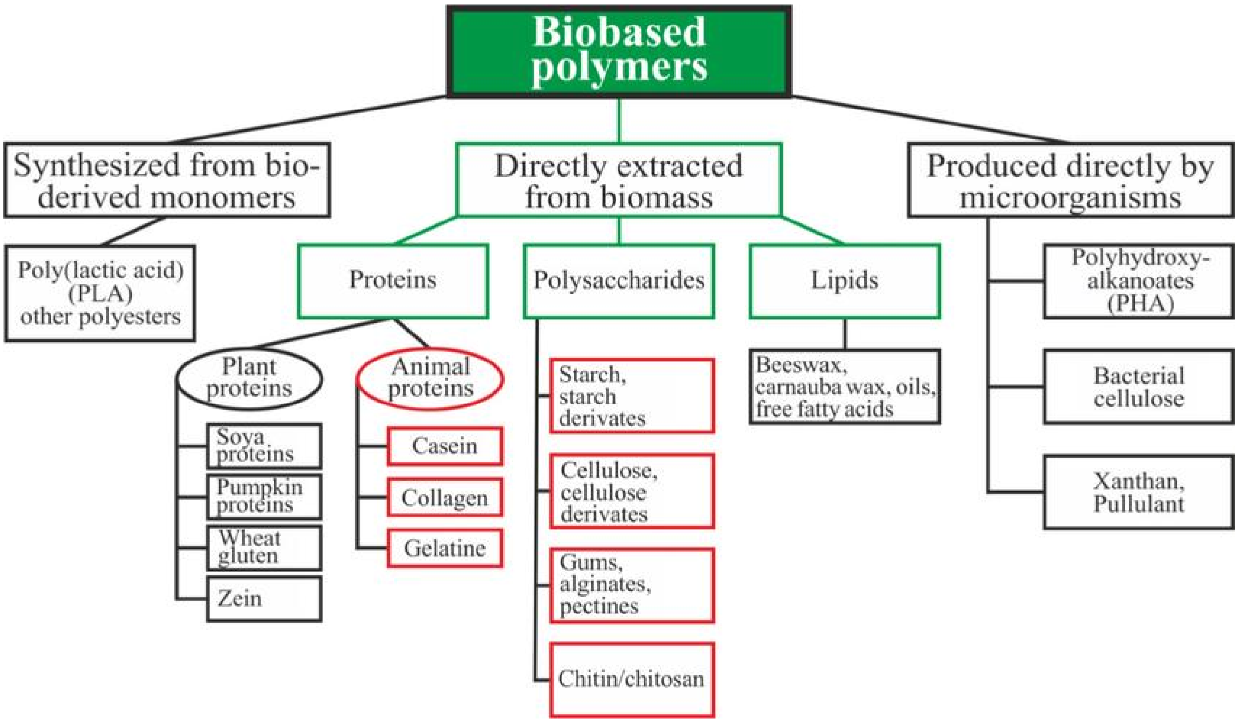


Figure 2. Classification of biopolymers (60)

It should be emphasized that biopolymers may be transformed to polymer in the following sequence: biomass > fermentation > intermediate product (eg. bioalcohol, starch) > monomer > polymer.

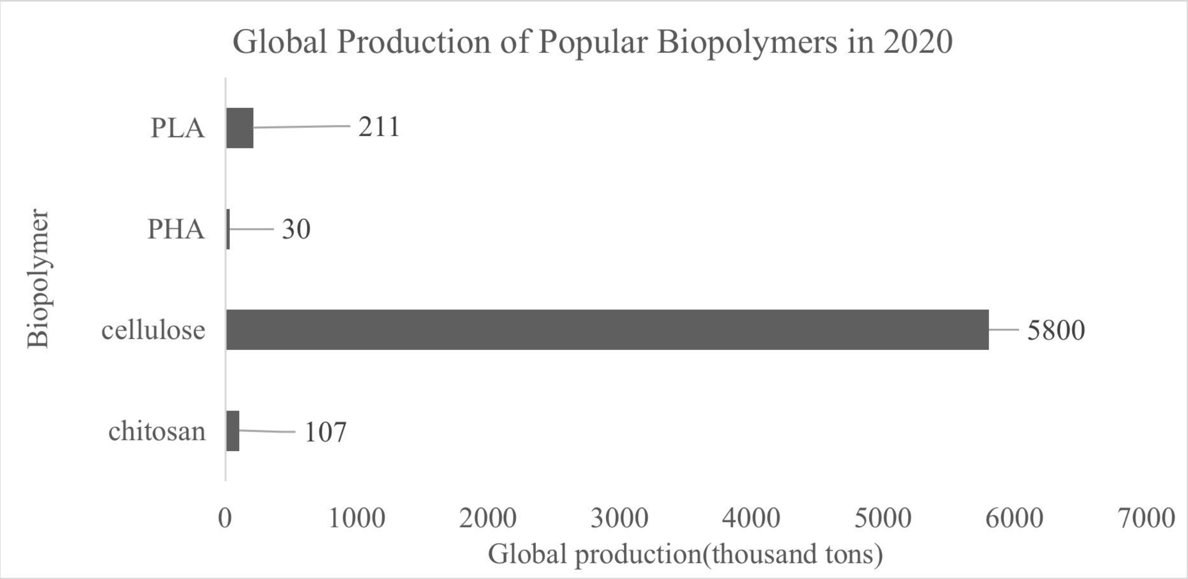


Figure 3. Global production of Biopolymers in 2020 (61)

3.1 Popular biomaterials used in packaging

3.1.1 Polysacharide based materials

3.1.1.1 Starch

Starch has been considered one of the most promising natural biopolymer-based food packaging materials due to its low cost, biodegradability, and simplicity of availability. Starch is a white powder without taste or smell, insoluble in cold water. Chemically, it is consists from two -glucose polymers, linear amylose and highly branched amylopectin. The 200–20,000 glucose units that make up amylose molecules tangle together because of their binding angles. With 30 glucose unit side chains linked to every 20–30 glucose units along the chain, amylopectin is a highly branched polymer. Molecules of amylopectin may contain up to two million units of glucose(9). Films made of starch can be made edible and biodegradable.

The thermoplastic characteristic of starch is triggered by the addition of a plasticizer, like water or glycerol. Granular starch can be made into thermoplastic starch (TPS) by gelatinizing it with a plasticizer, heat, and pressure. By adjusting the moisture/plasticizer concentration, raw materials amylose/amylopectin ratio, extruder pressure and temperature, TPS products with different viscosities, water solubility, and water absorption have been produced[7]. Many applications cannot employ thermoplastic starch due to its poor mechanical characteristics and susceptibility to moisture content. They are typically utilized in expanded trays, soluble biodegradable foams, shape-molded products, and expanded layers as an alternative to polystyrene. Three thermoplastic starch product lines are available from BIOTEC (Emmerich, Germany): Biopur® foamed starch, Bioflex® film, and Bioplast® injection-molded granules.(7)

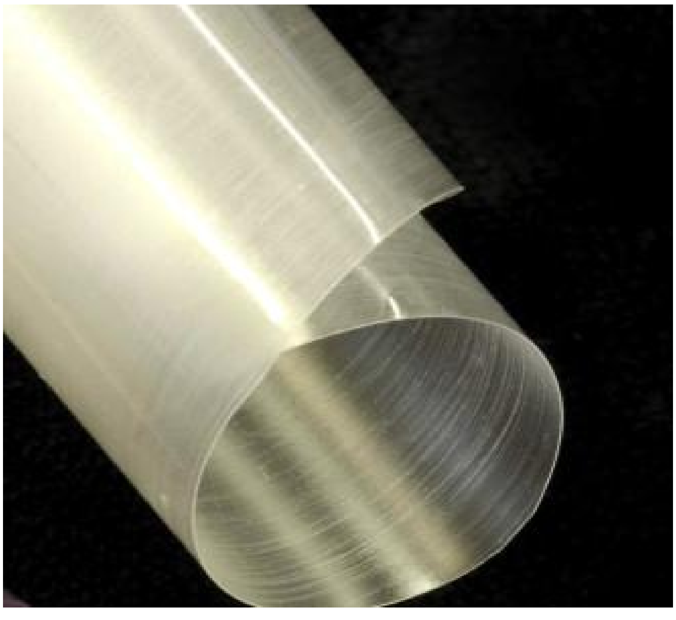


Fig 4. Cassava starch film incorporated with 0.4 g of cinnamon essential oil/100 g of filmogenic solution(70)

From starch is not possible only to produce package but also coating films. Different starch sources, including modified starch and high amylose starch (8), have been utilized to make self-supporting films from aqueous solution. But applicability of these coatings appears to be limited by their poor mechanical and moisture barrier properties combined with their insignificant oxygen barrier qualities. It is not out theme, but you can leave it here for interest or deleted the last paragraph describing coating by starch.

3.1.1.2 Chitin and Chitosan

Chitin, also known as poly(-(1-4)-N-acetyl-d-glucosamine), is a significant natural polysaccharide that was discovered in 1884. A huge number of living species produce this biopolymer. Chitin is found in nature as crystalline microfibrils that form structural components in arthropod exoskeletons or fungus and yeast cell walls (10). (citation format)

Chitosan is the deacetylated by-product of chitin alkali treatment (11). Chitosan is a copolymer of d-glucosamine and N-acetyl-d-glucosamine with a -(1-4) bond that is formed by alkaline or enzymatic deacetylation of chitin. It is a common polymeric product found in nature.

Casting from an aqueous solution can produce transparent, tough, and flexible chitosan films with good oxygen barriers. The impact of parameters such as plasticizer concentrations, storage time (12), and the degree of deacetylation of chitosan (13) on the mechanical properties and barrier properties of chitosan films have been investigated in greater detail. Chitosan films have the potential to modify the fresh fruit's environment and protect food against fungal deterioration(14).

Figure 5. A Picture of Chitosan Powder for Packaging

3.1.1.3 Cellulose

The most common natural polymer on Earth is cellulose, which is a polysaccharide consisting from linear polymer of D-glucose units. Wood, which contains 40–50% cellulose by weight, is the most plentiful source of cellulose. Cellulose is dissolved in a sodium hydroxide and carbon disulphide solution, then recast in sulfuric acid to create cellophane film. Despite its strong mechanical properties, cellophane is vulnerable to moisture. Its moisture barrier properties are often reinforced by coatings of polyvinylidene chloride or nitrocellulose wax (16).

Alternatively, hydroxyl groups on the polysaccharide backbone of cellulose can be esterified or etherified to derivatize it from the solvated form. Cellulose acetate, ethyl cellulose, hydroxyl-ethyl cellulose, and hydroxyl-propyl cellulose are among the derivatives that are available for purchase (17). Making cellulose ester biopolymers in powder form and extruding the ester powders in the presence of different plasticizers and additives is the process involved in producing these thermoplastic materials. In case of cellulose materials plasticizers like citrate and mixtures of citrate and derivatized oil are replacing the more harmful phthalate plasticizers (17) that were previously employed.

For food packaging, cellulose acetate's gas and moisture barrier characteristics are insufficient. However, because it permits respiration and avoids fogging, the film is ideal for high moisture applications (16).

3.1.2 Polyhydroxyalkanoates (PHAs)

Polyhydroxyalkanoates (PHAs) are biopolymers that accumulate as a source of carbon or energy in a variety of microorganisms when nutritional components are scarce. They are synthesized and accumulated by over 300 different microorganisms. Primarily polyhydroxybutyrates and copolymers of hydroxyl-butyrate (HB) and hydroxyl-valerate (HV), are the most well-known biopolymer forms of PHA(38). PHA-based packaging materials have exceptional film forming and coating properties because they have qualities like polypropylene (PP) (38). .

While a high quantity of polyhydroxyvalerate (PHV) increases toughness and flexibility, a high concentration of polyhydroxybutyrate (PHB) produces a material that is strong and stiff. Because polyalkanoates are more hydrophobic than polysacharide-based polymers, they have stronger moisture barrier properties comparing mentioned polysacharides.

A downside to PHA usage is their high manufacturing costs, brittleness, and poor gas barrier characteristics comparing traditional packaging materials.

3.1.3 Polylactic Acid (PLA)

Lactic acid (LA), a naturally occurring resource. LA is the basis for PLA, a manufactured, biodegradable polyester. When bacteria ferment carbohydrates like corn, sugarcane, potatoes, and other biomass, lactic acid is created. Although PLA is not easily found in nature, it can be made by humans employing naturally occurring biological sources.

The biodegradability of PLA is widely acknowledged. Furthermore, because PLA is a thermoplastic polymer, it is easily processed with the tools and techniques already used in polymer processing. PLA can be made into fiber, film, sheet, and 3D products via the processes of fiber drawing, film blowing, extrusion, and injection molding. Moreover, polyethylene glycol (PEG), triethyl citrate (TC), and partial fatty acid esters can be used to plasticize PLA (37).

PLA is generally distinguished by high brittleness, strong thermal stability, and poor toughness and elasticity. This material offers remarkable optical purity in its amorphous condition. PLA is regarded as the bioplastic with the most potential to replace various applications of petroleum-based plastics because of its good optical qualities, high temperature tolerance, and low environmental effect, particularly when it comes to food packaging. From the perspective of the packaging business, however, the issue of its high permeability for gases, like carbon dioxide and oxygen, must be resolved because it restricts its industrial application for processed goods that need a long shelf life [18].

The ratio between the two mesoforms, D and L, has a significant impact on PLA's characteristics. L-PLA has a higher crystallinity, which can result in brittleness and higher melting temperatures (37).

PLA presents a medium water and oxygen permeability level comparable to polystyrene. With that said, PLA is a brittle polymer with a tensile strain at break of less than 6% thus restricting its applicability.

3.1.3.1 Synthesis of PLA

In the evolution of PLA, Pelouze first condensed lactic acid by a distillation process of water to generate low-molecular-weight PLA in the early 1800s, which led to the discovery of PLA. This is however low-molecular-weight PLA and lactide are created during the early polycondensation of lactic acid. The transformation of lactide into high-molecular-weight PLA uses lactide as a pre-polymer or intermediate product. Low yield and low purity PLA are the only products of this polycondensation technique.

To enhance the commercialization of PLA, Cargill and Dow Chemical established a joint venture called Cargill Dow Polymer LLC in 1997. Their efforts have paid off, as the Ingot-branded products have been produced. In this joint venture, Cargill has strived to speed up the hardening of PLA goods while Dow has concentrated on producing PLA (Economic

Assessment Office, 2007). Typically, dextrose, which originates from plant starch, is fermented by bacteria to produce lactic acid, which is the monomer that constitutes PLA.

High-molecular-weight PLA may be produced by three distinct methodologies: direct condensation polymerization, azeotropic dehydrative condensation, and lactide ring-opening polymerization.

Direct condensation polymerization is the least expensive method, but it can only produce low-molecular-weight PLA due to the difficulty of thoroughly removing water from the reaction mixture

3.1.3.1.1 Ring-Opening Polymerization

Ring opening polymerization is used to produce high molecular weight polylactide from lactide monomer (ROP). Purification of lactide, a cyclic dimer of lactic acid generated by condensation of free lactic acid, is required for this approach. Aluminum and tin alkoxides (21) are common catalysts for lactide polymerization**.**

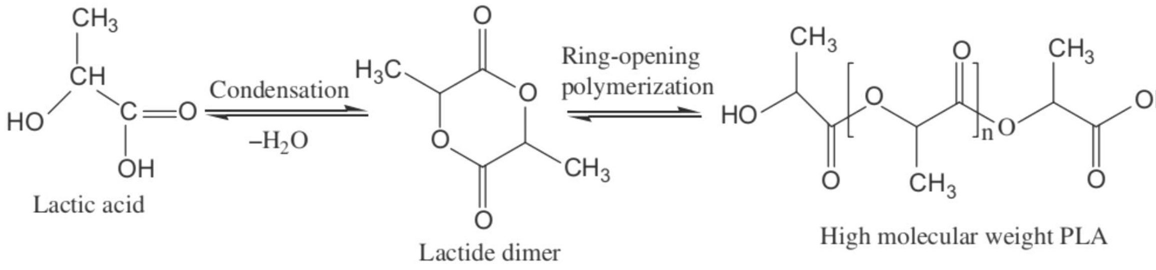


Figure 6. Ring-opening Polymerization of PLA(66)

Tin-based and aluminum-based catalysts differ primarily in that the former are more effective in catalyzing trans-esterification in contrast to the latter. When used in polymerizations, tin catalysts can be simpler to work with and more hydrolytically stable than aluminum catalysts. In the relatively fast synthesis time of PLA homopolymers , tin 2-ethylhexanoate (also known as stannous octoate, or Sn (Oct)2) and lauryl alcohol (1-dodecanol) have both been employed as initiators and co-initiators with high conversion and low racemization(21).

3.1.3.1.2 Polycondensation reaction

Lactic acid can be directly transformed to polyester by a polycondensation reaction because it possesses hydroxyl (-OH) and carboxyl (-COOH) groups. In order to shift the equilibrium reaction to the right or the product (lactic acid), water molecules must always be present in very small amounts in the lactic acid polycondensation reaction to produce PLA. Alternatively, the water in the feed must be eliminated by evaporation at temperatures above the boiling point of water and atmospheric pressure. Solid catalysts like SnO_2 and $SnCl_2$ can be used to remove the generated water and speed up PLA production (22).

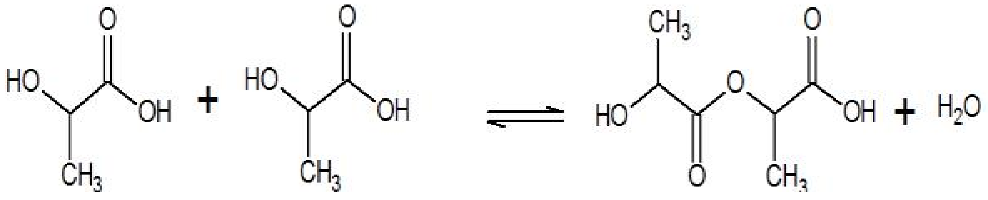
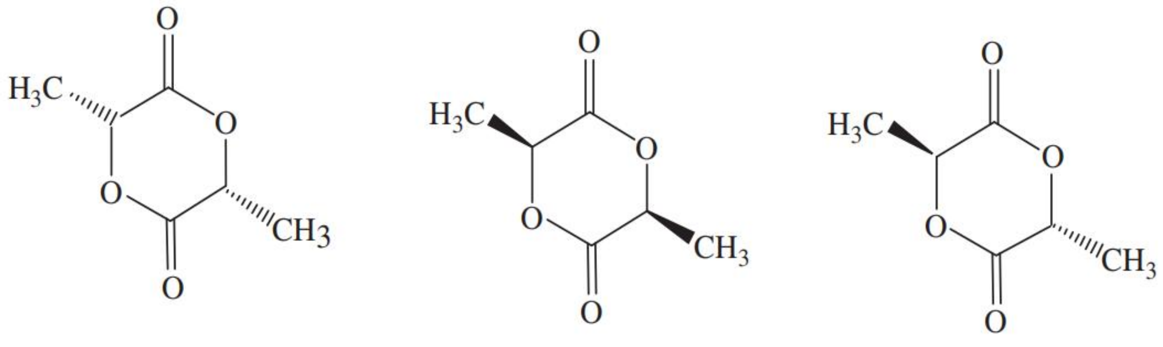


Figure 7. Chemical reaction of Direct Polymerization of LA to PLA(68)

3.1.3.2 Diastereomeric forms of lactides

The chirality of the lactyl unit gives rise to three diastereomeric forms of lactide, which are represented in Fig. 9 as L-lactide, D-lactide, and meso-lactide. The crystalline polymers poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) are optically pure polymers with melting temperatures of approximately 180 °C [17]. The glass transition temperature of Poly-(DL-lactide) is between 50 and 57°C, making it an amorphous atactic polymer (18).

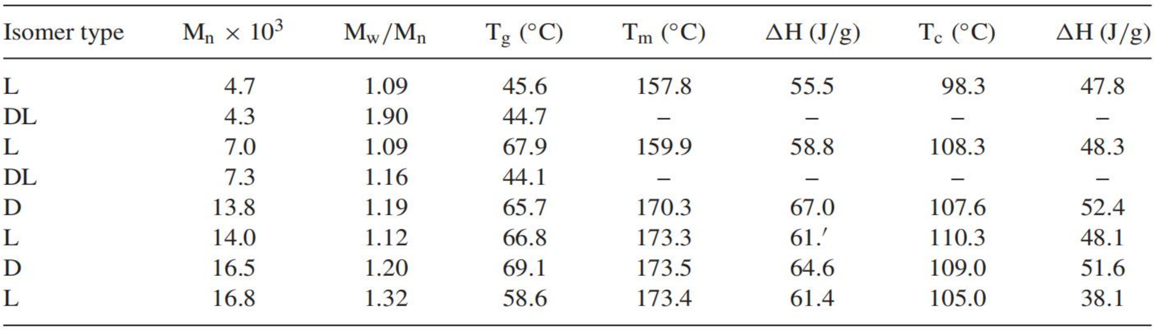
Polylactide characteristics are known to be highly dependent on the molecular weight of the polymer and the ratio and distribution of its two isomers.



D-lactide L-lactide D, L-lactide

Figure 8. Chemical formualr of the Diastereomeric forms of Lactides(67)

Based on isomer nature (D, L, and DL) and number average molecular weight (Mn), Ahmed et al. reported on a thermal examination of a variety of polylactides (PLA) (20). PLA's glass transition temperature (T_g) was shown to rise with molecular weight, irrespective of the kind of isomer, with the exception of samples that had a high polydispersity index (Table 1). The L-isomer's melting temperature (T_m) and enthalpy of crystal fusion (H_f) increased as M_n was raised from 1100 to 27500.



Isomer type	$M_n \times 10^3$	M_w/M_n	T_g (°C)	T_m (°C)	ΔH (J/g)	T_c (°C)	ΔH (J/g)
L	4.7	1.09	45.6	157.8	55.5	98.3	47.8
DL	4.3	1.90	44.7	–	–	–	–
L	7.0	1.09	67.9	159.9	58.8	108.3	48.3
DL	7.3	1.16	44.1	–	–	–	–
D	13.8	1.19	65.7	170.3	67.0	107.6	52.4
L	14.0	1.12	66.8	173.3	61.′	110.3	48.1
D	16.5	1.20	69.1	173.5	64.6	109.0	51.6
L	16.8	1.32	58.6	173.4	61.4	105.0	38.1

Figure 9. Effect of various isomers on thermal properties of PLA (67)

Among all the isomers, one of the most useful biodegradable PLA polymer materials is PLLA, in part because its L-lactide building block is produced by fermentation of starch from agricultural plants. PLLA has a crystallinity of approximately 37% with a melting point of the crystalline fraction of approximately 170-180 °C, a glass transition temperature of 60-67 °C, and a cold crystallization temperature of 80-120 °C (18),(19). Therefore, this material is brittle at room temperature and softens at a relatively high temperature. In terms of melting point, it is very similar to Polypropylene PP (18).

3.1.3.3 Properties of PLA

Aside from biodegradability, polylactic acid products exhibit strong biocompatibility, gloss, transparency, mechanical and heat resistance, as well as specific microbial resistance, flame retardancy, and UV resistance properties (69).

3.1.3.3.1 Crystallinity of PLA

The level of crystallinity in a polymer is a crucial characteristic. Numerous polymer properties, including hardness, tensile strength, modulus, stiffness, and melting temperatures, are influenced by crystallinity (43). The glass transition temperature and melting point rise with increasing crystallinity because more thermal energy is required to destroy the polymer's structure.

The molecular weight, percentage of d-lactic acid, and processing conditions all have an impact on the crystallization behavior and crystal form of PLA. Thus far, four different crystal forms—designated α, β, γ, and ε—as well as one disordered form, δ, have been discovered (44),(45),(46). At high temperatures (over 120°C), the α form crystals grow via solution, melt, or cold crystallization. They have an orthorhombic unit cell with a 10/3 helix shape and X-ray diffraction peaks at 14.8°, 16.9°, 19.1°, and 22.5°.The δ form crystals arise by melt or cold crystallization at low temperatures (below 100 °C), and a mixture of the α and δ form crystals is often created between 100 °C and 120 °C [46]. The chain conformation is similar to the α form's, but more disorganized. Processing conditions specific to the β, γ, and ε forms are necessary for the creation of the further crystal forms.

Recently, there has been a lot of interest in SC-PLA (stereocomplex PLA), another sort of PLA crystal structure. Units of PDLA and PLLA alternate in its makeup (1:1). SC-PLA offers better mechanical and physical qualities than homochiral PLA varieties because of its 50 °C higher melting point (48).

3.1.3.3.2 Mechanical properties of PLA

The basic mechanical properties include stiffness, strength, plasticity, elasticity (or elasticity) and hardness. Most of these quantities are dependent mainly on the production process and the raw material used (28),(30). The mechanical properties of PLA, such as hardness, stiffness, strength, and elasticity, are comparable to PET, which is the most used plastic in the production of bottles. PLA has the highest modulus of elasticity (E - 3.5 GPA) of common packaging materials. General purpose PLLA is considerably stronger (60 MPa) and has a considerably greater modulus (3 GPa) than many other commodity fossil oil-based polymers. HDPE, for example, has an average strength and modulus of 20 MPa and 1 GPa, respectively, whereas polypropylene (PP) has a typical strength and modulus of 30MPa and 1.5GPa.

To predict the behavior of the polymers, T_g and T_m are important parameters for determining the temperatures of use in various applications. Below T_g, PLA behaves like a creep glass until cooled to the β-transition temperature of approximately -45°C where PLA behaves only like a brittle polymer. Above the T_g temperature, amorphous PLA transitions from a glassy phase to a rubbery state, and upon further heating will behave as a viscous liquid (42).

3.1.3.3.3 Barrier Properties of PLA

The barrier properties of PLA make it a restricted material for use in the packaging sector. The shelf life of products is first and foremost restricted to 3 to 4 months, depending on the weight of the packaging, as the permeability to water vapor is significantly higher than that of PET, PP, or PVC. In the food industry for instance, packaging should protect packaged food not only from contamination, but also from loss of quality food (49).

The most used barrier properties that are used to describe a characterize packaging materials are oxygen and water vapor permeability tests. Their transfer through the packaging must be kept as low as possible to prevent contact of moisture with food or the ingress of oxygen. For oxygen, PLA is a medium barrier, and for water vapor, it is a relatively weak barrier (50). According to Drieskens et al., PLA crystallization reduces oxygen permeability, but not necessarily in a way that is proportional to a reduction in amorphous volume. The effect of crystallization on the barrier properties of PLA thus appears to be influenced by additional factors (50). By calculating the oxygen transmission rate (OTR), which represents the volumetric flow rate of oxygen per unit membrane area and over time, along with the thickness of the membrane, the oxygen diffusion process can be evaluated. The amount of oxygen that permeates the packaging material per unit area and time is also expressed using oxygen permeability coefficients, or OPCs (oxygen permeability coefficients) [$kgmm^{-2}s^{-1}$ Pa^{-1}] (49).

WVTR (Water vapor transmission rate), which is the amount of water vapor that permeates through the packaging material per unit area and time, is used to express vapor permeability. WVP (Water vapor permeability [$m^3mm^{-2}s^{-1}Pa^{-1}$]) is an alternative and superior expression that also considers the gradient of the water vapor partial pressure and the impact of material thickness.

Packaging fresh fruits and vegetables with PLA is advantageous due to its higher water throughput. The permeability to gases (CO_2, O_2) is better than HIPS but still significantly lower than PET, PP, and PVC; as a result, PLA products are not suitable for carbonated beverages but are suitable for bottled water, fruit juices, yoghurt drinks, and chilled dairy products with a limited shelf life.

Table 1: Permeability of commonly used packaging materials (50) .

MATERIAL	**WVP AT 23^{O}C [cm^3 ·mm·m^{-2} ·day^{-1} ·atm-^{1}]**	**O_2 PERMEABILITY AT 23^{O}C [g·mm·m^{-2} ·day^{-1} ·atm-^{1}]**
PET	1-5	0.5-2
PP	50-100	0.2-0.4
PS	100-150	1-4
PVOH	0.02	30
EVOH	0.001-0.01	1-3
PLA	3.5-15	1.6-3.6

3.2 Biopolymer properties enhancement

For good packaging application, biopolymer must be sufficiently stiff and strong during it useful cycle to fulfil the targeted uses, yet eventually biodegrade. It is very difficult to extract the right mix of properties from biopolymers because of their intrinsic water sensitivity and poor stiffness and strength, especially when humid. To achieve this balance, biopolymers are blended with other materials to enhance their properties for better application. Numerous studies (63),(64),(65) have concentrated on lowering the hydrophilicity and enhancing the mechanical properties of biopolymer-based films to improve their physical qualities.

The two major methods that have produced promising results are the formation of biopolymer blends and the use of nanofillers for the formation of biopolymer nanocomposites.

3.2.1 Biopolymer Blends

A suitable method in area of biopolymer modification is blending different biopolymers to permits for the alteration of biopolymer properties while minimizing the total cost of the material. To boost biodegradability and lower costs, PLA is frequently combined with starch. The initial starch and PLA combinations were made by pressing the ingredients into translucent films while they were sealed in a mixer (28). Jacobsen and Fritz (1996) investigated the thermal behavior of PLA with native corn starch when polyethylene-glycol was added as a plasticizer. PEG lowered PLA's glass transition temperature and raised PLA crystallization at ambient temperature (31). In 1998, Kim et al. combined PLLA and high amylose maize starch to a 40% concentration and found that the blends' tensile strength and elongation at break increased with the blends' starch concentration (32).

The blend that resulted from combining PHB and starch has poor mechanical properties because of their high crystallinity (29). In a separate investigation conducted in 2007, Parulekar and Mohanty found that the ageing issue with starch and PHA blend materials could be effectively mitigated by restricting the starch component's moisture uptake, hindering the glycerol leaching, and preventing the PHA component's secondary crystallization in the films (30).

The primary hindrance to the industrial applications of PHB might be its poor formability and processability. An alternate strategy for bringing it to market is to combine it with PLA, which also improves PLA's attributes. The degree to which PLA and PHB mix well depends on a number of criteria, including the processing temperature, the amount of each polymer in the final blend, and their molecular weight (33).

Blümm and Owen examined blends of low-molecular-weight PLA (Mn = 1759) and high-molecular-weight PHB (Mn = 222,000, Mw = 794,000gmol1). While a combination of high-molecular-weight PLLA (Mn = 159,400) and PHB showed biphasic separation, they found that the blends were miscible in the melt over the whole composition range (34). Dynamic TGA study indicates that adding PHB lowers PLA's thermal stability. PLA-PHB blends show two stages of thermal degradation, the first of which is linked to PLA degradation and the second to PHB disintegration(35). However, the PHB component in PLA-PHB blends has higher degradation temperatures than pure PHB, and in the second degradation stage, with the higher degradation temperatures, PLA thermal stability is shown to be diminished. Their strong compatibility, with PLA functioning as a shielding barrier to extend the PHB component of the blend's thermal degradation process, has been linked to the close association between the PHB and PLA degradation curves (36).

3.2.2 Biopolymers modification by fillers

The most practical method of regulating the material properties of natural biopolymer films is to use fillers with certain qualities. To cut costs or boost performance, mineral fillers including talc, silica, and clay have been employed in film preparation in amounts ranging from 10 to 50% by weight. Nonetheless, the mechanical strength of the films generally declines in the presence of fillers (23). A suitable modification could offer also natural fibers, proteins and starch (24). Polymer nanocomposites represent a superior alternative to these conventional polymer composites, are being developed by the application of nanoscale fillers (25). Polymer-clay nanocomposites show significant advantages in mechanical and physical properties above pure polymer or traditional composites. Improved features include enhanced strength and modulus, reduced gas permeability, increased solvent and heat resistance, and lowered flammability (26).

3.2.2.1 Nanocomposites

3.2.2.1.1 Sources of nanofillers

Among the nanoclays that have been utilized as fillers in packaging systems are saponite, kaolinite, and montmorillonite (MMT). Montmorillonite has attracted the greatest interest in the packaging industry, especially in food packaging, because of factors such as its cost effectiveness, availability, processability and improvement in performance in the final product. Natural MMT which are hydrophilic in nature do not perform well when mixed with hydrophobic polymers (67). To increase the affinity between the filler and the matrix and ultimately improve final properties, the inorganic cations (Na^+, Ca^{2+}, etc.) inside the galleries are usually replaced by ammonium or phosphonium cations bearing at least one long alkyl chain and possibly other substituted groups.

In certain works, the organically modified cloisite 30B and 20A have been employed to improve the interactions with organic polymers, enhance the interlayer spacing, and create hydrophobic surfaces. During the research of nanocomposites based package modified by MMT it was found out that organically modified nanoclays' have got ability to withstand bacteria. This property is attributed to the presence of quaternary ammonium groups in them. Before inducing cell lysis, the ammonium group interacts with the bacteria's cells and damages their membrane (51). Due to its more hydrophilic nature and ability to readily absorb and interact with bacteria, Cloisite 30B has been shown to have higher antimicrobial activity than Cloisite 20A (51).

3.2.2.1.2 Nanocomposite preparation

Polymer nanocomposites are made by dispersing inorganic or organic nanoparticles into a thermoplastic or thermoset polymer. The characteristics of polymer-nanocomposites are significantly influenced by their preparation process(27). Polymer nanocomposites can be made using one-dimensional disc-like nanoparticles, like clay platelets, two-dimensional nanofibers, or three-dimensional spherical and polyhedral nanoparticles, like colloidal silica.

In-situ polymerization, solvent intercalation/exfoliation, and melt intercalation/exfoliation are the three well recognized methods of preparation. In the in-situ polymerization process, monomers are introduced to layered clays and subsequently polymerized by heat, radiation, or a catalyst (39). In case of solvent intercalation/exfoliation method, layered clays are exfoliated into individual platelets using a solvent, and the clay suspension is mixed in to help the polymer adsorbed onto the platelets. In this procedure, the clay is initially allowed to swell in the solvent before the polymer (intercalant) is dissolved in it. After the two solutions are combined, the polymer chains intercalate and push the solvent out of the clay's interlayer (39). In the case of melt intercalation/exfoliation the clays are added directly to the polymer melt in processing equipment.

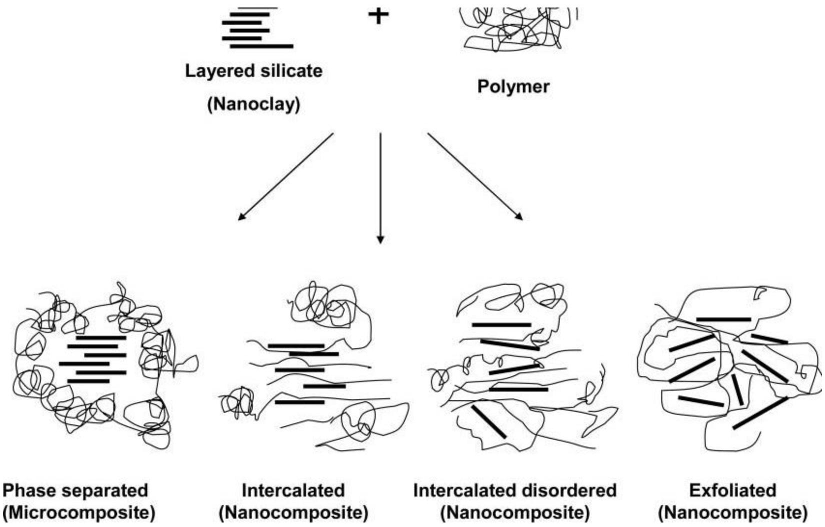


Figure 10. Composite structures of polymer-layered silicate clay materials (66)

3.2.2.2 Additives

Chemicals known as polymer additives are added to the polymer matrix to enhance certain qualities of the polymers, such as their processability or the length of their product's life. They are employed to alter the polymer material in order to fulfill the product's particular end-use specifications(72). These include blowing agents (azodicarbonamide), stabilizers(antioxidants), fillers(calcium carbonate, silica, kaolin), plasticizers (such as oils and adipates that change the Tg and processability of materials), modifiers of optical characteristics, and modifiers of surface qualities(72).

3.2.2.2.1 Orotic Acid (OA)

Orotic acid (OA) is a naturally occurring heterocyclic compound that is produced by living organisms. Its chemical name is 2,6-dioxo-1,2,3,6-tetrahydropyrimidine-4-carboxylic acid. The highest concentrations are found in animals with low levels of arginine and uridine-5'-monophosphate activity [52]. It is primarily found in ruminant milk. There are amounts of 20–100 mg/L in cow's milk and slightly higher amounts in goat's and sheep's milk. According to the range of cow's milk, orotic acid has also been found in infant formula in concentrations of 15 to 118 mg/L [52]. Orotic acid's role as a growth factor in feed deficiencies and as a liver protector makes it important nutritionally (53).

Orotic acid can be used also in the field of polymer . Studies indicate that orotic acid might function as a nucleating agent in the field of biodegradable polymers in the area of macromolecular chemistry. To change the optical characteristics of polymers, nucleating additives are used. As the polymer melt cools, these nucleating additives have an impact on crystallinity and speed up the crystallization process. The physical characteristics of spherulites are impacted by their size, which increases brightness and transparency.

Orotic acid was found to be an effective nucleating agent in a 2019 Yancun et al study investigating the effects of orotic acid on the crystallization, rheological, thermal, and mechanical properties of bacterially produced poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P34B) (55). The addition of OA resulted in an increase in both the isothermal and non-isothermal crystallization rates. An further observation about polymers was their enhanced rheological and thermal stability characteristics(55). Mechanical characteristics were improved, including yield strength and elongation at break. The yield strength was enhanced by 25% and the elongation at break by 119% with the addition of 5% OA (55). It is noted in the same article that adding OA resulted in a decrease in spherulite size and an increase in nucleation density. However, it had little effect on the crystalline structure (55).

Another group that looked into using OA as a PLLA nucleating agent was Song et al. They selected OA in two commercially accessible forms: OA-a, or anhydride, and OA-m, or monohydride. The isothermal and non-isothermal crystallization of PLLA from melt were the subjects of the investigations. The PLLA nucleation density, non-isothermal T_c, and crystallization of both variations improved. The nucleation efficiency of the two is different, with OA-a being more efficient than OA-m. The fact that OA-m's water binding and dehydration transitions negatively impact the nucleation of PLLA crystallization is one explanation for this.

4. OBJECTIVES

With the advent of new legislation, there is pressure to develop new materials for packaging applications. Furthermore, most bioplastics have limitations and as such they should be modified to achieve good packaging properties. For instance, the high hydrophilicity of these polymers makes them poor options for food packaging application. In view of this fact, the thesis will deal with the study of biopolymeric materials in terms of their possible applications in the packaging industry.

In this work, PLA L175 will be tested in combination of orotic acid and nanoclay fillers (cloisite Na^+, 10A and 20A). Barrier test including water, air and oxygen will be carried out on prepared materials. Also, the mechanical properties will be tested. Next methods like DSC and XRD will be used to observe the changes in thermal behavior and structure of mixtures.

II. EXPERIMENTAL PART

5. MATERIALS AND SAMPLE PREPARATION

5.1 Polylactic Acid

The trademarked Luminy® PLA L175 produced by Total Energies Corbion was used in this experiment. The polymer is a homopolymer PLA with high heat resistance and high viscosity. These properties makes it suitable for film extrusion. Thermoforming and spinning. Stereochemically, it is 99% L-isomer (57). The properties of PLA L175 are described in the table below.

Table 2. Selected features of PLA L175 from the manufacturer (57)

Properties	PLA L175
Density [g/cm^3]	1.24
Optical purity [% L-isomer]	99
Tg [°C]	60
Tm [°C]	175
Young modulus (ISO 527-1) [MPa]	3500
Tensile strength (ISO 527-1) [MPa]	50
Elongation (ISO 527-1) [%]	≤5

5.2 Orotic acid and nanoclays

The orotic acid used for this study was the P-LAB a.s produced anhydrous orotic acid (uracil -6-carboxylic acid) which has a molar mass of 156.1g/mol

Three different nanoclays, cloisite Na$^+$, 10A and 20A were used in the preparation of the nanocomposites.

The concentration of the orotic acid were varied in 0.1%, 0.3%, 0.5% and 1% while the concentration of the nanoclays were kept constant at 1%.

5.3 Preparation of PLA mixtures

The PLA sample, orotic acid and clays were all dried in a Vacucell vacuum dryer for 1 hour at a set temperature of 80 °C.

The two screw Labtech Engineering company LTD compounding machine was used for the mixing. The temperatures of the various chambers of the extruder were set as 180, 185, 195, 195, 200, 200, 210, 210, 210 and 210. The speed of the extrusion screw and the feeding screws were set at 25 rpm and 20 rpm respectively. The mixing was done twice for better dispersion of the orotic acid and nanoclay. The mixture was pelletized for further processes.

Figure 11. Labtech Engineering Co LTD made twin screw extruder for compounding

Table 3. Composition of PLA mixtures

PLA Mixture	PLA (dl)	Orotic Acid (dl)	Cloisite Na+ (dl)	Cloisite 10A (dl)	Cloisite 20A (dl)
PLA L175	100	0			
PLA L175/ 0.1 %OA	100	0.1			
PLA L175/ 0.3 %OA	100	0.3			
PLA L175/ 0.5 %OA	100	0.5			
PLA L175/ 1 %OA	100	1			
PLA L175/ 0.1 %OA/ 1% NA+	100	0.1	1		
PLA L175/ 0.3 %OA/ 1% NA+	100	0.3	1		
PLA L175/ 0.5 %OA/ 1% NA+	100	0.5	1		
PLA L175/ 1 %OA/ 1% NA+	100	1	1		
PLA L175/ 0.1 %OA/ 1% 10A	100	0.1		1	
PLA L175/ 0.3 %OA/ 1% 10A	100	0.3		1	
PLA L175/ 0.5 %OA/ 1% 10A	100	0.5		1	
PLA L175/ 1 %OA/ 1% 10A	100	1		1	
PLA L175/ 0.1 %OA/ 1% 20A	100	0.1			1
PLA L175/ 0.3 %OA/ 1% 20A	100	0.3			1
PLA L175/ 0.5%OA/ 1% 20A	100	0.5			1
PLA L175/ 1 %OA/ 1% 20A	100	1			1

5.3.1 Compression Molding of Samples

The hydrophilic PLA composites are first dried in the Vacucell vacuum dryer for 1hour at a temperature of 80 °C. The planned tests required to mold sheets of 0.1mm and 1mm thickness. For testing, mold of dimension 150x150mm were used. The amount calculated for 1mm sheet and 0.1mm film were 30 g and 3 g respectively. The pressing was conducted using the hand press with both the upper and lower heating plate temperatures set at 210°C. The mold plates were heated to 210°C temperature too. After the plates were tempered to this temperature, separation PET foil was placed on the bottom of mold and the 0.1mm mold placed on the foil, 30 g of the prepared PLA L175 nanocomposite was placed in the center and another separation PET foil placed on top. The top of mold was then transferred to its position and the whole sample placed in the press and pressed for 2 mins. After 2 mins the mold with sample was transferred to the hydraulic press where it was allowed to cool for 10mins. The process was repeated for all the 1mm and 0.1mm sheets. The equipments used for compression molding are in Figure 13 and 14.

Figure 12 . Vacucell vacuum drier

Figure 13. Manual press compression molding machine and hydraulic press for cooling

6. CHARACTERIZATION OF SAMPLES

Prepared samples were characterized by evaluating properties such as barrier, mechanical and thermal properties. Next crystallinity was evaluated using WAXRD.

6.1 Barrier properties

Two major barrier properties were studied in this work. The first was the permeability of water vapor through the polymer. The films were also tested for permeability to air and oxygen, which are basic gases whose permeability is researched in packaging materials, particularly in relation to food shelf life.

6.1.1 Water vapor permeability

For packaging, information about the permeability of water vapor through polymer is essential. A good packaging material should have the optimum amount of water vapor permeation for its intended purpose. Excessive water loss can result in undesirable drying of the packaged product. On the other hand, for food packaging, water vapor permeation through the packaging material toward the food can cause the growth of microbes.

The evaluation of WVT were processed in accordance with standard E95-96. In this work, three test specimens with thickness approximately 0.1 mm were cut out of the prepared foils for each material. The foil was placed on an aluminum dish containing 10 ml of distilled water and two pieces of rubber seal placed on each side of the sample. The cap was then tightened securely to ensure a good system sealing.

Figure 14. Complete assembly for water permeability test

The dishes were then moved to climate chamber from company PolEko. The conditions for measurement were set at 50 % humidity and 37 °C temperature. The measurement was done for 32 days with the three readings taking please in the first 5 hrs of the first day. Thereafter, samples were measured approximately every 5 days (measurement day and time was recorded).

Figure 15. Climate chamber for WVP testing

6.1.2 Gas Permeability Test

Another critical barrier property to characterize was the penetration of gas molecules through the packing material. If oxygen penetrates the packaging, oxidation process occurs inside the package. Especially the food components such as lipids (rancidity) are sensitive to this process. Oxidation resulting in a change in flavor, color, or nutritional value. Another area where the barrier properties of packing material must be addressed is the use of a protective inert atmosphere (N_2) and its possible leaking from the packaging due to poor barrier to gases, resulting in a reduction in food shelf life. These properties are very important for pharmaceutic products or cosmetics.

To determine gas barrier properties, the measurement standard ČSN 640115 was used. A circular specimen of diameter 80 mm and thickness averaging 0.1 mm was cut from the pressed material and used. The measurement was conducted at 3 bar pressure and 35 °C temperature.

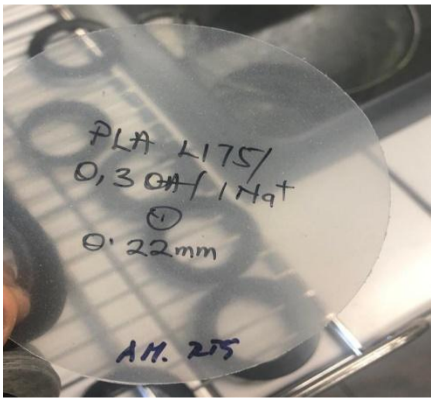


Figure 16. Specimen for gas permeability measurement

Figure 17. Instrument for gas permeability measurement

6.2 Mechanical properties

The main test done to ascertain the mechanical properties of the various samples was the tensile test. The test gave information on properties such as the tensile strength, elongation at break and Young’s modulus. The test procedure was done in accordance with ĆSN EN ISO 527-1.

The specimens were cut out to the required shape (dog-bone A5) using a hydraulic cutter. The cut specimen with average thickness 1mm were loaded into a Galdabini Quasar 25 tearing machine. A constant uniaxial load at a speed of 50 mm/min was applied. To determine Young's modulus, a speed of 1 mm/min was set at the beginning of the tensile test.

Figure 18. Galdabini Quasar 25 tensile test machine

6.3 Thermal Properties

6.3.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a method in which the thermal properties of materials such as melting point, glass transition and crystallization process are examined [58]. This thermal analytical instrument determines the temperature and heat flow associated with material transitions as a function of time and temperature. The sample of interest is heated linearly, then cooled, and the rate of heat transfer in the sample varied. An inert material in which no phase change (mostly air) occurs is used as a reference sample, because phase transformations of the first and second order are observed in the analyzed material, manifested by a step change in the DSC curve [59]. In this work, the samples were prepared in small aluminum dishes weighing approximately 6 mg and sealed with a cover using a crimping press. The cap was perforated for examination. For the measurement, a Mettler Toledo DSC1/700 laboratory instrument with STARe System software was utilized. Nitrogen was used as the inert medium. The heating program was set to two heating and two cooling cycles with a heating rate of 10 K/min in the temperature range of -80 to 200 °C.

6.4. X-Ray diffraction

6.4.1 Wide angle X-Ray Diffraction (WAXD)

Inorganic or organic polymeric materials' crystalline structure can be determined using this X-ray diffraction method. This measurement method applies to Braggs analysis peaks that are distributed at large angles of 2θ greater than 1 [54]. In this work, the determination was performed by X ́Pert PROPANalytical Instrument. On the bases of the obtained rentgenogram was determined the crystallinity using Peakfit software. The condition for measurement was set at 40.1 kV of energy, for the continous scan. The angle of measurement

2θ was set from 1.5-30. It should also be noted that the beam geometery was set as monochromatic for this measurement.

Figure 19. Diffractometer

7. RESULTS AND DISCUSSION

7.1 Barrier properties

7.1.1 Water vapor permeability

To quantify the resistance of packaging materials to water vapor, WVTR (Water Vapor Transmission) and WVP (Water Vapor Permeability) values are used. These two can be calculated using the equations given below.

$$\mathrm{WVTR} = \frac{\mathrm{m_w}}{\mathrm{A.t}}\ [\frac{\mathrm{g}}{\mathrm{m^2h}}]$$

where

m_w … the difference in the mass of water in the vessel at a given time [g]

A … the tested area [m^2]

t … time it took for the change in mass [h]

$$\mathrm{WVP} = \frac{\mathrm{WVTR}}{\Delta \mathrm{p}}.\mathrm{L} = \frac{\mathrm{m_w}}{\mathrm{A.t.S\ (R_1 - R_2)}}.\mathrm{L}\ [\frac{\mathrm{g}}{\mathrm{Pa}}.\mathrm{s.m^2}]$$

where

L … the thickness of the foil [m]

S … the saturated water vapor pressure at the test temperature [mm Hg = 133.2 Pa]

R_1, R_2 … the relat. humidity levels in the test vessel and in the surrounding environment [%].

In the table and figures below are presented measured weight changes in tested samples in dependence on time of measurement.

Table 4. Average weight loss for each sample with time

Number of hours	Change in mass [g]												
	PLA L175	**PLA L175 0.1 OA 20A**	**PLA L175 0.3 OA 20A**	**PLA L175 0.5 OA 20A**	**PLA L175 1 OA 20A**	**PLA L175 0.1 OA 10A**	**PLA L175 0.3 OA 10A**	**PLA L175 0.5 OA 10A**	**PLA L175 1 OA 10A**	**PLA L175 0.1 OA Na+**	**PLA L175 0.3 OA Na+**	**PLA L175 0.5 OA Na+**	**PLA L175 1 OA Na+**
0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
2	0.0033	0.0050	0.0200	0.0033	0.0033	0.0067	0.0000	0.0050	0.0067	0.0067	0.0000	0.0100	0.0000
4	0.0067	0.0150	0.0600	0.0133	0.0067	0.0067	0.0067	0.0100	0.0067	0.0067	0.0033	0.0167	0.0067
24	0.0167	0.0650	0.2667	0.0567	0.0533	0.0533	0.0533	0.0300	0.0300	0.0500	0.0433	0.0933	0.0367
48	0.0367	0.1250	0.4933	0.1000	0.1067	0.1033	0.1033	0.0550	0.0567	0.0933	0.0867	0.1800	0.0633
72	0.0533	0.1700	0.6767	0.1400	0.1567	0.1500	0.4767	0.0750	0.0767	0.1400	0.1233	0.2500	0.0967
168	0.1167	0.3250	1.0933	0.2900	0.3567	0.3433	0.2933	0.1700	0.1700	0.3167	0.2733	0.4900	0.2200
264	0.1667	0.4200	1.3133	0.3867	0.4967	0.4567	0.3967	0.2400	0.2367	0.4267	0.3733	0.6333	0.3133
360	0.2300	0.5300	1.5667	0.5100	0.6733	0.5567	0.5133	0.3300	0.3233	0.5533	0.5000	0.8133	0.4400
456	0.3033	0.6450	1.8167	0.6333	0.8533	0.6567	0.6333	0.4250	0.4167	0.6933	0.6300	0.9900	0.6133
552	0.3733	0.7700	2.0500	0.7567	1.0467	0.7500	0.7567	0.5300	0.5167	0.8433	0.7733	1.1900	0.8633
648	0.4400	0.8750	2.2300	0.8467	1.2000	0.8367	0.8600	0.6200	0.6033	0.9667	0.8933	1.5667	1.0600
768	0.5233	1.0050	2.4167	0.9600	1.3867	0.9400	0.9900	0.7350	0.7133	1.1200	1.0533	3.0067	1.2967

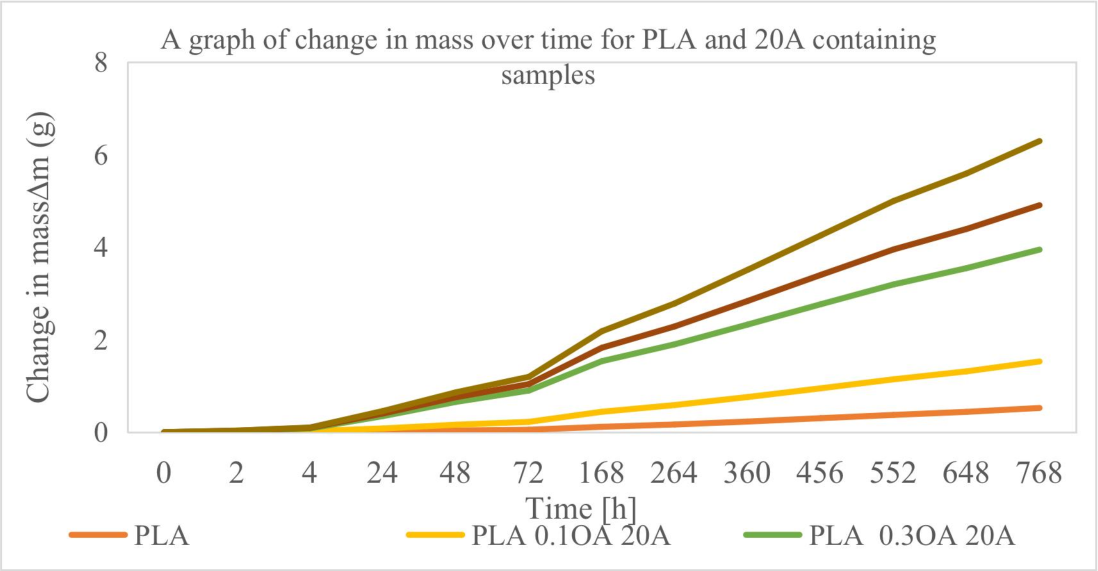


Figure 20 . A graph of change in mass over time for PLA and 20A containing samples

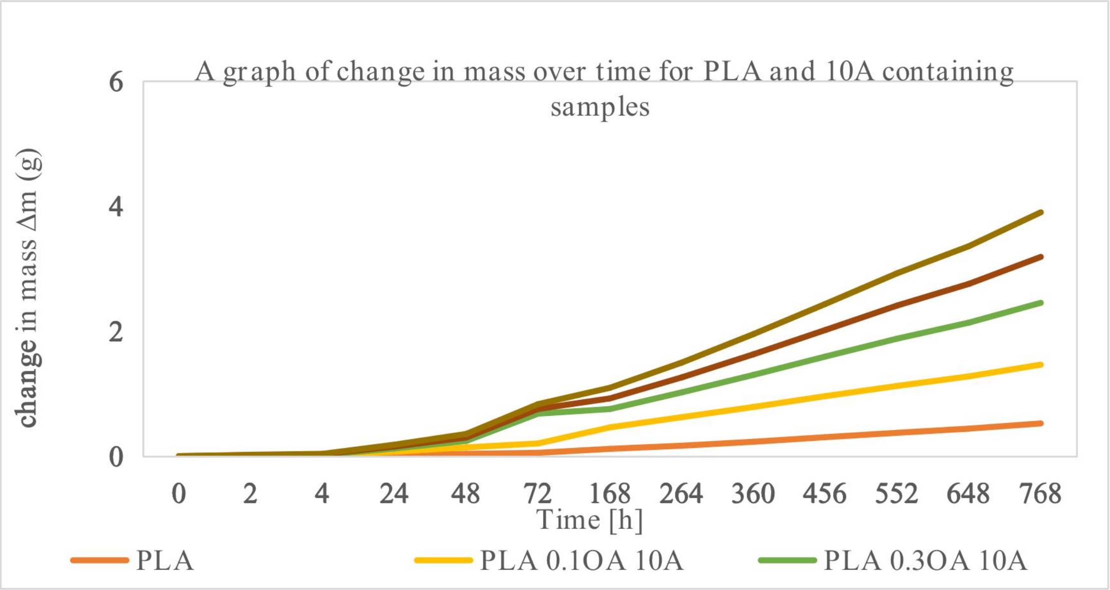


Figure 21 . A graph of change in mass over time for PLA and 10A containing samples

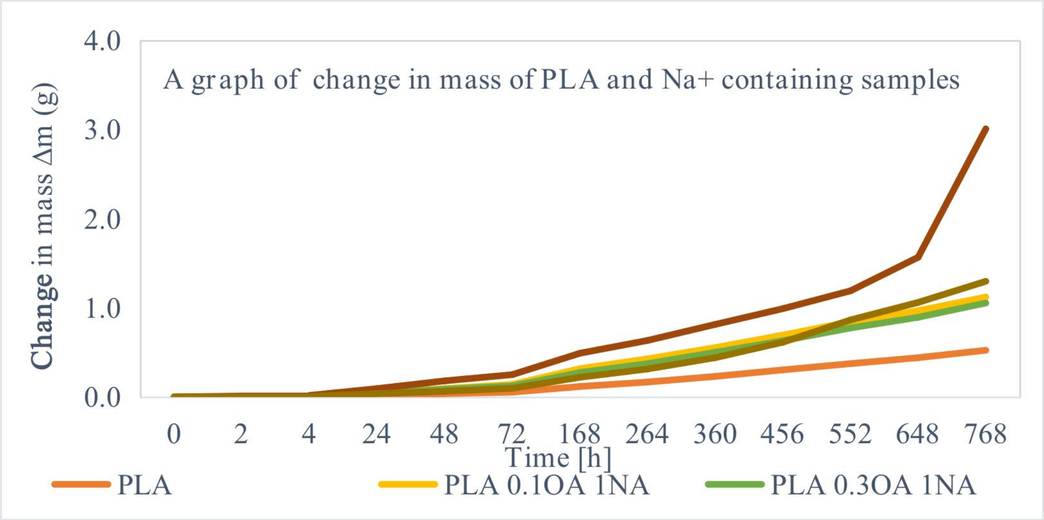


Figure 22 . A graph of change in mass over time for PLA and Na+ containing samples

The trend of the loss of mass by the various samples are illustrates in table 4 and figures, 20-22. The major observation here is that the samples barrier properties changed as with time. While there was a gradual change in mass at the beginning for every one of the samples, their permeability differed greatly after the initial 24hrs of measurement.

Table 5. A table of average WVP and WVT measured after 24hr

Sample	Average wvt after 24 hr (g/h.m^2)	Average wvp after 24 hrs (g/Pa.s.m^2)
PLA PURE	0.6822	7.58643E-05
PLA L175 0.1 OA 1 20A	2.6608	2.16E-04
PLA L175 0.3 OA 1 20A	2.4561	2.16E-04
PLA L175 0.5 OA 1 20A	2.3196	0.000203189
PLA L175 1 OA 1 20A	2.1832	0.000154912
PLA L175 0.1 OA 1 10A	2.1331	0.000171358
PLA L175 0.3 OA 1 10A	2.1831	0.000138466
PLA L175 0.5 OA 1 10A	1.2280	9.78809E-05
PLA L175 1 OA 1 10A	1.1210	9.86767E-05
PLA L175 0.1 OA 1Na+	2.0467	0.000162339
PLA L175 0.3 OA Na+	1.7738	0.00011194
PLA L175 0.5 OA Na+	3.8205	0.000239264
PLA L175 1 OA Na+	1.5009	9.70851E-05

Table 6. WVT And WVP values for PLA mixtures after 32 days

MATERIAL	WVT after 32 Days ($g/h.m^2$)	STANDEV WVT ($g/h.m^2$)	WVP after 32 Days ($g/Pa.s.m^2$)	STANDEV WVP ($g/Pa.s.m^2$)
PLA L175	0.7708	3.7142E-01	8.47E-05	4.2857E-05
PLA L175 0.1 OA 20A	1.8432	5.5790E-01	1.51E-04	5.0319E-05
PLA L175 0.3 OA 20A	1.6983	1.2705E+00	1.53E-04	1.0288E-04
PLA L175 0.5 OA 20A	1.6106	1.0132E+00	1.40E-04	8.7583E-05
PLA L175 1 OA 20A	1.7573	1.7243E+00	1.25E-04	1.0657E-04
PLA L175 0.1 OA 10A	1.6695	1.2467E+00	1.31E-04	1.0155E-04
PLA L175 0.3 OA 10A	1.7164	1.1299E+00	1.11E-04	7.5773E-05
PLA L175 0.5 OA 10A	1.1397	3.7534E-01	9.15E-05	2.8423E-05
PLA L175 1 OA 10A	1.1345	4.8313E-01	9.17E-05	3.6542E-05
PLA L175 0.1 OA Na+	1.6632	1.1239E+00	1.30E-04	9.9627E-05
PLA L175 0.3 OA Na+	1.2182	5.6424E-01	7.68E-05	3.4293E-05
PLA L175 0.5 OA Na+	2.9104	1.1613E+00	1.80E-04	7.3567E-05
PLA L175 1 OA Na+	1.1947	3.0768E-01	7.70E-05	1.7780E-05

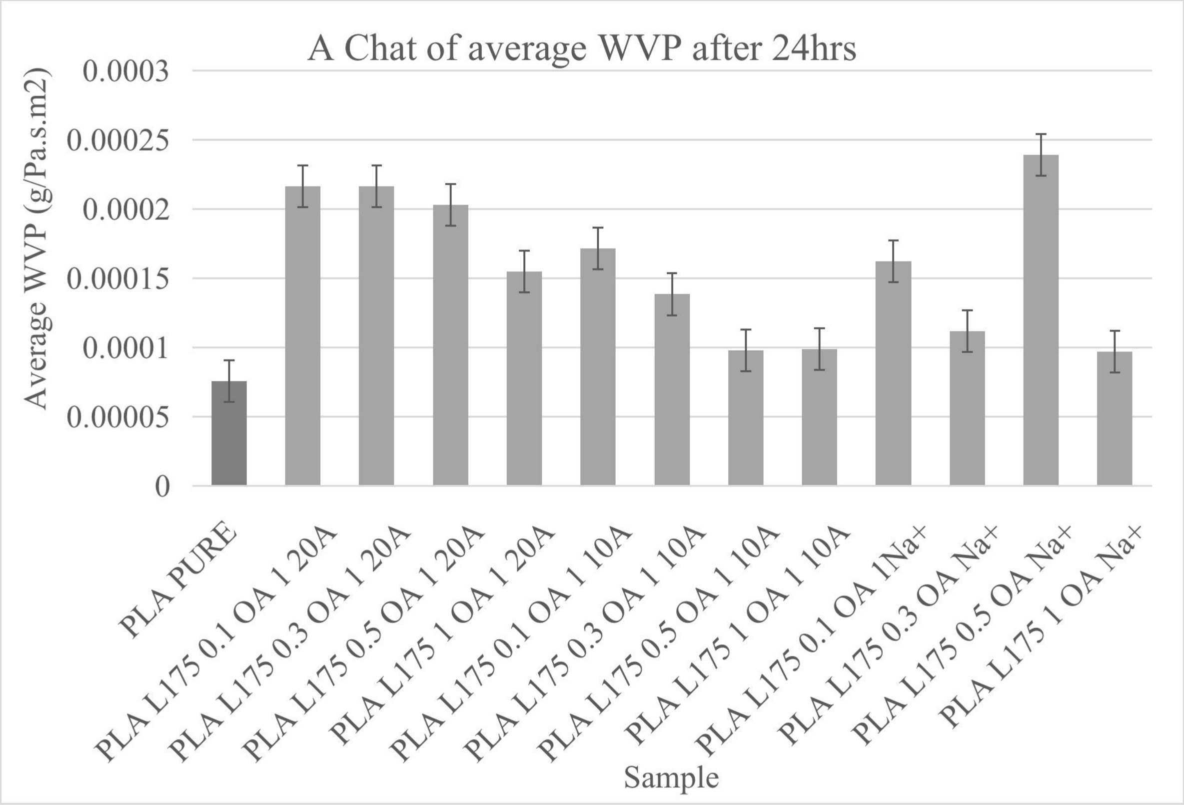


Figure 23. A chat of WVP measured after 24 hrs

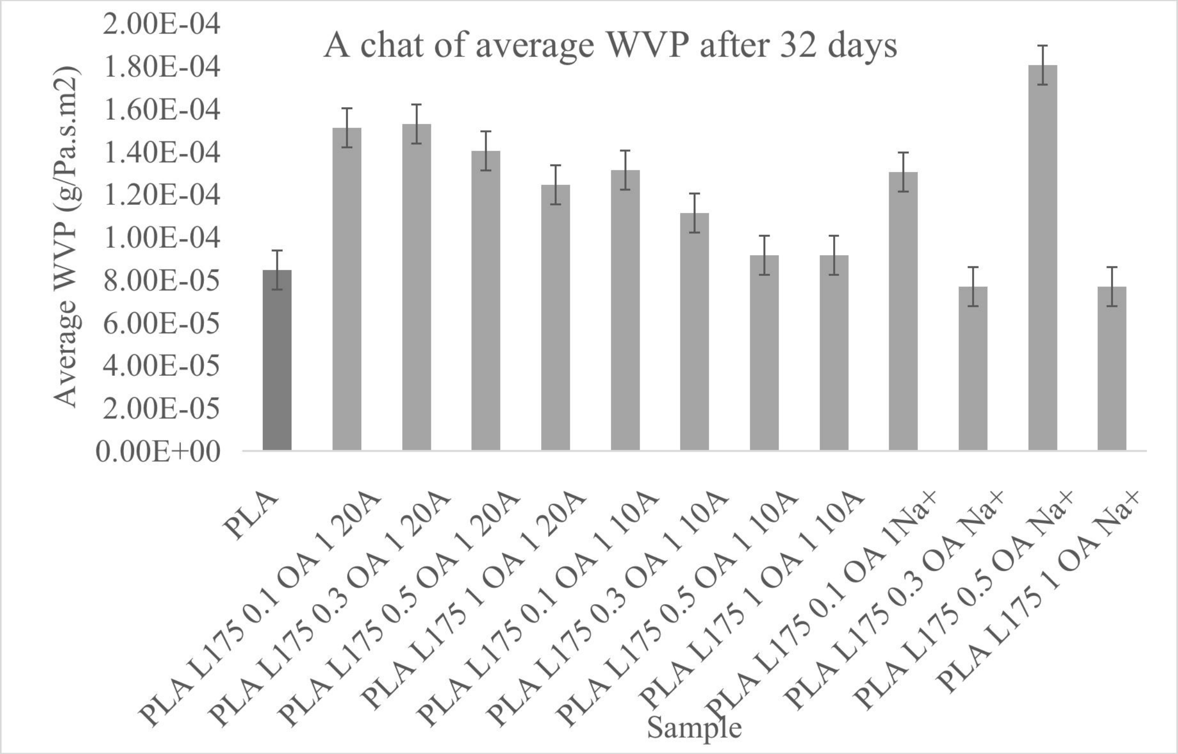


Figure 24. A graph of average water vapor Permeability after 32 days

Water vapor transmission (WVT) and water vapor permeabilities (WVP) for a period of 32 days were computed for all materials based on changes in the weight of the water in the test cup, which were determined using the gravimetric method. The WVP results of the pure PLA sample was 8.47×10^{-5}g/Pa. s. m2. The lowest value of WVP was marked for composition PLA L175 0.5OA 10A and PLA L175 1OA 10A (9.2×10^{-5} g/Pa.s.m^2). The difference comparing pure PLA make approximately 9 %. Also sample with Na show value of WVP relatively near the value for pure PLA, 7.7×10^{-5} g/Pa.s.m^2. Majority of samples surprisingly show worsening of tested property because clays are known to improve these properties. It is supposed that problem could be caused both by sample preparation or the influence of OA in composition.

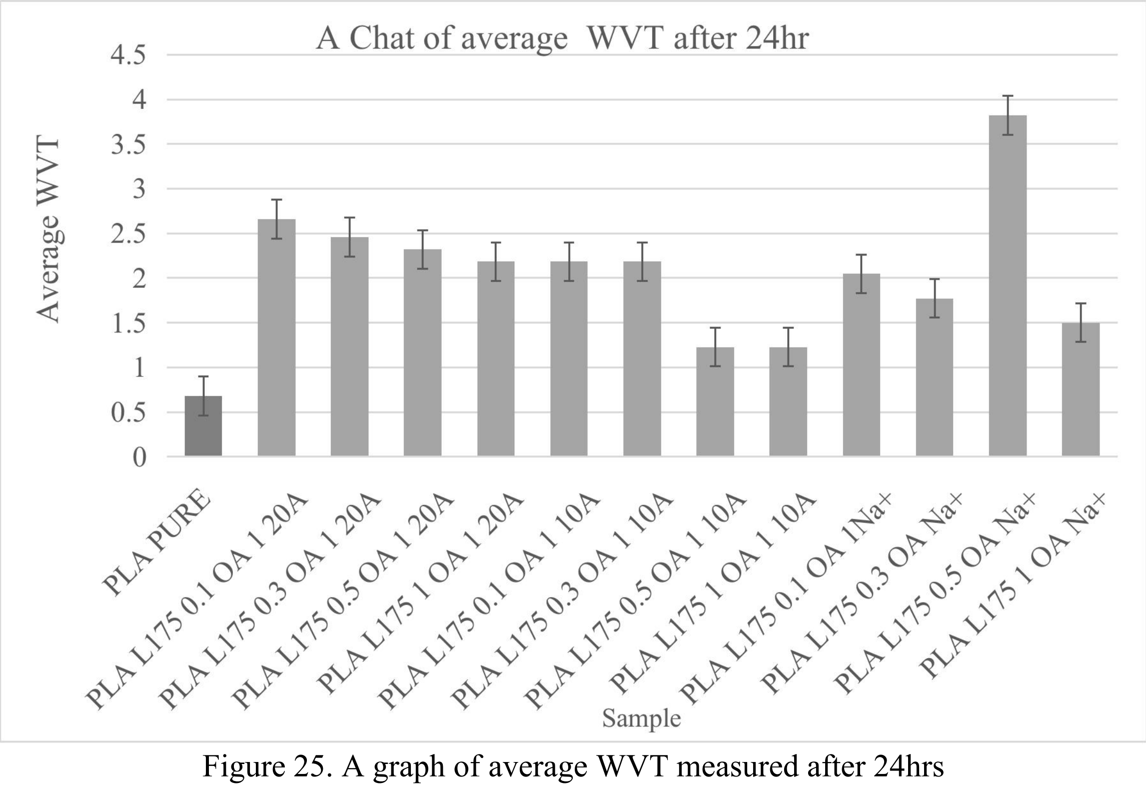


Figure 25. A graph of average WVT measured after 24hrs

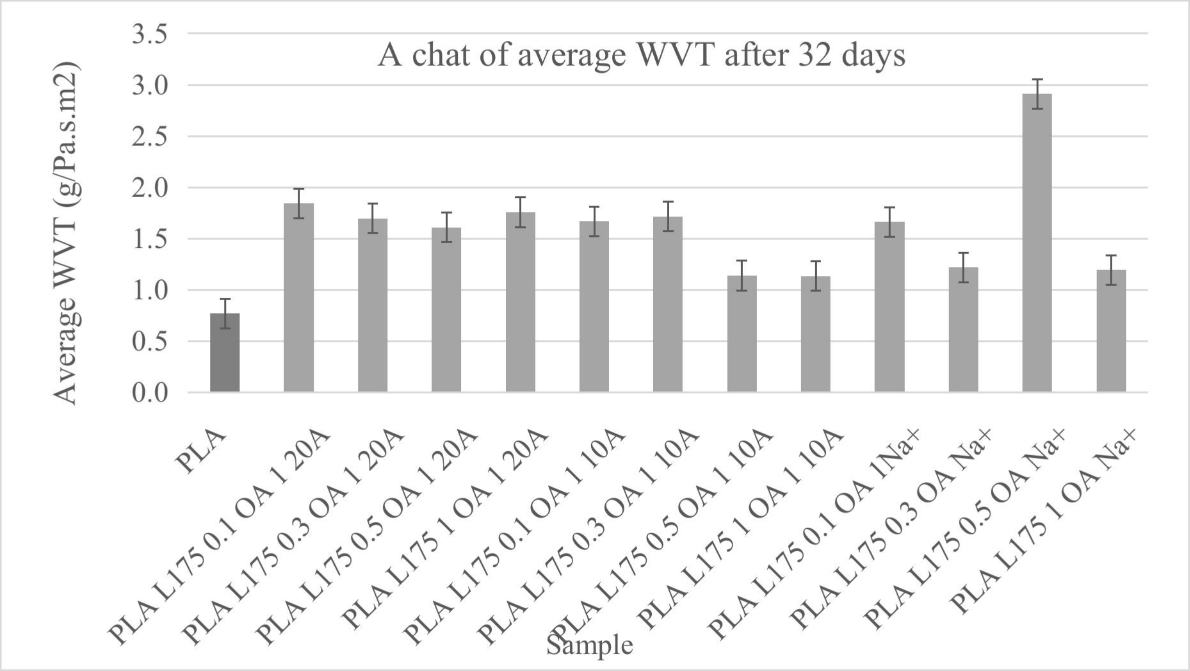


Figure 26. A graph of average water vapor transmission after 32 days

Water vapor transmission (WVT) which is the standard measurement by which films are compared for their ability to resist moisture transmission. Lower values of WVT indicate better moisture protection. Generally acceptable values for WVT for packaging materials are values less than 0.2 for food packaging.

The values obtained from the experiments indicates that all of the samples lower resistance to moisture transmission and hence poor barrier to moisture. Their high WVT values make them not suitable for packaging purposes.

Table 7. A table of Percentage change to pure PLA for WVT.

Sample	% change to pure PLA for WVT after 24hrs	% change to pure PLA for WVT after 32 days
PLA L175	100	100
PLA L175 0.1 OA 20A	-290.03	-139.13
PLA L175 0.3 OA 20A	-260.03	-120.33
PLA L175 0.5 OA 20A	-260.40	-108.95
PLA L175 1 OA 20A	-220.02	-127.98

Sample	% change to pure PLA for WVT after 24hrs	% change to pure PLA for WVT after 32 days
PLA L175 0.1 OA 10A	-212.68	-116.59
PLA L175 0.3 OA 10A	-220.01	-122.68
PLA L175 0.5 OA 10A	-80.01	-47.86
PLA L175 1 OA 20A	-64.32	-47.18
PLA L175 0.1 OA Na^+	-200.01	-115.78
PLA L175 0.3 OA Na^+	-160.01	-58.04
PLA L175 0.5 OA Na^+	-460.03	-277.58
PLA L175 1 OA Na^+	-120.02	-54.99

Comparing the WVT values of the samples with pure PLA leads to the conclusion that the presence of the additives reduced the samples capacity to withsatand moisture transmission.

When the nanocomposites' WVT was compared to that of the pure PLA, all the sample showed negative values which means they have poorer barrier to moisture than PLA in both the short peroid and and long term. The sample PLA L175 0.5OA Na^+ had the poorest moisture resistance properties when compared to PLA.

7.1.2 Gas permeability

The aim of this part of the work was to determine the permeability of four gases: air, oxygen, carbon dioxide and oxygen. However, the test came out with results for only air and oxygen. The permeability for CO_2 and N_2 coulded not be calculated due to the sample behavior. Some of them provided data for permeability calculation for less than 10mins hence ignored. For this reason, the discussions will be limited to the values obtained for oxygen (O_2) and air permeability. By calculating the oxygen transmission rate (OTR), which represents the volumetric flow rate of oxygen per unit membrane area and over time, along with the thickness of the membrane, the oxygen diffusion process can be evaluated [49]. The transmission of air is also calculated using the same method.

Table 8. Calculated coefficient of permeability for oxygen and air

Sample	**Coefficient of permability $\times10^{-15}$ [mol/m.s.Pa] O_2**	**Coefficient of permability $\times10^{-15}$ [mol/m.s.Pa] Air**
PLA L175	2.4075	3.5106
PLA L175 0.1OA 20A	1.9803	1.0087
PLA L175 0.3OA 20A	2.0787	2.0603
PLA L175 0.5OA 20A	3.9714	2.6661
PLA L175 1OA 20A	2.1319	2.0847
PLA L175 0.1OA 10A	2.2786	1.0701
PLA L175 0.3OA 10A	3.8464	3.7142
PLA L175 0.5OA 10A	1.8675	1.5139
PLA L175 0.1OA Na	3.6746	1.5748

Table 9. A table of the percentage change in permeability of O_2 and air for all samples compared to PLA

Sample	% change of permeability of O_2 compared to PLA	% change of permeability of Air compared to PLA
PLA L175	100	100
PLA L175 0.1OA 20A	82.26	28.73
PLA L175 0.3OA 20A	86.34	58.69
PLA L175 0.5OA 20A	164.96	75.94
PLA L175 1OA 20A	88.55	59.38
PLA L175 0.1OA 10A	94.65	30.48
PLA L175 0.3OA 10A	161.36	105.80
PLA L175 0.5OA 10A	77.57	43.12
PLA L175 0.1OA Na	157.64	44.86

Obtained and calculated data are presented in table and . It is possible to see, that addition of clay leads to the decreasing permeability of air in all samples expect for PLA L175 0.5OA 10A whose pwermeability is about 5% higher. The samples with clay exhibited decrease of permeability when compared to PLA. The lowest permeability was observed for sample PLA L175 1OA 20A. It must be noted that the permeability of this sample is just 28.73% compared to that of pure PLA.

In the case of OTR it is quite similar only three samples having a higher permeability than PLA. However, unlike in the permeability of air, the permeability of these samples are quite high and closer to that of the PLA.

Samples with loading 1% of clay were problematic from the viewpoint of barrier properties measurement. Clay affected the mechanical properties and the materials started to be brittle. In this case, too much fragility and not desirable.

7.2 Mechanical properties

As was mentioned above the tensile test is one of the most used testing method to determine mechanical properties. The result of the Young's modulus, tensile stress and elongation at break determined by the tensile test are shown in the table and graphs below.

Table 10. A table of Tensile test data

SAMPLE	YOUNGS MODULUS (MPa)	STDEV OF MODULUS (MPa)	TENSILE STRENGTH (MPa)	STDEV OF TENSILE STRENGTH (MPa)	ELONGATTION (%)	STDEV OF ELONGATION (%)
PLA L 175	2003.64	±133.06	52.53	±1.6	3.85	±0.38
PLA L175 0.1 OA 20A	2160.10	±282.19	55.62	±8.48	4.42	±1.62
PLA L175 0.3 OA 20A	2346.39	±267.44	58.41	±6.86	3.45	±0.77
PLA L175 0.5 OA 20A	2363.86	±230.35	57.07	±5.73	2.93	±0.45
PLA L175 1 OA 20A	2161.29	±286.28	52.53	±2.58	3.41	±0.37
PLA L175 0.1 OA 10A	2147.29	±258.2	61.19	±1.29	3.22	±0.45
PLA L175 0.3 OA 10A	2238.67	±243.26	59.8	±5.12	2.44	±0.2
PLA L175 0.5 OA 10A	2223.21	±261.04	61.59	±5.57	2.95	±0.14
PLA L175 1 OA 10A	1898.86	±188.9	55.45	±2.72	3.5	±0.56
PLA L175 0.1 OA Na	1867.90	±280.42	58.72	±8.08	3.29	±0.09
PLA L175 0.3 OA Na	2222.16	±228.41	61.02	±2.13	3.47	±0.87
PLA L175 0.5 OA Na	1875.93	±320.44	61.5	±1.88	3.22	±0.23
PLA L175 1 OA Na	2247.49	±179.89	57.48	±2.99	2.44	±0.2

The mechanical properties of the samples were measured for the different mixtures. The Young´s modulus, tensile strength and elongation were measured to determine the durability of the different samples. The value of all these samples at different concentrations of OA were compared to determine which concentration of OA and which nanoclay gave the better mechanical properties. The comparison was done this way because the concentration of the nanoclays were kept at 1%.

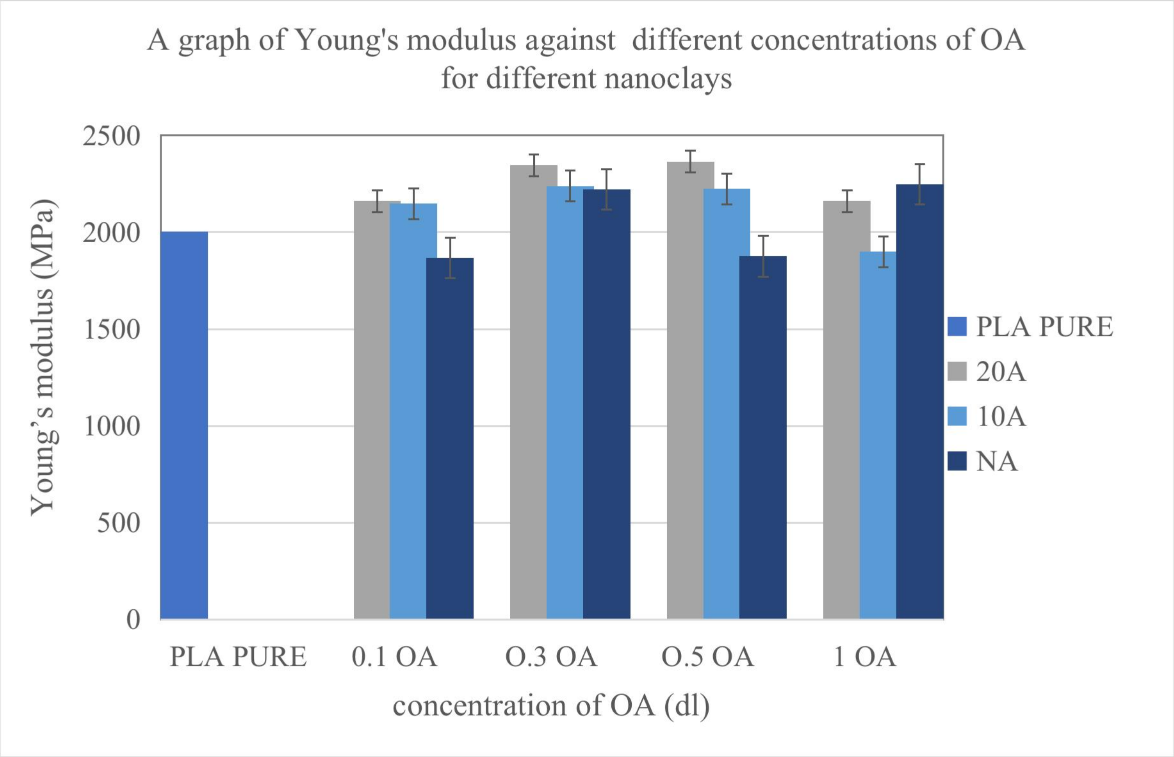


Figure 27. Young's modulus for samples prepared with different OA concentration

Youngs modulus describes the relative stiffness of a material and is determined by the equation: $E = \frac{\text{stress}}{\text{strain}}$. This equation indicates that a stiff material will have a high E value while a flexible material will have a low E value. For good packaging materials, the E value should not be so low that the sample cannot withstand tearing.

It was observed that most of the prepared samples have higher modulus compared to pure PLA. This fact is connected with presence of clay in the mixture. It is generally known that filler increased stiffness of material. In case of OA concentration, the E modulus growth with increasing OA concentration to loading 0.5% for mixtures containing cloisite 10A and 20A. After that, it dropped down. In case of Na+, there was no marked trends and the values varied around 2000 MPa. The highest value was noticed by composition PLA L175 0.5 OA 20A, where the change was in range 17 %.

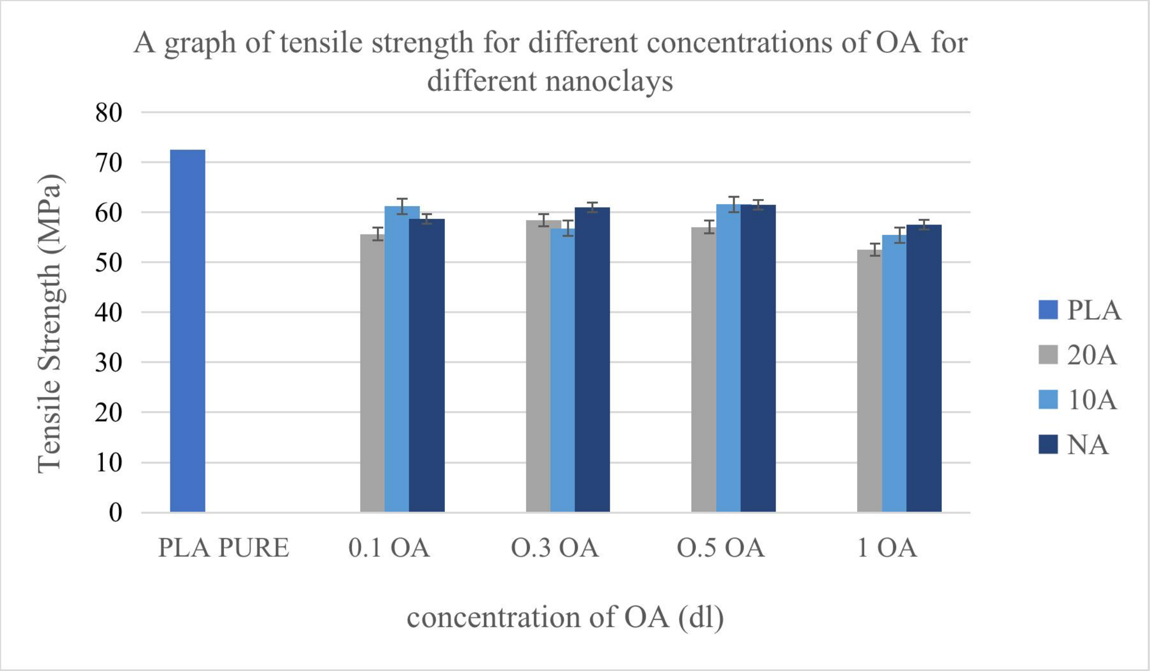


Figure 28. A graph of Tensile strength for samples prepared with different concentration of OA

Tensile strength can be defined as the maximum stress that a material can bear before breaking when it is stretched. High tensile strength materials are often used to create strong and durable products that can withstand heavy loads and forces.

From the view point of tensile strength, the shift to higher values was marked for composition with 10A and Na+. For all compositions varied around 60 MPa. In case of mixtures with 20A, the values increased till loading 0.5% and then the value decreased. The highest values was shown by sample PLA L175 0.5 OA 10A (61.6 MPa). Percentual change is 17.3 % comparing pure PLA L175. Mixture with cloisite Na show the highest value of tensile strength by loading 0.5 OA too (61,5 MPa, +17 %). The mixture with 20A exhibit highest value at OA loading 0.3 (58.4 MPa, +11%). The presence of the additives altered the crystal lattice structure of the PLA hence increasing it tensile strength.

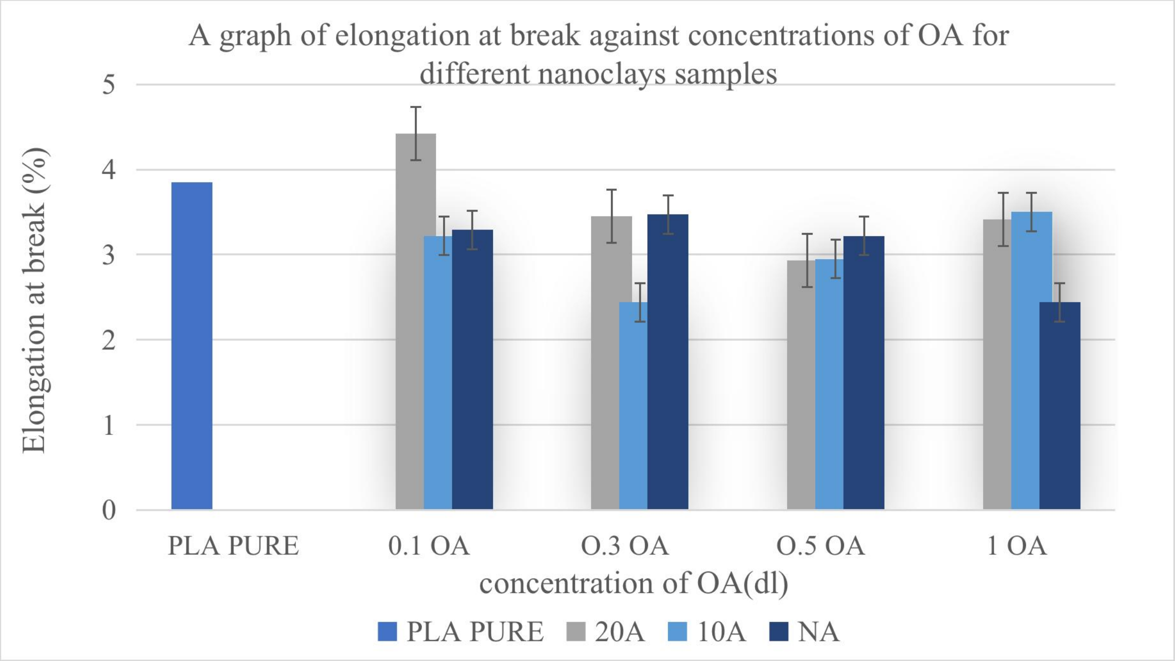


Fig 29 A graph of elongation at break against concentrations of OA for different nanoclays samples

Last tested parameter was elongation at break. Elongation at break or fracture strain could be defined as the ratio of the test specimen's altered length to its starting length following breakage. It is measured in percentages. Materials with a higher elongation at break have higher ductility. High ductility implies that a material will be more likely to deform and not break. Whereas low ductility suggests that a material is fragile and will fracture before deforming substantially under a tensile stress. As it is possible to see from table 10 and graph 29 above, the highest elongation at break (4.42%) exhibit sample PLA L175 0.1OA 20A with improvement 15 % comparing to pure PLA. On the other hand, with increasing concentration of OA the decrease of elongation was observed. The lowest value was market for PLA L175 1OA Na (2.44%, drop -36 %). Common decrease is around 10%. At the same concentration of OA, the percentage elongation was dependent on the nanoclay used. The lowest changes in elongation at break notices mixtures with cloisite 20A.

7.3 Wide Angle X-Ray diffraction(WAXD)

DSC analysis revealed that PLA L175 crystallizes considerably in the presence of OA and nanoclay. The WAXD approach which is regarded as the most accurate for analysis confirms and elaborates on the crystalline fraction concentration. The graph and tables below displays computed crystallinity curve and values for the samples and are compared to the crystallinity of PLA.Fig 30. A graph of XRD curve up to 7° 2Q for all samples

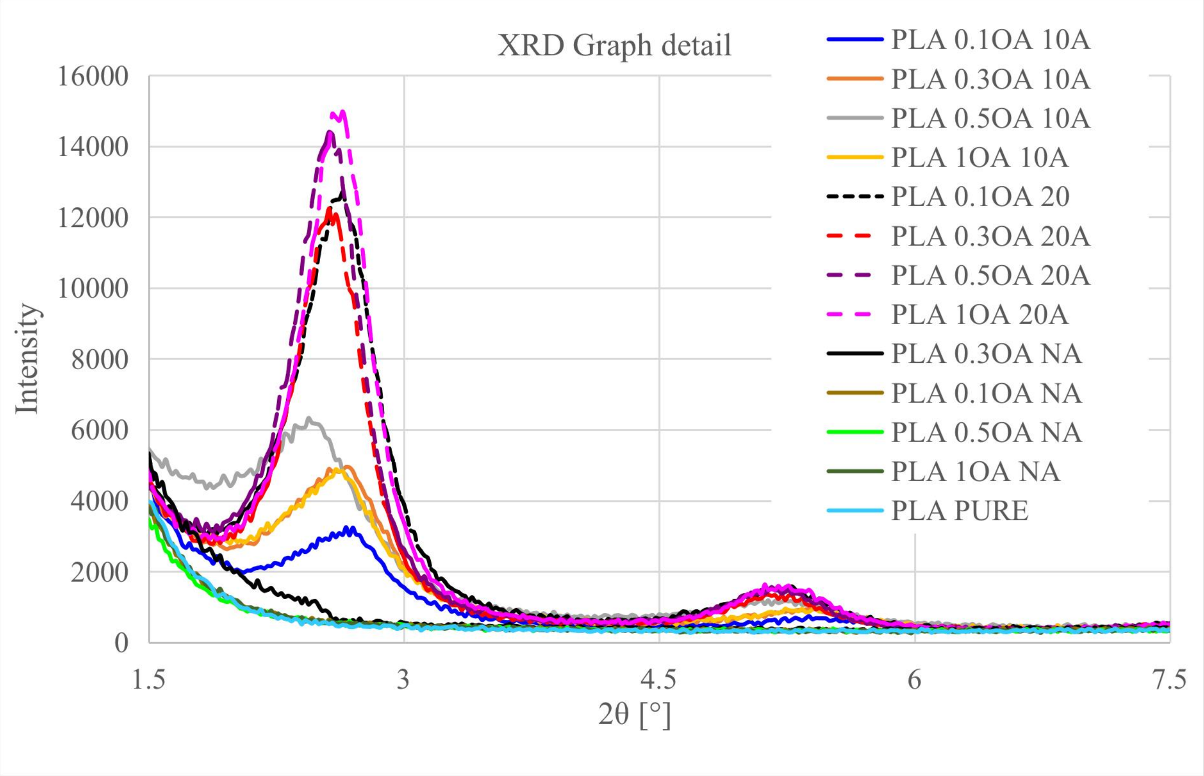


Fig 30. A graph of XRD curve up to 7° 2Q for all samples

In Figure 30-33 could be visible process of intercalation or exfoliation of clay filler in polymer matrix. In case of cloisite 20A it is possible to see relatively sharp peaks at position 2,7 ° 2Q. This indicates organized structure in polymer matrix and intercalated structure of clay, not fully exfoliated.

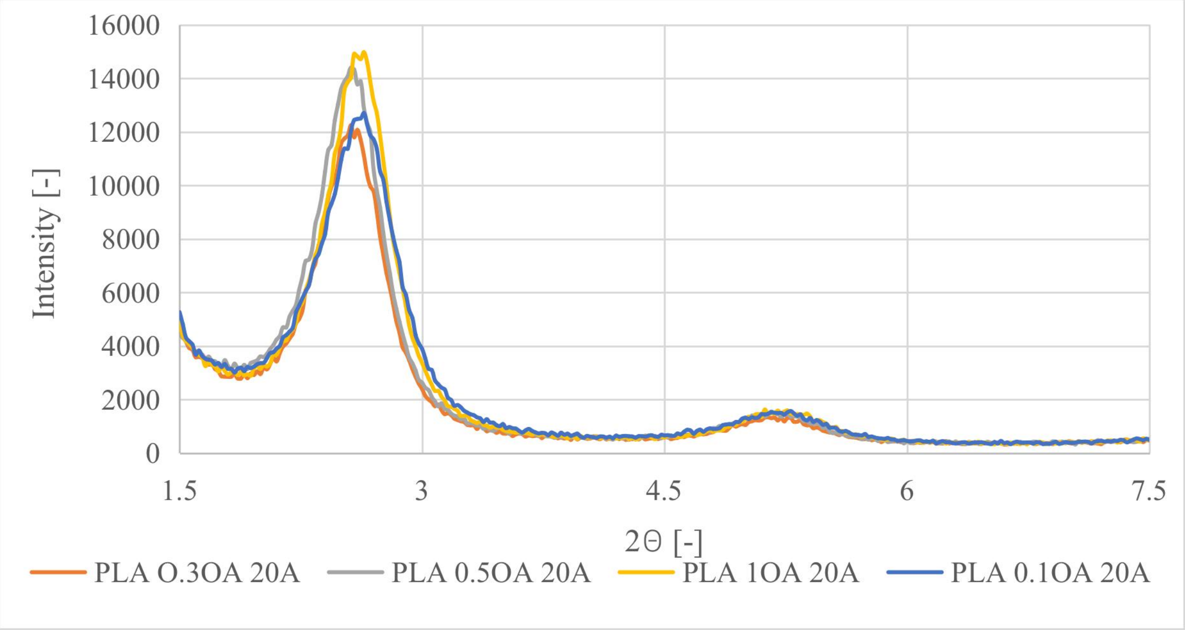


Fig 31. A graph of XRD curve for PLAL175/20A series

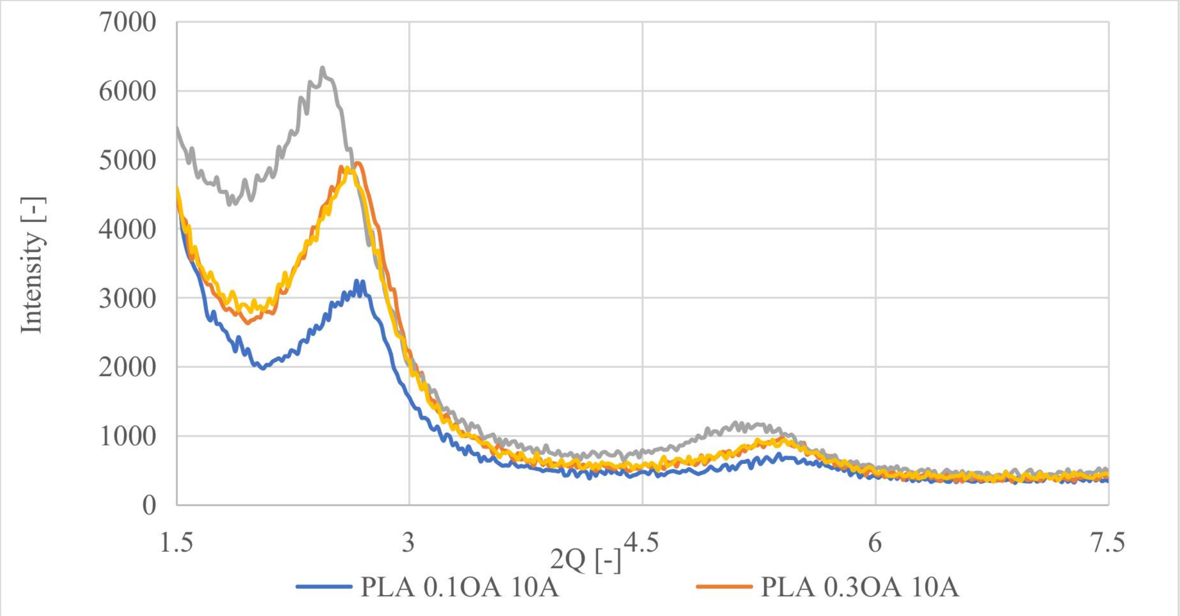


Fig 32. A graph of XRD curve for PLAL175/10A series

For mixtues with 10A it was noticed the shift of peak to lower values of angle with increase level of OA. This effect is connected with increasing interlayer distance with increasing level of OA in PLA mixture. The position was changed from 2.7 to 2.4 ° 2Q. The observed maxima are not so sharp like in case of Cloisite 20A. This fact indicated, that there is less order strucrure of clay in polymer matrix. It could be supposed that we could have the combination intercalated and particularly exfoliated structure of clay.

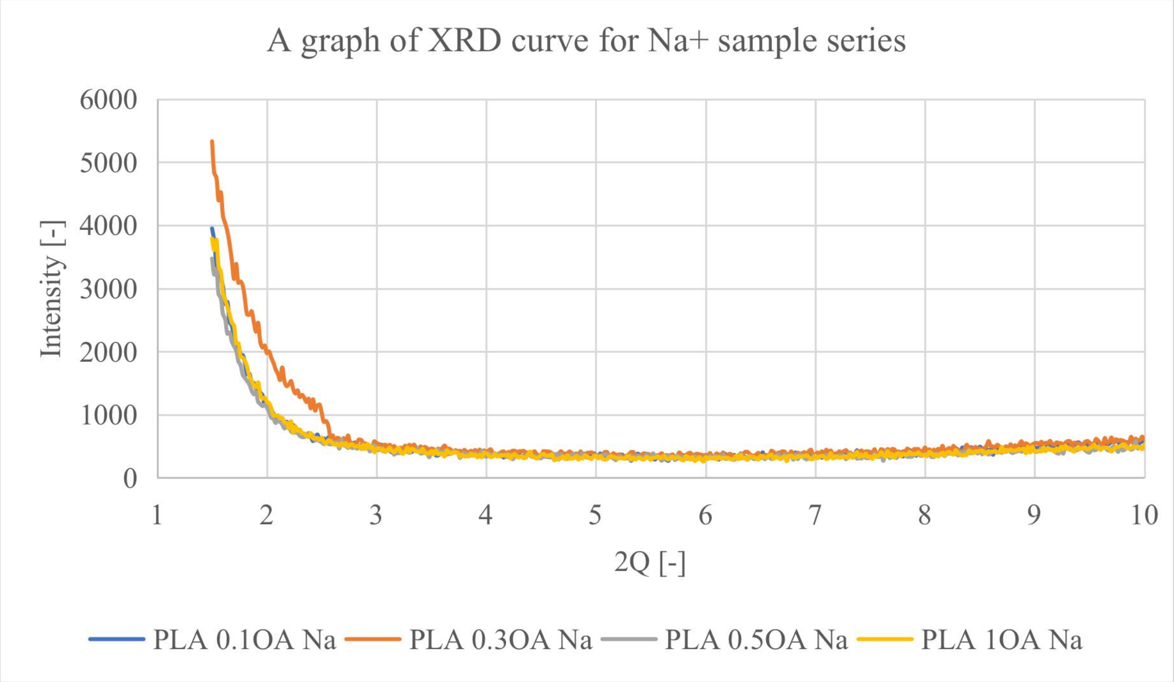


Figure 33. A graph of XRD curve for PLAL175/Na series

Last graph presented PLA/Na composition. In this mixture it is not possible to see any peaks. Only in case of 0.3 OA there is some hint of peak at 2.4 ° 2Q. On the base of XRD results we could suppose to obtained exfoliated structure of clay in polymer. To confirmed these results, it will be necessary to check these results by other method (e.g., microscopy).

The curves in the whole measured range are presented in figures 34-36. In case of 20A we can mark some relatively small peak around 16 ° 2Q, and 26 ° 2Q. In Figure 35m, which is connected with 10A it is visible only non-intensive maximum at 19 ° 2Q. On the other hand, last Figure 36 exhibited very sharp and intensive peakt in area 16, ° 2Q. Next peak with lower intensity were notice at 19 and 29 ° 2Q. In this composition, an increase in the crystalline fraction in polymers mixtures can be expected.

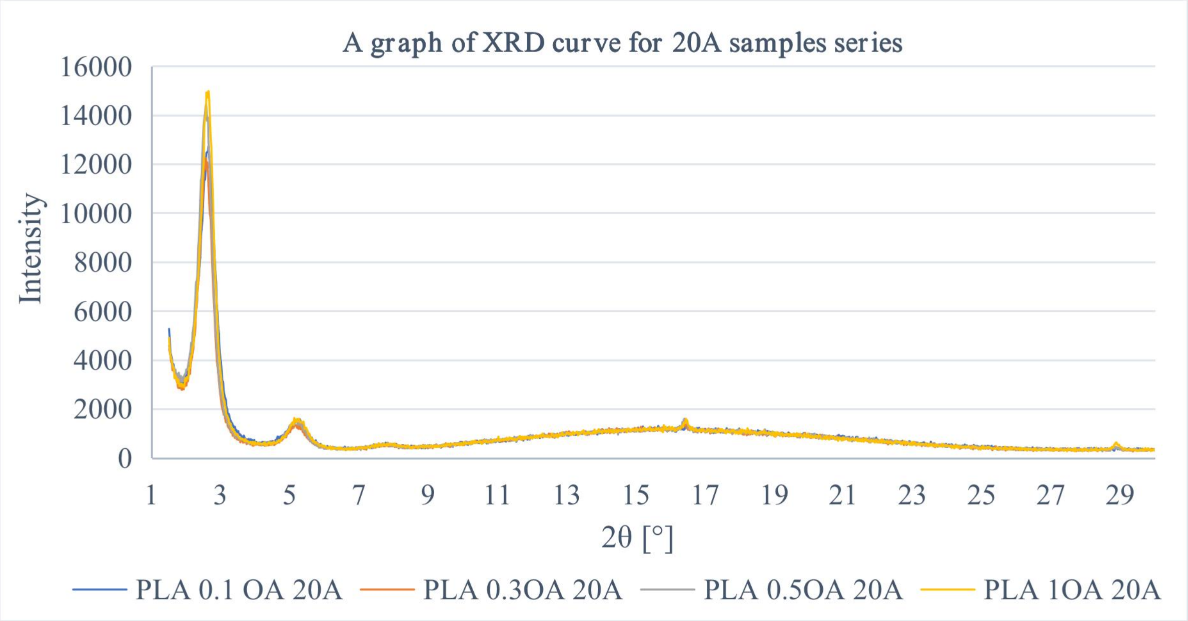


Figure 34 :A graph of XRD curves for PLA L175 OA 20A samples series

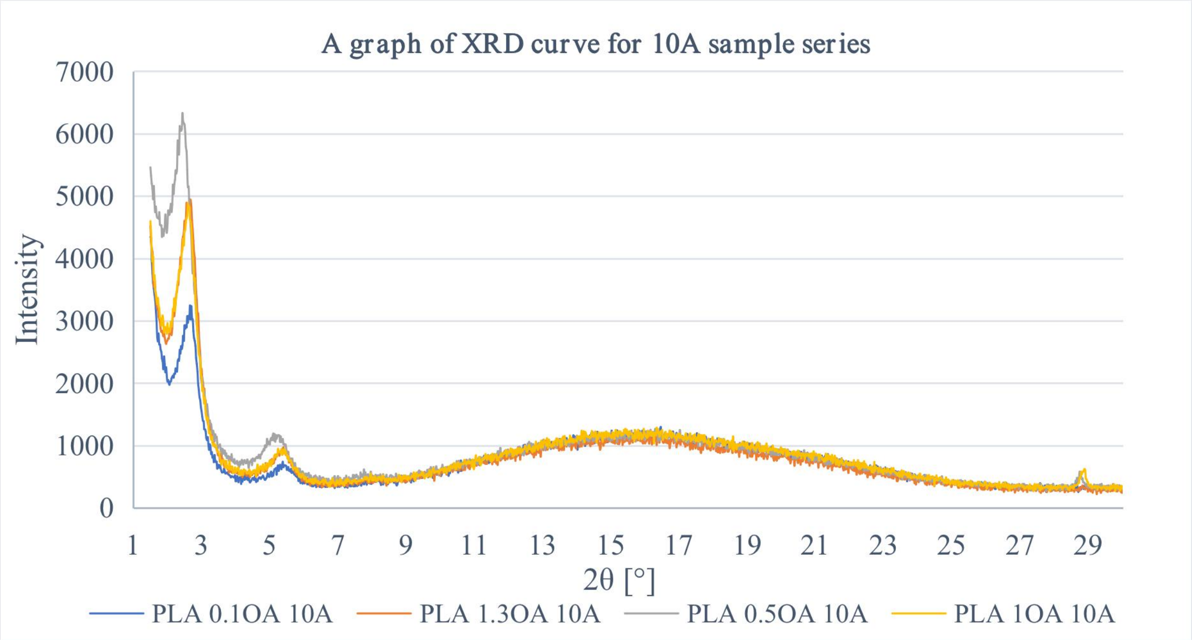


Figure 35. A graph of XRD curves PLA L175 OA 10A samples series

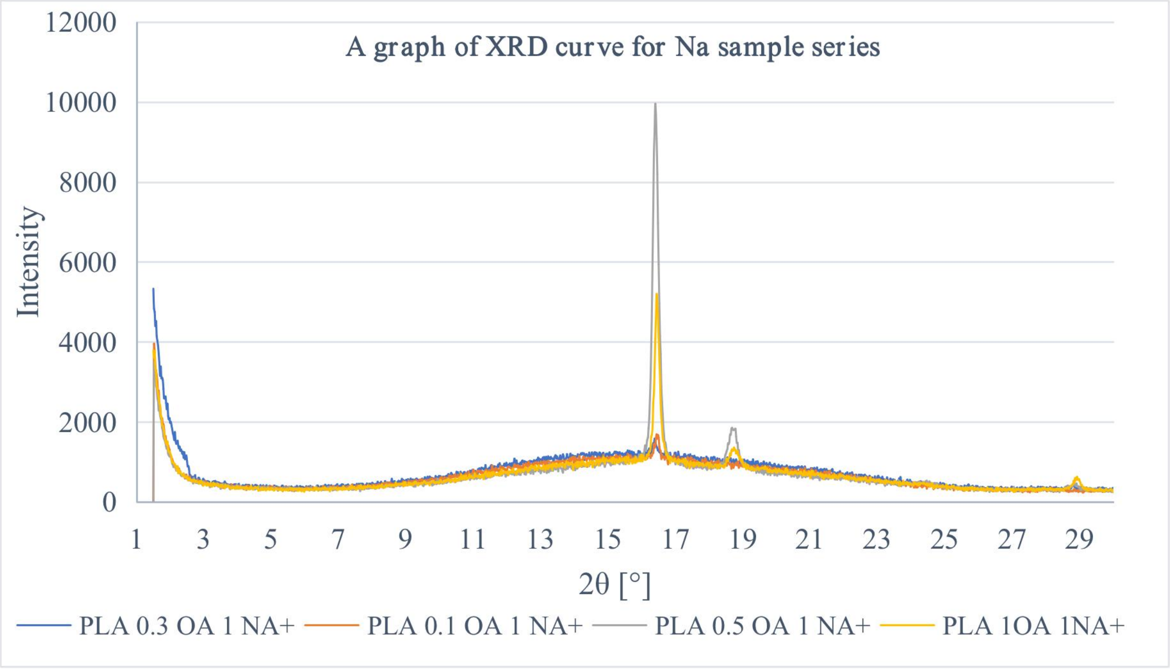


Figure 36 : A graph of XRD curves for PLA L175 OA Na samples series

7.4 Thermal Properties -DSC

The results of the thermal properties measured by the DSC technique are shown in the table and graphs below. The result clearly indicate the effect of the additives on the thermal properties of the prepared samples. Each nanoclays had a different effect on the samples.

Table 11. A table of the Thermal Properties as measured by DSC

Sample	T_g [^oC]	T_c [^oC]	T_m [^oC]
PLA L175	63.16	102.92	173.48
PLA L175 0.1OA 20A	61.78	-	175.18
PLA L175 0.3OA 20A	63.42	105.02	175.71
PLA L175 0.5OA 20A	62.99	106.13	174.89
PLA L175 0.1OA 10A	59.83	97.94	174.29
PLAL175 0.3OA 10A	71.1	101.68	174.45
PLA L175 0.5OA 10A	-	118.67	173.49
PLA L175 1OA 10A	67.84	106.45	174.37
PLA L175 0.1OA NA	59.28	115.72	174.16
PLA L175 0.3OA NA	63.6	120.31	175.54
PLA L175 0.5OA NA	61.23	129.28	172.76
PLA L175 1OA NA	61	133.44	173.51

The Glass Transition temperature, Crystallization temperature and Melting temperatures measured for the prepared sample as shown in the table above do differ greatly from the values obtained from the Pure PLA sample except for a few instances.

The melting point for all the samples did not show much variation from the pure sample. All the samples have Tm within the range 173 ^oC- 175^oC. The measured value of the melting temperature for the pure PLA sample 173.48^oC. The lowes value was noticed for PLA L175 0.5OA 10A with Tm 173.49, highest for PLA L175 0.3OA 20A, 175.71 °C.

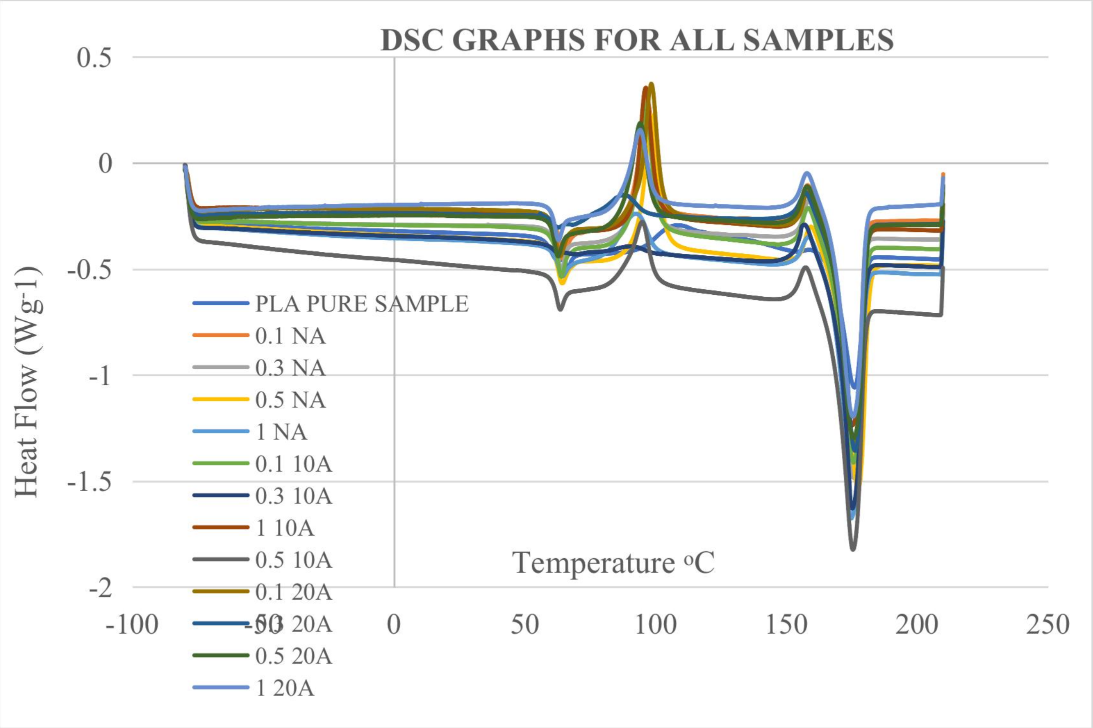


Figure 37. A graph of the full spectrum of DSC measurement for all samples

The presence of the additives OA and nanoclays did not greatly alter the Tm. The highest Tm, 175.54°C, which was recorded by PLA 0.3OA Na$^+$, is approximately the same as the Tm rported by the manufacturer for pure PLA.

The measured glass transition temperature T_g of of the Na samplesseries were similar to that of the value of the pure PLA with the value ranging between 59-63°C. PLA 0.3OA NA showed a higher Tg value than the rest. This Tg value is similar to that of the pure PLA with other samples showing relatively lower values.

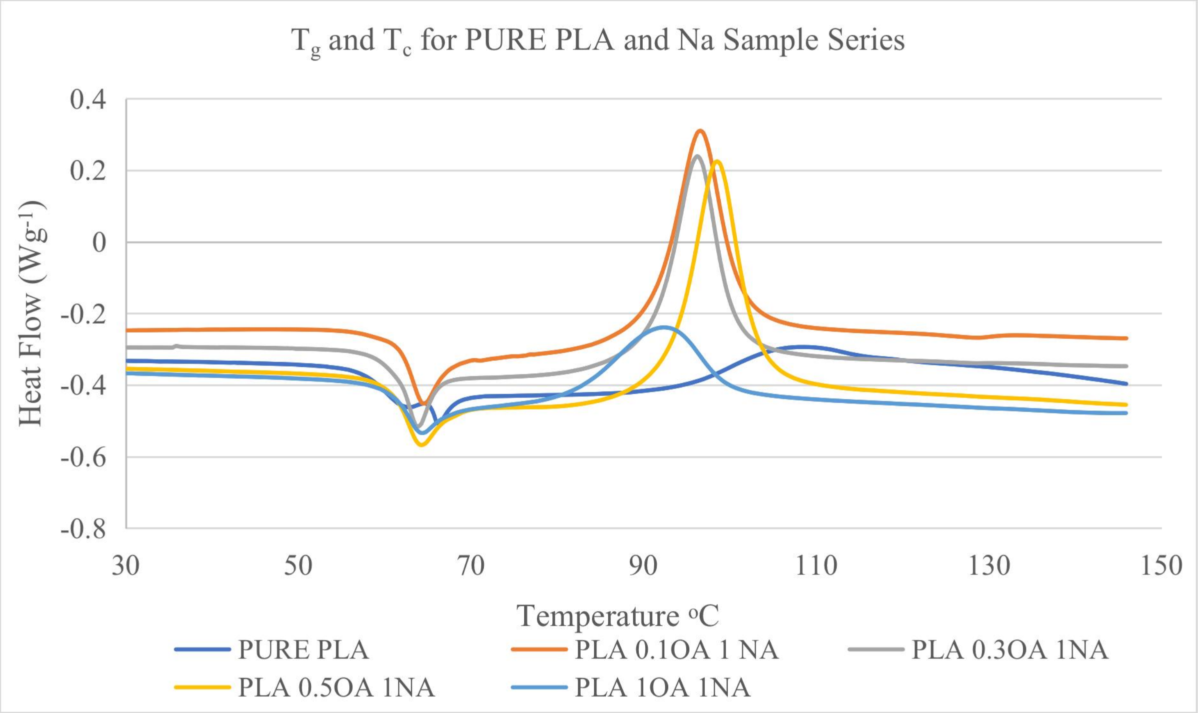


Figure 38. A graph of T_g and T_c for Na+ Samples Series

The difference in the values are as a result of the processing conditions and the presence of additives which alter the structure of the matrix. The twice mixing during the compounding is a very major factor on the values recorded.

The crystallization temperature on the other hand differs greatly from one sample to the other. The trend observed is higher Tc for higher concentration of OA samples.

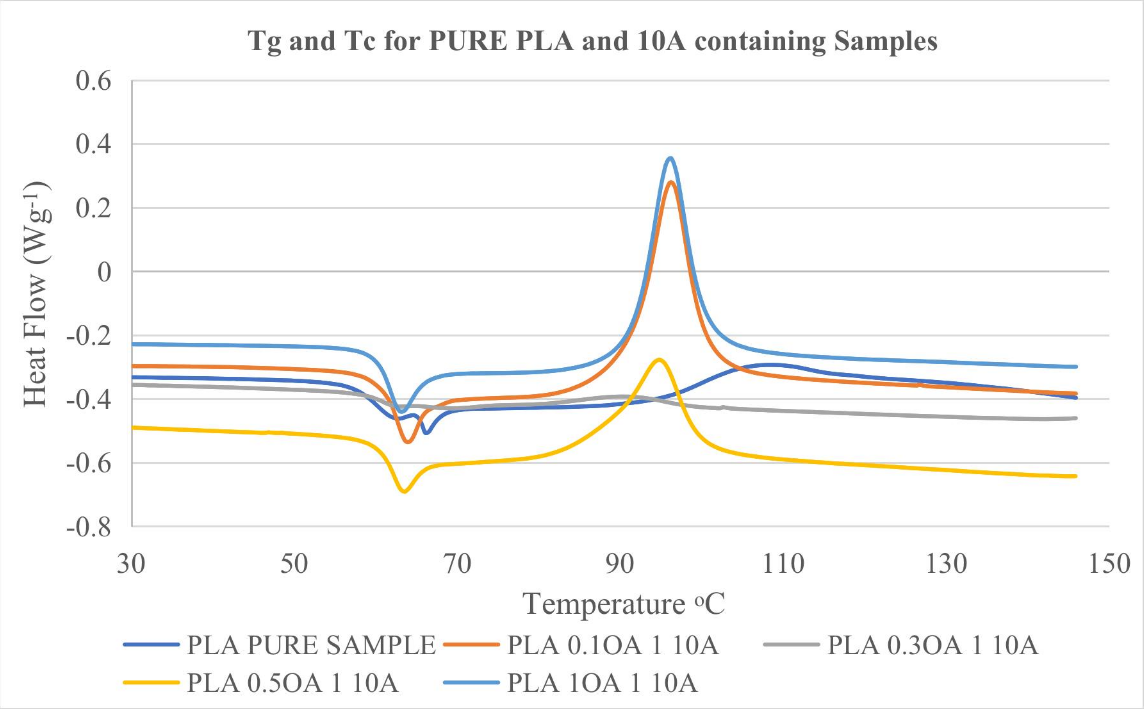


Figure 39 . A graph of T_g and T_c for Pure PLA and 10A sample

In the determination of the T_g and T_c for the 10A sample series, it was observed the results show the Tg was in the range of 60°C - 71°C. The sample containing 0.3% of OA showed the highest Tg value of 71°C and the lowest T_g at 0.1% OA. Compared to the measured value of pure PLA, it was observed that the higher concentrations of OA had higher T_g.

The T_c values for these samples showed and increasing trend from the lowest concentration of OA until the highest value was reached at 0.5% OA. the highest value of Tc was 118.67°C. beyond this concentration of OA, the T_c decreased. when compared to the values of the pure PLA, it can be deduced that the T_c values of the 10A containg samples were lower at the lower concentations of OA and higher than that of the pure PLA at higher concentrations of OA.

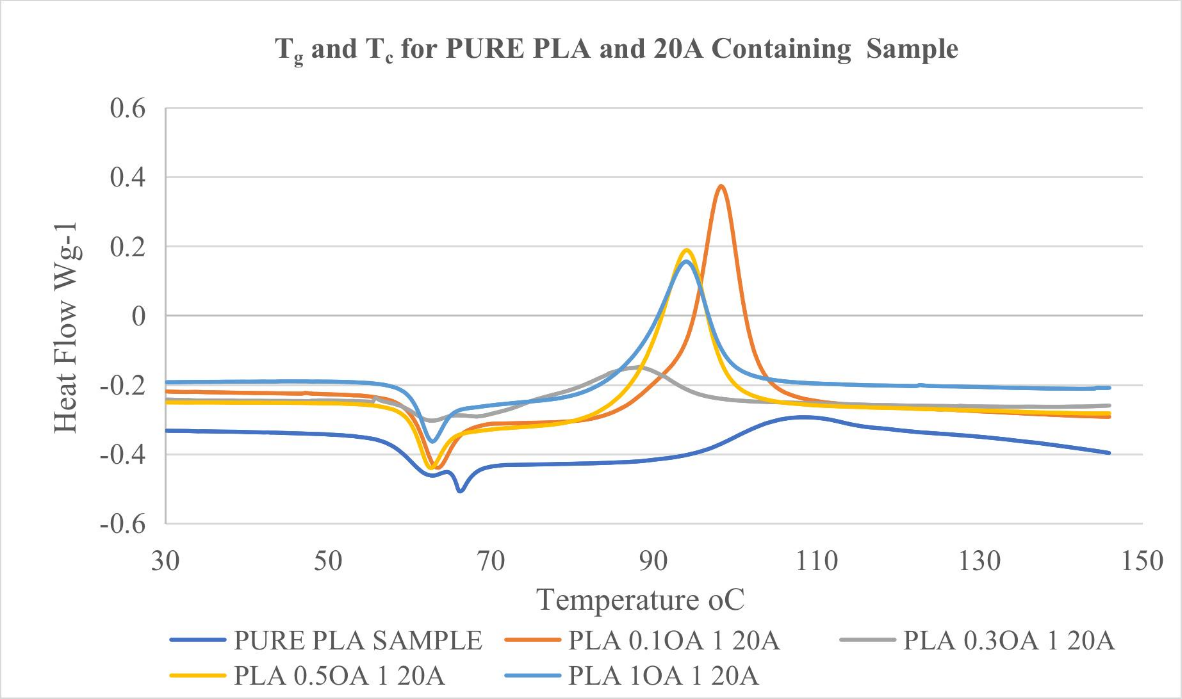


Figure 40. A graph of T_g and T_c for Pure PLA and 20A sample series

Just like in the previous prepared samples, the concentation of the OA was the determining factor in the values of T_g and T_c. As the concentration of OA changed, the glass transition temperature and crystallization temperatures also varied.

The T_g values recorded for the 20A containing samples deviat from the measured value of pure PLA by a few degrees.

In the case of crystallization T_c, the highest value is showed by the sample with 1% concentration of OA**.** At this concentration**,** the value of Tc is 123.87°C. This temperature is about 20°C higher than the Tc of pure PLA.

CONCLUSION

The diploma thesis' objective was to synthesize nanocomposite materials for packaging purposes using degradable biopolymer—in this case, PLA—and assess the composites' barrier, mechanical, and thermal qualities by pertinent testing. Above all, these qualities are crucial in the packaging sector.

The most important parameter for the application in packaging is the measurement of the barrier properties. The gas barrier properties were determined by measuring the coefficient of gas permeability for oxygen and air. The values showed all the samples have lower permeability to air except PLA L175 0.3OA 10A meaning the samples have better air permeability resistance than pure PLA. On the other hand, most of the nanocomposite samples have worse resistance to oxygen. The two samples PLA L175 0.5OA 10A and PLA L175 1OA 10A are the exception.

The water vapor permeability and water vapor transmission rates values also indicate that the samples with additives have poorer moisture barrier than the pure PLA.

The Young´s modulus, tensile strength and elongation were measured to determine the durability of the prepared samples. The different concentration of OA and nanoclay affected greatly tensile property values. All the prepared nanocomposite showed higher tensile strength values expect mixtures with 10A and 20A whose tensile strength value is equal to the pure PLA sample. The presence of the additives altered the crystal lattice structure of the PLA hence increasing it tensile strength. The sample PLA L175 0.5 OA 10A showed the highest value.

The different prepared samples showed different ductility hence different elongation at break values. Low ductility suggests that a material is fragile and will fracture before deforming substantially under a tensile stress. The highest elongation value is exhibited by the sample

PLA 0.1OA and 20A. This sample's elongattion is about 0.57% higher than that of the pure PLA.

The 10A and Na samples both showed their highest Young´s modulus (E) values at 0.5%OA while the 20A sample's greatest modulus is showed by the sample with 0.3% concentration of OA. Overall the PLA L175 0.5 OA 20A sample (2363.86 MPa) showed the highest modulus value and has the better stiffness amongst all the prepared sample.

The WAXD test confirms the effect of some additives (orotic acid and nanoclay) on the crystallinity of the sample

The thermal properties were determined by the DSC technique. The crystallization temperature raised in the presence of OA and nanoclay in almost all samples except for PLA 0.1OA 10A and PLA 0.3OA 10A , as demonstrated by the DSC experiment data. The T_g for the samples were also affected slightly while the T_m did not show any significant change for all samples.

Based on their relatively better barrier and mechanical properties, the best material from the prepared mixtures the purpose of packaging is PLA 0.5OA 10A.

RECOMENDATION

The degradability of the modified PLA should also be investigated to determine the effect of the nanoclay and orotic acid on it.

Further study should also be conducted on the antimicrobial activities of the resulting films. This will provide enough information about the usability of the nanocomposites in the food packaging application process.

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LIST OF SYMBOLS AND ABBREVIATIONS

PLA	Polylactic acid
OA	Orotic acid
LDPE	Low-density polyethylene
HDPE	High-density polyethylene
PP	Polypropylene
PCL	Polycaprolactone
PBS	Polybutylene succinate
CA	Cellulose acetate
CN	Cellulose nitrate
PGA	Polyglycolic acid
PHA	Polyhydroxyalkanoate
PVOH	Polyvinyl alcohol
PET	Polyethylene terephthalate
PBT	Polybutylene terephthalate
PVC	Polyvinyl chloride
SBR	Butadiene-styrene rubber
PU	Polyurethane
PS	Polystyrene
PBAT	(1,4-butylene adipate-co-1,4-butylene terephthalate);
LA	Lactic acid
PDLA	Poly-D-lactic acid
PLLA	Poly-L-lactic acid
PDLLA	Poly-D,L-lactic acid
MW	Molecular weight

SC-PLA	Polylactic acid stereocomplex
T_m	Melting point
T_g	Glass transition temperature
T_{cc}	Temperature of cold crystallization
T_c	Crystallization temperature
PEG	Polyethylene glycol
ATC	Acetyl Triethyl Citrate
WVTR	Vapor Permeability
WVP	Water vapor permeability
OTR	Oxygen Transmission Rate
OPC	oxygen permeability coefficient
UV	Ultraviolet
NA	Nucleating agent
DSC	Differential scanning calorimetry
Hc	Enthalpy of crystallization
WAXD	Wide angle X-ray diffraction
CO_2	Carbon dioxide
O_2	Oxygen
XRD	X-ray diffraction
SEM	Scanning electron microscopy
HB	Hydroxyl-butyrate
HV	Hydroxyl-valerate
PHV	Polyhydroxyvalerate
PHB	Polyhydroxybutyrate
E	Youngs modulus

FMCG	Fast-moving consumer goods
TPS	Thermoplastic starch
TC	Triethyl citrate
ROP	Ring-opening polymerization
MMT	Montmorillonite

LIST OF FIGURES

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