DEVELOPING THE MECHANICAL PROPERTIES OF BIO-BASED FILMS USED IN FOOD PACKAGING INDUSTRY

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ABSTRACT

DEVELOPING THE MECHANICAL PROPERTIES OF BIO-BASED FILMS USED IN FOOD PACKAGING INDUSTRY

Waste management becomes more important day by day because of increasing population of the world. Many methods have been considered as sustainability solutions. One of the popular methods for enhancing the sustainability is the disposal of the waste by biodegradable alternatives. PLA granule is the most common granule in packaging industry which is produced from biobased and biodegradable ingredients. In this study, biobased and biodegradable film production was evaluated. The PLA film is hard to form and more brittle than many films which are produced from petroleum based granules. This causes inefficiency in the food packaging and printing machine. Rigidity of PLA was reduced by using different raw materials used in shopping bags film. The shopping bags produced from Mater-Bi granules are more ductile than petroleum-based standard packaging materials. Mater-Bi granule is biobased and biodegradable like PLA granule. Both PLA and Mater-Bi granules were solved as 100% PLA, 80%PLA-20% Mater-Bi, 70%PLA-30%Mater-Bi, 60%PLA-40% Mater-Bi and 100% Mater-Bi films. Properties are changed with the difference of Mater-Bi percentage. Thickness, unit weight, efficiency, tensile strength and puncture resistance were tested for determining the mechanical properties. Another important criteria for food packaging is sealing performance, which is tested in order to ensure food safety. Marketing concerns are also important; so optical properties of the produced packaging films were tested. Films were produced between the yellowish appearance of Mater-Bi and the transparent appearance of PLA. FTIR analyzes were also conducted for analytical characterization Gas Chromatography test was performed in order to check that it is suitable for regulations in terms of food safety. The formulations were evaluated according to the test results.

ÖZET

GIDA PAKETLEME ENDÜSTRİSİNDE KULLANILAN BİYO BAZLI FİLMLERİN MEKANİK ÖZELLİKLERİNİN GELİŞTİRİLMESİ

Canlı popülasyonun artmasıyla birlikte dünyamızda atık yönetimi günden günde daha önemli bir hale gelmektedir. Sürdürülebilirlik için ambalaj atığı yönetiminde de birçok yöntem gündeme gelmiştir. Bu popülaritesi artan yöntemlerden biri de biyobozunma ile atık bertaraf edilmesidir. Yapılan bu çalışmada da biyobazlı ve biyobozunur ambalaj üretimi üzerine çalışılmıştır. Markette en yaygın olan biyobazlı ve biyobozunur ambalaj filmi PLA granülünden üretilen filmlerdir. PLA filmi mekanik özellikleri bakımdan petrol bazlı granüllerden üretilen birçok filme göre daha rijit ve şekil verilmesi zordur. Bu da paketleme makinalarında ambalaj filmine form vererek torba haline getirilmesinde kopma ve şekil verilmesi verimliliği kaynaklı problemler çıkarmaktadır. Bu problemler üzerine odaklanılarak PLA filmin rijitliğini bir miktar azaltmak için alışveriş torbalarında kullanılan Mater-Bi granülü kullanılmıştır. Mater-Bi granülünden üretilen alışveriş torbaları petrol bazlı standart ambalaj filmlerine göre daha sünek bir yapıdadır. Mater-Bi granülü de PLA granülü gibi hem biyobazlı hem de biyobozunur yapıdadır. Hem PLA hem de Mater-Bi granülleri solvente çözülüp %100PLA, %80PLA-%20Mater-Bi, %70PLA-%30Mater-Bi, %60PLA-%40Mater-Bi ve %100 Mater-Bi olarak farklı oranlarda ambalaj filmi üretilmiştir. Bu oranlarda üretilen ambalaj filmindeki Mater-Bi oranının artışı ile ambalajın özelliklerindeki değişim incelenmiştir. Mekanik özellikler kapsamında kalınlık, birim ağırlık, verimlilik, çekme-gerdirme dayanımı, delinme direncine bakılmıştır. Form verilen filmlerin yapışma performansı da gıda güvenliği için önemli bir kriter olduğundan dolayı yapışma performansındaki değişim de test edilmiştir. Gıda güvenliği ve raf ömrü için kullanılan ambalaj filminin diğer bir amacı da pazarlamadır. Bu sebeple üretilen ambalaj filminin optik özelliklerindeki değişim de test sonuçlarında bulunmaktadır. PLA'nın transparan görünüşü ile Mater-Bi'nin sarımtırak görünüşü arası optik özellikte filmler üretilmiştir. Farklı oranlarda üretilen ambalaj filmlerinin analitik olarak inceleyerek FTIR analizleri yapılmıştır. Gıda güvenliği açısından regülasyonlara uygun olduğunu görmek için solvent kalıntısı tespit testi yapılmıştır. Formülasyonlar yapılan testlerin sonuçlarına göre değerlendirilmiştir.

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CHAPTER 1

INTRODUCTION

Plastic wastes become a bigger issue day by day because plastic garbages are randomly thrown into environment. This waste management issue has become a global problem because of aggressively increasing world population, irregular urbanization and industrialization. In the absence of a solution to this problem, not only human, but also the animals suffer. It is obvious that waste management issue will pose a great threat to future generations according to statistics of waste management. On the other hand, approximately 448 million tons of plastic produced each year consumes about 8% of the world's fossil resources. If the plastic consumptions continue to increase as expected, the plastics industry will consume 20% of total crude oil production by 2050. In this case, the price of fossil-based granules will increase. It will create a commercial and technical difficulties for the packaging industry. Due to the shortage of raw materials; competition between packaging companies will increase and price of the packaging will be affected. The use of biodegradable and bio-based materials for packaging applications will be important alternative in the future for the environment in terms of sustainability. With the widespread use of bio-based packaging, oil consumption would decrease for packaging; so world oil reserves can be used in other sectors. Therefore, importance of biobased film industry is increasing, but there are some limitations such as forming difficulties of biobased films and optical properties regarding marketing.

Mechanical properties are important for flexible films. Tension settings vary according to films and printing, lamination, slitting and packaging machines. If the desirable mechanical properties are not achieved, breakage, puncture, wrinkle and deformation occur. Especially, proper tension in roller is one of the important point for packaging technology. It can be difficult to adjust the tension settings of some machines. These films produced only for petroleum-based flexible packaging film (BOPP, CPP, PET, PE, BOPA, CPA etc.) especially in the production of old-style machines. For this reason, difficulties are experienced especially in adjusting the machine tensions [1]. Biobased flexible packaging films takes more setup time compared to petroleum-based packaging films. According to European Bioplastics, it is predicted that after 2030, bio-based plastics will have a share of 70-100% in the flexible packaging industry. However, mechanical properties need to be improved for flexible biofilms, especially for machinery. Food products are also another important point for the packaging industry. For example, if we consider almond ice cream, the food product has sharp corners. These sharp corners may perforation the package. Therefore, it should be worked with a biomaterial in accordance with its puncture resistance. [2]

There are especially Poly Lactic Acid (PLA) films are pre most common bio-based films on the market. However, PLA films create problems in printing, lamination, slitting and packaging machines due to their brittle structure. When PLA film runs at the packaging machines, there are some of the mechanical issues. At the same time, perforation can be observed for sharp edged food products because of extremely brittle nature of PLA[3].

Mater-Bi films are generally used as shopping bags. These bio-based bags are weak due to their ductile nature. Due to this ductile behaviour, it causes problems in the converting and packaging process. [4]. Highly transparent and clear looking flexible packaging films are preferred in the market. Optically, PLA is preferred with its transparent feature compared to Mater-Bi which has a yellowish appearance. Boizidi kept the rate of Mater-Bi more than PLA in his study which is not common in the market, because visuality is an important marketing element for food packaging films[5]. The transparency of PLA is one of the key properties for packaging industry considerations. In this study, the plastic film that is optically more suitable for the market was produced by keeping the PLA ratio higher. Therefore, we expect the more transparent visuality.

There are several methods for producing flexible packaging films. Solvent casting is one of these methods, which granules are dissolved in suitable solvents and conditions. Flexible packaging is produced by pouring solution into the appropriate mold. The important thing in this method is to find most suitable ratio and component. It is necessary to wait enough time under suitable ambient conditions for solvent to evaporate.

In this study, solvent casting method was used to PLA by dissolving PLA and Mater-Bi granules in variable proportions. Considering the brittle nature of PLA and the ductile nature of Mater-Bi, blend biobased films were produced to reach optimum parameters. Tensile strength at break, elongation at break, puncture resistance, sealing strength, optical properties and solvent residue were measured and effect of PLA and

Mater-Bi ratios on the properties were evaluated. Each formulation analyzed in FTIR. All tests were conducted according to ASTM standards.

CHAPTER 2

FLEXIBLE PACKAGING FILMS

Plastic consumption in the global market has increased aggressively with the increasing population. Since the 1950s, approximately 450 million metric tons of plastic have been produced annually. In this period, more than 340 million tons of plastic waste was produced. It has been reported in Figure 1 that approximately 46% of this waste originates from the packaging industry [6]

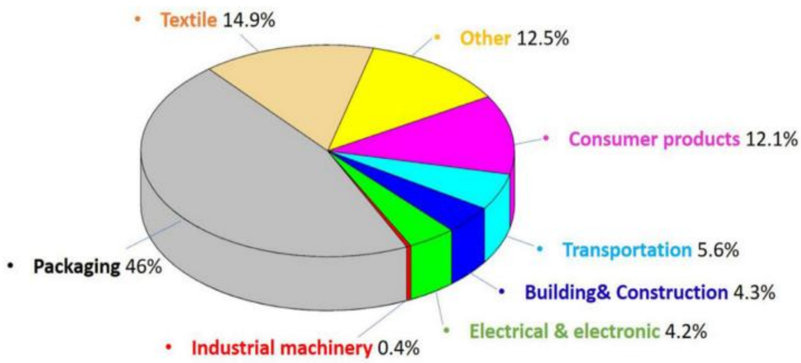

Figure 1. Classification of global plastic waste generation by industry sector in 2018 (source: O. Awogbemi et al., [6])

Packaging materials have a huge impact to population increase of the world, since suitable packaging materials improved preserving, protecting and distributing food products. Also, printed packaging materials give information about ingredients of the food products for consumers. Generally, there are flexible and rigid packaging materials are common in the world. Especially plastic films, papers, foils, some vegetable fibers, sealed and unsealed plastic bags are members of flexible packaging industry. Large part of this flexible packaging industry uses petroleum based raw materials for their products. These petroleum-based packages are not bio-based and cannot be easily degraded in nature. Approximately 95% of flexible packaging materials are made of polyolefins and polyethylene terephthalate. Printing, lamination, slitting and packaging operations on petroleum-based flexible packaging are easy on many machines because of good mechanical properties. PLA material is popular bio-based food packaging material because of availability and processibility. Main disadvantage of PLA material is brittleness. This causes processibility issues, especially in converting and packaging process. Therefore, the amount of bio-based films in the flexible packaging industry isn't as common as petroleum based packaging material. On the other hand, it is possible to find little amount Mater-Bi materials as a bio-based food packaging. The fact that Mater-Bi contains high percentage of bio-based raw materials shows significant advantages in the entire waste management cycle which reduces environmental negative impact. Some of Mater-Bi materials are very ductile such as Mater-Bi® EF05B which is used for shopping bag[4].

2.1. Petroleum Based Flexible Packaging Films

There are more than 30 types of polymers in the packaging industry. The majority of these are produced from petroleum-based raw materials. The most common types of polymers are polyolefins, polyvinyl and polyesters which are also petroleum based. CPP films and PE films are generally used for sealing layer of packaging films. PET films are generally used for printing layer. BOPP films are generally used for both printing and sealing performance of packaging films. Table 1 contains a list of some petroleum-based polymers.

Table 1. Common abbreviations for different plastic films and coating materials

Abbrevetion	Full Form
PE	Polyethylene
PP	Polypropylene
PET	Polyethylene terephtalate
PC	Polycarbonate
EVA	Ethylene vinyl acetate
PA	Polyamide
PVC	Polyvinylchloride
PVdC	Polyvinylidene chloride
PS	Polystyrene
EVOH	Ethylene vinyl alcohol

Some of the granules are also used as an additive or extra co-extrude layers in order to improve it better properties. For instance, Ethylene vinyl alcohol can be used for better oxygen transmission rate.[7]

2.1.1. Recyclable Process of Petroleum Based Packaging Materials

Recyclability is the reuse of waste materials by going through some chemical and mechanical processes. Plastics, papers, glasses and cans material can be recycled in suitable recyclable conditions and sorting centers. There are 2 types of recycling process for the plastic material.

Mechanical recycling process is including sorting and separation of wastes. During the sorting and separation contaminants are removed. Then separated plastic materials are reduced size by grinding and crushing. After that grinded and crushed plastic wastes are extruded and mechanical recycled granules are produced. However, they aren’t used for food packaging again, because food contact status isn’t available due to the contamination. Generally, they can be used non-food contact applications such as hygiene products. Polyolefins (PP and PE) cannot undergo the same mechanical recycling as PET. Because LLDPE's melting point is 115C°, HDPE's melting point is 137 C°, polypropylene's melting point is 168-176 C°. However the melting point of PET is 255 C°. There is not much difference between the melting point of PP and PE. But the melting point of PET is much higher than that of PP and PE. That's why PET can't go into the same mechanical recycling with PE and PP materials[8]. The recycling process is given in Figure 2.

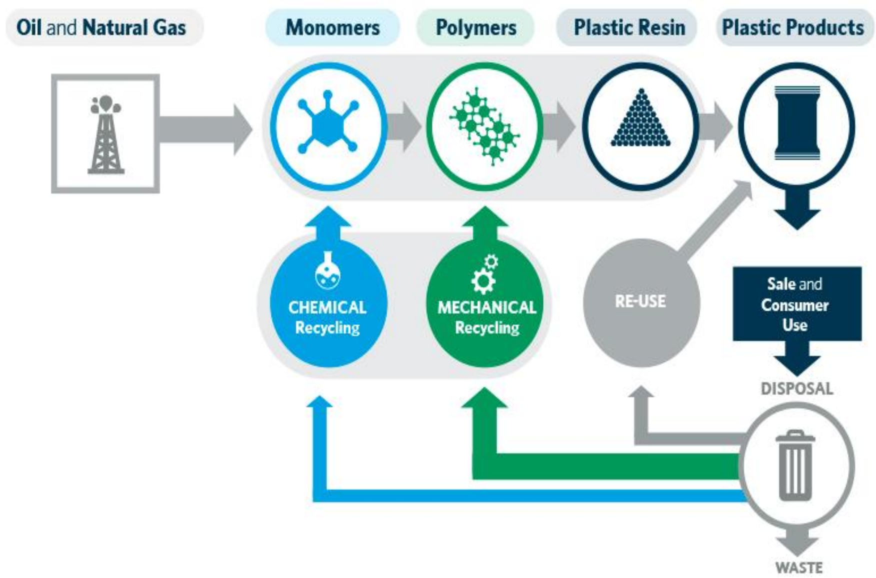

Figure 2. Recycling Process of Flexible Packaging Material
(url 9, 2023)

Chemical recycling process is including pyrolysis, gasification. After that chemical depolymerization and catalytic cracking and reforming process applied. Following the hydrogenation, chemically recycled granules can be used in industry. Chemically recycled granules' can be used in food industry. Because there is no contamination risk after chemical recycling process [10],[39].

2.2. Bio-based Packaging Films

Bio-based packaging materials are generally produced from renewable raw materials. PLA, Mater-Bi, Bio PE, Bio PP, paper materials are bio based raw materials. Generally, bio-based materials are produced from renewable materials such as sugar cane, corn stretch, and wood fibers. Therefore, biobased packaging materials are considered as environmental-friendly. According to European Bioplastics, biopolymers are biodegradable, compostable polymers derived from renewable resource [11] It is considered the most promising alternative to replace synthetic polymers in the packaging machinery industry for food products. It can be classified as thermoplastic and hydro plastic biopolymers. In general, the implementation of biopolymers is a problem for industry due to their challenging mechanical properties.[12] Bioplastics are generally available in two forms in the market. Thermoplastic scratch-based material is formulated with starch as with minor changes, Mater-Bi material is used with natural or synthetic biodegradable polymer. Scratch based materials are first fermented to obtain lactic acid. It is then polymerized to polylactic acid.[13] Bio-based packaging, which is produced from bio-based raw materials instead of using petroleum-based raw materials, is becoming increasingly popular. However, there is not only one type of bio-based packaging in the food packaging industry.

A classification can be made for the raw materials for this type of packaging. Figure 3 shows the classification of bio-based polymers used in food packaging. In the packaging sector, there are different types of bio-based raw materials used not only as the main material of packaging but also as coatings. The most widely used and commercialized bio-based packaging raw material is Poly lactic acid. For this reason, the most easily accessible bio-based raw material is Poly lactic acid. Poly lactic acid raw material, which is one of the biobased granules used in the food packaging industry, is a member of the thermoplastic polymer group.

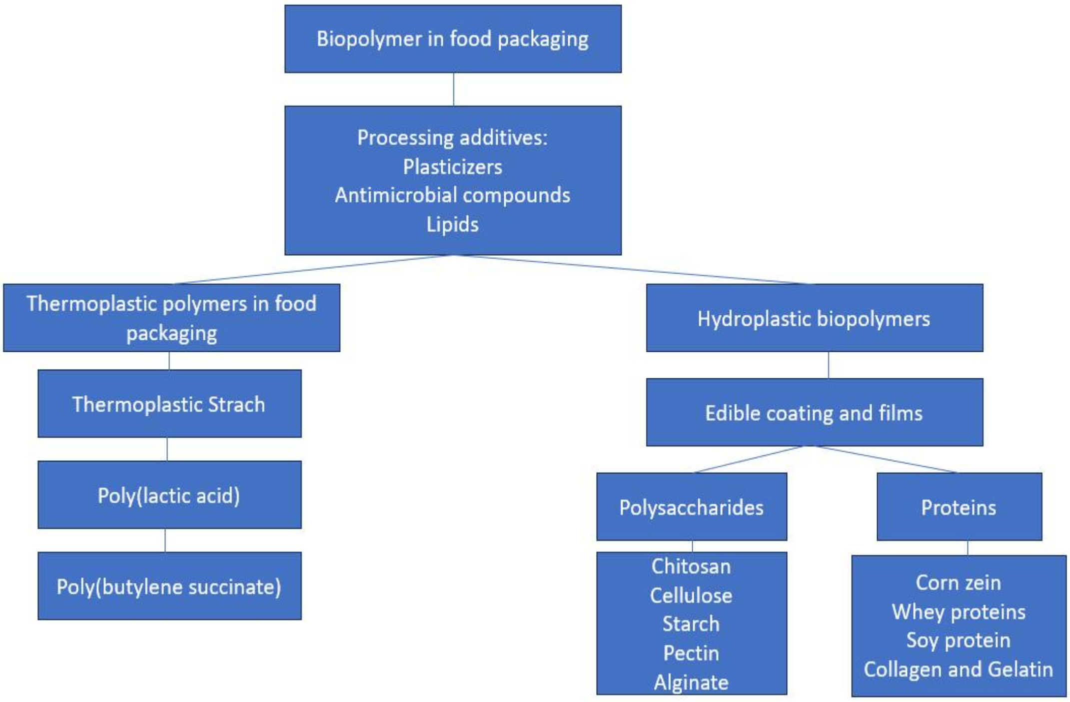

Figure 3. Classification of Food Packaging Films
(source: A. Moeini et al., [12])

2.2.1. Mater-Bi Polymer

Mater-Bi has been gaining popularity lately with the popularity of biodegradable and compostable bioplastics. At the environmental summit in Bologna, Novamont committed to providing at least 40% bio-based ingredients across the entire Mater-Bi bioplastic range [14] . Mater-Bi has compostable and biodegradable properties and a high content of renewable raw materials. It enables promising organic waste management and reduces the harmful effect on the environment. It contributes to the development of advantages for the entire production-consumption-disposal cycle[15]

Mater-Bi is starch-based and can be produced with different films in different synthetic components according to the needs of the industry. According to Bastioli, the mechanical properties of Mater-Bi films were tested with the different behavior of starch-based materials produced with these different synthetic components in terms of processability, chemical- mechanical properties, and biodegradation propensity[16].

In their study of M. Barbale et al. used Mater-Bi film in their study, which is also used in their study. They explained that the Mater-Bi film consists of biodegradable polyesters, corn starch and polyol-based plasticizers. Mater-Bi film, according to EN

13432 standard, at least 90% degradation occurs in less than six months under controlled composting conditions [17], [18],[38].

In their study of Cavallaro et al., Mater-Bi, a Novamont brand used in food packaging, has worse mechanical properties than petroleum-based films in terms of mechanical properties. Selvam and Dinaharan used different types of nanoclays to increase their mechanical properties. The changes in the mechanical properties of these nanoclays were investigated. Nanoclays used with Mater-Bi were produced by using solvent casting method. The nanoclays used in this method are alloysite, sepiolite and laponite. 30% dissolution was achieved in this blend. According to the measurements taken, mechanical properties of sepiolite nanoclay was improved as seen in Figure 4.

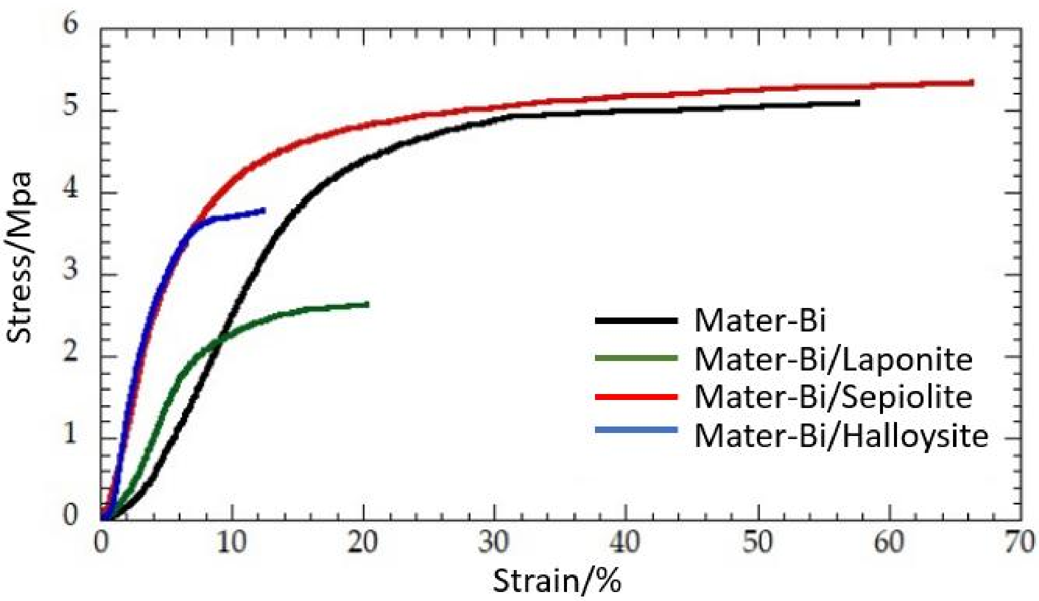

Figure 4. Stress/ Strain Diagram of Mater-Bi mechanical properties with different types of nanoclays (Source: G.Cavallaro et all., 2018 [19])

Halloysite strongly increased the hardness of Mater-Bi-based films, expanding the potential. Compared to standard petroleum-based films a relatively close performance has become possible. Sepiolite and halloysite induced an improve of the Mater-Bi rigidity of 146% and 240%, respectively [19].

In the study of S. Bouzidi et al. ,the main component of the blends studied is a thermoplastic starch-based polymer named Mater-Bi®_YI0140/C (MB) of the Novamont brand. PLLA, Ingeo® biopolymer 3D870 Natureworks (Blair, Nebraska) was used in. Compounder Joncryl-ADR® 4468 combined with two biopolymers is a commercial type of multifunctional epoxide.

In the studies conducted at different rates, the results were obtained as in the table below. Some mechanical properties were observed by forming blend with PLA material and Mater-Bi at different ratios. It has been observed that the brittle structure of PLA makes it more ductile by using Mater-Bi, as we can see Figure 5 below.

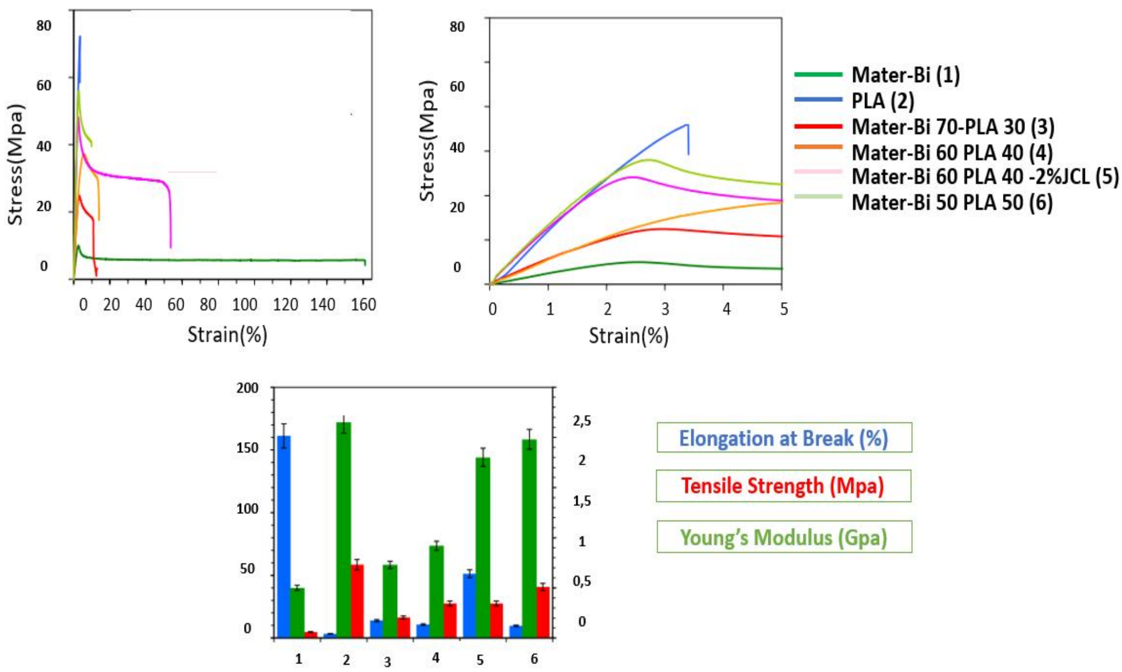

Figure 5. Change of mechanical properties of films produced at different rates (Source: S. Bouzidi et all.,2023 [37])

The inclusion of PLLA on Mater-Bi® in different proportions increased the strength and hardness of the mixture much more as PLLA increased. [37]

In the study of D. Briassoulis et al., the properties of biobased films were measured. Tests were made on the mechanical properties of samples from some trademarks. These tests were also compared with the data declared by the suppliers. These test results were compared with a standard BOPP film.

The following results were obtained according to the tensile stress values. As we can see from the test results, PLA film has a more brittle structure compared to the Mater-Bi in Figure 6 [20].

The puncture strength was also examined to see the difference in the mechanical properties of the Mater-Bi film and PLA film in Figure 7. According to test results, higher force is required for PLA puncture resistance, if we compare Mater-Bi material and other bio-based food packaging films. BOPP film's puncture resistance is higher than other bio-based food packaging.

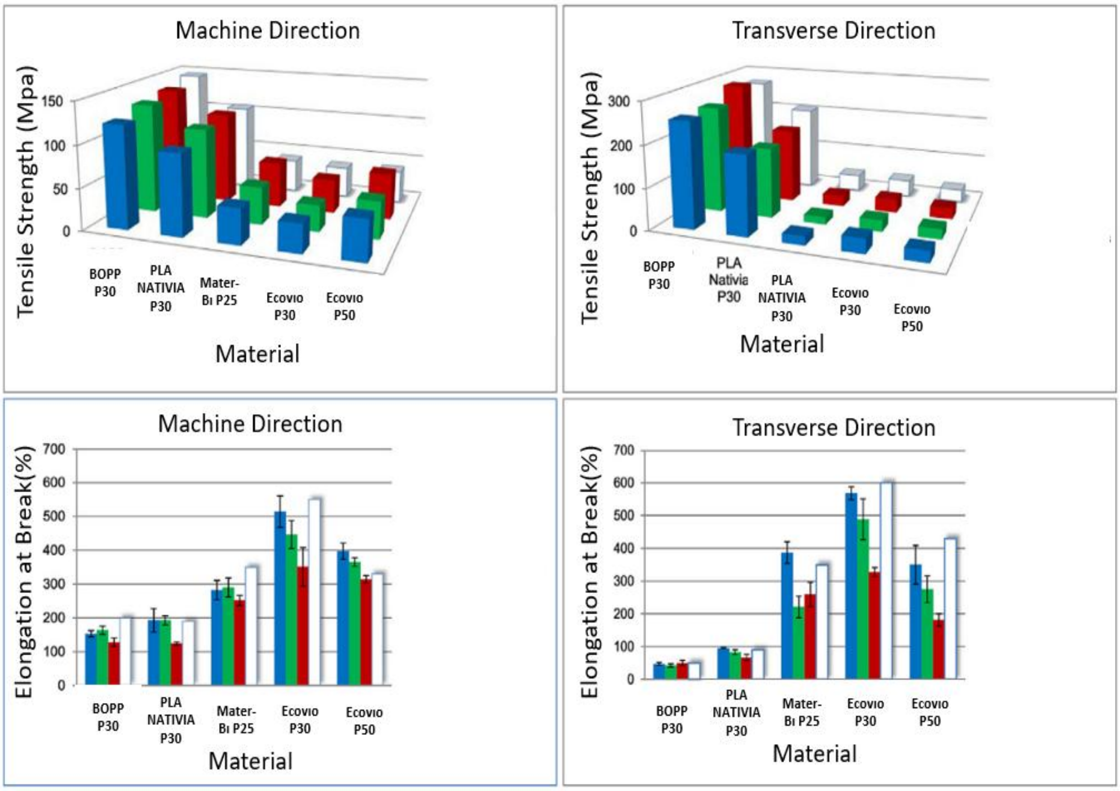

Figure 6. Change of mechanical properties of commercialized films

(Source: D. Briassoulis et all., 2018 [20])

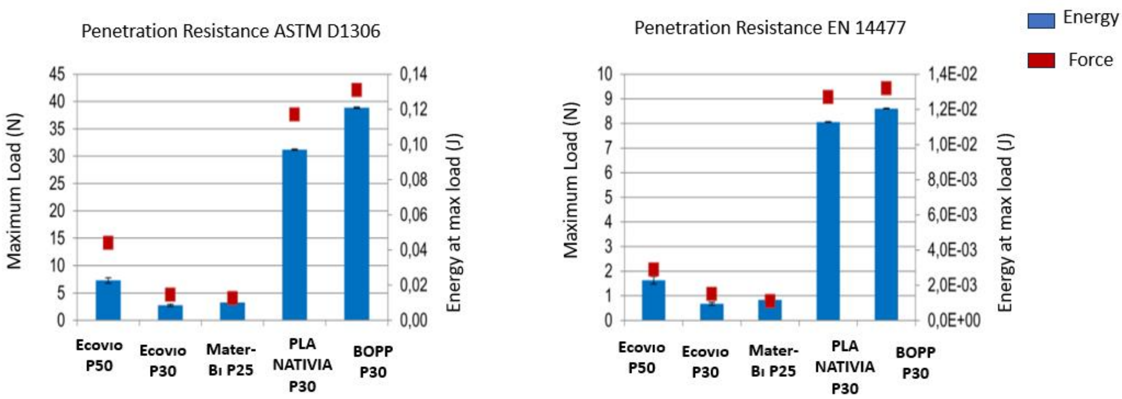

Figure 7. Change of puncture resistance of commercialized films in Briassoulis Study

(Source: D. Briassoulis et all., 2018 [20])

Sealing performance was tested from materials taken from different materials. According to the test results, the adhesion strength of PLA is higher than BOPP. BOPP's sealing performance is also higher than Mater-Bi as below in Figure 8 [20]

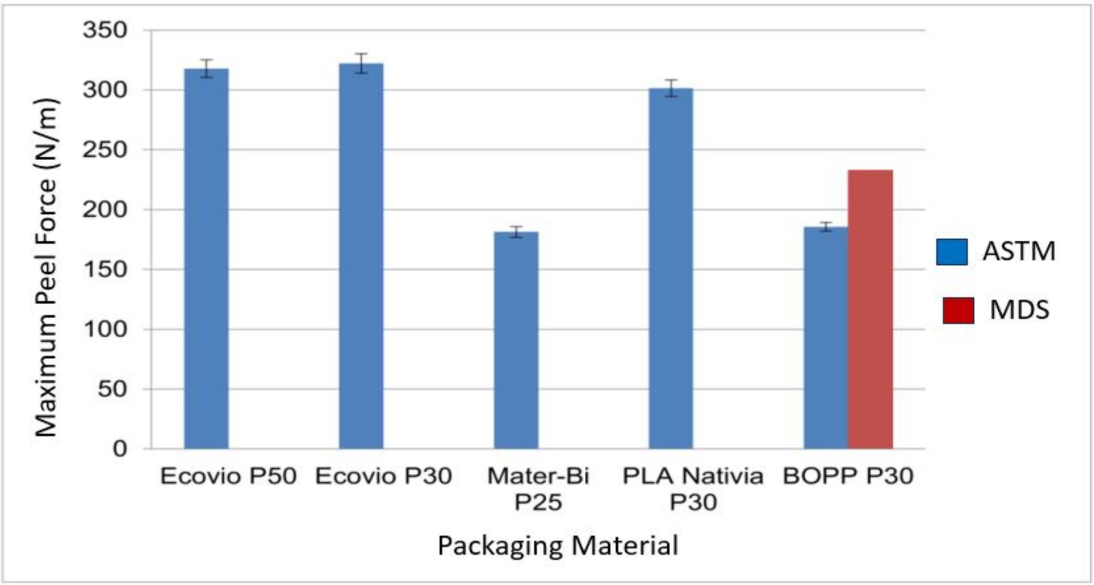

Figure 8. Change of sealing performance of commercialized films
(Source: D. Briassoulis et all., 2018 [20])

2.2.2. PLA Material

PLA is obtained from renewable resources, attracts attention as a biodegradable material in the industrial compost environment. PLA is approved by the United States Food and Drug Administration (FDA) for the current food packaging application of the traditional plastics manufacturing industry. It is in the field of use of the plastic industry, which is used in the production of widely used products and packaging materials as films, bottles and trays. PLA is biodegradable under certain conditions such as the presence of oxygen and moisture. Since PLA is biodegradable, it significantly reduces the negative impact of waste on the environment[21].

In terms of tensile, puncture and optical properties, PLA is comparable to those of synthetic polymers derived from fossil fuels such as PE, PP, PS, and PET. [12] PLA material is derived from 100% renewable resources such as starch, sugar and corn.[24] It is converted to lactic acid by fermentation or chemical synthesis. There are two ways to synthesize PLA which is shown in Figure 9. These are either direct polycondensation of lactic acid units or ring-opening polymerization in the presence of catalysts[22].

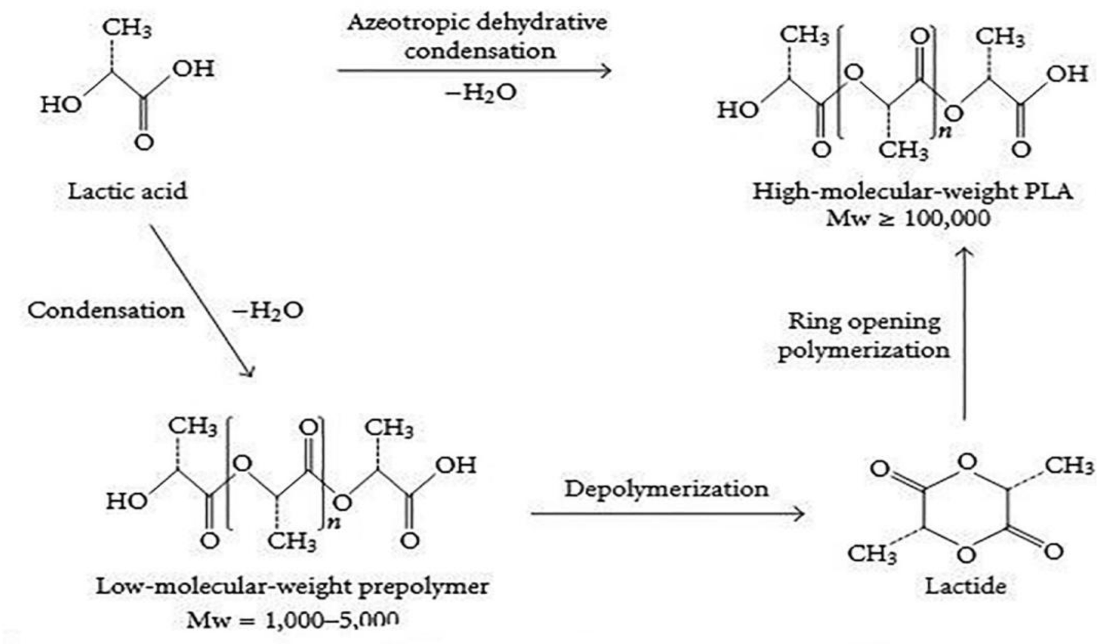

Figure 9. Production Route of PLA

(Source: S.Mohan et all., 2021 [22])

According to Ahmed J et al. study, mechanical parameters of PLA shown brittle behavior. Studies have shown that the tensile strength is 32 MPa and young's modulus was calculated as 2.3 GPa. PLA is hard and brittle with low plastic deformation ability below the glass transition temperature (Tg) (50–60◦C). It is necessary to plasticize PLA [23].

R. Plavec et al. study, changed extruder temperatures in this study 170-190-185-180 ℃ with L/D=25. Mechanical properties were examined from the films produced. From the results shown in this study, the PLA/PHB blend had better resistance to degradation under multiple thermomechanical stresses compared to the PLA and PHB polymers themselves. It has been observed that the tested material has a positive effect on the machining process and mechanical properties.

Bio-based polymeric materials have great potential in packaging because of the extreme environmental and human health benefits compared to petroleum-based films. PLA is the most famous biodegradable packaging material among all biopolymers when compared to other type petroleum based flexible packaging films. However PLA has its own limitations, such as brittleness, high gas permeability, low thermal stability, and low antibacterial activity. According to Mohan S. et al., it has been determined that the inclusion of various organic, inorganic and essential oil fillers in PLA-based blend films reduces the flexibility of PLA-based films.[22]

In the study of Nudem Deniz et al., biodegradable blends of PLA and PCL were prepared by solution mixing method based on properties between both brittle PLA and ductile PCL in Table 2. Mixtures of different ratios were prepared to examine the mechanical properties at different ratios. [25]

As PLA, they used the 4043D granule they used in their work as well. PCL65 (CAPATM6500) and PCL68 (CAPATM6800) polymers with α-Toc used as antioxidant as an additive. In Table 2 below, the mechanical changes of flexible packaging films are produced at different rates.

Table 2. Change of mechanical properties of commercialized films
(Source: Nudem et all., 2020 [25])

Sample	Tensile Strength	Elongation at Break	Young's Modulus	Thickness
P1	44,86	2,62	3208,34	23
P2	3,63	232,85	286,96	10
P3	9,74	1,44	1192,39	20
P4	19,79	2,96	1915,7	16
P5	4,71	8,21	388,79	12
P6	12,41	561,99	324,02	18
P7	19,75	5,86	1979,63	16
P8	24,53	6,08	1807,22	22
P9	11,37	4,31	823,25	23
P10	8,2	115,33	512,21	18
P11	11,86	422,45	274,87	30

With the increase of PCL ratio in PLA/PCL blends, the modulus of elasticity decreased and the elongation at break increased. In addition, with the addition of α-Toc to PLA-20%/PCL-80% mixture, the elongation at break increased compared to this film prepared without α-Toc.[25]

In this study of Trongsatitkul et al., aimed to investigate the effects of the blend films on the packaging-related properties of poly(lactic acid) (PLA). In order to improve the ductility of PLA with low-density polyethylene (LDPE) blown films, the blown film production technique was used. In extrusion grade LDPE (InnoPlus LD2426H, PTT

Chemicals, Thailand) was used as a matrix due to its ease of processing and good mechanical properties. Multipurpose extrusion grade PLA (Indigo 4043D, NatureWorks®, USA) was used. Blended films were produced in different ratios and their mechanical properties were examined. PLA/LDPE blends can combine the beneficial properties of the two polymers, such as improvements in processability and mechanical and barrier properties. Slower degradation rate can also be expected, which helps extend the service life of the PLA/LDPE product Table 3 below. [26]

Table 3. Change of mechanical properties of commercialized films
(Source: T. Trongsatitkul et all., 2017 [26])

	Modulus (Mpa)		Tensile Strength (Mpa)		Elongation at Break (%)	
	MD	TD	MD	TD	MD	TD
LDPE	134,3±23,9	7,6±2,4	14,6±3,1	14,8±1,9	361,7±86,7	525,7±42,7
5PLA	233,3±72,6	16,4±9,6	17,9±7,4	6,8±0,8	216,8±84,2	38,6±28,7
10PLA	246,9±154,4	11,5±6,2	17,8±6,3	5,6±0,9	251,4±70,2	13,0±3,3
15PLA	219,6±106,5	10,0±2,5	13,7±3,2	4,8±0,5	246,7±25,1	22,5±2,9
20PLA	1000,5±137,0	30,1±13,0	13,7±6,3	3,4±0,3	137,3±59,1	5,3±1,2

In the thesis of Ceren Özbay et al., it was aimed to prepare homogeneous blends with PLA by modifying natural rubber (DK) because of increasing its mechanical properties as Figure 10 below. In order to find a homogeneous blend, DK was first epoxied, then epoxy groups were acetylated and ester groups were added to the structure, thus ensuring compatibility with PLA in the ester structure. The mechanical properties of the films prepared at different ratios were tested in a tensile strength device.

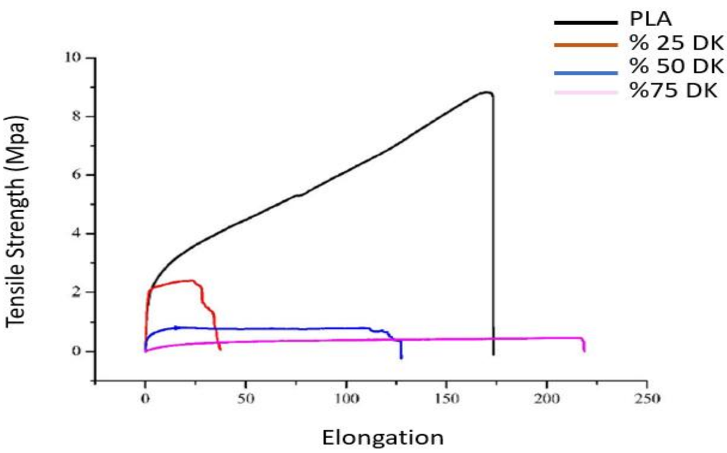

Figure 10. Change of mechanical properties of commercialized films
(Source: Ceren Özbay et all., 2019 [27])

It was observed that the tensile strength increased as the PLA ratio increased, while the elongation at break increased as the DK ratio increased. While the highest elongation at break was reached at 75% DK content, both the elongation at break and tensile strength of the other blends were lower than PLA[27].

In the study of Phetphaisit et al., modified natural rubber powder was used to increase the toughness of PLA films. The changes in mechanical properties of PLA and hydroxyl epoxidized natural rubber (HENR) by melting mixing process with twin screw extruder and blowing machine was used. Tensile test was performed on formulations prepared at different ratios. According to the test results, the following results were obtained in Figure 11 below.

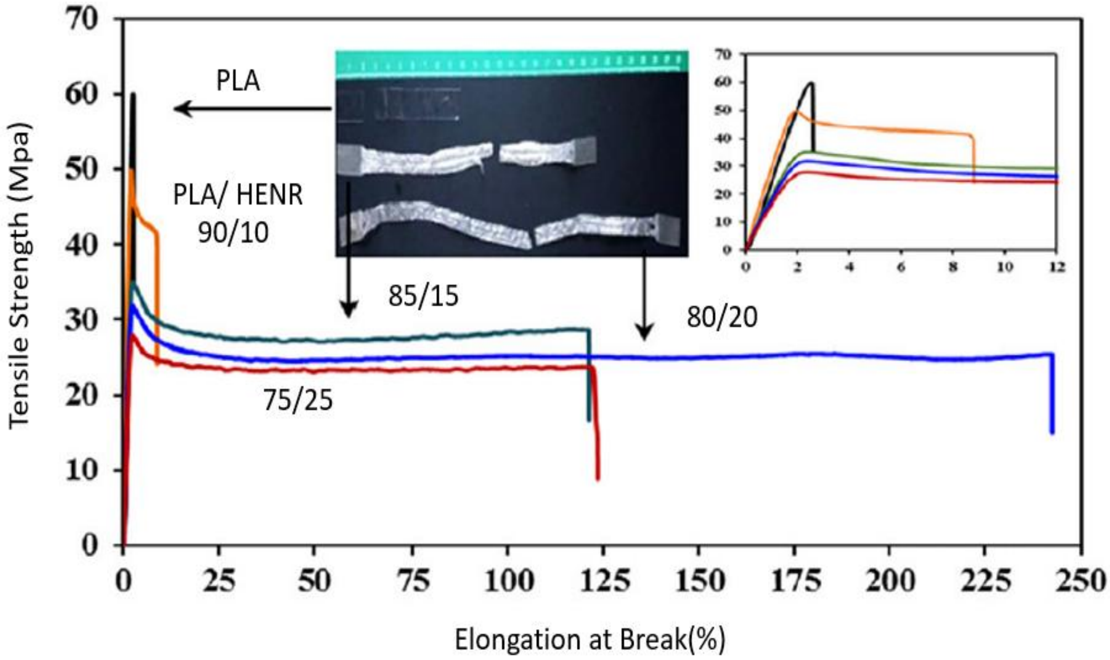

Figure 11. Change of mechanical properties of commercialized films
(Source: C. W. Phetphaisit et all., 2019 [28])

The elongation at break improved with increasing HENR content in the blend film in comparison with that of pure PLA. After the addition of 15–25 wt % HENR, the elongation of the blend increased significantly in both directions to 100–230% tensile strength of 30–40 MPa. It is also tested impact strength as a mechanical property in Figure 13. The notched Izod impact strengths of the PLA and PLA–HENR blends. The impact strength improved with HENR content from 5 to 20 wt %. It developed from 5.1 kJ m2 of pure PLA to 27.9 kJ m2 for 80/20 PLA–HENR as seen in Figure 12. [28].

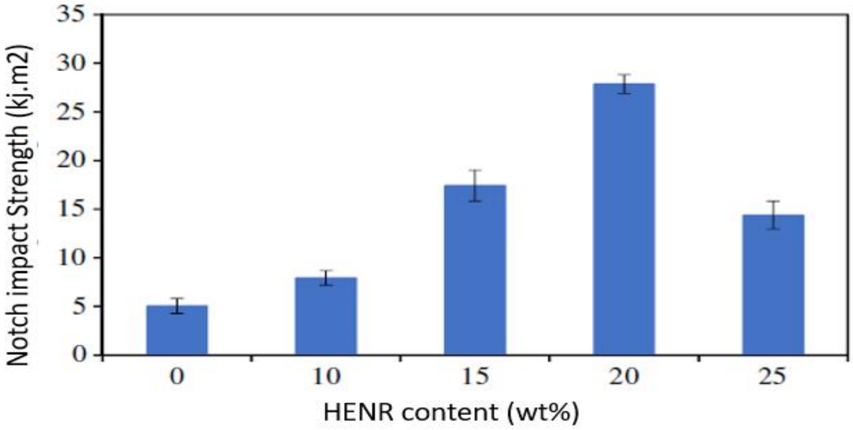

Figure 12. Change of penetration resistance of commercialized films
(Source: C. W. Phetphaisit et all., 2019 [28])

2.3. Compostable Flexible Packaging Films

Compostable food packaging materials are made from paper, plants such as palm leaf, sugar cane, potato starch and certain bioplastics. Compostable materials can be broken down in natural conditions. Composting process takes between 3-24 months. Regarding the term of the composting process, specific conditions and human-driven circumstances should be provided according to type of compostable materials. Human interventions are necessary for composting. For instance, industrial composting process is needed higher temperatures than home composting process as seen in Figure 13 below There are 2 type of compostable flexible packaging materials in the world as a home compostable and industrial compostable.

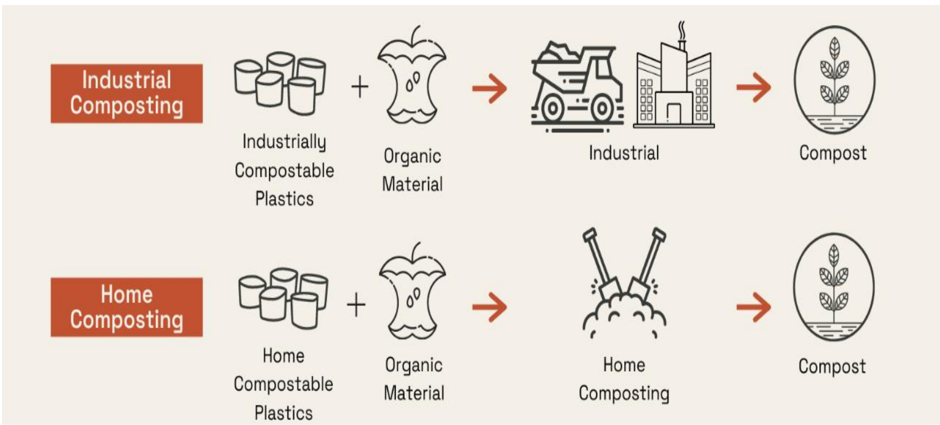

Figure 13. Difference of Home Compostable and Industrial Compostable Plastic Waste
(url 30, 2023)

Home compostable materials can be composted with household waste materials. Regarding the home composting process needs a much lower temperature and approximately 1 year. During this time, materials should be decomposed into organic soil.

Some of the conditions should be controlled specific conditions in industrial composting process. Optimal moisture, temperature and oxygen conditions should be provided. Industrial composting is more complex than home composting. The advantage of industrial composting is that large volumes of solid wastes can be composted easily in provided conditions. On the other hand, composting process doesn't take a long period as 1 year[29]–[31]

2.4. Bio- Degradable Flexible Packaging Films

Products that can be consumed by fungi and bacteria are called biodegradable products. Fungi and bacteria help to biodegrade products into microorganisms. There are some key differences between compostable flexible packaging materials and biodegradable flexible packaging materials. Regarding the compostable packaging materials, some specific conditions must be provided to degrade in nature. These specific conditions are provided in some of the special landfills. However, biodegradable flexible packaging materials can be biodegraded in nature without these specific conditions. But under suitable conditions, compostable flexible packaging materials can be degraded in a shorter time in Figure 14 below. Both solutions are better than petroleum-derived plastic flexible packaging materials that create waste in nature for centuries [30], [32].

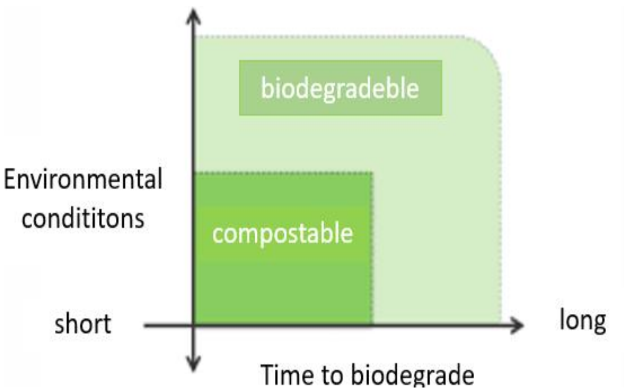

Figure 14. Difference of Compostable and Biodegradable Process
(Source: J. H. Song et all., 2009 [31])

2.5. Flexible Packaging Machines

Packaging machines differ according to the type of food and the desired packaging per minutes. The main purpose of the packaging machines is to shape the packaging material in the form of a reel and to fill the food into it. There are 2 types of packaging machines, horizontal and vertical packaging machines.

In horizontal packaging machines, the food filling cannot be vertically dropped. Food packaging is packed by dragging the food coming from the filling line horizontally. Form is shaped to the package in reel form before filling. During the forming phase, the tensions are adjusted with rollers. Sealing is provided to the formed reel with the jaws. Generally, this is achieved by temperature and pressure with jaws.

In vertical packaging machines, food filling is done vertically by falling method. The reel takes form as it passes through the dancer rollers, collar and belts. Sealing is provided by pressure and heat. In general, this type of packaging machines are used in food packaging for chips, pasta, nuts products. [34] [35] Vertical packaging machine units consist of feeding unit, collar and belts. The packaging machine driven by the motor passes through the rollers and the tension of the packaging is adjusted. For this reason, the tension of the packaging film produced is one of the most important criteria in packaging development. [33]

CHAPTER 3

EXPERIMENTAL STUDY

In the Experimental Study, films were produced using brittle PLA granules and ductile Mater-Bi granules. The mechanical properties and optical properties of these films were tested. The change in the properties of these films to be produced at different ratios was evaluated.

3.1. Materials

In this study on biodegradable packaging, studies were carried out on the mechanical and analytic properties of PLA films. In order not to change the biodegradable properties of PLA material, a search for a more ductile biodegradable film has been started. As a result of the research, 4043D polymers were supplied from Naturaworks company. This polymer has been approved by the FDA in the USA to be suitable for food packaging. In Europe, it is suitable according to EU Plastic regulations. The mechanical and physical properties of 4043D PLA granule are given in the table 4 below.

Table 4. Typical Properties of PLA 4043 D

Typical Material Properties (1)		
Physical Properties	**Ingeo Resin**	**ASTM Method**
Specific Gravity, g/cc	1.24	D792
MFR, g/10 min(2)	6	D1238
Relative Viscosity(3)	4.0	D5225
Clarity	Transparent	-
Peak Melt Temperature, °C	145-160	D3418
Glass Transition Temperature, °C	55-60	D3418
Mechanical Property		
Tensile Yield Strength, psi (MPa)	8700 (60)	D882
Tensile Strength at Break, psi (MPa)	7700 (53)	D882
Tensile Modulus, psi (MPa)	524,000 (3.6)	D882
Tensile Elongation, %	6	D882
Notched Izod Impact, ft-lb/in (J/m)	0.3 (16)	D256
Flexural Strength, psi (MPa)	12,000 (83)	D790
Flexural Modulus, psi (MPa)	555,000 (3.8)	D790
Heat Distortion Temperature, °C 66 psi (0.45 MPa)	55	E2092

Aim of the study to produce for suitable materials in the market in order to improve the mechanical properties of the brittle PLA material. Since PLA is biodegradable, a biodegradable material research was conducted again.

The Mater-Bi film series of Novamont company was considered in Table 5. Ductile materials in the Mater-Bi series were preferred to change the brittleness. It was worked with Mater-Bi® EF05B fiber, which is mostly used to produce shopping bags.

A declaration of conformity with Commission Regulation (EU) 10/2011 (PIM) on plastic materials and articles intended to come into contact with food is available for Mater-Bi® EF05B. The table contains the physical and mechanical properties of the MaterBi® EF05B material.

Table 5. Typical Properties of Mater-Bi® EF05B

Property	Unit	Test	Value	Note
THERMAL				
Melting temperature	°C	ASTM D3418	115	raw pellets
RHEOLOGICAL				
Melt Flow Rate (MFR)	g/10'	ASTM D1238	3	raw pellets, at 160°C; 5kg
MECHANICAL				
Tensile strength at break	MPa	ASTM D882	30 29	film thickness 23 µm (MD) film thickness 23 µm (TD)
Elongation at break	%	ASTM D882	300 580	film thickness 23 µm (MD) film thickness 23 µm (TD)
Young modulus	MPa	ASTM D882	390 250	film thickness 23 µm (MD) film thickness 23 µm (TD)
OTHER				
Density	g/cm^3	ASTM D792	1.28	raw pellets, at 23°C
Water Vapour Transmission Rate (WVTR)	$g/(m^2 \cdot 24h)$ $(g \cdot 30\mu m)/(m^2 \cdot d)$	ASTM E96	235 180	23°C; 50%ΔRH; film thickness 23 µm
	$g/(m^2 \cdot 24h)$ $(g \cdot 30\mu m)/(m^2 \cdot d)$		890 680	38°C; 90%ΔRH; film thickness 23 µm
Tear Resistance (Elmendorf)	N	ASTM D1922	4.5 2.5	film thickness 23 µm (MD) film thickness 23 µm (TD)
Coefficient of Friction (CoF)	adimens.	ASTM D1894	0.28 0.25	static dynamic

A suitable solvent is required to dissolve Mater-Bi® EF05B granules from Novamont and PLA 4043 D granules from Naturaworks. A solvent liquid that can dissolve both granules 100% should be used.

To dissolve both PLA 4043 D and Mater-Bi® EF05B, Tetrahydrofuran solvent product number 1.08114 of the Tetrahydrofuran EMPLURA® series supplied from Supelco was used as liquid.

In the Table 6 below, there are the components of the liquid product number 1.08114 of Tetrahydrofuran EMPLURA®, which is used as a solvent.

Table 6. Component of Tetrahydrofuran 1.08114 EMPLURA®

Component		Classification	Concentration
Tetrahydrofuran			
CAS-No. EC-No. Index-No.	109-99-9 203-726-8 603-025-00-0	Flam. Liq. 2; Acute Tox. 4; Eye Irrit. 2; Carc. 2; STOT SE 3; H225, H302, H319, H351, H336, H335 Concentration limits: >= 25 %: Eye Irrit. 2, H319; >= 25 %: STOT SE 3, H335;	<= 100 %

3.2. Blend Film Preparation

Flexible packaging films were used by using solvent casting method. A solution of 1 gram of granules was prepared in 100 ml of solvent. Flexible packaging films were used by using solvent casting method. A solution of 1 gram of granules was prepared in 100 ml of solvent. Mater-Bi® EF05B granule in 3 different ratios as 20%, 30% and 40% of the solution, 1 gram in total in different ratios, was added to the PLA 4043 D granule. For comparison, 1 gram of pure Mater-Bi® EF05B and PLA 4043 D were dissolved in 100 ml Tetrahydrofuran EMPLURA® as well. With the help of magnetic fish, the granule was dissolved in Tetrahydrofuran EMPLURA® for 40 minutes at 60 degrees temperature at 1200 cycle/min. It was rotated for 40 minutes in each solution to dissolve. In order to prevent Tetrahydrofuran from volatilizing, the mouth of the beaker was closed with an aluminum container during dissolution. After 40 minutes, the dissolved solutions were poured onto the glass petri dishes and allowed to evaporate at room temperature and relative humidity. After the evaporation of tetrahydrofuran, the flexible food packaging films produced at different mixing ratios were separated as films by peeling from the glass plate as Figure 15 below.

5 different film formulations were produced and the formulations of these films were prepared as follows in Table 7.

Blend films were poured to be casted into petri dishes as 6 ml as Figure 16 below. The technical properties of food packaging films produced in different formulations produced under the same conditions above were tested. All of the films produced were tested under the same conditions. Considering that there may be inaccuracies in the test results of the film if any different conditioning is applied, all the results have been produced same certain ASTM standards. In order to keep the test results stable, no different conditioning was applied both during the film production and during the test.

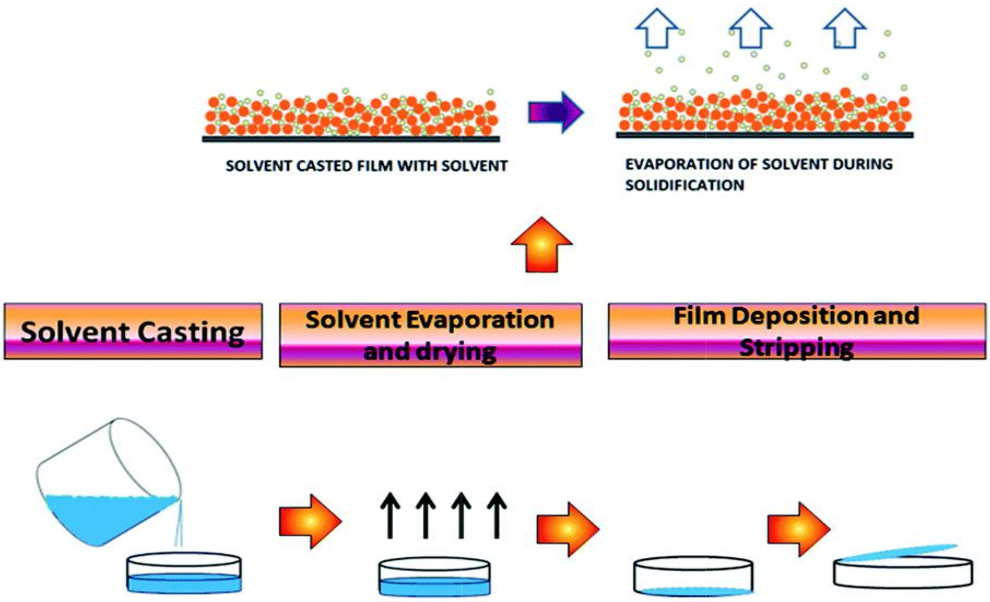

Figure 15. Schematic diagram of the Solvent Casting method

Table 7. Formulations of the produced films

- 100 % PLA (1 g PLA 4043 D with 100 ml Tetrahydrofuran)
- 80% PLA 4043 D 20 %Mater-Bi® EF05B (0.8 g PLA 4043 D + 0.2 g 20 Mater-Bi® EF05B with 100 ml Tetrahydrofuran)
- 70% PLA 4043 D 30% Mater-Bi® EF05B (0.7 g PLA 4043 D + 0.3 g 20 Mater-Bi® EF05B with 100 ml Tetrahydrofuran)
- 60% PLA 4043 D 40% Mater-Bi® EF05B (0.6 g PLA 4043 D + 0.4 g 20 Mater-Bi® EF05B with 100 ml Tetrahydrofuran)
- 100% Mater-Bi® EF05B (1 g Mater-Bi® EF05B with 100 ml Tetrahydrofuran)

Figure 16. Solvent Casted Blend Liquid

3.3. Flexible Packaging Film Properties

All the flexible packaging films' mechanical properties are different. Therefore, correct material should be used according to converting and packaging machine characteristic. In order to find the suitable film, the formulations in the different films produced were tested.

3.3.1. Determination of Thickness with Different Formulation Biodegradable Flexible Packaging Films

An electronic digital micrometer (ID -C 112 BS, Mitutoyo) in Figure 17 below with a sensitivity of 0.001m was used to measure the thickness of bio compostable flexible packaging films with different formulations. Considering that there may be surface fluctuations, the test is performed by taking 10 measurements from different parts of the produced films.

Figure 17. Micrometer for thickness measurement

3.3.2. Determination of Unit Weight and Density with Different Formulation Biodegradable Flexible Packaging Films

Unit weight calculation was tested by cutting from an area with the help of the TF513A apparatus in Figure 20 below. Density was calculated by dividing the unit weight by the thickness. Commercial agreements are made with the unit weight and density parameter.

Figure 18. Apparatus for 1dm2 area separation

3.3.3. Determination of Tensile Strength and Elongation at Break with Different Formulation Biodegradable Flexible Packaging Films

There are rollers that adjust tension in printing, lamination, slitting and packaging machines. Printing, lamination, slitting and packaging processes are carried out by passing flexible packaging film through these rollers. Packaging film is developed according to the capacity of machinery tension. If appropriate tension values cannot be adjusted for the machines, some of the mechanical problems occurs such as breakage, unexpected elongation.

Lloyd Instrument equipment was used in Figure 19 below for tensile strength and elongation at break test. Lloyd Instruments' LS materials testing machines are testing machines for materials testing up to 5 kN (1124 lbf). The machines use highly accurate interchangeable YLC Series load cells for tension, compression and cycling via zero force measurements and have an accuracy of ±0.5% from 1% to 100% of the load cell rating.

Figure 19.Equipment Tensile Strength and Elongation at Break test

3.3.4. Sealing Strength

Shelf life is one of the important point for packaging materials to protect food long term. Packaging materials should have appropriate barrier properties and hermetic seal to provide shelf life. Hermetic seal can be provided with temperature, pressure, welding time on the packaging machine side. But, not only the packaging machine, but also the packaging film is effective in hermetic adhesion. Therefore, flexible film sealing property should be considered for hermetic sealing property.

Seal strength is performed using the LS 2.5 test equipment. However, in order to sealing bond the produced films, first of all, a sealing jaw is used to ensure appropriate sealing strength. For precise measurement of the heat sealability of flexible packaging, the HSE-3 heat seal jaw of RDM company with a length of 300 mm and a width of 5 to 25 mm is used in Figure 20 below.

3.3.5. Puncture Resistance

Lloyd Instruments in Figure 21 below was used to measure the puncture resistance of flexible packaging films. The flexible film is compressed using a table by removing the clamps used in tensile stretching. With a piercing needle, a force is given until the film is perforated at certain standards. Since perforation problems may occur in products with sharp corners, the puncture resistance is tested.

Figure 20. RDM-HSE-3 Sealing Jaw

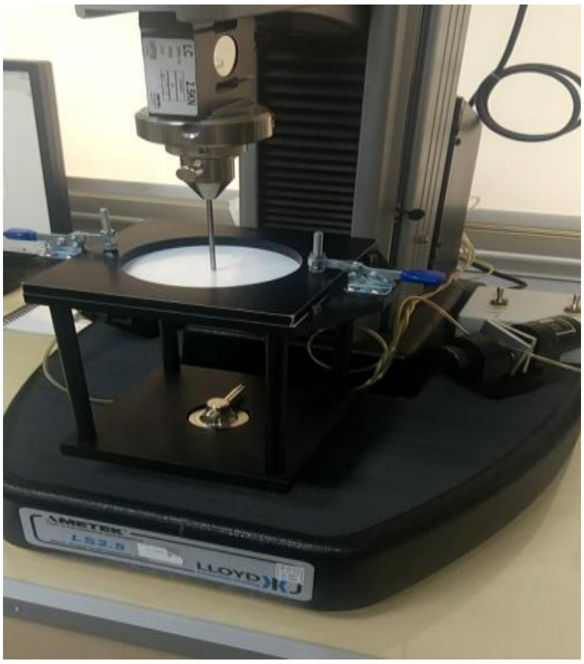

Figure 21. LS 2.5 Puncture Test

3.3.6. Optical Properties

Another purpose of packaging production is marketing the food product. For this reason, optical properties are very important to increase of commercialization. The optical properties of the packaging film to be printed on are also important. Therefore haze, gloss, transmittance, clarity measurements were measured by BYK Gardner GmbH in Figure 22 below.

Figure 22. Optical Properties Meter BYK-Gardner GmbH

3.3.7. Solvent Residue

Solvent Residue test is an analytical technique that allows the components of an organic product mixture to be separated and measured. This definition can be obtained by comparing with examples. This technique is applied in the packaging industry by separating and quantifying reagents from products and to demonstrate their results. The mixture should be dissolved in a solvent and injected into the gas chromatograph. All components are separated from the capillary column at different rates and pass through the detector, ultimately allowing the separation and quantification of compounds with similar chemical properties [36] . These films were considered to measure the solvent residue in the produced films. The solvent residue tested in the NEPTUNE 801 laboratory equipment in Figure 23 below.

3.3.8. Fourier-transform infrared (FTIR) spectroscopy

FTIR is an advanced analytical technique used to study polymeric materials. It is widely used to study microscopic fields in polymers by connecting the infrared interferometer with some detectors to the microscope. When IR radiation is passed through a material, some of the radiation is absorbed by the material and some passes through it. A signal appears in the detector. This sample has a spectrum that represents one with the molecules. The usefulness of infrared spectroscopy is due to the fact that different chemical structures (molecules) produce different spectral fingerprints as Figure 24 below.

Figure 23. NEPTUNE 801 Gas Chromatography Equipment

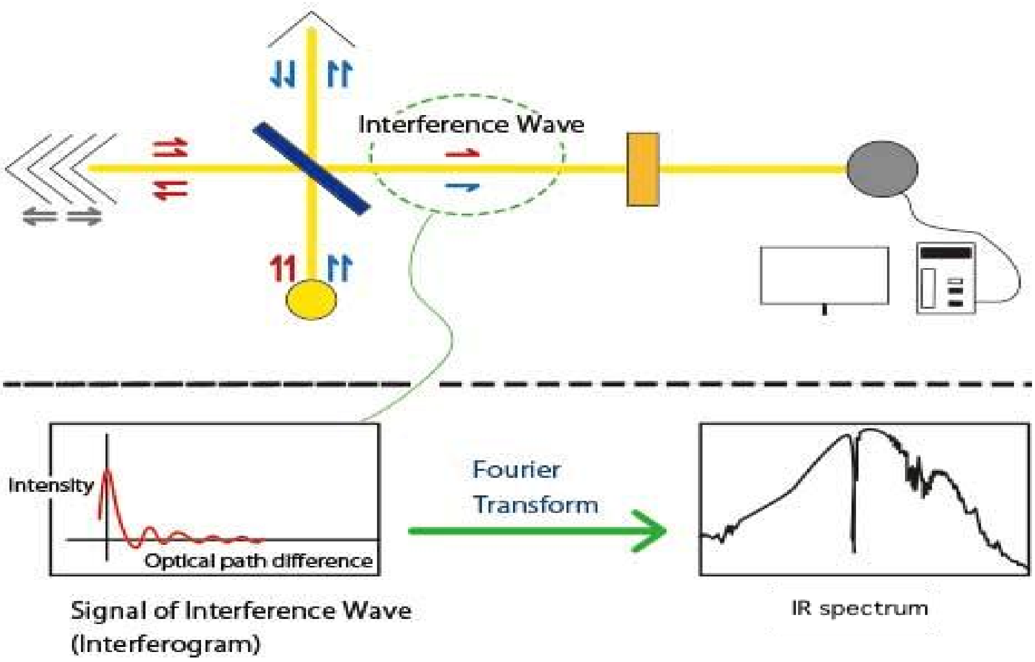

Figure 24. Working Principle of FTIR

The material content of the bio-based granules used in this study was examined using FTIR. Perkin Elmer's FTIR 100 model in Figure 25 below was used for the characterization of this materials.

Figure 25. FTIR 100 from Pelkin Elmer

CHAPTER 4

RESULTS AND DISCUSSION

The change in the mechanical properties of the produced films and the change in their optical properties according to these different ratios are tested. Different formulations have been developed according to the product to be packaged and the packaging machine capability.

4.1. Produced Films Formulations

The aim of the study is increasing the forming capability in the machine by making the brittle structure of PLA more ductile, by making it blend with the more ductile Mater-Bi material at different rates. Mechanical properties of the films produced under the same conditions in 5 different formulations were examined in Table 8 below. In order to properly compare the mechanical properties of the produced films in Figure 26 below, the thickness of each produced film is produced to be the same. Because different thicknesses directly related with the mechanical properties of the films. Tensile strength, elongation at break, sealing strength, puncture resistance, thickness, unit weight, yield and density were measured as mechanical properties. Based on these properties, the changes in mechanical properties were tested.

Table 8. Blend Films Produced at Different Ratios

- 100 % PLA (1 g PLA 4043 D with 100 ml Tetrahydrofuran)
- 80% PLA 4043 D 20 %Mater-Bi® EF05B (0.8 g PLA 4043 D + 0.2 g 20 Mater-Bi® EF05B with 100 ml Tetrahydrofuran)
- 70% PLA 4043 D 30% Mater-Bi® EF05B (0.7 g PLA 4043 D + 0.3 g 20 Mater-Bi® EF05B with 100 ml Tetrahydrofuran)
- 60% PLA 4043 D 40% Mater-Bi® EF05B (0.6 g PLA 4043 D + 0.4 g 20 Mater-Bi® EF05B with 100 ml Tetrahydrofuran)
- 100% Mater-Bi® EF05B (1 g Mater-Bi® EF05B with 100 ml Tetrahydrofuran)

Figure 26. Produced Films with Different Formulations

FTIR tests was evaluated for the structural analysis of these produced films. Haze, clarity and transmittance were measured as optical properties. Solvent residue test which is an important point for food packaging were tested as well. After the test results, the use of the film produced in food packaging technology was evaluated.

4.2. Mechanical Properties

The mechanical properties of the films planned to be produced with the granules planned to be used were tested. Tensile strength, elongation at break, sealing strength, puncture resistance, thickness, unit weight, yield and density were measured as mechanical properties.

4.2.1. Thickness Measurements of Produced Films

The aim is to test the mechanical properties of flexible packaging produced with different formulations. Therefore, the films are produced to be of the same thickness. Thickness measurements were made according to ASTM D6988 – 13 standard. The thicknesses of 5 different formulations produced in different formulations were measured to be 10 microns in Figure 27 below. The average of 10 micron thickness was tested by making 10 measurements from each different formulation.

Figure 27. Thickness of 70% PLA 4043 D 30% Mater-Bi® EF05B

4.2.3. Density, Unit Weight and Yield Measurements of Produced Films

The unit weights and densities of the films produced at different rates are as Table 9 below. Produced films were tested according to ASTM D 4321 standards.

Table 9. Unit Weight, Density and Yield Measurements at Different Ratios

Material	%100 PLA	%100 Mater-Bi	%80 PLA %20 Mater-Bi	%70 PLA %30 Mater-Bi	%60 PLA %40 Mater-Bi
Unit Weight (gr/m2)	12,10	13,02	12,31	12,42	12,82
Density(g/cm3)	1,21	1,30	1,23	1,24	1,28
Yield(m2/kg)	82,64	76,80	81,23	80,52	78,00

Densities, unit weights and yields of the produced films were tested for commercial side. If we compare the selling price of 1000 kilos, the 4043D PLA costs 3810 USD. 1000 kilos of Mater-Bi cost 3380 USD. Produced films with different ratio on purchase will be advantageous. Because the unit price of Mater-Bi is lower.

Unit weights, yield and density of Mater-Bi and PLA are close to each other. Therefore, the performance in the packaging machine will not change for each formulation.

Since the unit weight of Mater-Bi is higher, the feeling of market in the formed unit pack will be better. This will have a positive impact on marketing.

4.2.4. Tensile Strength

The tensile stresses in Figure 28 below of the films produced at different ratios were measured. Measurement results were tested in ASTM D 882 - 12 standard. The test results obtained at different rates are as follows.

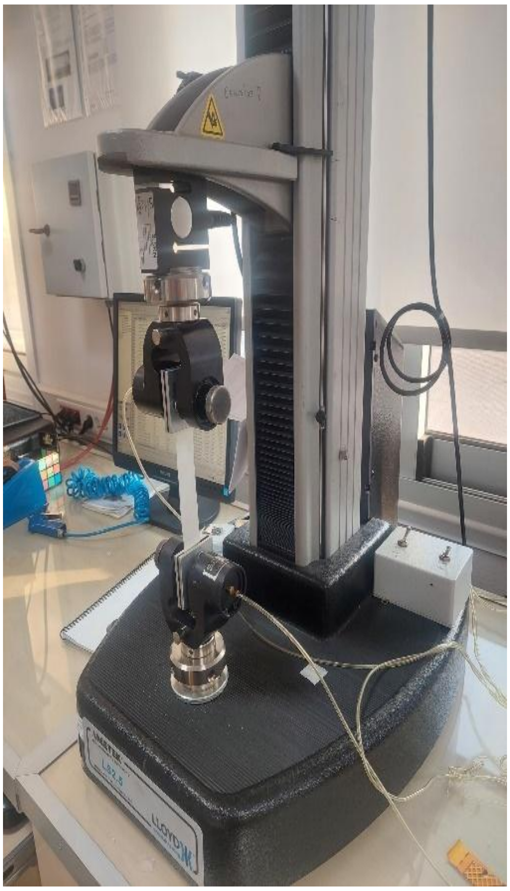

Figure 28. Tensile Strength of 100 %Mater-Bi® EF05B Measurement

According to the test measurement results made from 100% PLA material and 100% Mater-Bi® EF05B material the following results were obtained as Figure 29 and Figure 30.

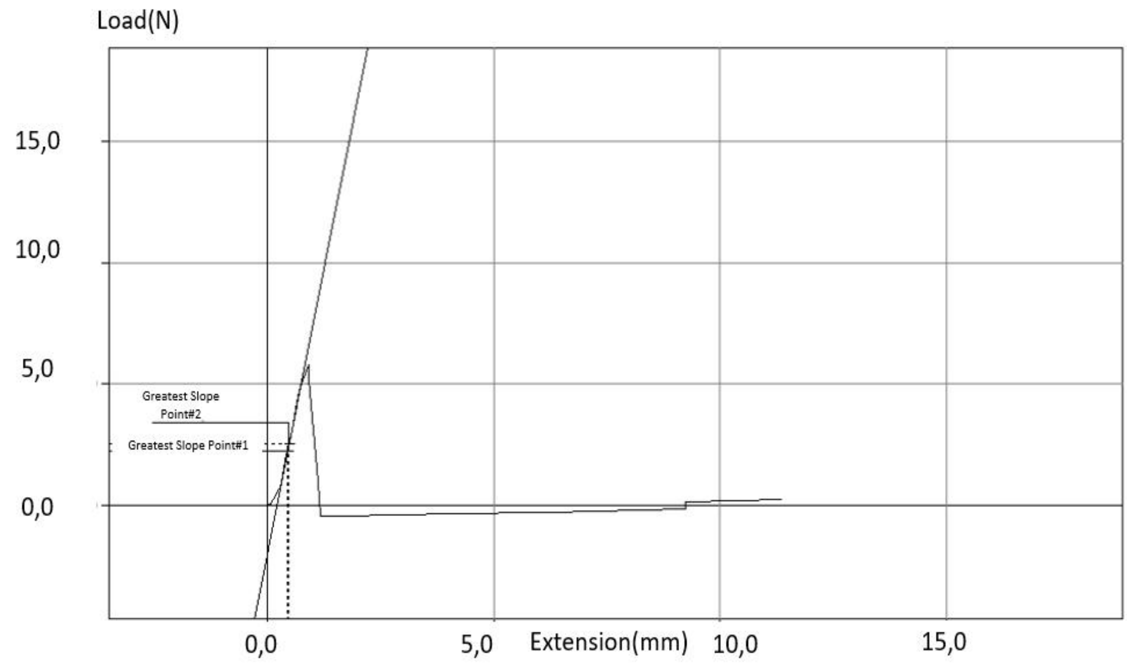

Figure 29. Tension Test Graph 100% PLA Film

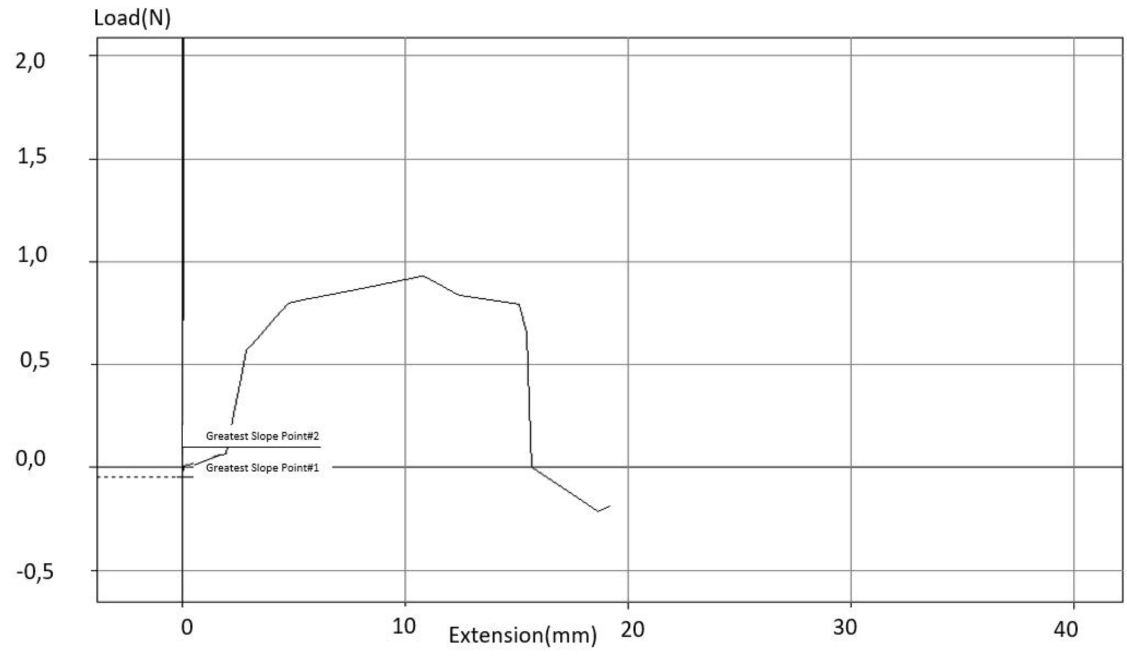

Figure 30. Tension Test Graph 100% Mater-Bi® EF05B Film

10 tests were performed from each formulation. According to the average test results, the following test results were obtained. These formulated films were tested by cutting test specimens with a width of 15 mm.

You can find the tensile strain curves for each formulation in Appendix. Comparison table of the test results in the table 10 below.

Table 10. Comparison table of the stress-strain test results

Formulation	Load at Maximum	Extension at Maximum Load	Tensile Strength	Strain at Maximum Load	Strain
%100 PLA	5.766 N	0.89926 mm	38.44 Mpa	1.9	11.3
%100 Mater-Bi	0.930 N	10.833 mm	6.2 Mpa	11.3	19.2
80% PLA 4043 D 20% Mater-Bi	4.508 N	1,5905 mm	30.053 Mpa	2.5	11.9
70 %PLA 4043 D 30% Mater-Bi	3.533 N	1.8712 mm	23.553 Mpa	2.7	13.2
60 %PLA 4043 D 40% Mater-Bi	2,759 N	2.3396 mm	18.3933Mpa	2.8	17.8

According to our tests, the mechanical properties of the films are graphically as follows in Figure 31, Figure 32, Figure 33, Figure 34 and Figure 35.

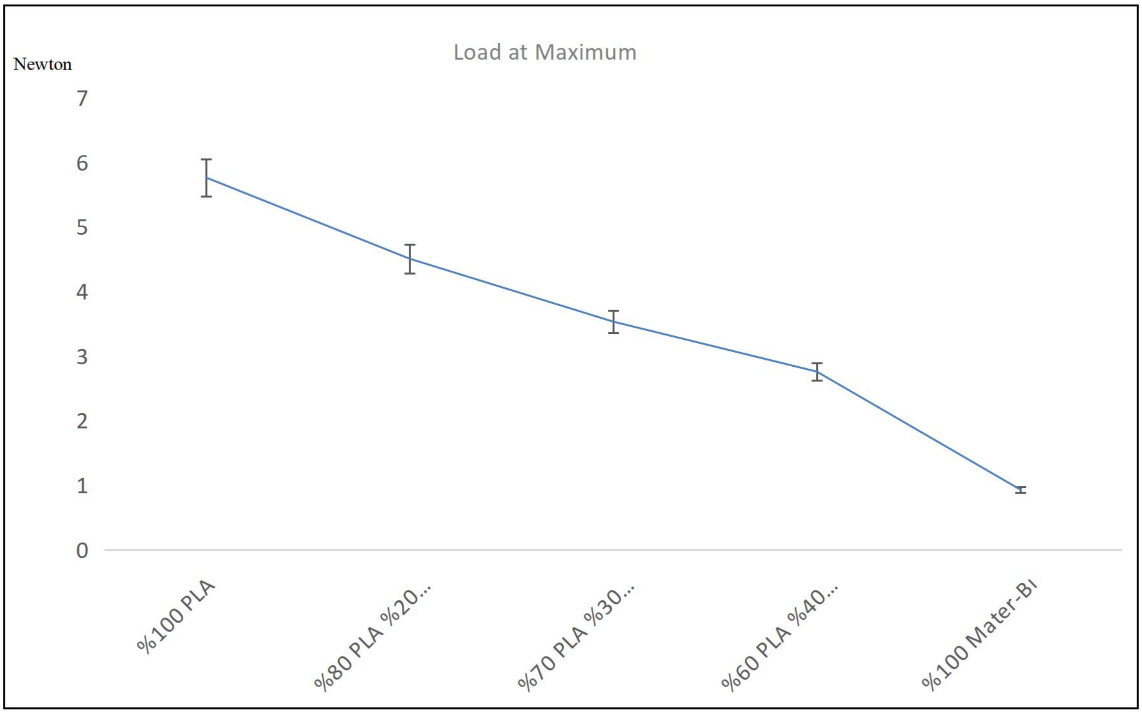

Figure 31. Load at Maximum at Tensile Test with Different Formulations

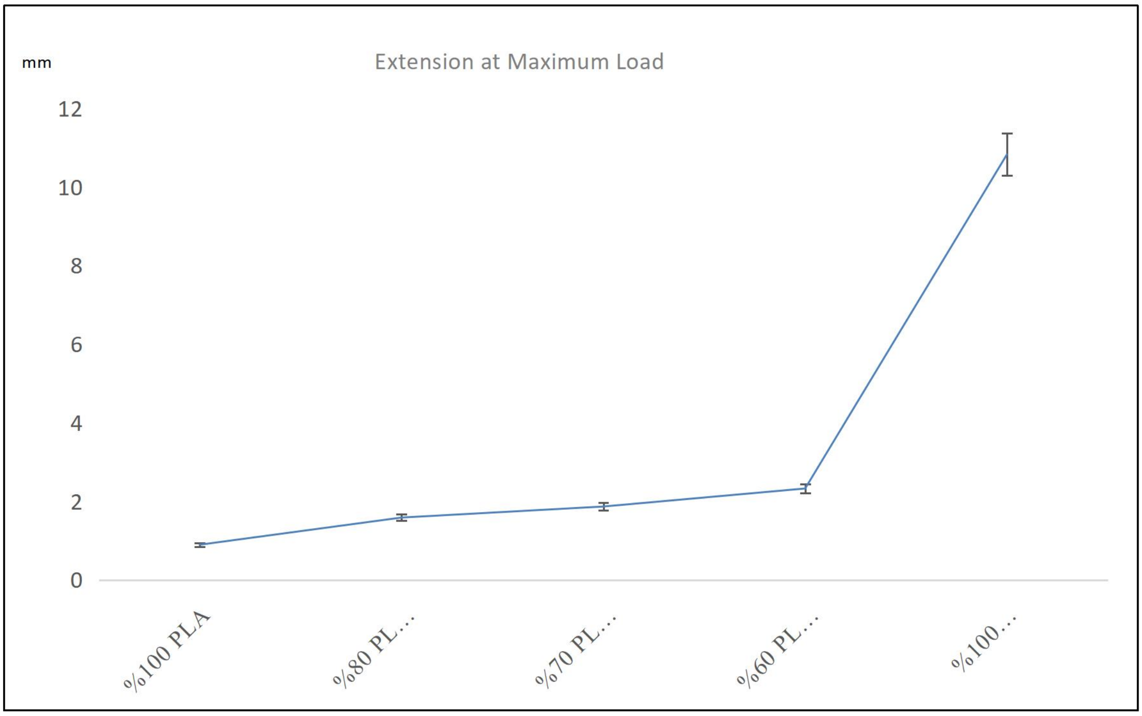

Figure 32. Extension at Maximum Load at Tensile Test with Different Formulations

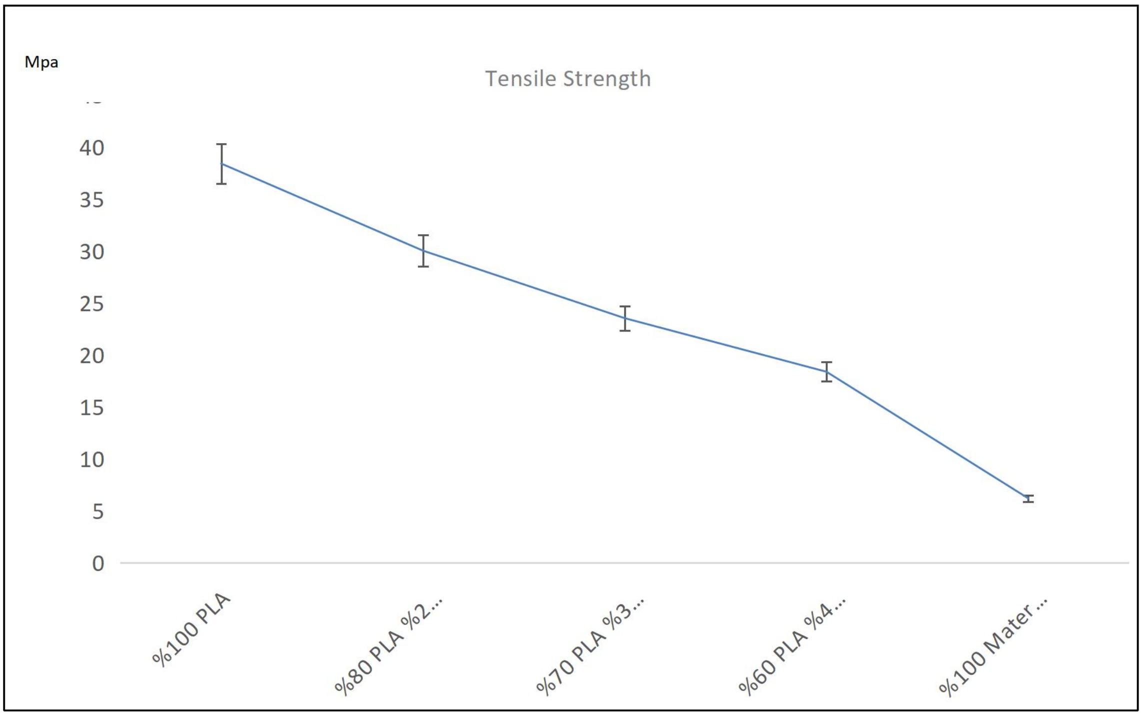

Figure 33. Tensile Strength at Tensile Test with Different Formulations

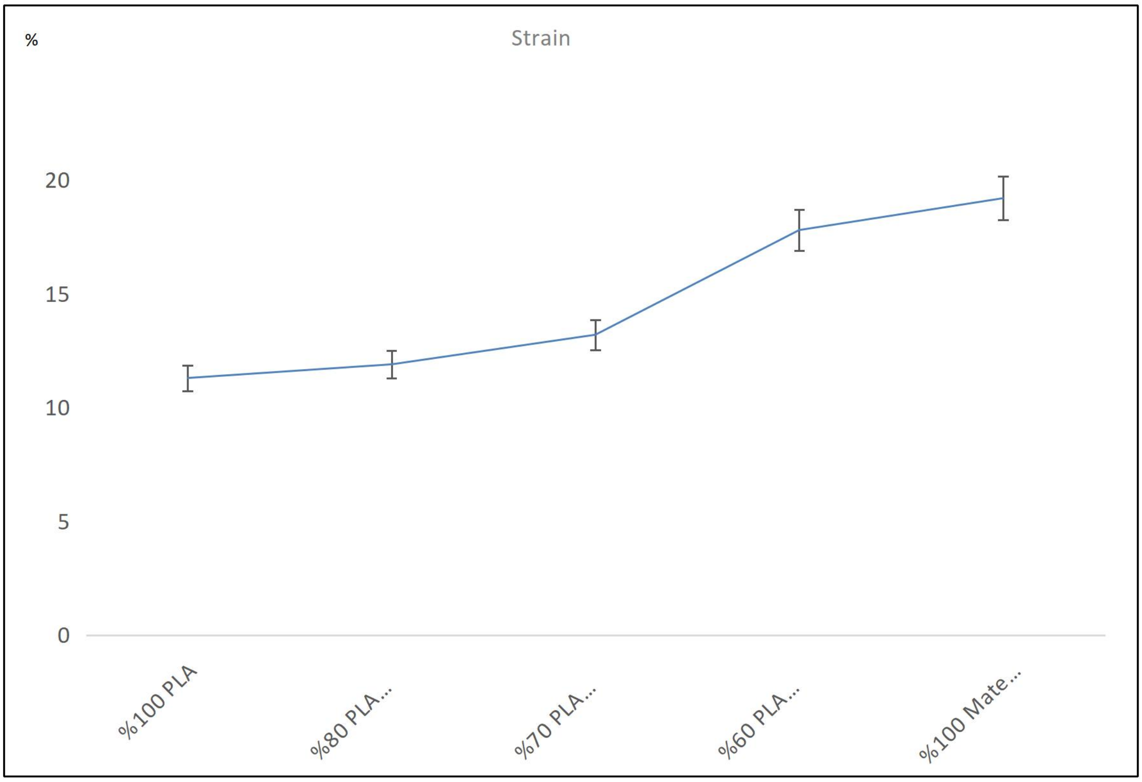

Figure 34. Strain at Tensile Test with Different Formulations

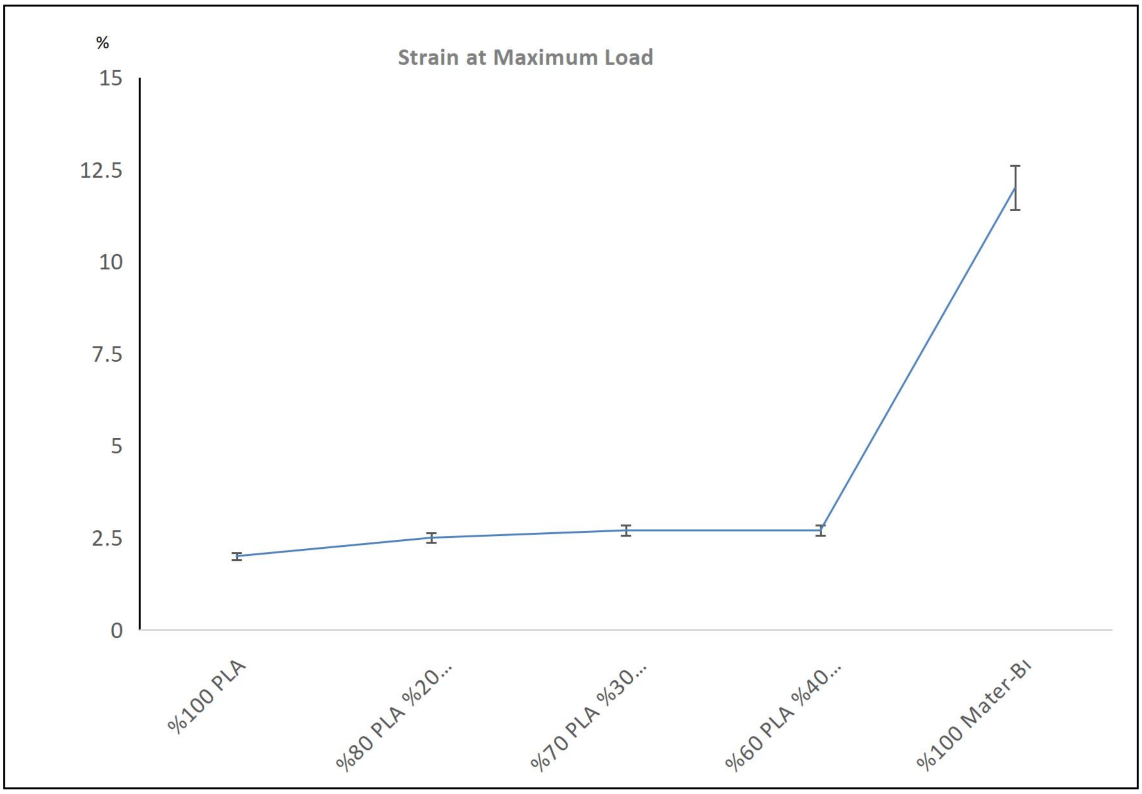

Figure 35. Strain at Maximum Load at Tensile Test with Different Formulations

It is found in the literature studies that PLA material is a more difficult structure to shape than Mater-Bi material [21]–[23]

According to the tensile test performed in the thesis, it was tested that PLA material has a more brittle structure than Mater-Bi. In the study of Y. Bouzidi, the tensile strength and strain data of 100% Mater-Bi and 100% PLA materials are close to the data in my thesis. However, Boizidi tested the mechanical property change by keeping the Mater-Bi ratio higher than PLA in his study. In my thesis, the PLA ratio is higher than the Mater-Bi ratio. In Boizidi's study, as PLA increases from the formulation, the tensile strength increases and the strain decreases. In my study, as in Boizidi's study, as the Mater-Bi ratio decreases, the tensile strength increases and the strain decreases. In particular, a very soft change was measured in strain at maximum load compared to 100% PLA.

However, as in Bouzidi's study, when the Mater-Bi ratio in the formulation is from PLA, the change in tensile strength and strain values becomes more aggressive. This shows that the mechanical properties will change more aggressively if the Mater-Bi ratio is higher than PLA. But since the optical properties of PLA and Mater-Bi are different, the scenario where PLA ratio is higher than Mater-Bi is also important for marketing studies[37]

In the test results, the material becomes more ductile as the ratio of Mater-Bi in the formulation increases. For example, in 70% PLA 4043 D 30% Mater-Bi® EF05B formulation, Tensile strength decreased by about 39%, while strain value increased by about 16%. This shows that PLA can become more ductile with this experiment.

In the printed film, strain at maximum load will be important in order to protect the quality of the printing film visuality and prevent it from shrinking. An increase in the Mater-Bi ratio has a positive effect. However, strain at maximum load data increased approximately 0.4% with 10% increase in Mater-Bi in each formulation.

As we will see in the test results, the increase in the ratio of Mater-Bi in each formulation increases the processability.

4.2.5. Puncture Resistance

The puncture test results were checked for the possibility of sharp corners of the food product to be placed in the packaging. The test in Figure 36 results of the films produced at different ratios using the ASTM F 1306 - 16 standard are as follows. According to the test measurement results made from 100% PLA material, the following results were obtained as Figure 37.

Figure 36. Puncture Resistance of 100% Mater-Bi® EF05B Measurement

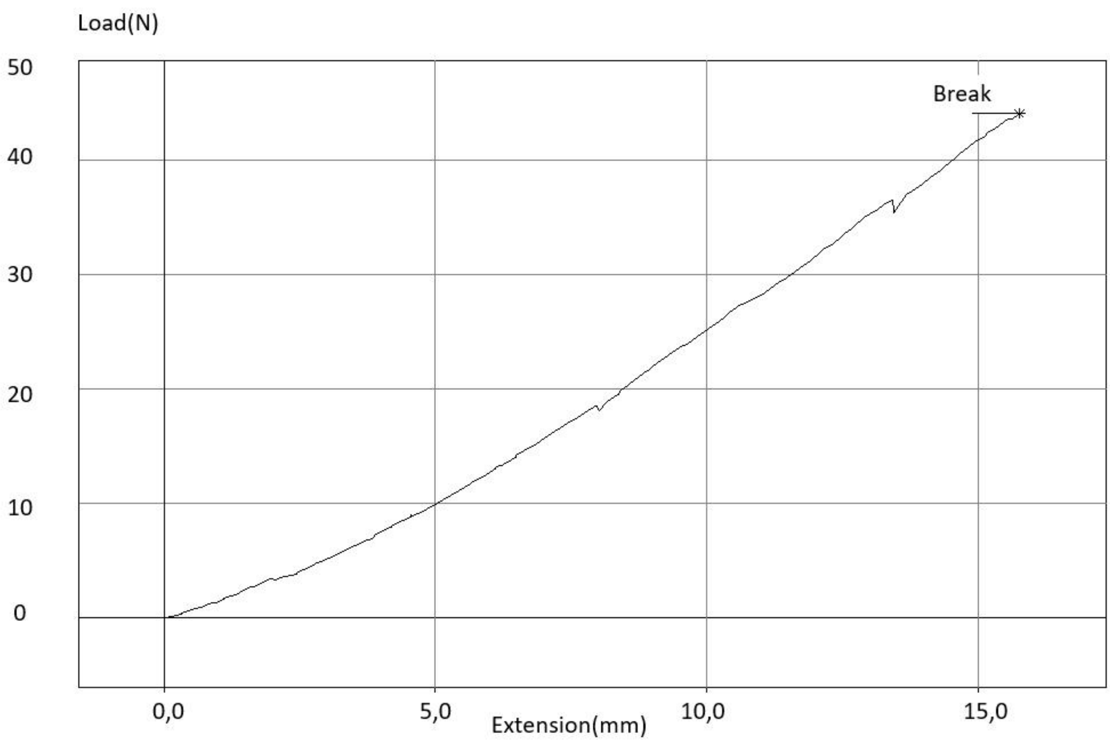

Figure 37. Puncture Resistance Graph of 100% PLA Film

According to the test measurement results tested from 100% Mater-Bi® EF05B material, the following results were obtained as Figure 38.

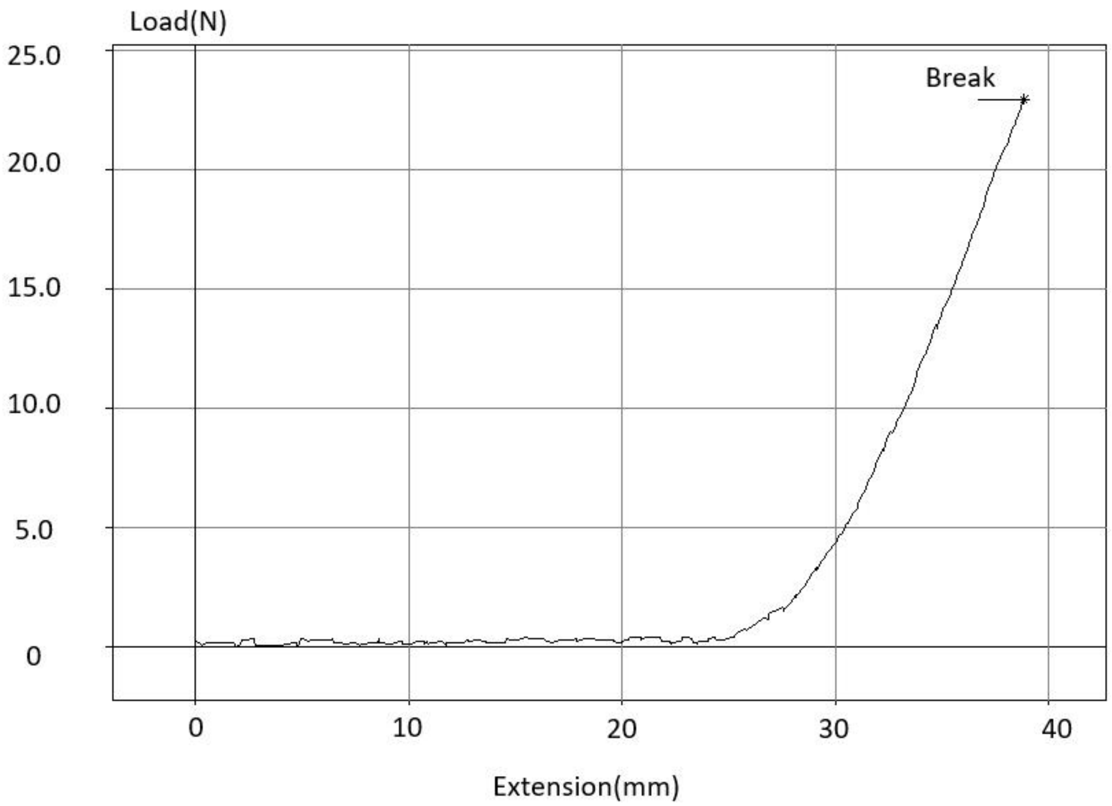

Figure 38. Puncture Resistance Graph of 100% Mater-Bi® EF05B Film

You can find the puncture test graph for each formulation in Appendix. Comparison table of the test results in the table 11 below. 3 tests were performed from each formulation. According to the average test results, the following test results were obtained.

Table 11. Comparison table of the stress-strain test results

Formulation	**Load at Break**	**Extension at Break**	**Stress Break**
%100 PLA	44.082 N	15.768 mm	5.5503 N/mm²
%100 Mater-Bi	22.904 N	38.813 mm	2.8838 N/mm²
80% PLA 4043 D 20% Mater-Bi	41.874 N	19.17 mm	5.2723 N/mm²
70 %PLA 4043 D 30% Mater-Bi	35.517 N	24.29 mm	4.4719 N/mm²
60 %PLA 4043 D 40% Mater-Bi	29.537 N	25.180 mm	3.7190 N/mm²

According to our tests, the mechanical properties of the films are graphically as follows in Figure 39, Figure 40 and Figure 41 below.

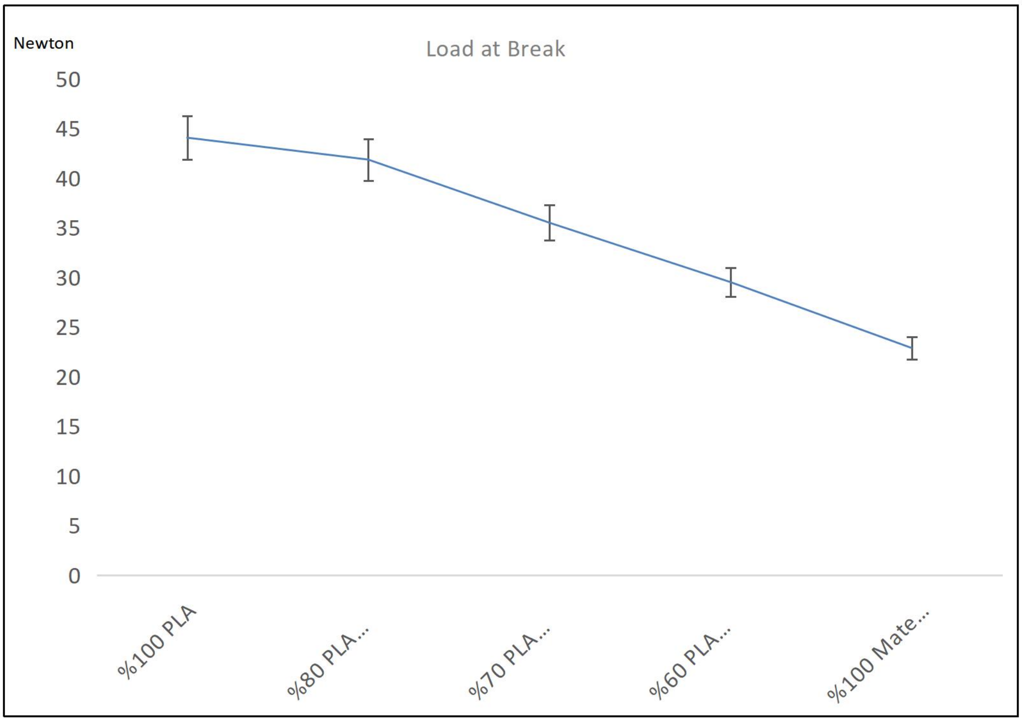

Figure 39. Load at Break Comparison with Different Formulations for Puncture

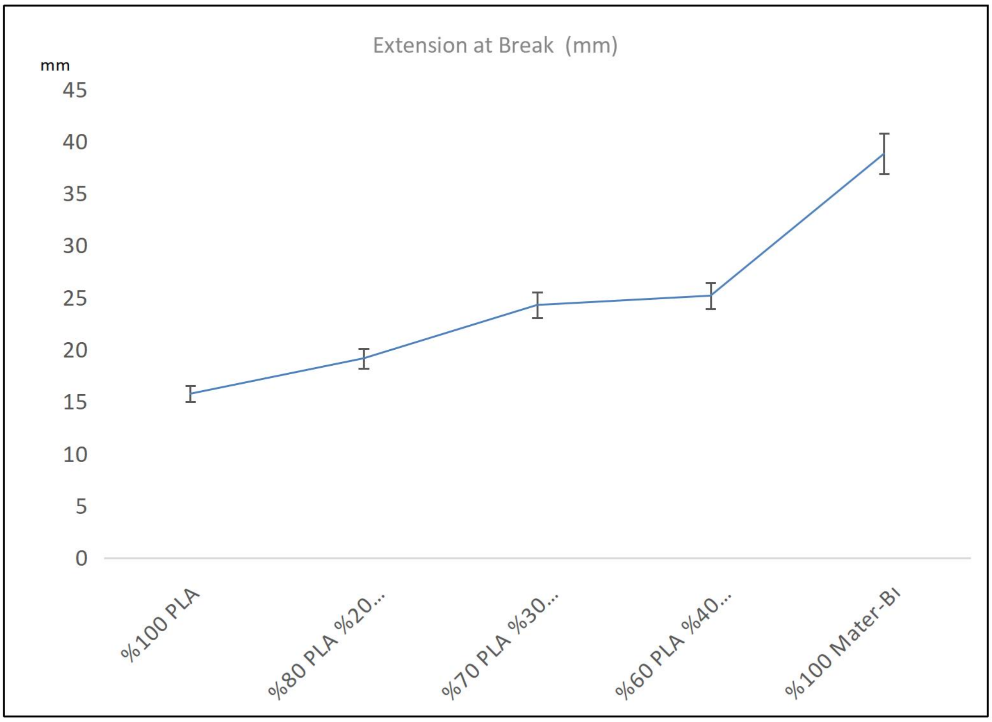

Figure 40. Extension at Break Comparison with Different Formulations for Puncture

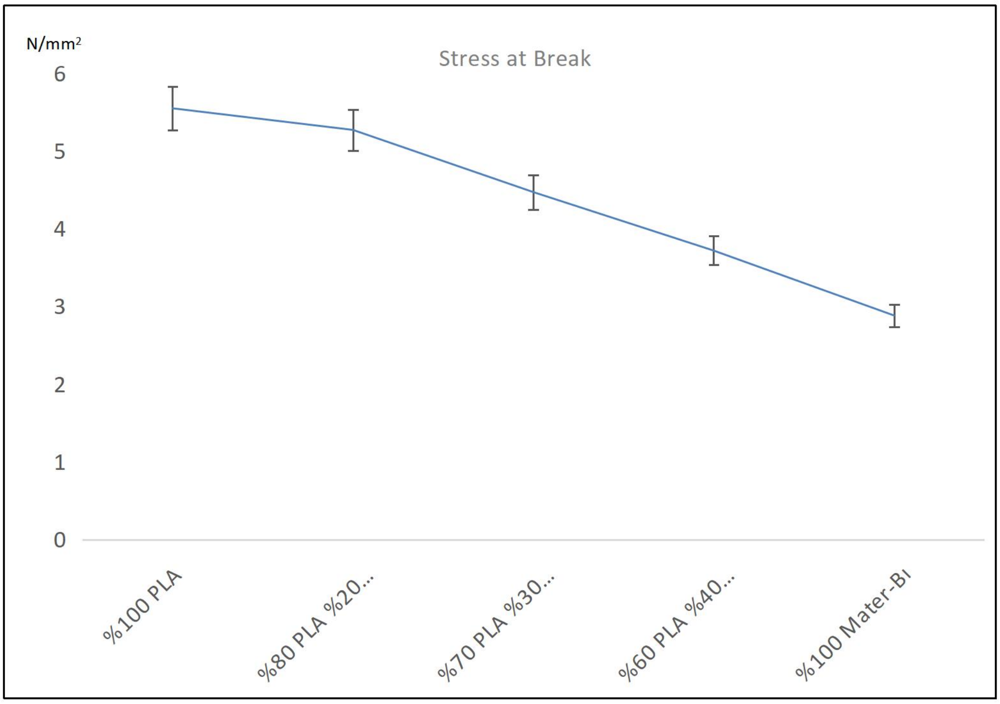

Figure 41. Stress at Break Comparasion with Different Formulations for Puncture

According to the study, the puncture force of PLA is nearly 2 times that of Mater-Bi. Although the extension of Mater-Bi film is higher than PLA, the energy it absorbs is less than PLA. In general, Mater-Bi was not very dominant in extension. Therefore, it does not provide puncture resistance in products with sharp edged products. Therefore, the produced films are not suitable for packaging sharp edged products in terms of puncture strength. In parallel study of Brisasoulis with different PLA and Mater-Bi granules, PLA is more convenient than Mater-Bi for sharp edged food products [20] The puncture performance of PLA 4043 D film tested to be better than Mater-Bi® EF05B film. As the ratio of Mater-Bi increases in different formulations, the puncture strength decreases.

4.2.6. Sealing Properties

The sealing force must be provided in order to ensure the integrity of the packaging. Even if the desired sealing force changes from the product to be packaged, it is necessary to take measurements of more than 3 Newtons at 15 mm. The measurements were tested in ASTM F 88 standard at 130 degrees 3 bar 0.8 seconds.

According to the test measurement results made from 100% PLA material, the following results were obtained as Figure 42 below.

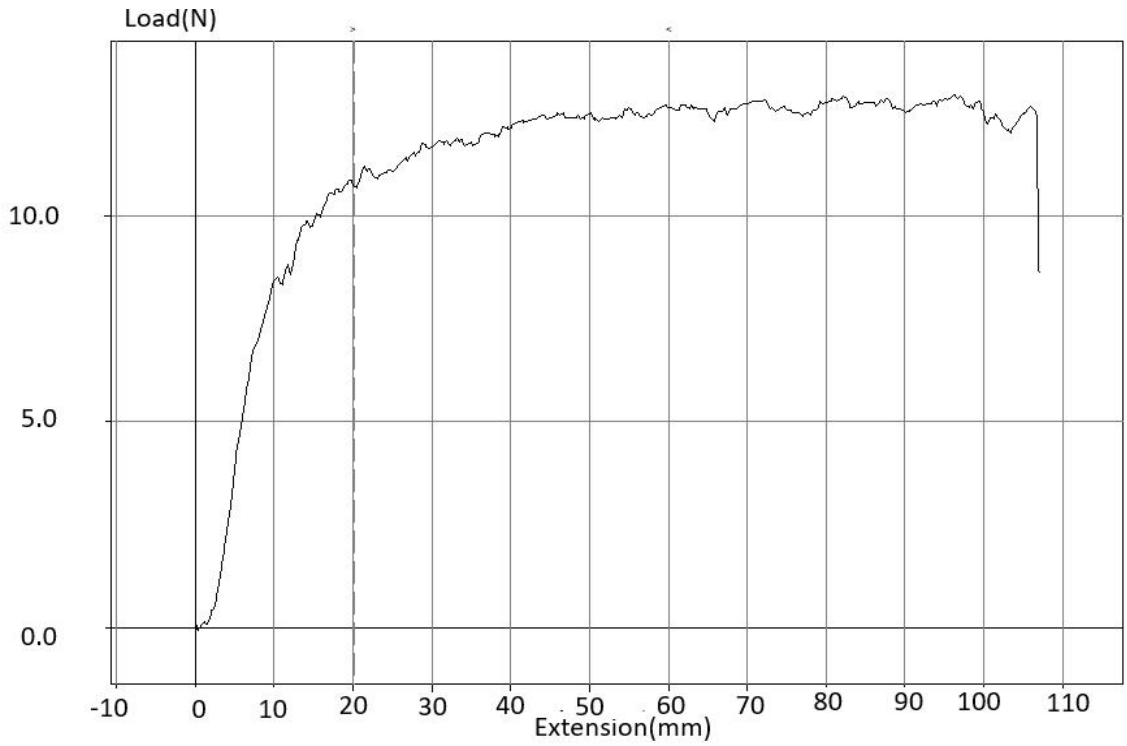

Figure 42. Sealing Test Graph of 100% PLA 4043 D

According to the test measurement results tested from 100% Mater-Bi® EF05B material, the following results were obtained as Figure 43 below.

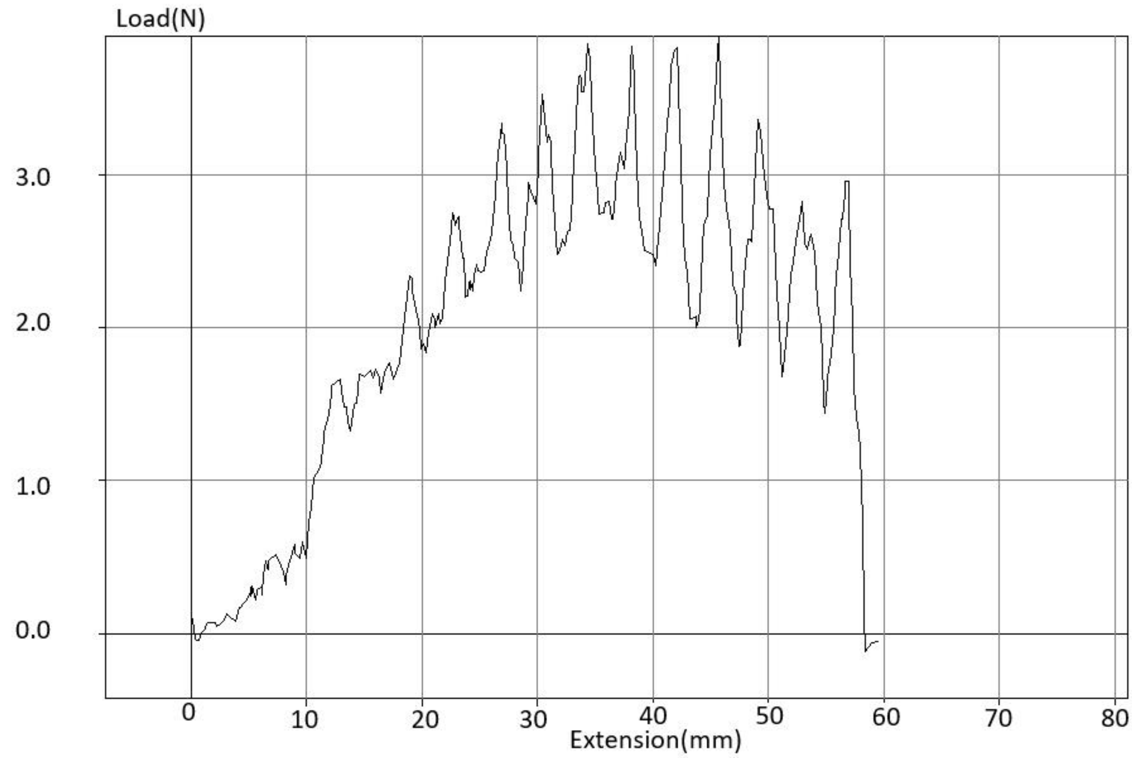

Figure 43. Sealing Test Graph of 100% Mater-Bi® EF05B

You can find the sealing test graph for each formulation in Appendix. Comparison table of the test results in the table 12 below. 3 tests were performed from each formulation. According to the average test results, the following test results were obtained.

Table 12. Comparison table of the sealing test results

Formulation	Load at Maximum
%100 PLA	11.89 N
%100 Mater-Bi	3.89 N
80% PLA 4043 D 20% Mater-Bi	8.88 N
70 %PLA 4043 D 30% Mater-Bi	7.02 N
60 %PLA 4043 D 40% Mater-Bi	6.91 N

According to our tests, the sealing properties of the films are graphically as follows in Figure 44 below.

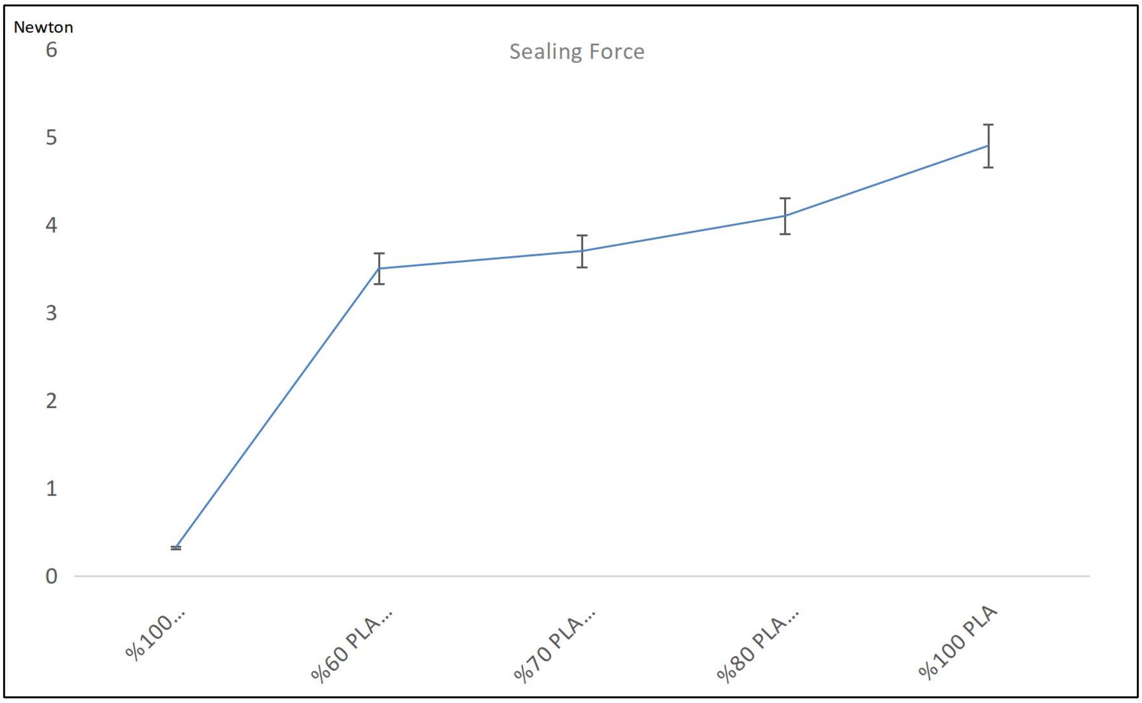

Figure 44. Sealing Force Test with Different Formulations

Looking at commercialized packaging films, different seal forces declared. For healthy sealing, it is expected to take a minimum of 3 Newtons at 3 bar 0.8 sec, 130 C. This type of packaging is referred to as easy peelable packaging.

According to our test results, the sealing force of each formulation is greater than 3 Newtons at 130°C at 3 bar, 0.8 sec. Test results show that we have achieved sufficient seal force for each formulation. Sufficient seal force can be achieved for packaging integrity and shelf life.

4.3. Optical Measurements

Since the optical properties are important for the packaging material, the change in the optical properties of the produced films has been tested. Produced samples were tested in ASTM D 2457 for gloss of the film. ASTM D1003 standard was used for haze, clarity, and transmittance as Table 13 below. Each formulation was tested 3 times.

Table 13. Optical Measurements of Films with Different Ratios

Avarage Opt. Pro.	%100 PLA	%100 Mater-Bi	%80 PLA-%20 Mater-Bi	%70PLA-%30 Mater-Bi	%60PLA -%40 Mater-Bi
Gloss(%)	14,97	8,97	13,25	11,8	10,65
Haze(%)	11,15	81,57	63,12	68,57	74,57
Clarity(%)	90,95	65,75	72,37	71,77	68,47
Transmittance(%)	90,67	89,57	90,62	89,72	89,62

In general, transparent materials such as PLA are preferred in the market. A more transparent appearance was obtained in those with a high PLA ratio. The haze, clarity and transmittance values are almost close to each formulation. In terms of reaching the customer, marketing studies should focus on by considering these optical properties as Figure 45, Figure 46, Figure 47 and Figure 48. Each measured optical property differs in terms of marketing strategy. Marketing activities vary according to age, consumption habits, gender and income level. Optical properties also differ according to the marketing strategies of companies. Therefore, each optical property should be evaluated differently. In the food packaging industry, optical properties should be considered according to user consumption habits.

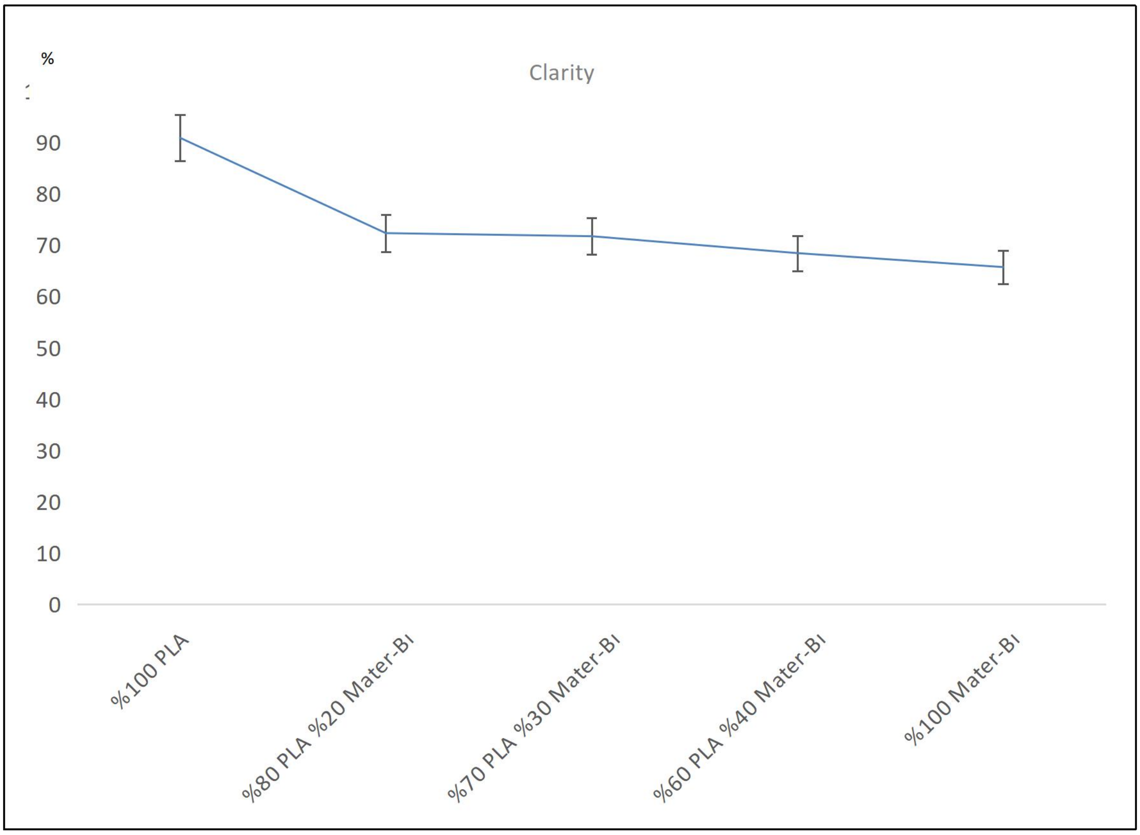

Figure 45. Clarity Measurements of Films with Different Ratios

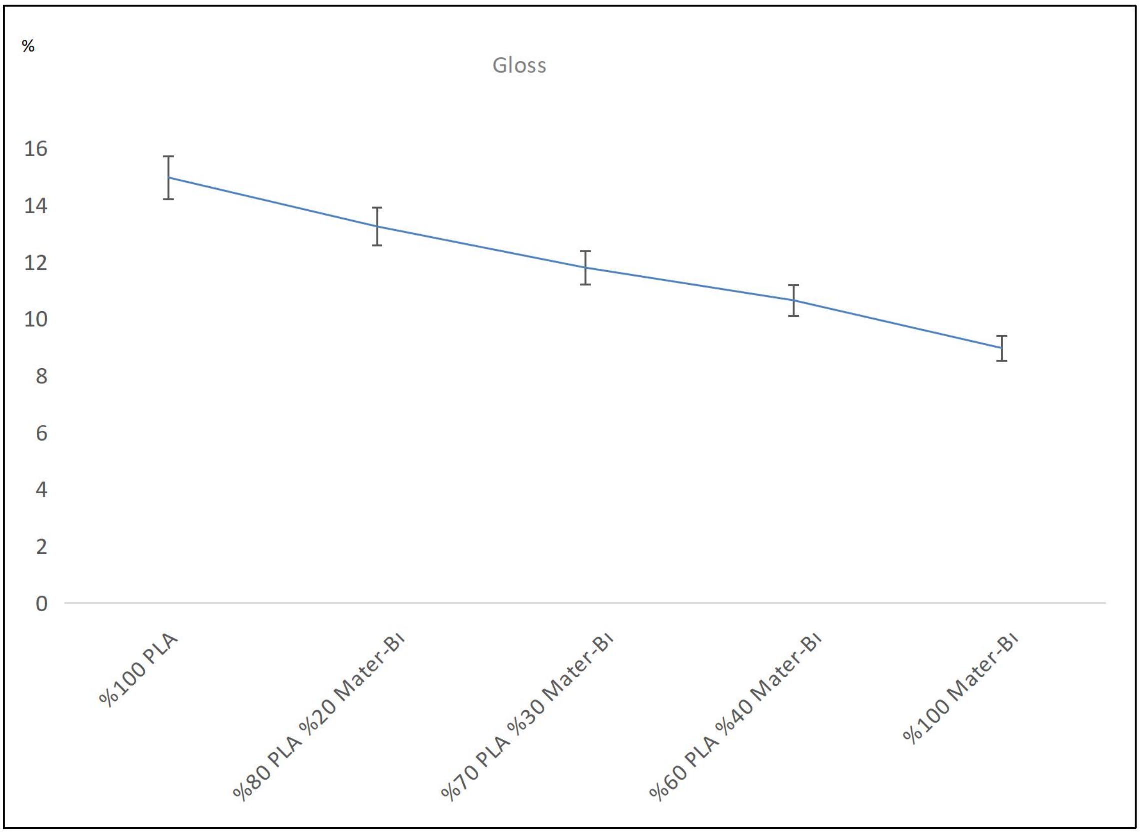

Figure 46. Gloss Measurements of Films with Different Ratios

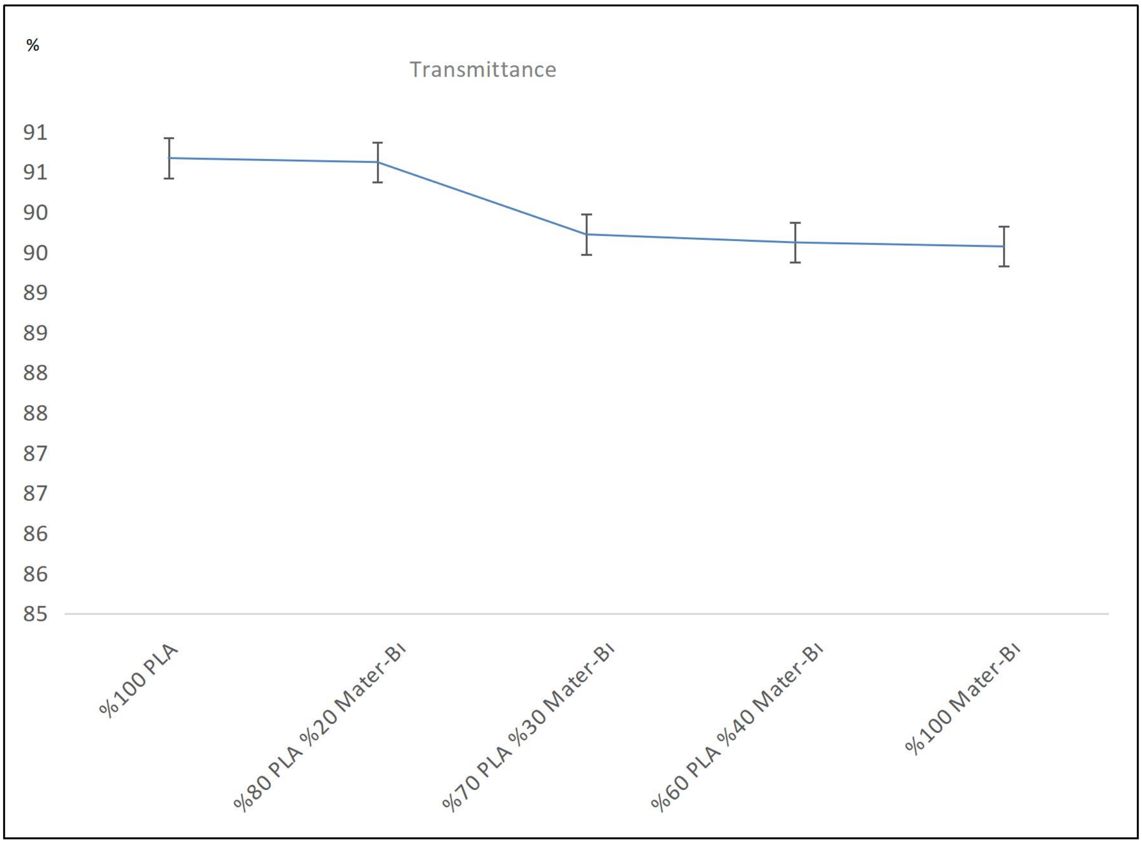

Figure 47. Transmittance Measurements of Films with Different Ratios

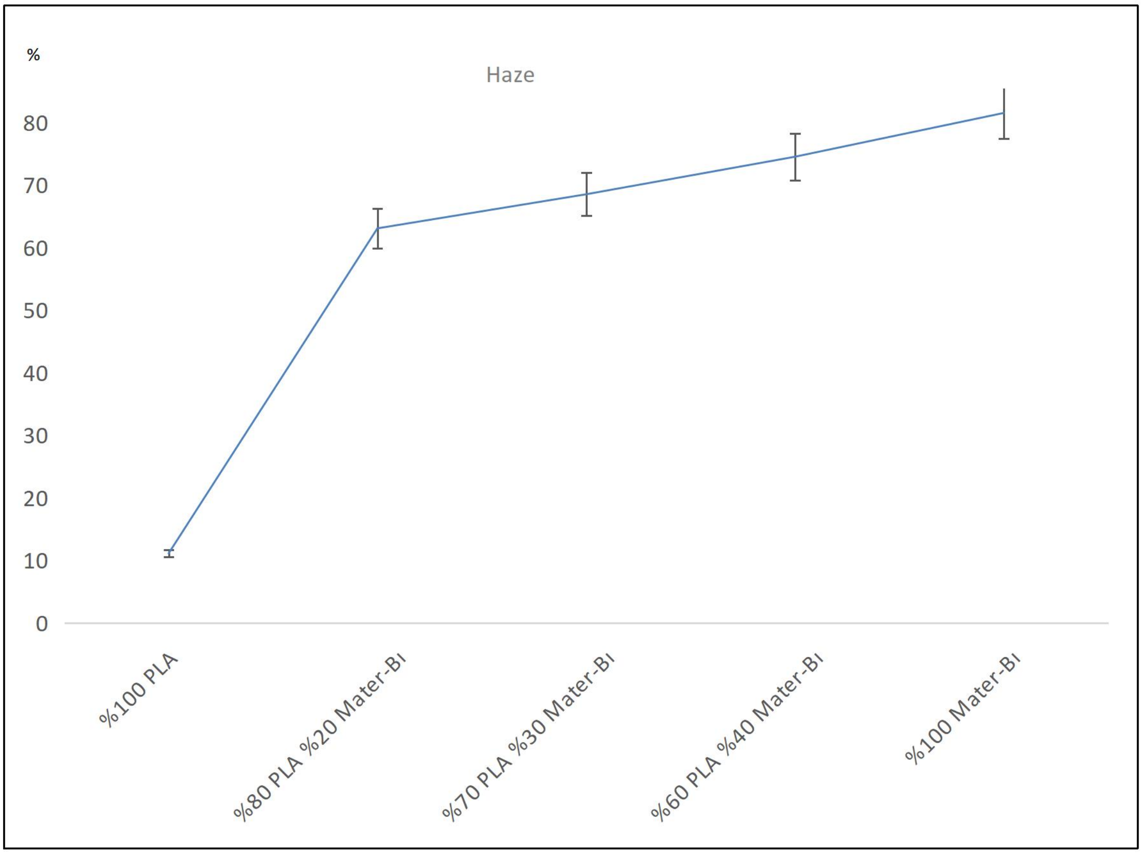

Figure 48. Haze Measurements of Films with Different Ratios

4.4. Gas Chromatography

Measuring the solvent residue in the packaging material is important for the packaging material. Therefore, all produced samples' solvent retention were tested. You can find the solvent residue report of one of the formulations as Table 14 below.

Table 14. 80% PLA 4043 D 20% Mater-Bi® EF05B Material Solvent Retention Test

Component Name	Ret Time(min)	Area(Uv-sec)	Area(%)	Adjusted Amount(mg/m2)
Methyl alcohol	1,212	0,00	0,00	0,0000
Ethyl alcohol	1,391	2453,43	74,4	0,2330
iso-propyl alcohol	1,565	0,00	0,00	0,0000
N- propyl alcohol	1,89	0,00	0,00	0,0000
Mek	2,182	0,00	0,00	0,0000
Ethyl Acetate	2,317	844,07	25,60	0,0864
iso-propyl acetate	2,861	0,00	0,00	0,0000
Methoxy propanol	3,111	0,00	0,00	0,0000
N-propyl acetate	3,644	0,00	0,00	0,0000
N-heptane	3,784	0,00	0,00	0,0000
Ethoxy propanol	4,509	0,00	0,00	0,0000
Acethyl acetone	5,297	0,00	0,00	0,0000
Buthyl Acetate	6,216	0,00	0,00	0,0000
		3297,50	100,00	0,3194

Measurement results were test using ASTM F 1884-04. Total solvent residue should be less than 20 mg/m^2 according to Food Packaging Product Stewardship Considerations. For instance, the total solvent residue ratio of 80% PLA 4043 D 20% Mater-Bi® EF05B material is 0.3194 mg/m^2. All formulations' test reports in appendix. According to the Food Packaging Product Stewardship Considerations, all films are at the acceptable level for food safety. Because the measurement results in each formulation are less than 2 mg/m^2.

4.6. Fourier-transform infrared spectroscopy

The FTIR results of each formulation were tested. The approaches were examined according to the similar formulations that showed the most similarity among the data recorded in the library. 100% PLA film's peak point in Figure 49 below. The formula is % 62,2 similar to propanoic acid ethyl ester.

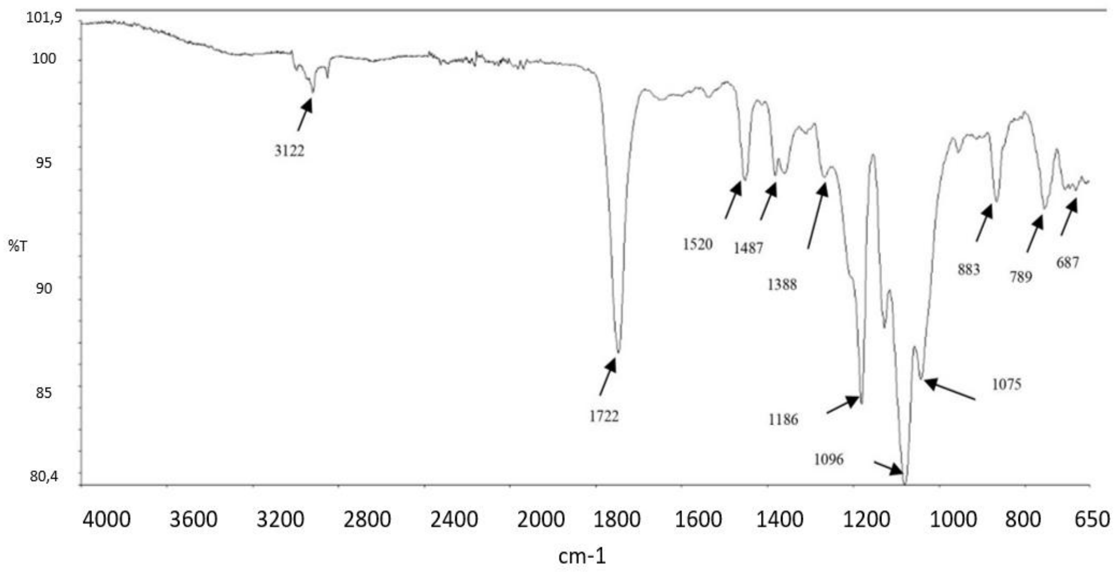

Figure 49. 100% PLA Film FTIR Test Graph

100% Mater-Bi film’s peak point in Figure 50 below. The formula is % 70,6 similar to PBT (Polybutylene Terephthalate).

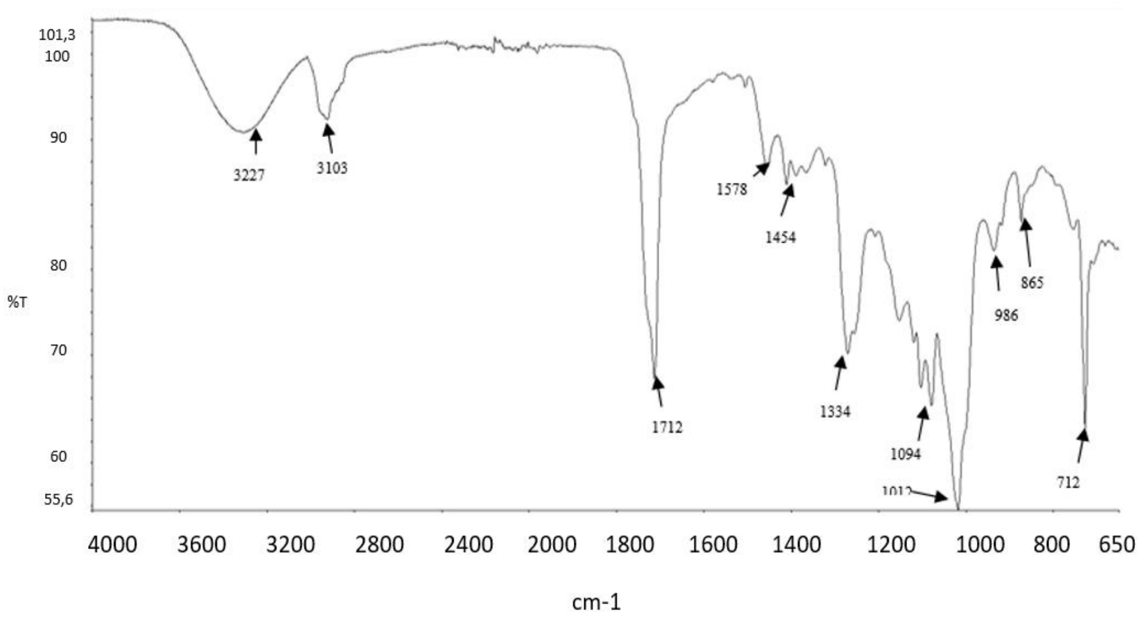

Figure 50. 100% Mater-Bi Film FTIR Test Graph

According to the spectrum, it was shown as 70 % Polybutylene Terephthalate PBT similarity. It is a semi-crystalline engineering thermoplastic material. Formulation is $(C12H12O4)_n$ [40]. PBT block copolymer is biodegradable [41].

80% PLA 4043 D 20% Mater-Bi® EF05B film's peak point in Figure 51 below. The formula is % 64,4 similar to propanoic acid ethyl ester.

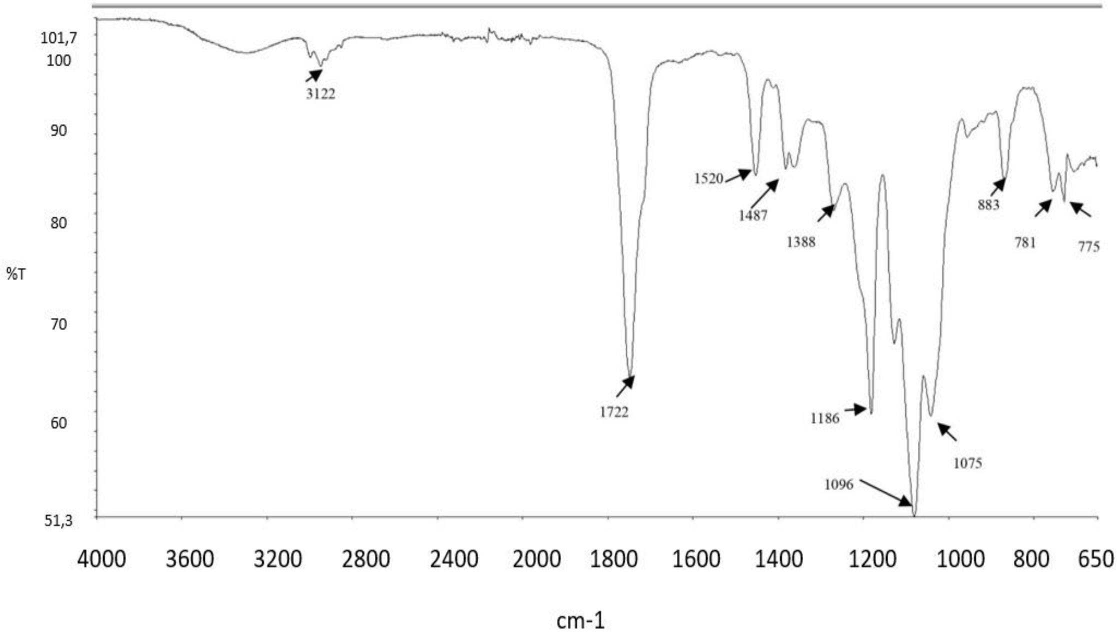

Figure 51. 80% PLA 4043 D 20% Mater-Bi® EF05B FTIR Test Graph

70% PLA 4043 D 30% Mater-Bi® EF05B film's peak point in Figure 52 below. The formula is % 62,7 similar to propanoic acid ethyl ester.

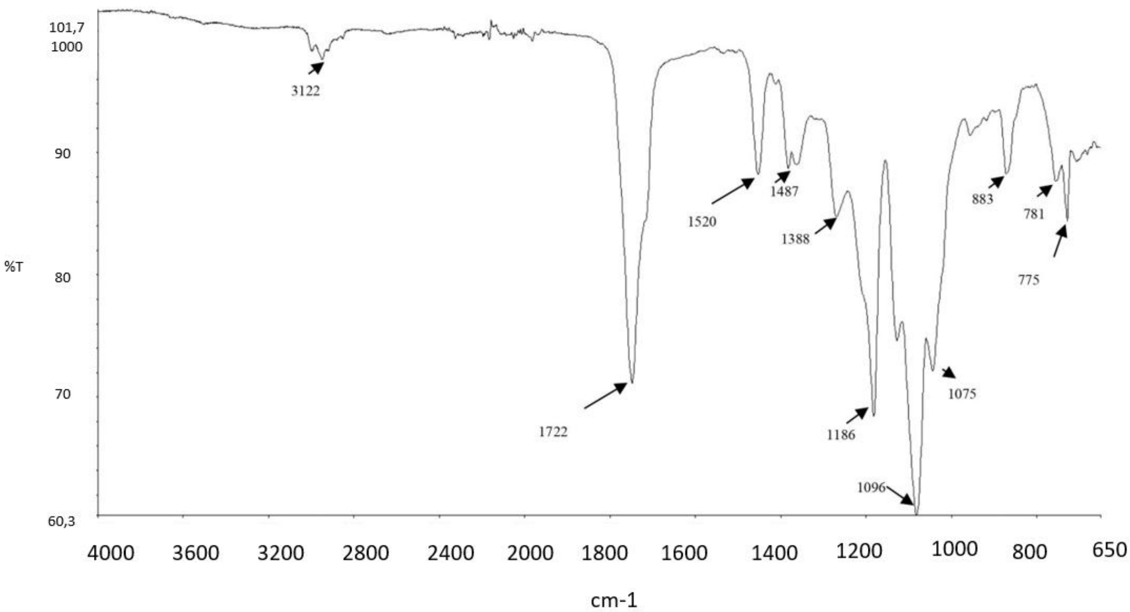

Figure 52. 70% PLA 4043 D 30% Mater-Bi® EF05B FTIR Test Graph

The spectrums of 80% PLA 4043 D 20% Mater-Bi® EF05B , 70% PLA 4043 D 30% Mater-Bi® EF05B and 100% PLA formulations were examined. According to these spectra, 60% similarity was found to propanoic acid ethyl ester in each of them. Ethyl propionate is kind of organic formula. Formulation is $C_5H_{10}O_2$ .Propionic acid is in the ethyl ester group . It is volatile liquid with a pineapple-like odor. Some fruits contain ethyl propionate in small amounts as kiwi, strawberry. Since PLA 4043D is biobased, the formula we expect to see at the highest rate should also be biobased.

You can find 60% PLA 4043 D %40 Mater-Bi® EF05B film's peak point in Figure 53. The formula is % 64,7 similar to propanoic acid ethyl ester.

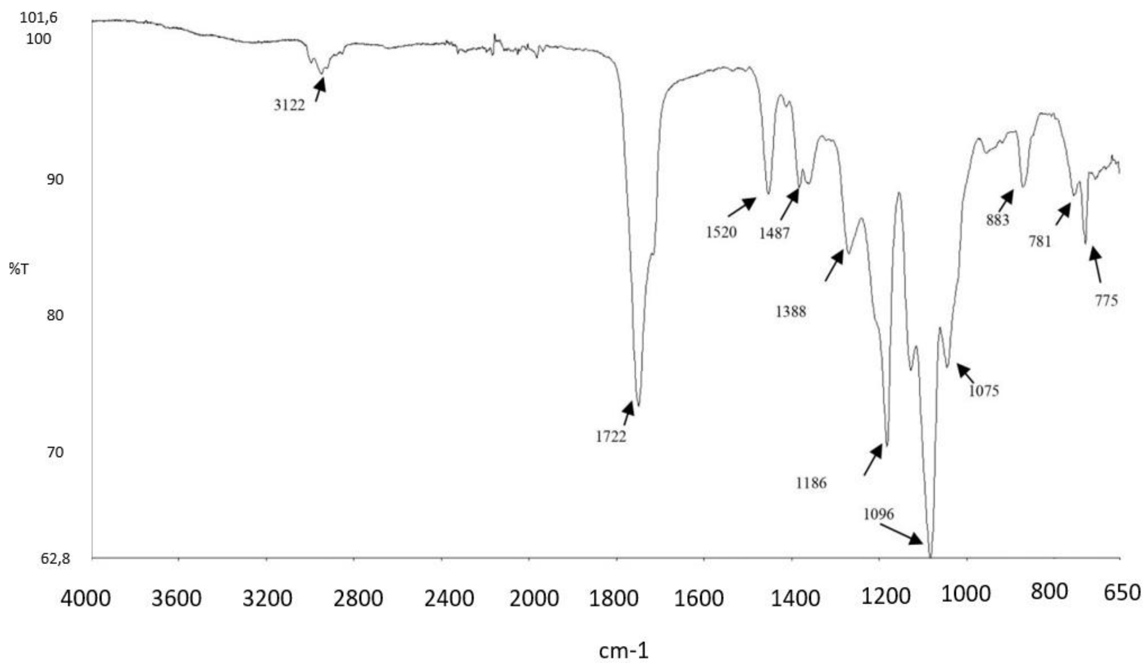

Figure 53. 60% PLA 4043 D %40 Mater-Bi® EF05B FTIR Test Graph

Tartaric acid is an organic acid found naturally in many fruits. It is found in grapes, but also in bananas, tamarinds and citrus fruits. Its formulation is C4H6O6. 60% PLA 4043 D 40% Mater-Bi® showed 64% similarity to tartaric acid in the EF05B spectrum. Since bio-based films are used, it is expected to have these organic ingredients.

If we superimpose the spectrums of all formulations and interpret them. They show 60% PLA-40% Mater-Bi pink line, 70% PLA-30% Mater-Bi red line, 80%PLA-20%Mater-Bi green line, 100% Mater-Bi blue line and 100% PLA black line in the spectrum at Figure 54. In the figure see that the properties of PLA are more dominant than Mater-Bi in all formulations.

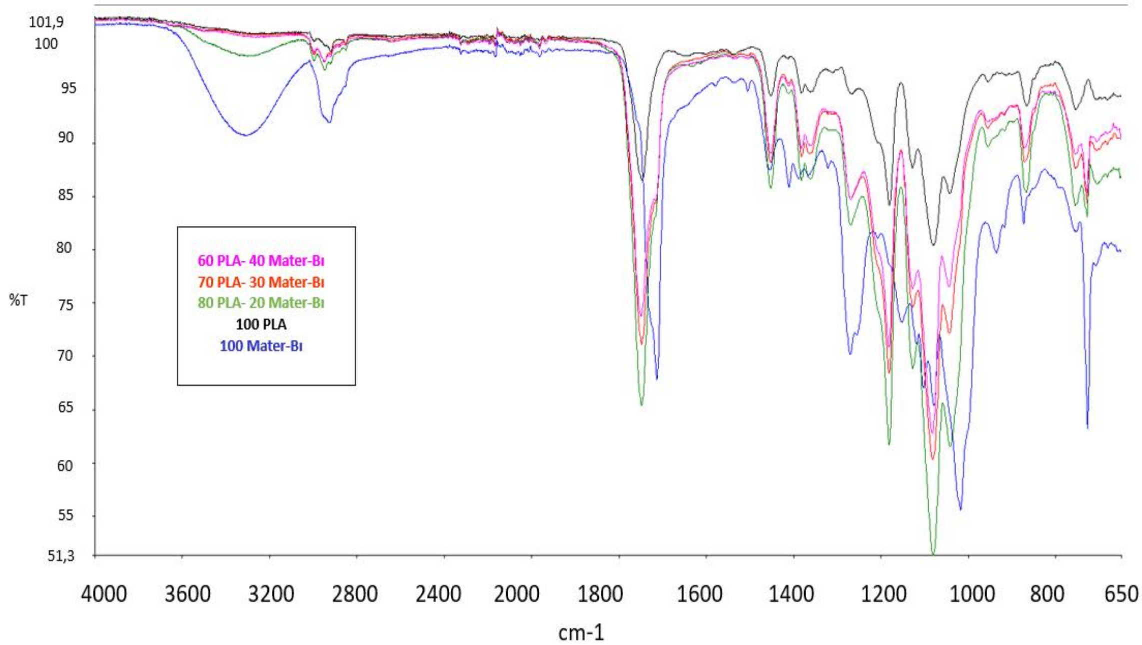

Figure 54. Spectrum Behaviour of Differently Formulated Films

CHAPTER 5

CONCLUSION

With the increasing population in our world, the waste management process is getting more difficult. Different solutions have been produced on different solutions in the waste management process. Biobased and biodegradable packaging also plays an important role in the waste management process. PLA and Mater-Bi granules were used in studies carried out within the scope of sustainability solutions. The Mater-Bi granule I used in my study is mostly used in shopping bags. These types of bags are quite ductile and have low strength. Flexible packaging films produced only from PLA granules are very brittle. This brittleness causes difficulties in processability.

The aim of the study is to increase the formability of the flexible packaging film produced from %100 PLA granules. For this reason, PLA granule and Mater-Bi granule are solved in different proportions to form a flexible film blend. It is produced by dissolving as %100 PLA, %80 PLA 4043 D %20 Mater-Bi® EF05B, %70 PLA 4043 D %30 Mater-Bi® EF05B , %60 PLA 4043 D %40 Mater-Bi® EF05B, %100 Mater-Bi® EF05B. Commercially, Mater-Bi® EF05B granule is less expensive than 4043 D under current conditions. Regarding the packaging film produced at different formulations, the properties are changing with the increasing of Mater-Bi percentage. Thickness, unit weight, efficiency, tensile strength and puncture resistance were tested for mechanical properties. The ductility of the material increases as the ratio of Mater-Bi increases. The puncture force of PLA is nearly 2 times that of Mater-Bi. Although the extension of Mater-Bi film is higher than PLA, the energy it absorbs is less than PLA. In general, Mater-Bi was not very dominant in extension. Therefore, it does not provide puncture resistance in products with sharp edged products. Sealing performance is one of the important criteria for food safety. Sealing test results were appropriate for each formulation.

Optical properties of the produced packaging films were tested. In general, transparent materials such as PLA are preferred in the market. A more transparent appearance was obtained in those with a high PLA ratio. FTIR analyzes were considered as analytical review. Gas Chromatography test was performed in order to check that it is suitable for regulations in terms of food safety. As the Mater-Bi ratio increases, the mechanical properties of the film increase. The formulation can be selected according to the tested properties for different type optical properties. Mechanical properties were improved in each formulation compared to base PLA. It can be used by choosing different formulations according to different packaging machine capabilities.

Appropriate packaging formulation with appropriate optical properties can be selected according to the customer's request in marketing. If there is a need for a barrier, packaging structure can be developed by laminating it with different biodegradable and biobased films. The industrial processability of the films produced by the industrial blown method in the same formulations can be tested as a future study. Oxygen and moisture barrier can be provided by adding bio-based additives for the next step of the study. As a future step, the optical properties of the films can be differentiated by using different bio additives.

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APPENDIX A

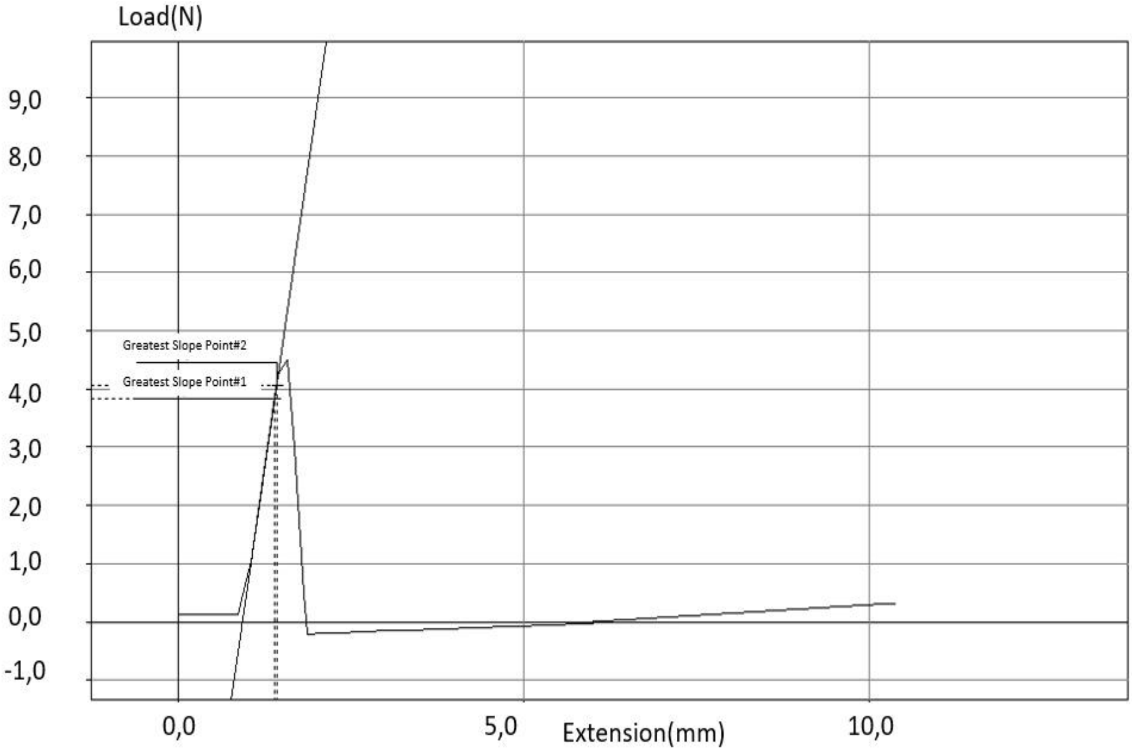

Figure 55. Tension Test Graph 80% PLA 4043 D 20% Mater-Bi® EF05B

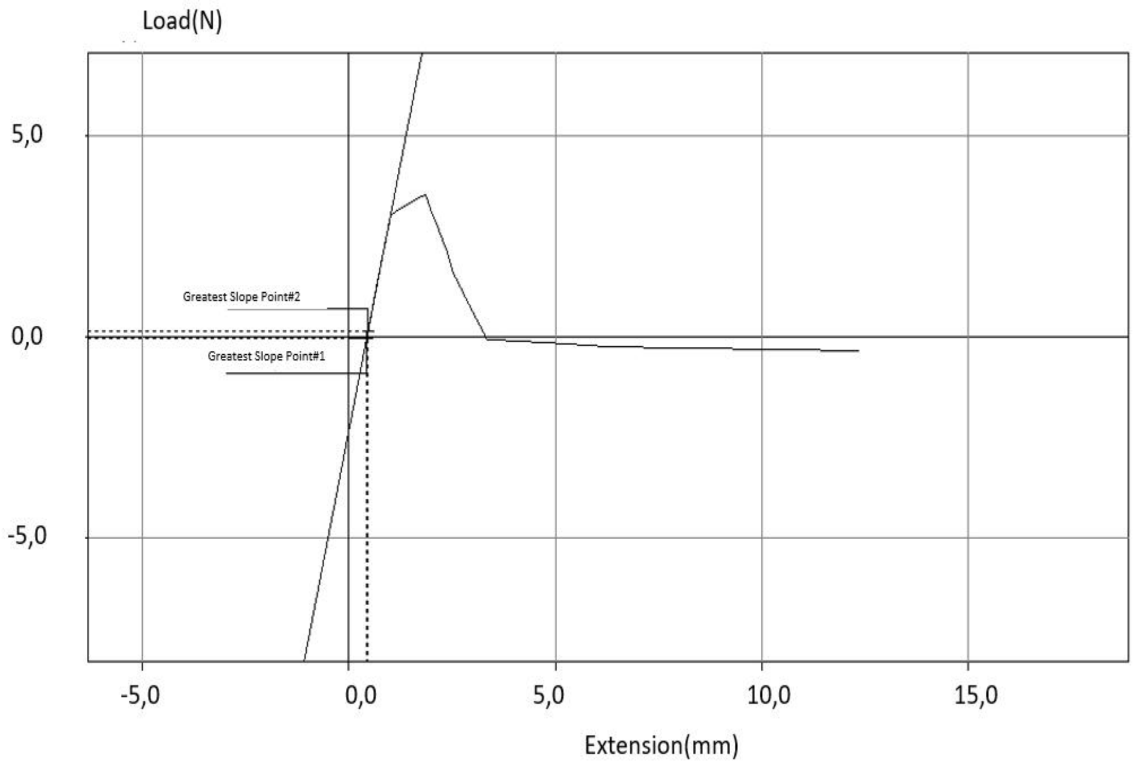

Figure 56. Tension Test Graph 70% PLA 4043 D 30% Mater-Bi® EF05B

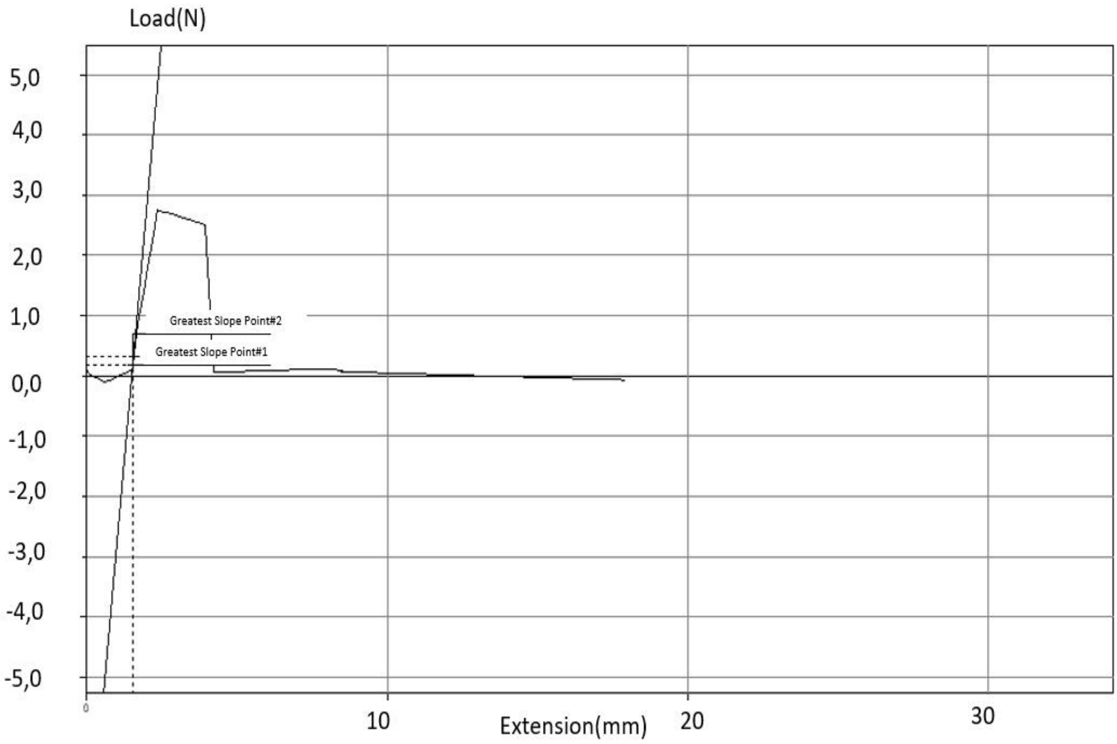

Figure 57. Tension Test Graph 60% PLA 4043 D 40% Mater-Bi® EF05B

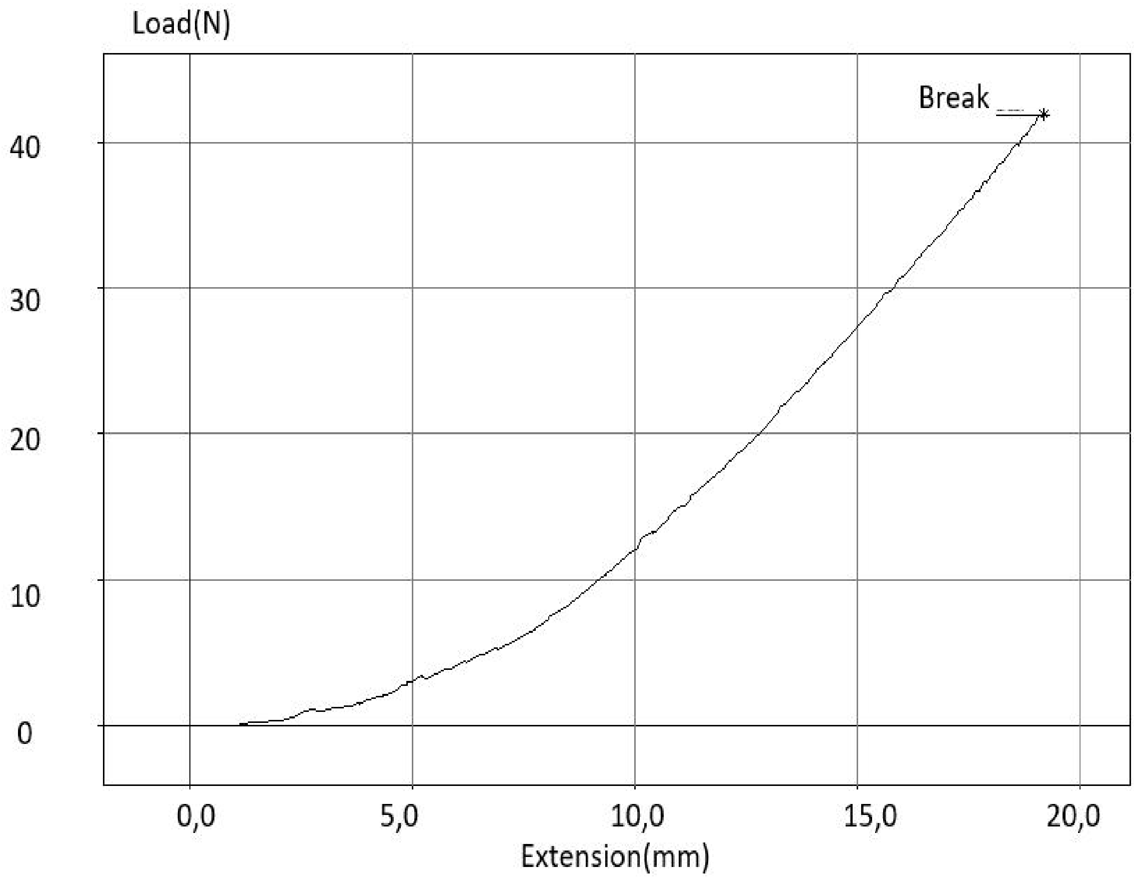

Figure 58. Puncture Resistance Graph of %80 PLA 4043 D %20 Mater-Bi® EF05B

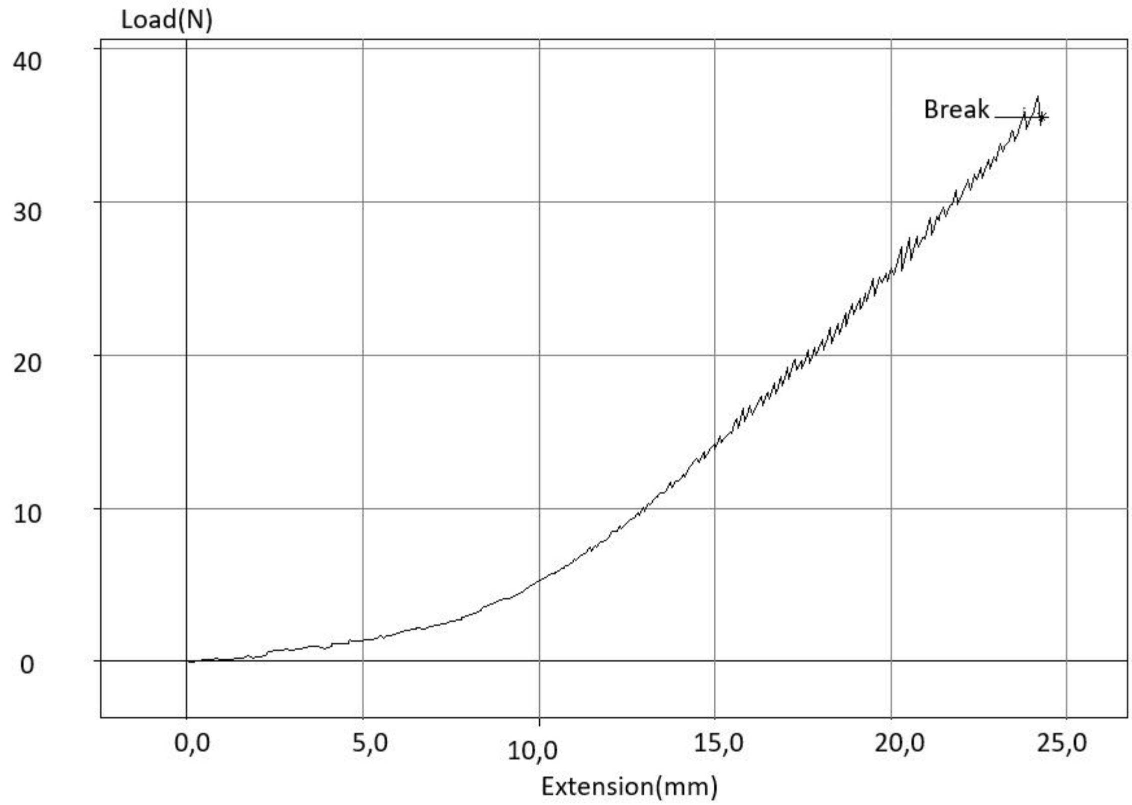

Figure 59. Puncture Resistance Graph of 70 % PLA 4043 D 30% Mater-Bi® EF05B

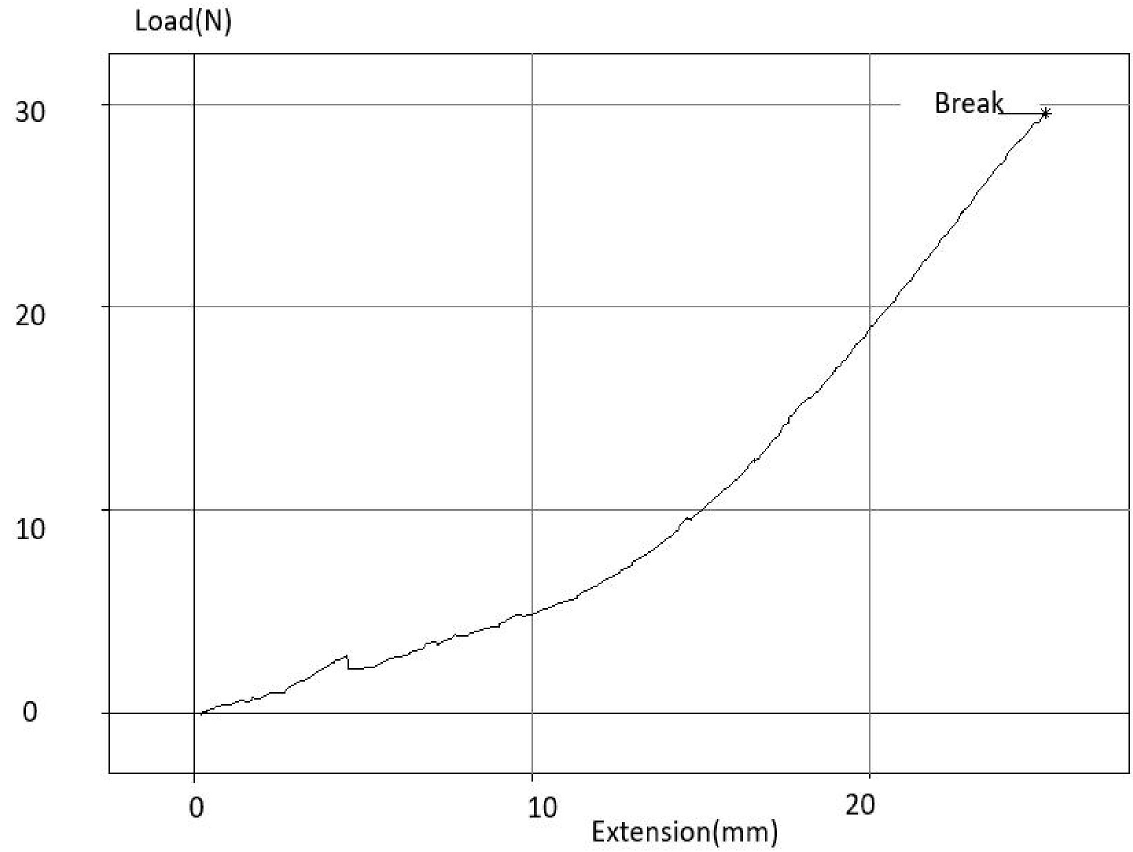

Figure 60. Puncture Resistance Graph of 60% PLA 4043 D 40% Mater-Bi® EF05BI

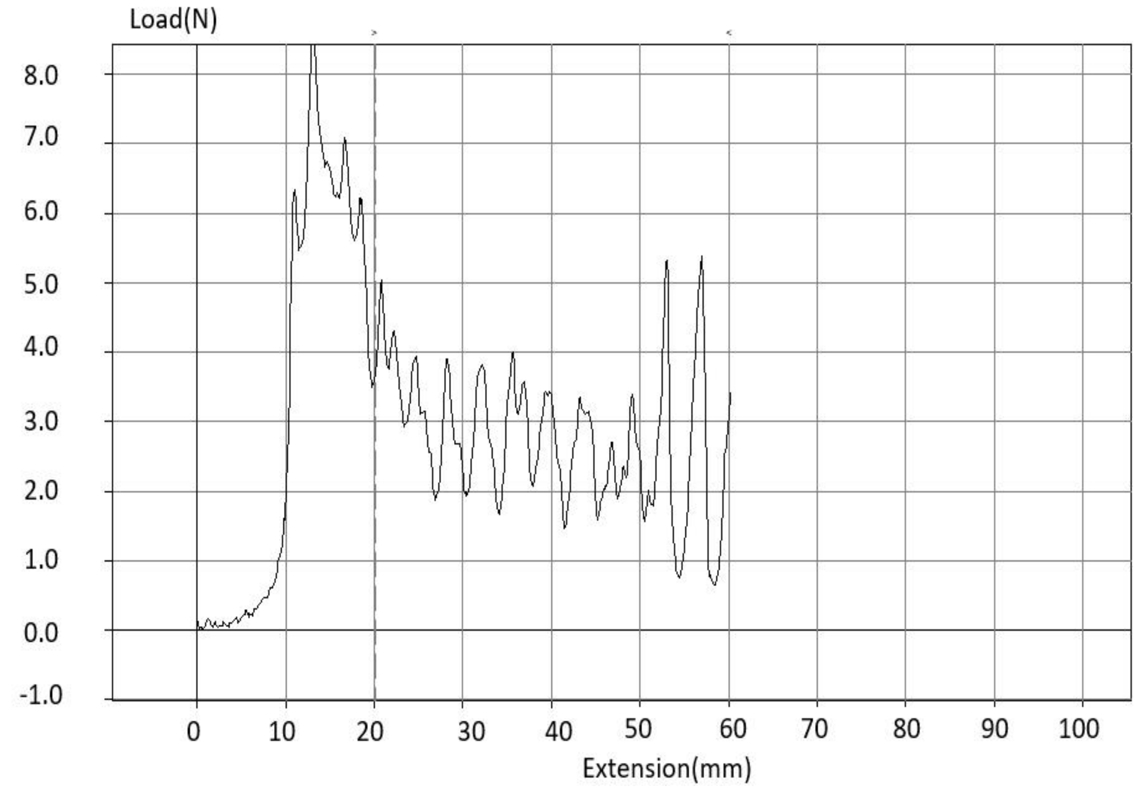

Figure 61. Sealing Test Graph of 80% PLA 4043 D 20% Mater-Bi® EF05B

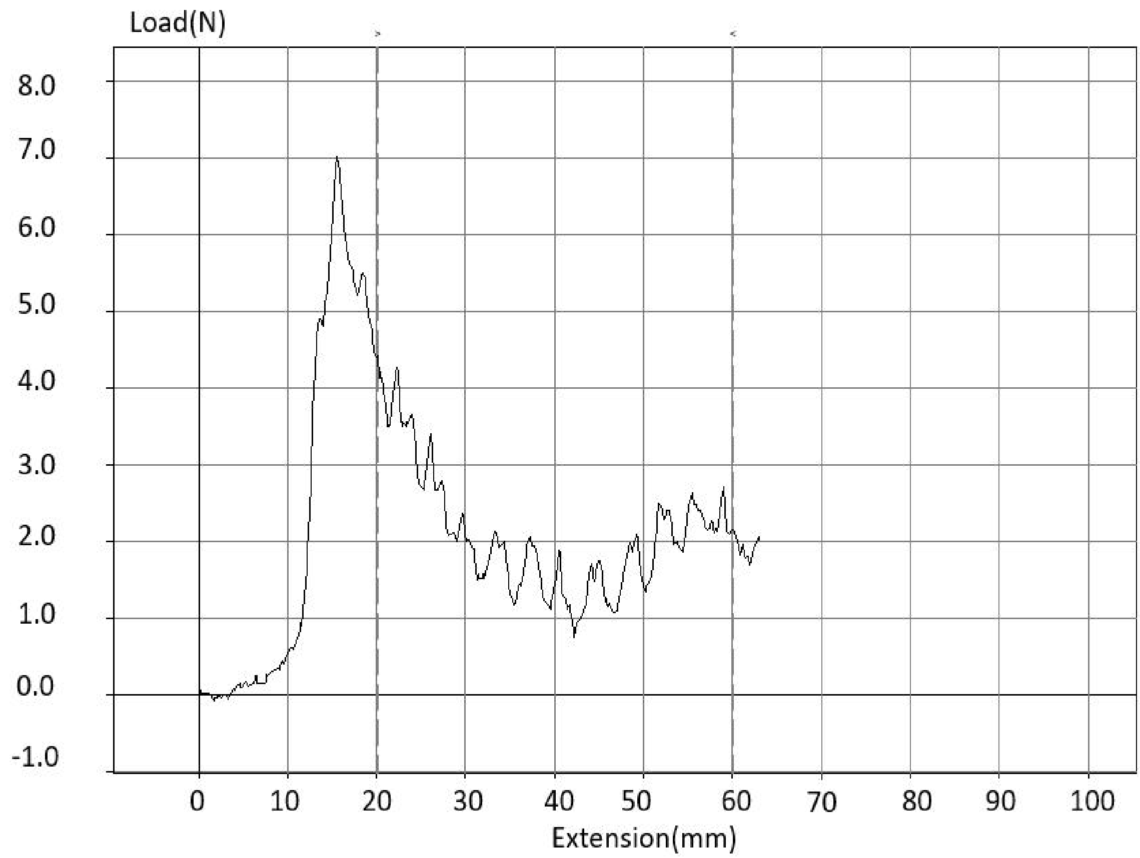

Figure 62. Sealing Test Graph of 70% PLA 4043 D 30% Mater-Bi® EF05B

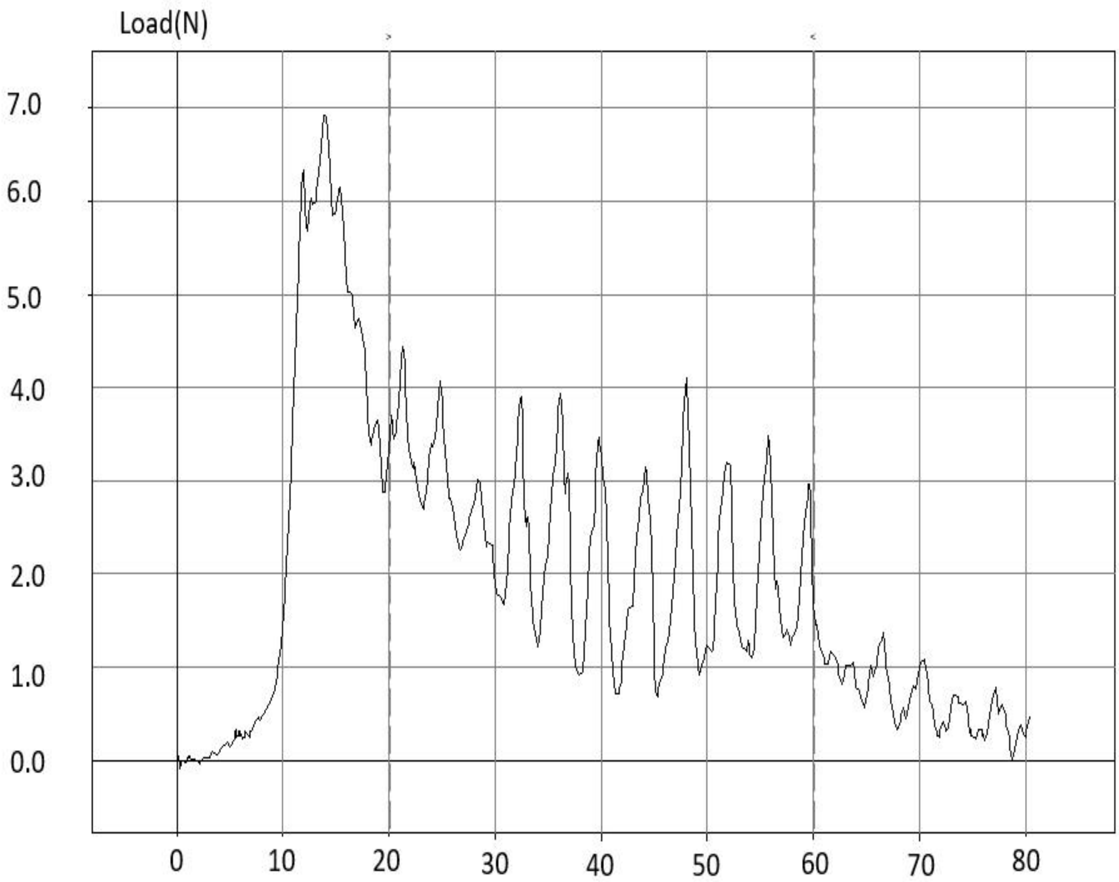

Figure 63. Sealing Test Graph of 60% PLA 4043 D 40% Mater-Bi® EF05B

Table 15. 100% PLA Material Solvent Retention Test Table

Component Name	Ret Time(min)	Area(Uv-sec)	Area(%)	Adjusted Amount(mg/m2)
Methyl alcohol	1,212	0,00	0,00	0,0000
Ethyl alcohol	1,391	1105,76	9,99	0,1050
iso-propyl alcohol	1,565	0,00	0,00	0,0000
N- propyl alcohol	1,89	0,00	0,00	0,0000
Mek	2,182	0,00	0,00	0,0000
Ethyl Acetate	2,325	0,00	0,00	0,0000
iso-propyl acetate	2,861	0,00	0,00	0,0000
Methoxy propanol	3,083	9960,43	90,01	1,2091
N-propyl acetate	3,644	0,00	0,00	0,0000
N-heptane	3,784	0,00	0,00	0,0000
Ethoxy propanol	4,509	0,00	0,00	0,0000
Acethyl acetone	5,297	0,00	0,00	0,0000
Buthyl Acetate	6,216	0,00	0,00	0,0000
		11066,19	100,00	1,3141

Table 16. 100% Mater-Bi® EF05B Material Solvent Retention Test Table

Component Name	Ret Time(min)	Area(Uv-sec)	Area(%)	Adjusted Amount(mg/m2)
Methyl alcohol	1,212	0,00	0,00	0,0000
Ethyl alcohol	1,391	307,41	100	0,0292
iso-propyl alcohol	1,565	0,00	0,00	0,0000
N- propyl alcohol	1,89	0,00	0,00	0,0000
Mek	2,182	0,00	0,00	0,0000
Ethyl Acetate	2,325	0,00	0,00	0,0000
iso-propyl acetate	2,861	0,00	0,00	0,0000
Methoxy propanol	3,111	9960,43	0,00	1,2091
N-propyl acetate	3,644	0,00	0,00	0,0000
N-heptane	3,784	0,00	0,00	0,0000
Ethoxy propanol	4,509	0,00	0,00	0,0000
Acethyl acetone	5,297	0,00	0,00	0,0000
Buthyl Acetate	6,216	0,00	0,00	0,0000
		307,41	100,00	0,0292

Table 17. 70% PLA 4043 D %30 Mater-Bi® EF05B Material Solvent Retention Test

Component Name	Ret Time(min)	Area(Uv-sec)	Area(%)	Adjusted Amount(mg/m2)
Methyl alcohol	1,212	0,00	0,00	0,0000
Ethyl alcohol	1,391	369,41	100	0,0351
iso-propyl alcohol	1,565	0,00	0,00	0,0000
N- propyl alcohol	1,89	0,00	0,00	0,0000
Mek	2,182	0,00	0,00	0,0000
Ethyl Acetate	2,325	0,00	0,00	0,0000
iso-propyl acetate	2,861	0,00	0,00	0,0000
Methoxy propanol	3,111	0,00	0,00	1,2091
N-propyl acetate	3,644	0,00	0,00	0,0000
N-heptane	3,784	0,00	0,00	0,0000
Ethoxy propanol	4,509	0,00	0,00	0,0000
Acethyl acetone	5,297	0,00	0,00	0,0000
Buthyl Acetate	6,216	0,00	0,00	0,0000
		369,41	100,00	0,0351

Table 18. 60% PLA 4043 D %40 Mater-Bi® EF05B Material Solvent Retention Test

Component Name	Ret Time(min)	Area(Uv-sec)	Area(%)	Adjusted Amount(mg/m2)
Methyl alcohol	1,212	0,00	0,00	0,0000
Ethyl alcohol	1,388	874,12	100	0,0830
iso-propyl alcohol	1,565	0,00	0,00	0,0000
N- propyl alcohol	1,89	0,00	0,00	0,0000
Mek	2,182	0,00	0,00	0,0000
Ethyl Acetate	2,325	0,00	0,00	0,0000
iso-propyl acetate	2,861	0,00	0,00	0,0000
Methoxy propanol	3,111	0,00	0,00	1,2091
N-propyl acetate	3,644	0,00	0,00	0,0000
N-heptane	3,784	0,00	0,00	0,0000
Ethoxy propanol	4,509	0,00	0,00	0,0000
Acethyl acetone	5,297	0,00	0,00	0,0000
Buthyl Acetate	6,216	0,00	0,00	0,0000
		874,12	100,00	0,0830