OULUN AMMATTIKORKEAKOULU

Erik Rannaste

USAGE OF RICE HUSK AS FILLER MATERIAL IN PHBV BASED BIOPOLYMER

RIISINKUOREN KÄYTTÖ TÄYTEMATERIAALINA PHBV POHJAISESSA BIOPOLYMEERISSÄ

Erik Rannaste
Opinnäytetyö
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Oulun seudun ammattikorkeakoulu

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Tekijä(t): Erik Rannaste
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Tämä opinnäytetyö tehtiin osana espanjalaisen tutkimusryhmä PIMA:n tutkimusta biopolymeerien käytöstä pakkausmateriaaliteollisuudessa. Tämän opinnäytetyön päätavoitteena oli tutkia, voitaisiinko riisinkuorta käyttää vahvistavana täytemateriaalina PHBV pohjaisessa biopolymeerissä, joka on biohajoava. Opinnäytetyön tarkoituksena oli tehdä biohajoava biopolymeeri riisinkuoresta ja PHBV:stä, jolla olisi paremmat mekaaniset ominaisuudet verrattuna puhtaaseen PHBV:seen.

Metodi opinnäytetyötä varten kehitettiin kirjallisuuslähteiden avulla. Erään lähteen mukaan emäskäsitellyllä riisinkuorella on paremmat mekaaniset ominaisuudet kuin käsittelemättömällä. Kahta erilaista riisinkuorityyppiä (NaOH käsiteltyä ja käsittelemätöntä) testattiin ja verrattiin keskenään, jotta voitiin todeta pitikö kyseinen lähde paikkansa. Riisinkuorta käsiteltiin 5 % ja 10 % NaOH – liuoksella kahta käsittelyaikaa (24 ja 48 tuntia) käyttäen. Riisinkuoren pinnan morfologiaa tutkittiin SEM:illä ja mikroskoopilla. Todettiin, että paras tulos saavutettiin kun riisinkuorta käsiteltiin 24 tuntia 10 % NaOH – liuoksella. Kalvojen valmistuksessa käytetyt olosuhteet löydettiin kirjallisuudesta. Emäskäsitellystä riisinkuoresta ei saatu kalvoa aikaiseksi, koska emäskäsittely laski riisinkuoren viskositeetin niin alhaiseksi että se meni pilalle.

Adheesio on hyvin voimakasta riisinkuoren ja PHBV:n välillä. Mekaanisten ominaisuuksien määrityksen perusteella kimmokerroin kasvoi 20 % verrattuna puhtaaseen PHBV:seen, kun kalvon annettiin hajota 1 päivän ajan. Kun 15 päivän kuluttua näytteet mitattiin uudestaan, oli kimmokerroin enää 5 % parempi verrattuna puhtaaseen PHBV:seen. Polymeerisekoituksen kiteisyysaste oli säilynyt melkein yhtä suurena kuin puhtaan PHBV:n. Sulamis- ja kiteytymislämpötilat laskivat odotetusti alhaisemmaksi kuin puhtaan PHBV:n. Tämä johtui riisenkuoren lisäyksestä polymeeriin. Kaikki polymeerinäytteet olivat epämuodostuneita tai muuten epätäydellisiä lämpömuovauksen jälkeen, koska jauhetun riisinkuoren partikkelit olivat liian suuria verrattuna kalvon paksuuteen. Jotta riisinkuoresta ja PHBV:stä voitaisiin tehdä kalvoja, täytyisi kalvojen olla paksumpia kuin tässä opinnäytetyössä tehdyt (>140 µm).

Asiasanat: Biohajoava, biohajoaminen, biopolymeerit, PHBV, riisinkuori, ligniini

ABSTRACT
Oulu University of Applied Sciences
Bachelor of Laboratory Services, Biotechnology

Author(s): Erik Rannaste
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This thesis is a part of the research group PIMA’s research about the usage of biopolymers in the packaging industry. The objective of this thesis was to research the usage of rice husk (RH) as a strengthening fiber in PHBV based biocomposite that is biodegradable. The aim of this study was to make a biodegradable biocomposite, made of PHBV and RH that should have better mechanical properties compared to pure PHBV.

According to the literature review, alkaline treated RH has better mechanical properties than untreated RH. Two different types of RH (untreated and NaOH treated RH) were tested to see whether the chemical treatment of RH would improve its mechanical properties or not. RH was treated with 5% (w/w) and 10% (w/w) NaOH and it was left for 24 hrs or 48 hrs. The surface morphology of RH was investigated with Scanning Electron Microscopy (SEM) and microscope. According to the surface morphology, the best results were achieved with 10% (w/w) NaOH solution when treated for 24 hrs. Used melt blending & other processing conditions were discovered from literature. NaOH treated RH was not suitable for film pressing because it lowered too much its viscosity during the melt blending. All the NaOH treated RH was lost during the melt blending.

The adhesion between untreated RH and PHBV was great. According to the results from the determination of the tensile properties, the modulus of elasticity improved 20% (max.) compared to pure PHBV with the samples that were measured after 1 day of degradation. After 15 days of degradation in the desiccator, the modulus of elasticity was improved only slightly, with the increase of 5% (max.) in the modulus of elasticity. The degree of crystallinity of RH and PHBV polymer remained almost the same as the pure PHBV Mezclado. Melting temperatures of the RH blends were lowered, due to the addition of RH into the polymer. All the samples were ruptured during thermoforming. PHBV + RH films could not be thermoformed because the RH particles are too huge compared to the size of the film. In order to make films that could be thermoformed, the films would have to be thicker than 140 µm.

Keywords: Biodegradable, biodegradation, biopolymers, PHBV, rice husk, lignin

FOREWORD

Oulu, Finland

February 20th, 2015.

This thesis is a part of the research group Polímeros y Materiales Avanzados PIMA’s research about the usage of biopolymers in the packaging industry. The main part of this thesis was done between 1.9. - 5.12.2014 in the University of Jaume I, Castellón. PIMA was founded in 2010 and it soon gathered under its wings a group of talented researchers. Their expertise lies in the area of Materials Sciences and Engineering. Nowadays PIMA’s work is structured in five different lines: Polymers for the packaging industry, Polymers for clean energy, Materials for biomedical applications, Functional coatings and Corrosion protection.

I would like to thank my supervisor Ph.D. Luis Cabedo Mas and my instructor Ph.D. José Gaméz Pérez for giving me valuable advice and support always when needed. Other important persons considering my thesis are María Fernanda Bandres, José Ortega Herreros, Jennifer González Ausejo, Estefanía Lidón Sánchez Safont, Adria Monferrer and Sara da Silva Barros whom I would like to give my special thanks to for being awesome and wonderful people.

In the end, I would like to thank the whole PIMA research group and the University of Jaume I for giving me this great opportunity to make my thesis in their laboratories.

Erik Rannaste

Erik Rannaste

TABLE OF CONTENTS

VOCABULARY

Copolymer	Polymer that is made of two or more different repeating monomers
Homopolymer	Polymer that is made of one repeating monomer
PH3B	Poly-3-hydroxybutyrate
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate), biodegradable polymer used in this study.
PHV	Polyhydroxyvalerate
PE	Polyethylene, most used polymer that doesn´t degrade in the nature.
PUR	Polyurethane
RH	Rice husk

1 INTRODUCTION

This thesis researches the usage of rice husk (RH) as a strengthening fiber in PHBV based biocomposite that is biodegradable. This biocomposite consists of two matrixes: 1.) biodegradable polymer (PHBV) and 2.) natural fiber (rice husk) that improves the mechanical properties of polymers. The aim of this study is to make a biodegradable biocomposite, made of PHBV and RH that resulting in better mechanical properties compared to pure PHBV.

RH was chosen as the fiber matrix in biopolymer composite because in Castellon there is an abundance of RH as a by-product of rice industry. Millions of tons of RH are created every year from rice milling processes. According to FAOSTAT, in 2013 the estimated total world production of rice paddy was 745 million tons **[1]**. On average 20% of the rice paddy is husk, giving an annual total production of 150 million tons.

RH is considered waste by many rice milling companies, which is the reason why it is often left to compost in the nature or burnt as a source of fuel **[2]**. Both methods produce unwanted by-products (composting the RH produces methane and burning RH produces toxic fumes). It would solve quite many big problems regarding waste management of plastics and environmental protection if an economically reasonable way to combine RH to biodegradable polymer was developed. In the long run it would help the environment and ease the waste management of rice husk and polymers.

The use of RH as a strengthening fiber in biocomposite is not the best option everywhere in the world because you would have to have the infrastructure ready for growing & transporting rice and you have to have fresh water & fertilizer for growing it, which is not self-explanatory for example in the driest parts of Africa or Middle East. One of the main points in my thesis regarding this problem is that you have to focus on local possibilities. In Spain we have rice husk, in the Middle East they have almond shells and so on. In the world there are many good sources of usable fiber (wood fiber, bamboo, kenaf...) that are often by-products or waste of some processes. **[3]** As the old saying goes, one man’s trash is another man’s treasure.

This thesis was made as a part of research group PIMA´s (founded 2010) research about the biopolymers in the University of Jaume I, Castellón de La Plana, Spain.

2 POLYMERS AND FOOD PACKAGING

This chapter is about the theory of polymers, polymer classification and the usage of polymers in food packaging. Polymers are used in food packaging because they are cheap and easily available anywhere in the world.

2.1 Polymers

Polymers are composed of smaller structural units (monomers) that are attached together. This bonding forms longer chains of monomers that are called polymers. Monomers are molecules that have a double bond between two carbons and they have one or more side groups (e.g. H, CH_3, Cl, F...). Polymers are macromolecules, which can be composed of hundreds or even thousands units of monomers. These huge chains are the reason why polymers have their unique physical and chemical properties.

2.2 Polymerization

Polymers are formed by polymerization – a reaction in which monomer´s double bond opens up and bonds to another monomer with a single bond (Figure 1). In the case of polyethylene, the typical length of chain is $n \approx 20\,000$ **[4]**.

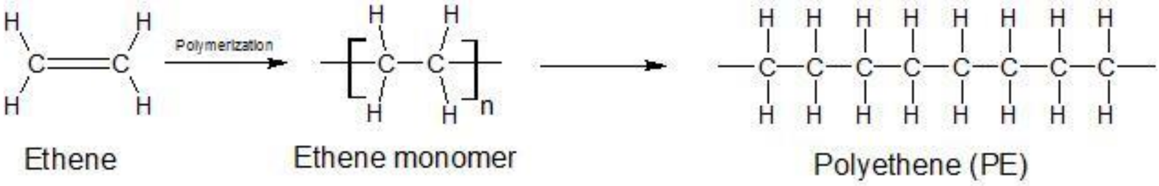


Figure 1 Polymerization of polyethylene

There are two types of polymerization: addition and condensation polymerization. In addition polymerization monomer units join together by breaking their double bonds without losing anything from their structure (See Figure 2). When the double bond breaks, the electrons available from the double bond are used to bond two monomers together **[5]**. When several monomers do this, long chains of monomers are formed. These chains are, as previously said, polymers.

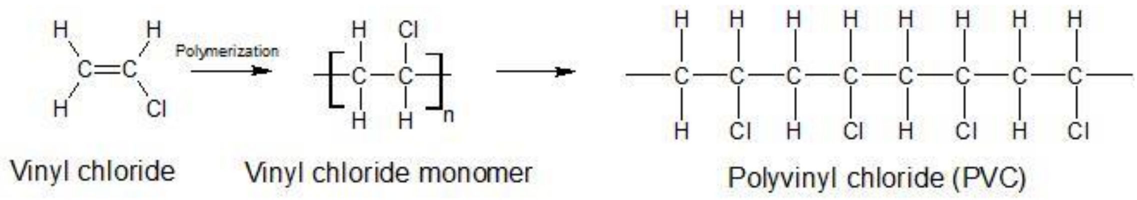


Figure 2 Addition polymerization of PVC

In condensation polymerization (See Figure 3) monomers join together by generating and eliminating a small molecule (e.g. H_2O) from their structure **[6]**. To put it shortly; homopolymers are formed in addition polymerization and copolymers in condensation polymerization.

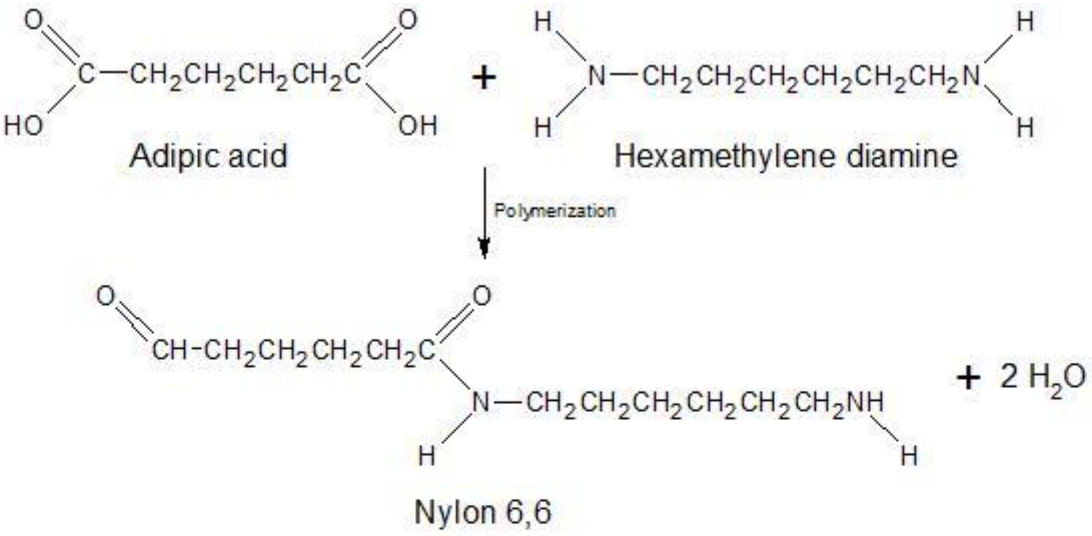


Figure 3 Condensation polymerization of nylon (6,6) **[7]**

2.3 Classification of polymers

Polymers are usually classified based on their chemical structure, but there are also other ways to classify them. For example, based on the origin of the polymer they can be classified as natural, semi-synthetic or synthetic polymers.

2.3.1 Homo- and copolymers

Polymers can be divided into groups based on their origin, structure, features, purpose of use, crystallinity and the way how monomers are attached together. Depending on how many different monomers polymer is composed of, it can be a homopolymer made out of one repeating monomer (Figure 4) or a copolymer that is made of two or more repeating monomers (Figure 5). This structural difference gives each polymer their unique mechanical and chemical properties.

- C - C - C - C - C - C - C - C - C - C -

Figure 4 Homopolymer made of monomer C

- C - A - C - A - C - A - C - A - C - A -

Figure 5 Copolymer made of monomers A & C

There are four different kind of copolymers (Random, Alternating, ABA –triblock and Graft copolymers) **[8]**, but only alternating copolymer is depicted above in the Figure 5. This is because this thesis is about PHBV and the polymerization of PHBV (Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)), where PH3B and PHV are polymerized, follows the order of alternating copolymerization. In Figure 6 below the four different types of copolymers are represented.

In random copolymerization monomers are organized in a random order. In block copolymerization the monomers of the same kind are in groups (blocks). Alternating copolymerization has monomers organized in alternating turns. In Graft copolymerization monomers form sc. “backbone” that has side chains. These side chains can tangle to each other and this phenomenon is known as cross-linking.

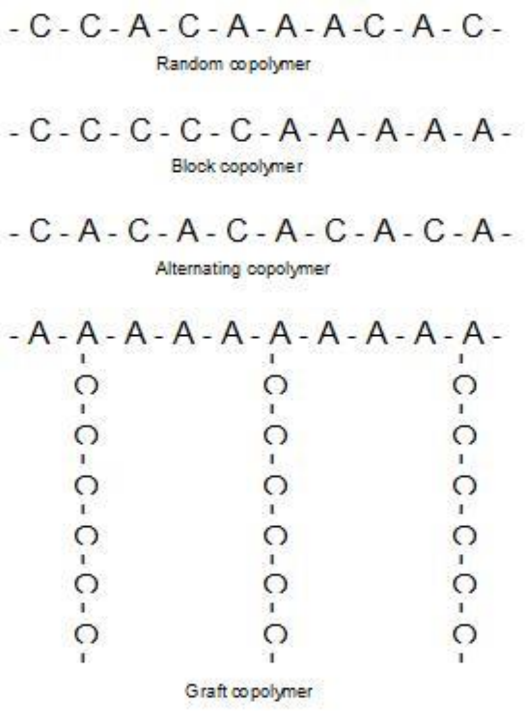


Figure 6 Types of copolymerization

2.3.2 Natural, semi-synthetic and synthetic polymers

Polymers can also be divided into three subgroups based on their origin and source of availability: natural polymers, semi-synthetic polymers and synthetic polymers **[9]**.

Natural polymers are polymers that are mostly made of mono- or polysaccharides. They can be obtained from plants and animals and they are vital for life because DNA and RNA are both composed of polysaccharides. Starch, cellulose, proteins and nucleic acids are natural polymers. Natural polymers are biodegradable.

Semi-synthetic polymers are natural polymers that have been treated chemically to have certain properties. Semi-synthetic polymers are trying to combine the good properties of natural and synthetic polymers. Natural polymers are e.g. vulcanized natural rubber, cellulose nitrate and cellulose diacetate **[10]**.

Synthetic polymers are produced in laboratories by chemical processes. They are mostly made of petroleum based raw materials and they are not biodegradable. It takes so long (in some cases hundreds of years or more) for synthetic polymers to degrade in the nature that they are called nondegradable polymers.

2.3.3 Thermoplastics

Polymers are usually divided into three major groups, based on their thermal processing behavior **[11]**. Those polymers that can be remolded after heating multiple times are called thermoplastics. There is no strong chemical bonding between thermoplastic polymers. Thermoplastics are hold together by long linear polymer chains that have a weak chemical bonding (van der Waals force) between them. When thermoplastics are heated, weak bonds between polymers break and the plastic 'melts'. It can be then remolded into new shape. When plastic is cooled, new weak bonds form between the polymers and plastic can keep its form.

2.3.4 Thermosets

Polymers that cannot be remolded after heating again are called thermosets. This is because of their chemical structure that has strong chemically bonded and cross-linked polymer chains. When heat is applied, thermoset polymers will not change their form because the energy used to break strong bonds between the polymers is not enough. If enough heat is used, thermosetting polymers will not return to their original state **[12]**.

2.3.5 Elastomers

Polymeric compounds that can be stretched and are capable to recover their original form rapidly are called elastomers **[13]**. Elastomers are polymers that have properties from both thermoplastics and thermosets. Elastomers have long chain-like molecules that are cross-linked to each other – similar to the structure of thermosets, but elastomers are not as cross-linked as thermosets. They have mostly ion and hydrogen bondings between molecules **[14]**. Most elastomers are thermoset elastomers, but some of them have the ability to be remolded after heating. These elastomers are called thermoplastic elastomers.

2.4 PHBV

PHBV aka Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) is a biodegradable co-polymer. It is produced by either indirectly by micro-organisms or directly by plants **[15]**. PHBV is a copolymer that is made of two different monomers as it can be seen from Figure 7. These two monomers are PH3B (Poly-3-hydroxybutyrate) and PHV (Polyhydroxyvalerate). Mechanical and thermal properties of PHBV are relative to the ratio of PH3B and PHV. The higher ratio of PH3B is compared to PHV, the stiffer PHBV becomes **[16]**. Higher ratio of PHV makes polymer more flexible and lowers the melting temperature **[17]**.

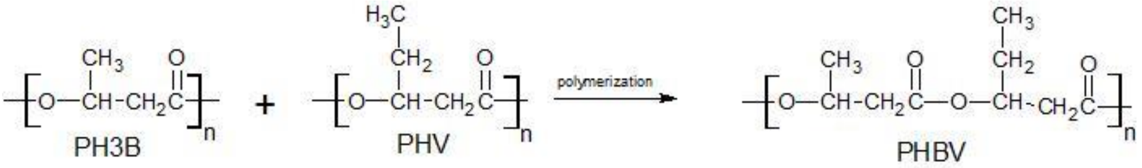


Figure 7 Polymerization of PHBV

PHBV as a material is hard, very brittle and it has low strain at break. It is also expensive compared to the petroleum based plastics, which is the reason why there has been a growing interest for finding a good filler material to cut the price of PHBV. The problem is that the filler material that is being used with PHBV has to have good adhesion properties with PHBV and it cannot lower the mechanical properties of PHBV.

2.5 Rice husk

Rice husk (or hull) is the exterior part of grain of rice (See Figure 8). During the milling processes rice grains and husks are separated from each other. It is made of mostly from lignin, cellulose and silica. Because of the materials it is made of, RH is mostly inedible for humans. Lignin reacts in the same way in our bodies as the cellulose does. Because humans do not have the same kind of enzymes as grass eating animals (like cows) do have, humans cannot digest cellulose or lignin to glucose. RH is considered waste by the rice milling industry and it is usually left to rot outside the factories or used as fuel for heating the factories **[18]**. RH is rich in silicone, which makes it a perfect source for e.g. electronics and cement manufacturing.

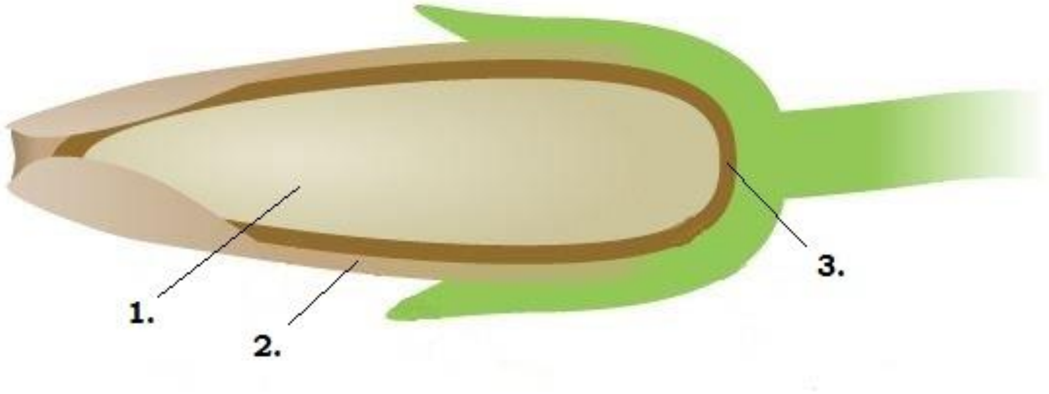


Figure 8 Cross-section of rice: 1. rice grain; 2. rice husk and 3. rice bran

2.6 Cellulose

Cellulose is a plant polymer that has a simple chain structure. It is a homopolymer that is made of repeating units of monosaccharides (glucose monomers), which can be seen in Figure 9. These long chains of monosaccharides are called polysaccharides. Polysaccharides form cellulose that acts as a strengthening component in the fiber walls of wood and plants. Depending on the size of the cellulose chain, the smaller the chain is the more hydrophilic (soluble to water) it is. Longer chains of cellulose are hydrophobic (insoluble to water). Cellulose can be degraded into monosaccharide units by certain enzymes or with an acid and high temperature treatment. This is due to the strong hydrogen bonds between monomers.

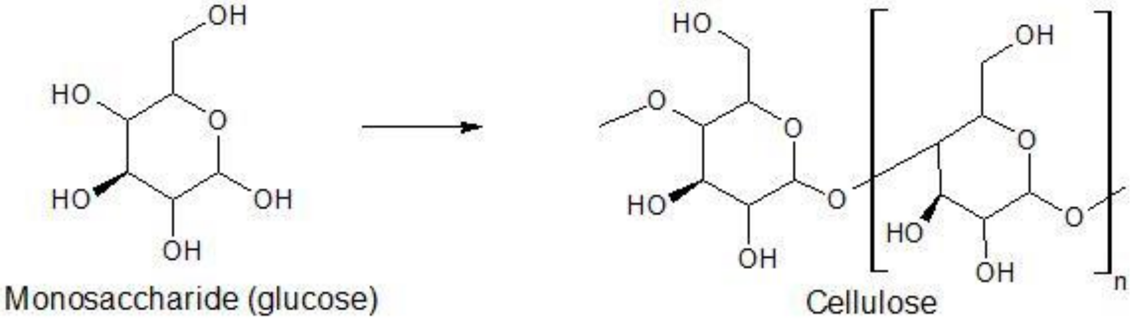


Figure 9 Structure of cellulose

2.7 Lignin

Lignin is a plant polymer that has a high molecular-weight and very complex structure, as it can be seen from the Figure 10 below. Lignin is the only polymer in plants that is not made of monosaccharide monomers.

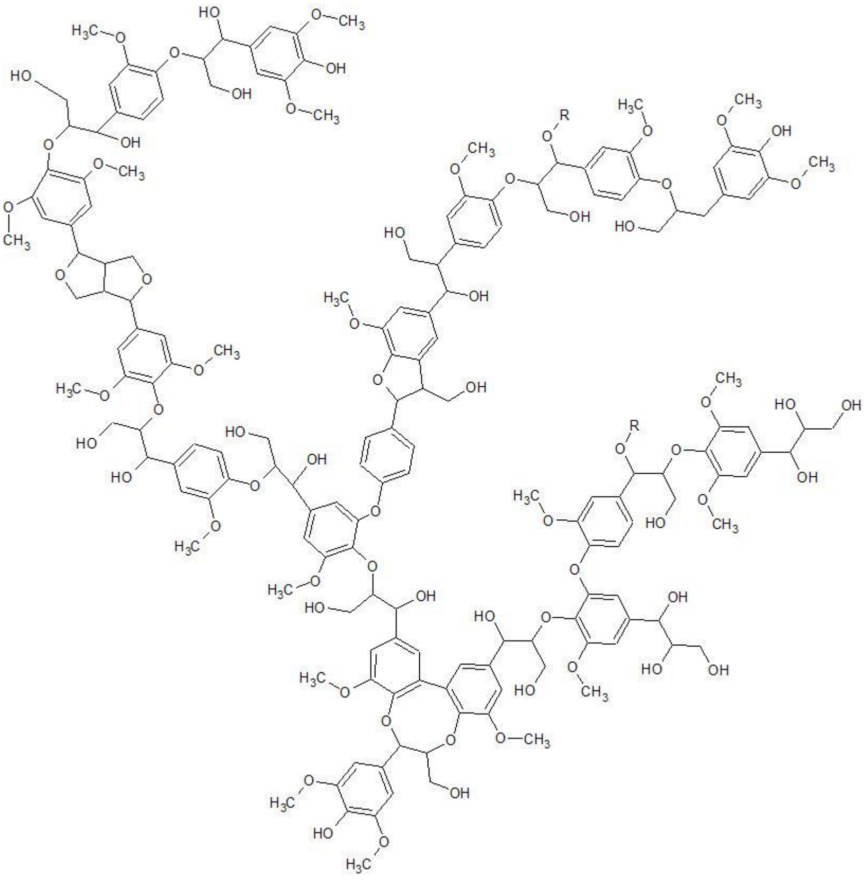


Figure 10 Structure of lignin

The structure of lignin is composed mainly of three different phenyl propane monomers (Figure 11) that are cross-linked to each other. There are many different bonding patterns that can occur between different phenyl propanes. Lignin provides structural stiffness to many plants and trees that would bend under their own weight without it. Lignin owns a chemical structure that makes it less hydrophilic **[19]**.

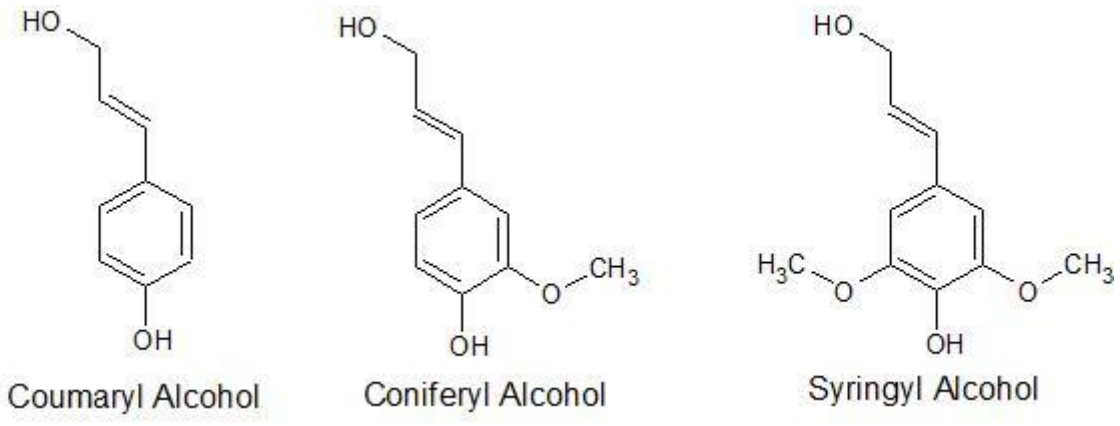

Coumaryl Alcohol Coniferyl Alcohol Syringyl Alcohol

Figure 11 Lignin alcohols

2.8 Polymers in food packaging

There are many ways to store food. The best way to do it is to wrap the food into a material that protects the food from outside environment and improves the transportability and storability of the food item. The packaging materials vary from metals to polymers. Depending on the purpose of use, certain packaging material is used that has the required properties to do its job. Metal, glass, plastics, paper and cardboard are used as packaging materials for food around the world.

In order to be a good food packaging material, it has to have the following properties: material has to withstand changes in the out and inside environments, it has to be safe for consumers to be used in food packaging, it has to protect the product and if food preservation gases are used, it has to be gastight. There are many other requirements too, but the presented ones are the main ones.

Polymers are most widely used in the food packaging industry because they are cheap and versatile for use in a large variety of applications. Polymers can be used to give products shock resistance, they can be used for restricting the movement of the product in the package and they can be used for creating an air-tight environment. Most commonly used polymers in food packaging industry are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyethylene terepthalate (PET) **[20]**.

Waste management of polymers has been done so far by recycling them, burning them or using them as s landfill. Recycling of polymers is hard because they are usually covered in other materials (food, metal, glass, wood…) that are not easy to remove. Because it is costly to recycle polymers, they are often just burned. Burning polymers releases high amounts of heat that can be used for producing electricity. However, burning certain polymers (like PVC) produces toxic gases that can be harmful to people. Using polymers as landfill is also problematic because it produces greenhouse gases like methane and it might be an unstable ground for buildings to be built on.

2.9 Problems with polymers in food packaging

The use of polymers in food packaging has been increasing steadily over the past 15 years. The latest trend in the packaging industry has been the increase in the usage of biodegradable biopolymers as packaging material for products instead of petrochemical plastics. Nevertheless, petrochemical polymers are used widely almost in every technical application that exists today. As a result of this, a huge amount of polymer waste is created every year. In 2012, a total of 32 million tons of plastic waste were created according to US EPA (United States Enviromental Protection Agency) **[21]**. Some polymers can be recycled and used again, but in most of the cases the plastic that has been used in food packaging will not be used again nor recycled. This is because of the remains of food in the polymer waste, which makes it harder and more expensive to recycle.

In order to reduce the amounts of polymer waste created every year, more effective measures than recycling & burning old materials has to be introduced. Even if 95% of all the polymer waste created every year were collected, there would still be left that 5% of waste in the nature. Some polymers (for example PE, polyethylene) degrade chemically into smaller pieces in the nature over long periods of time, so they can basically last forever. That does not mean that polymers cannot physically degrade into smaller pieces. When polymers are mechanically grinded into smaller pieces, it makes it almost impossible to collect those tiny pieces from water. A good example about this problem is the sc. the seventh continent of plastic also known as the Great Pacific garbage batch. This “continent” is made entirely out of polymer waste that has been grinded into smaller particles **[22]**. This garbage batch is not one of its kind, there are four other similar garbage batches but the one in the Pacific is the biggest.

There are also other reasons why interest in researching the usage of biopolymers has been growing constantly. The biggest reason after environmental protection is the diminishing sources of fossil fuels. The currently known sources of fossil fuels will probably last 40 - 100 years **[23]**. Without fossil fuels, we won´t have petrochemical plastics which are a necessity nowadays.

3 METHOD

This thesis researches the usage of rice husk (RH) as a strengthening fiber in PHBV based biocomposite that is biodegradable. This biocomposite consists of two matrixes: 1.) biodegradable polymer (PHBV) and 2.) natural fiber that improves polymer's mechanical properties (rice husk). The aim of this study is to make a biodegradable biocomposite made of PHBV and RH, that should have better mechanical properties compared to pure PHBV.

Before a method was developed, literature review had to be done in order to determine what kind of results there already are about PHBV based biocomposites and RH. Based on these findings a method was developed.

3.1 Literature review

According to the studies of Tran - Bénézet - Bergeret (24, p.58) and Mohammadi - Rovshandeh - Pouresmaeel-Selakjani - Davachi - Babak - Hassani - Bahmeyi (25, p.58) sodium hydroxide (NaOH) treated RH possess better mechanical properties than non-treated natural RH. This is caused by the lignin removal that improves composite by creating porosity and more roughness in the outer surface. NaOH treated RH should also produce more fiber-like structures that should improve biocomposites mechanical properties. In order to compare the difference in the mechanical results between NaOH treated RH and untreated RH, different concentrations of RH and PHBV should be tried. The concentration of NaOH and its effect on RH is also studied by making a test, in which two different concentrations of NaOH are used and the duration of treatment is varied.

An optimal amount of RH in the biocomposite is somewhere between15 (wt.%) – 20 (wt.%) according to Mohammadi (25, p.58) and Tran - Nguyen – Thuc – Thuc – Tan (26, p.58). In these studies the mechanical properties of RH and PLA based biocomposite were investigated. Higher concentrations of RH will lead to the reduction of mechanical properties, if the lignin is completely removed, according to the study of Mohammadi (25, p.58). Singh – Mohanty - Sugie - Takai - Hamada (27, p.59) concluded that higher filler concentrations would be achieved with other fiber types than RH, like bamboo fiber and kenaf. Based on these findings, four different concentrations of RH and PHBV are made (See Table 1).

Table 1 PHBV and RH blends

Blends (wt %)	Rice husk (g)	PHBV (g)	Total mass (g)
5	15	285	300
10	30	270	-//-
15	45	255	-//-
20	60	240	-//-

3.2 Experimental

In the experimental part of this thesis the mechanical properties and surface morphology of RH and PHBV based biocomposite were investigated.

3.2.1 Materials

Rice husk (RH) was supplied by Herba in Valencia, a company recently purchased by Ebro Foods. PHBV pellets (ENMAT Y1000P) were supplied by TianAn Biopolymer. Sodium hydroxide (NaOH) was from Panreac (141687.1211). Acetic acid (CH_3COOH) was obtained from Probus (010510).

Figure 12 PHBV pellets (ENMAT Y1000P)

For washing the lignin from RH, two alkaline solutions consisting of 10% (wt.) and 5% (wt.) sodium hydroxide (Panreac, 141687.1211) were prepared in distilled water. For neutralizing and washing the alkaline solution, an acidic solution consisting of 1% and 10% acetic acid (Probus, 010510) was also prepared. Bühner funnel and filter paper (1300/80) were used for suction filtration. Tri-color pH paper was used for determining the pH. Mortar and pestle were used for cracking the RH after suction filtration and drying.

JSM-7001F Scanning Electron Microscope and Leica DM-RME light microscope was used for observing the surface morphology of fine RH. Piovan Hot Air Dryer was used for drying the PHBV pellets. Thermo Haake Polylab System (equipped with Rheomix 3000p mixer and Roller-Rotors R3000 rotors) was used for mixing the PHBV pellets and RH. Carver Standard Press (Model 3851-0) was used forfilm pressing. Positest DFT was used to determine the thickness of the films. Perkin Elmer Differential Scanning Calorimeter 7 was used for determining the thermal properties of the films. Shimadzu AGS-X 500N was used for determining the mechanical properties (tensile testing) and Illig Skin and Blister Machine SB 53c was used for the thermoforming of the films.

3.2.2 Grinding of RH

Liquid nitrogen was used to freeze the material and then it was grinded into smaller particles with a coffee grinder. Rough RH was put into a sieve (Filtra Vibracion SL, mesh size of 140 µm) and it was put into a separator. Fine dust of the RH was left into the collection bag under the sieve and the rough RH that did not pass the sieve was processed again, until there was enough material to work with.

RH was characterized using JSM-7001F Scanning Electron Microscope. Using the SEM, the particle size & surface morphology were investigated. It was possible to achieve particle size of ≤ 0.140 mm (140 µm) with liquid nitrogen method.

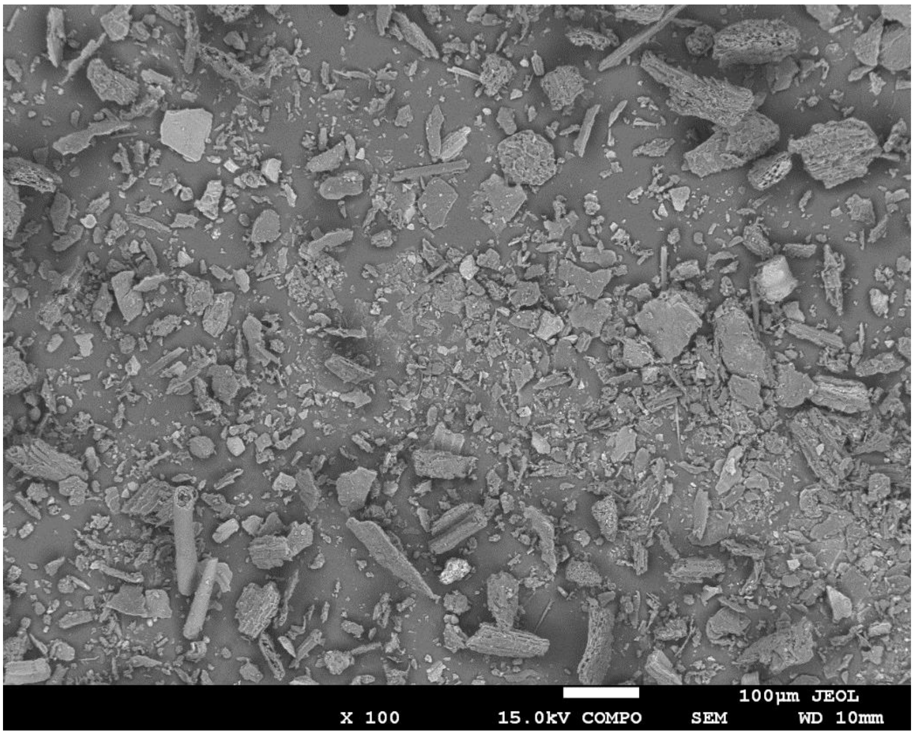


Figure 13 Grinded RH

As it can be seen in Figure 13 above, most of the RH particles are within the size limit of ≤ 0.140 mm (140 µm). Bigger particles than that would affect to the polymer film because the size of the film would not be too much bigger than 140 µm. This could weaken the film and its mechanical properties. The structure of fine untreated RH is not too fibrillated, so the adhesion between PHBV and RH could be weaker which would lower the tension properties of the PHBV film.

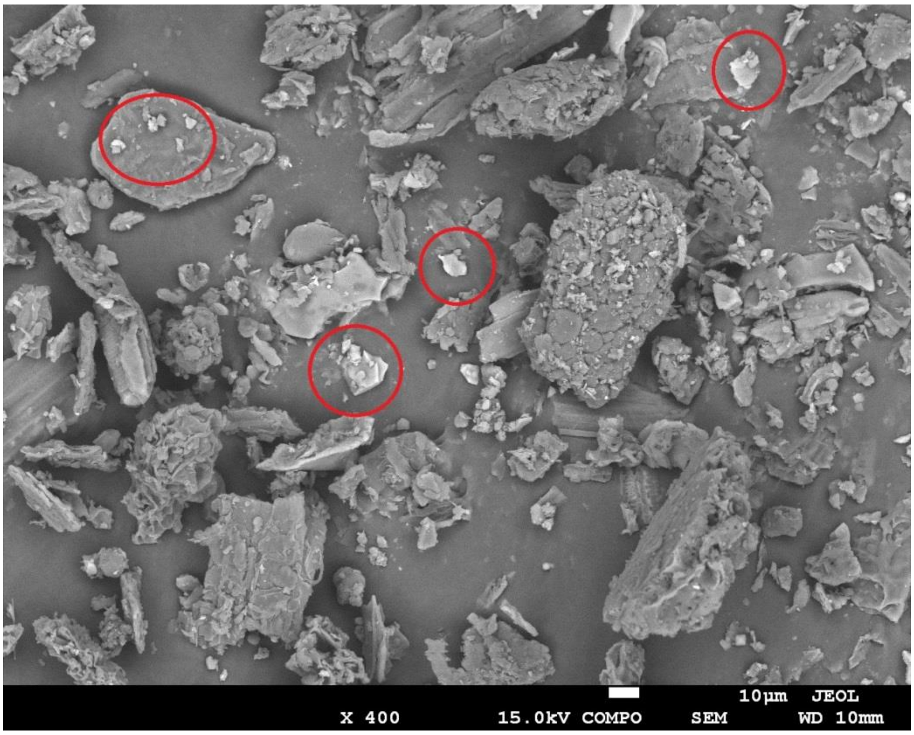


Figure 14 RH with silica particles (red rings)

SEM revealed that the RH wasn´t as pure as it was thought to be. Small particles of silica (See Figure 14) were found to be in the sample, but there is an explanation for this: those silica particles found were from RH itself. RH is full of silica and those particles in the sample were most likely from it. This was confirmed by the supplier of the RH.

3.2.3 NaOH treatment of RH

Rice husks were dried at 100°C for 24 h. Then small batches of RH were immersed in 5% (wt.) and 10% (wt.) sodium hydroxide (NaOH) solution for 24 and 36 hours. These batches were then left to be in room temperature.

Suction filtration equipment was prepared and wet RH was put into the filter paper. RH was washed with distilled water to eliminate NaOH, and then the RH was washed with acetic acid (1%). Sediment was washed with acetic acid, until the pH of filtrate was 7.0 (neutral). Finally, the RH was washed again with distilled water to wash any leftovers of acidic or alkaline solution. When RH was dry enough, a spoon was used gently to remove the RH from filter paper to a drying plate.

RH was dried at 100°C for 24 h and mixed occasionally to get rid of the moisture. Then RH was cracked into smaller pieces using a mortar and pestle. Fine RH was dried at 100°C for 2 h. Small batches of grinded RH were characterized with SEM & microscope. The surface morphology of NaOH treated RH was investigated to see if the treatment was successful.

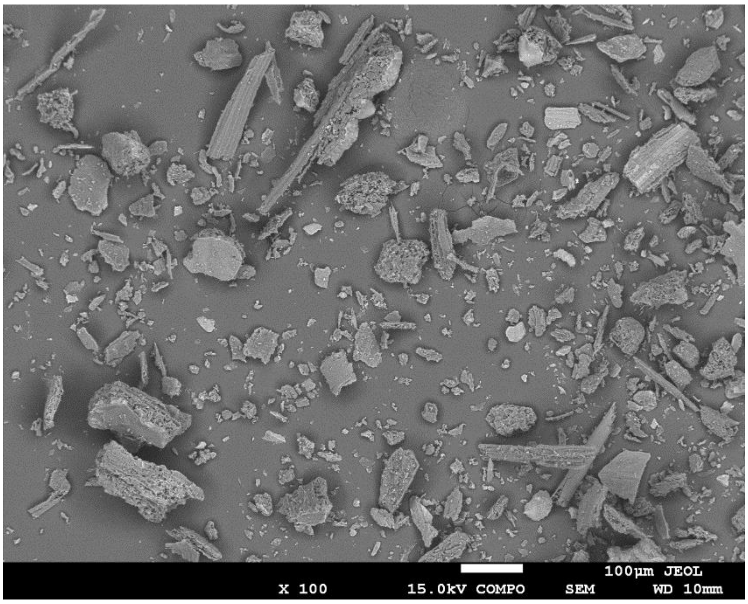


Figure 15 Untreated RH

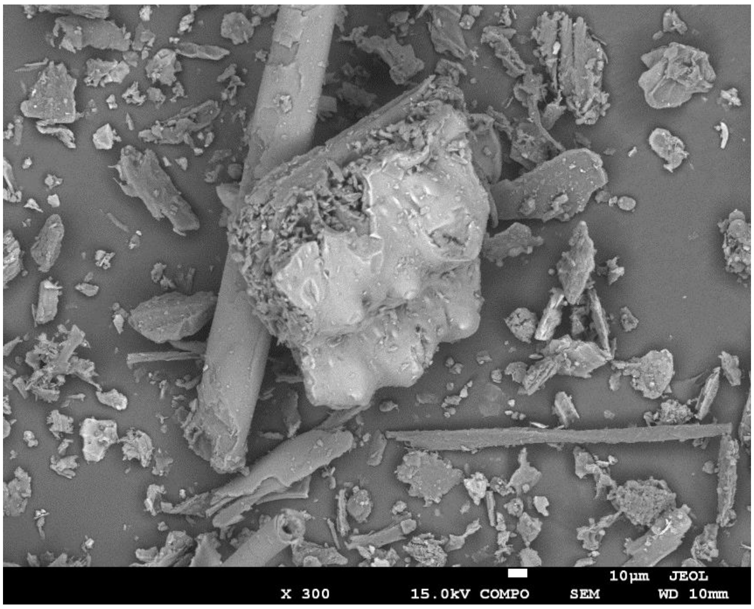


Figure 16 Untreated RH

As it can be seen from Figures 15 and 16, the untreated RH does not have too many fiber-like structures in it. The surface of RH is smooth, which does not help with the adhesion of PHBV and RH. In Figures 17 and 18 it can be seen that the structure of NaOH treated RH is rougher when compared to untreated RH.

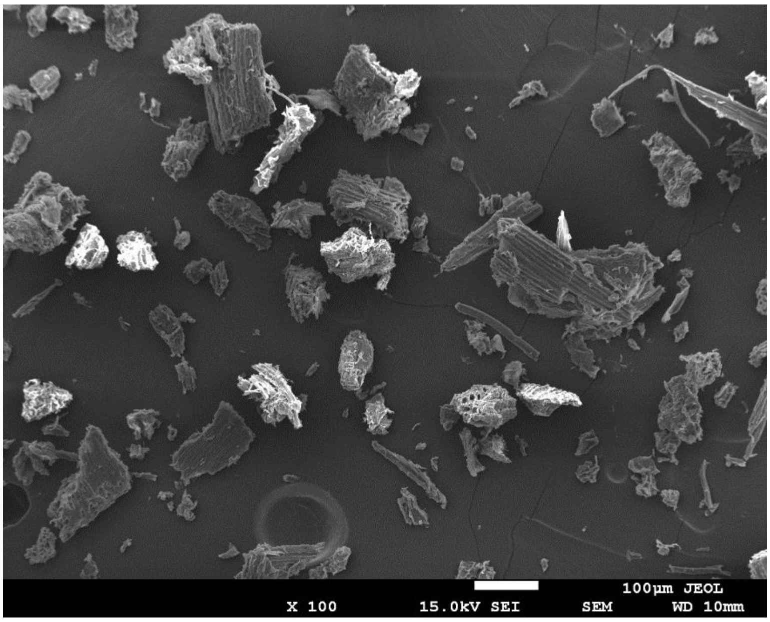


Figure 17 5% NaOH for 24 hrs

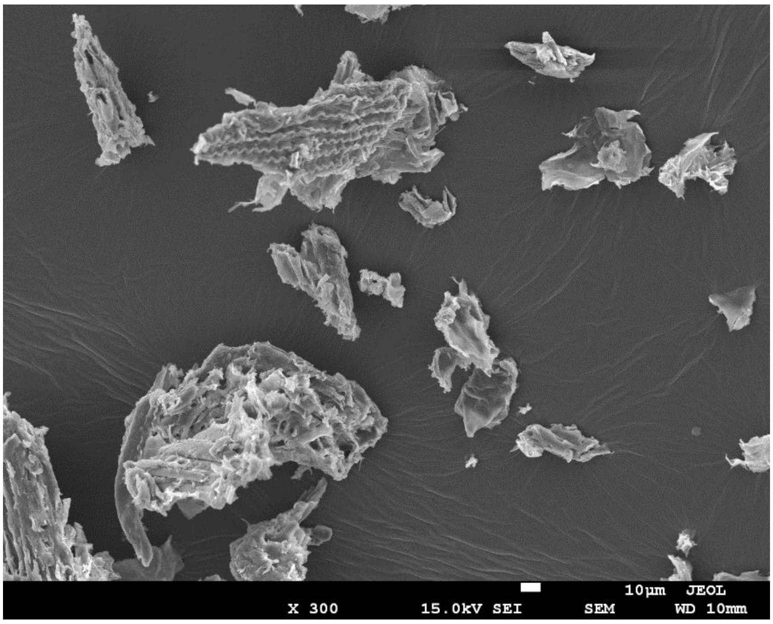


Figure 18 5% NaOH for 24 hrs

In an ideal case the RH has a very porous structure and it has many fiber-like structures, similar that can be seen in Figures 19 and 20.

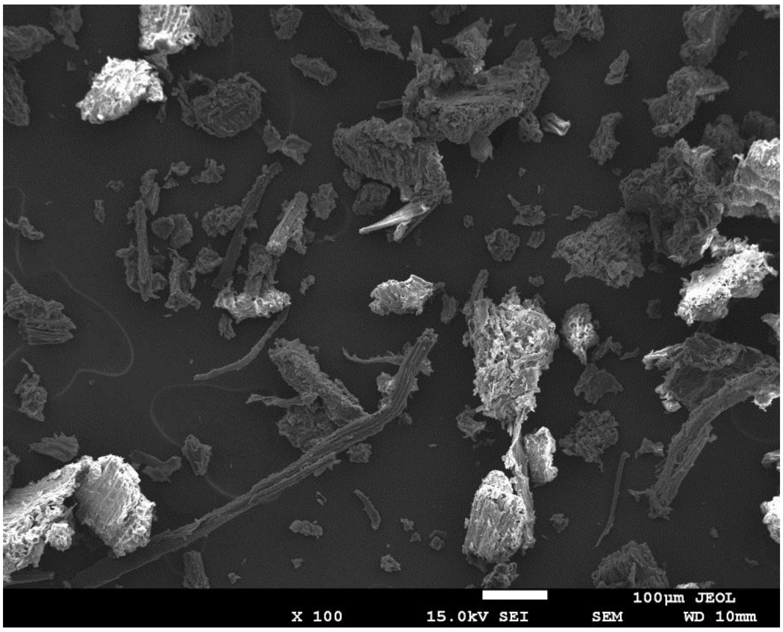


Figure 19 10% NaOH for 24 hrs

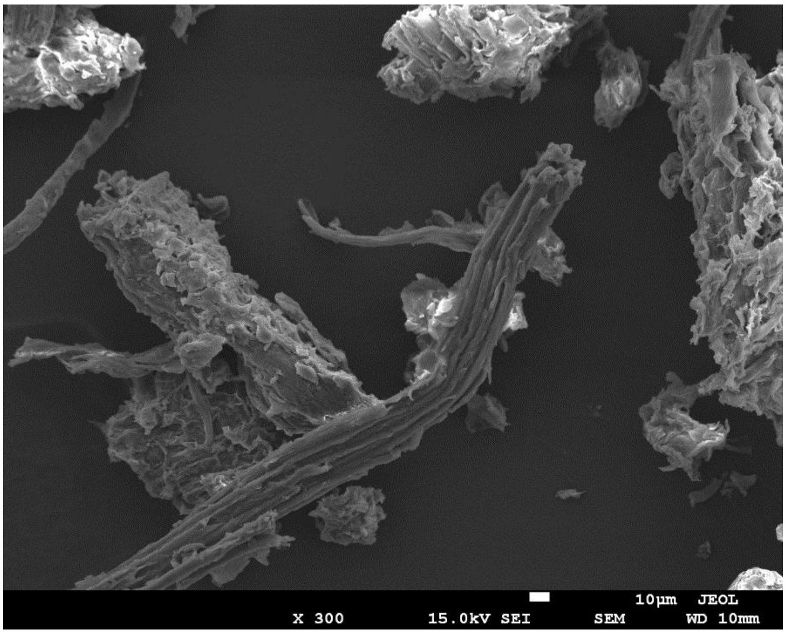


Figure 20 10% NaOH for 24 hrs

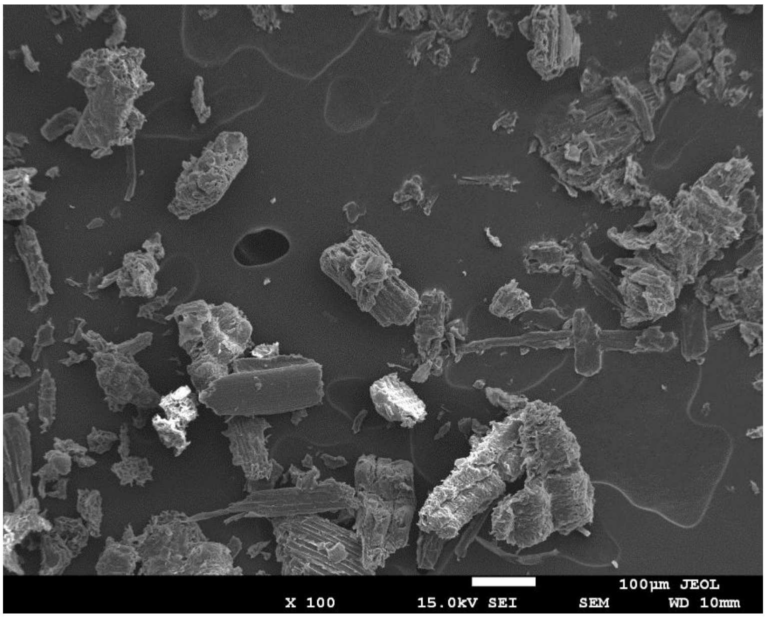


Figure 21 5% NaOH for 36 hrs

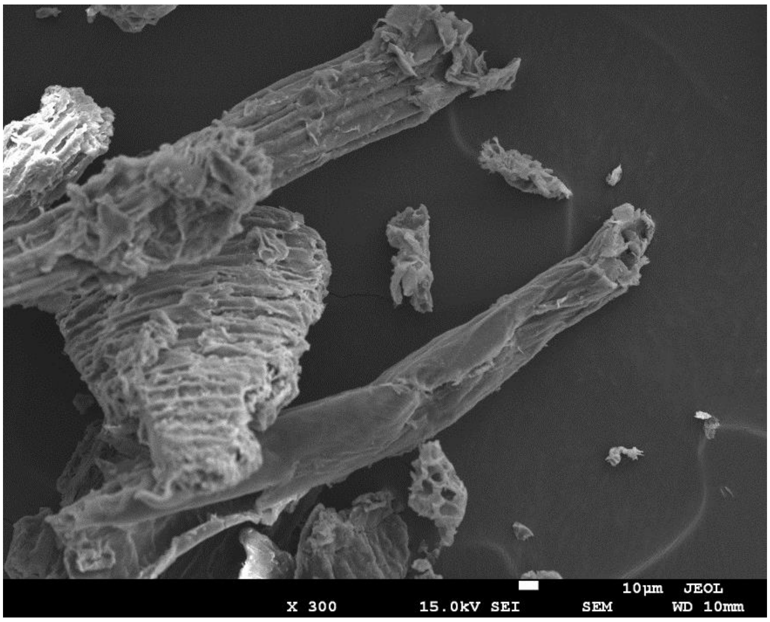


Figure 22 5% NaOH for 36 hrs

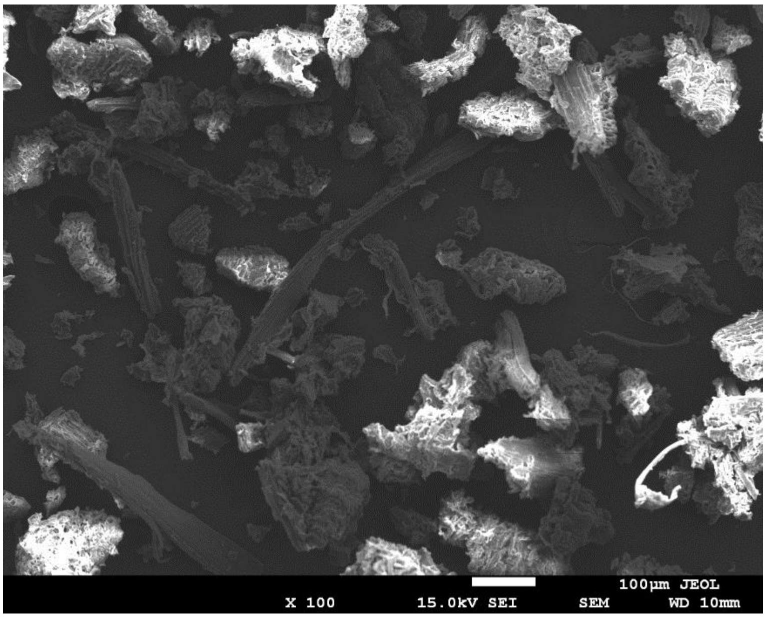


Figure 23 10% NaOH for 36 hrs

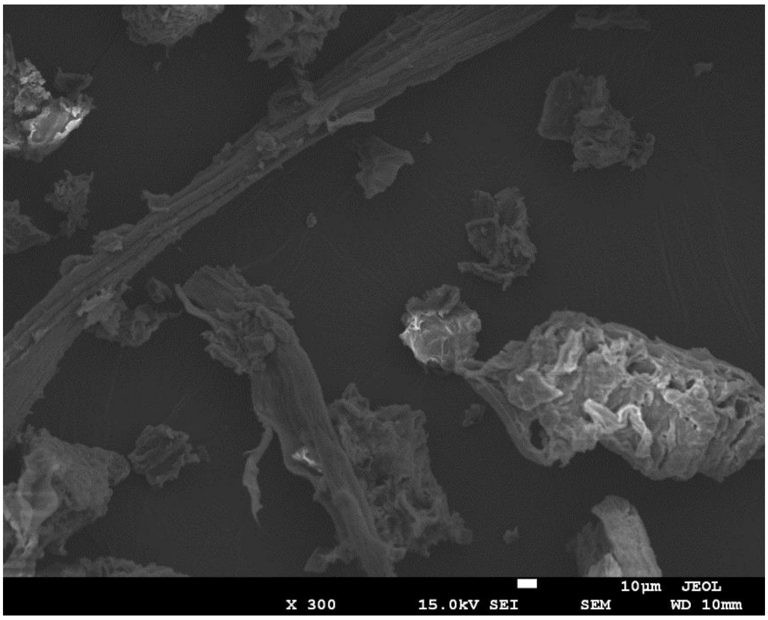


Figure 24 10% NaOH for 36 hrs

The increased porosity of RH can be seen from all the SEM Figures 17 - 24 above. Treated RH is more porous compared to untreated RH. It seems that higher concentrations of NaOH are more effective at washing lignin off than the lower concentrations. Also, there seems to be no additional benefits from longer chemical treatments of RH. NaOH treated RH after 24 hours of treatment looked the same as NaOH treated RH after 36 hours of treatment.

Leica DMR ME microscope was used to roughly estimate the amount of fibrillated particles in the sample. The measurements were conducted at room temperature (25°C) with the lens magnification of x50.

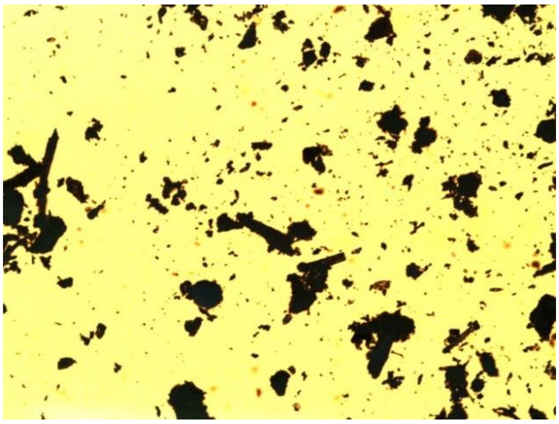


Figure A Untreated RH

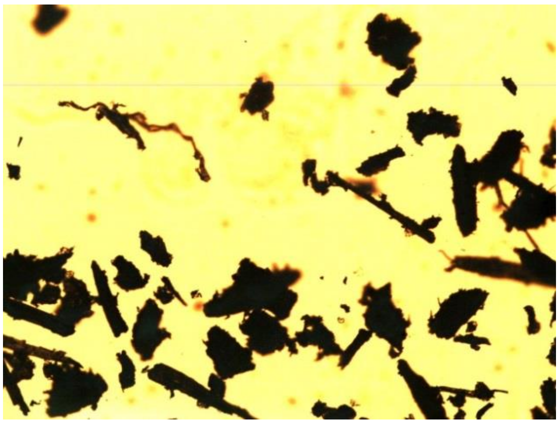


Figure B 5% NaOH 24 hrs

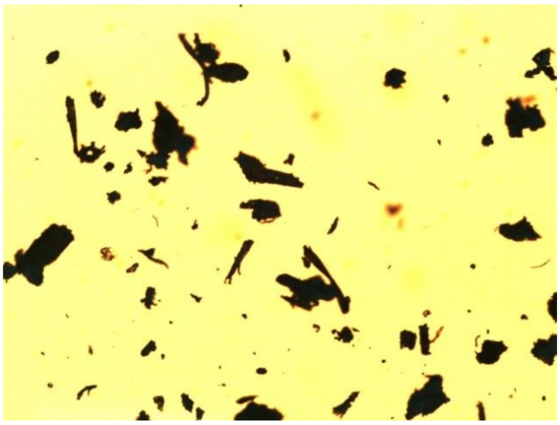


Figure C 10% NaOH 24 hrs

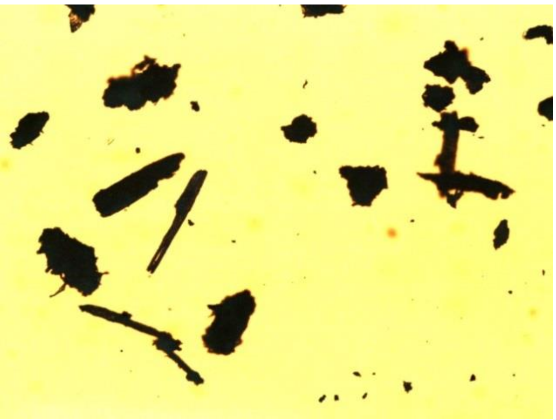


Figure D 5% NaOH 36 hrs

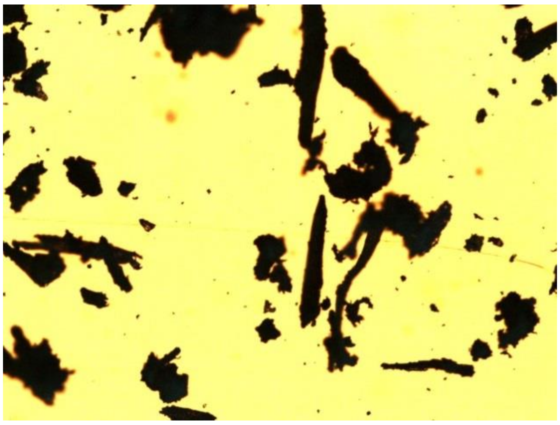


Figure E 10% NaOH 36 hrs

In Figure A there are many particles that have a round shaped structure. Round shape is not the ideal shape for a particle in this case because they do not have as much surface area as fiber-like structures. This might lead to the reduction of mechanical properties because PHBV and RH will not probably have a very good adhesion between each other.

In Figures B and C, the NaOH treatment has clearly had an effect to the amount of fiber-like structures. There are more fiber-like structures and the surface of the RH does not look as smooth as it does in Figure A. When the surface area of a RH particle is increased, the adhesion between PHBV and RH should increase too. This would increase the mechanical properties of the film.

Figures D and E show that RH has similar fiber-like structure and that there are fewer particles than in Figures B and C. This might be the cause of NaOH concentration. Even small concentrations of NaOH with enough time will dissolve all the lignin from RH. This would cause the structure to be so porous that it would crack very easily.

3.2.4 Melt blending

PHBV pellets (ENMAT Y1000P) were dried at 80°C for two hours. Piovan Hot Air Dryer was used for drying the pellets. This was done in order to remove the moisture from the pellets. If the pellets are not dry enough, PHBV would start degrading and it would affect to the mechanical properties.

Both untreated and treated RH was melt mixed into PHBV. Four different blends of RH were prepared as shown in the Table 1, page 22. The process of mixing was done as shown in Table 2. Total mass of each blend is 300 grams and the temperature, in which the blends are mixed, is 175°C. PHBV pellets and RH were mixed with Thermo Haake Polylab System (equipped with Rheomix 3000p mixer and Roller-Rotors R3000 rotors).

After melt blending all the blends of PHBV and RH into ´cakes´, they were visually inspected before processing them into films. This was done in order to check that there were no burnt spots or non-melted pieces of PHBV.

Table 2 Process table of melt blending

m= 300 g (total) **T= 175°C**

Process	**RPM (rpm)**	**Time (min)**
Feeding 1	20 rpm	≈ 1 min
Feeding 2	40 rpm	≈ 1 min
Mixing	100 rpm	≥ 3 min
Finishing	20 rpm	≈ 1 min
	Total time	**= 6 min**

Figure 25 Thermo Haake Polylab System equipped with Rheomix 3000p mixer

3.2.5 Film pressing

PHBV and RH cakes were broken into pieces with a hammer and a cloth. Using a laboratory scale around 1.3g ± 0.1g of polymer was then weighted for one film. Polymer was processed with Carver Standard Press (Model 3851-0) that is capable of polymer forming. It uses heat and pressure to reform the polymer cakes into polymer film.

Polymer was put between two stainless steel plates that were covered with a teflon sheet. Temperature was set to 180°C and the sample was put between clamps. Pressure was slowly raised to 1.0 metric tons, until the needle remained in its place. Pressure was raised to 2.0 metric tons and the pressure was released totally to let the polymer reshape. The clamps were put together again almost immediately. Pressure was raised to 3.0 metric tons and it was kept for 3 minutes. After 3 minutes the pressure was raised to 3.5 metric tons, temperature was lowered to 25°C, water cooling was activated and the pressure was kept in 3.5 metric tons until the film was cooled to room temperature.

Figure 26 Carver Standard Press

3.2.6 Determination of tensile properties

As a part of mechanical properties, tensile properties were determined with Shimadzu AGS-X 500N. AGS-X 500N was used for determining the force (F=Newtons) that is needed to break the sample. Thickness of the films were determined with Positest DFT. Tensile modulus (Young's modulus) of the sample can be calculated, after we know the cross-sectional area of the sample (A) and the force (F) needed to break the sample. Using the following Formula 1, the tensile strength (usually indicated in megapascals, MPa's) can be calculated.

Formula 1 Tensile strength of the sample

$$\text{Tensile strength } \left(\frac{N}{cm^2} / \text{ MPa}\right) = \frac{Force\ needed\ to\ break\ the\ sample\ (N)}{Cross\text{−}sectional\ area\ (cm^2)} \text{, where}$$

Cross-sectional area = thickness of the sample x width of the sample (5 mm)

Films were cut into bone-shaped samples (Figure 27) using a specific cutter for this. Twenty replicates were made for each blend. Pure PHBV Mezclado (Spanish word for ´mixed´) was used as a point of reference. In order to see the effect of PHBV degradation, ten samples were measured at day one and another ten after 15 days. In total, twenty replicates were made from each blend and PHBV Mezclado. Samples were stored in desiccator, until they were measured.

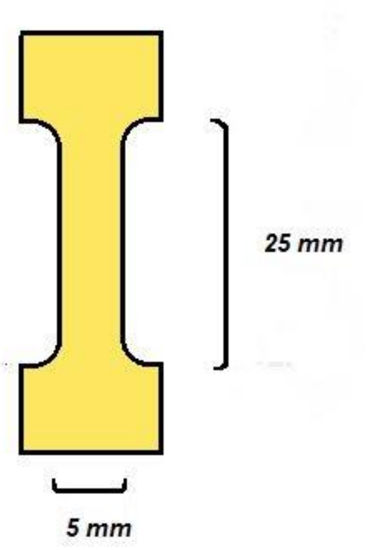


Figure 27 Measurements of tensile properties sample

Sample was placed between clamps straight up. The lower clamp of Shimadzu AGS-X 500N (Figure 28) was closed first. Total force was nulled at this point, so the results would stay consistent. A little dent was made in the sample before closing the upper clamp. This was done because the machine would stretch the samples with the programmed pre-force of 5.0 N and without that dent the sample would stretch unevenly. This would have otherwise distorted the results.

Figure 28 Shimadzu AGS-X 500N Universal Tester

In order to check the morphology of the films (what kind of adhesion RH had with PHBV) polymer samples were frozen with liquid nitrogen and then samples were cracked with forceps. The cracked samples were then observed with SEM to see if the RH had fiber-like structure in the melt blended polymer and if there was good adhesion between RH and PHBV.

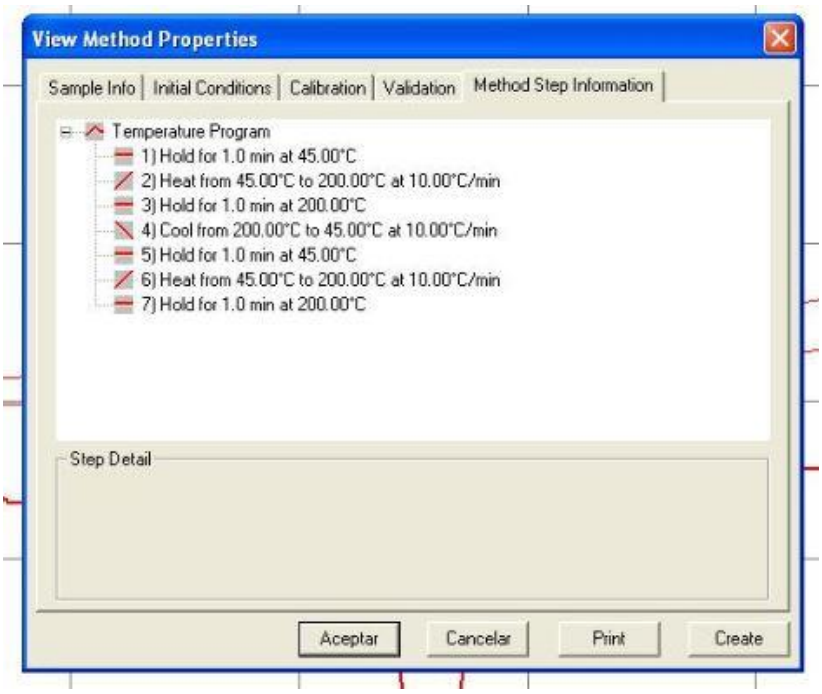
3.2.7 Differential Scanning Calorimeter (DSC)

Thermal properties and thermal degradation of PHBV and RH blends were investigated with Perkin Elmer Differential Scanning Calorimeter 7 (Figure 29) that used argon (Ar) as inert purge gas for DSC cell. Differential Thermal Analysis (DTA) is a technique where polymer sample is heated and effects of the heating to the sample and the reference material (empty aluminum dish) are investigated. Inside DSC there are two pans with their own heater units, one for reference material and another for the polymer sample. In this experiment two values are plotted in the graphs: the temperature (x-axis) and the differential temperature (y-axis) of the reference material and the sample (See Figure 31) **[29]**.

Figure 29 Perkin Elmer DSC 7

A two-hole punch was used to obtain the PHBV+RH film sample. Laboratory scale was used to measure a sample between 6.0 to 8.0 mg. Sample from the film was packed between two aluminum dishes and the weight of the sample was recorded. Forceps were used for sample handling because the amino acids on hands would increase the amount of material in the sample and therefore heat needed for warming the sample. Aluminum dishes were closed with Perkin Elmer

Universal Crimper Press. After this the samples were analyzed. The following temperature program (Figure 30) was used for PHBV+RH films.



Temperature Program
1) Hold for 1.0 min at 45.00°C
2) Heat from 45.00°C to 200.00°C at 10.00°C/min
3) Hold for 1.0 min at 200.00°C
4) Cool from 200.00°C to 45.00°C at 10.00°C/min
5) Hold for 1.0 min at 45.00°C
6) Heat from 45.00°C to 200.00°C at 10.00°C/min
7) Hold for 1.0 min at 200.00°C

Figure 30 Temperature program of DSC (Pyris Software version 9.0.2.0193)

Both pans inside the DSC undergo the same temperature program. DSC measures the temperature of both pans individually. Because in the sample dish there is more material than in the empty reference dish, it takes more heat in the sample pan to keep the temperature even in both pans. This heat difference is plotted in the graph and based on that graph the values of T_m (melting temperature), the degree of the crystallization and T_g (glass transition temperature) can be determined.

Knowing the melting temperature, the degree of the crystallization and the glass transition temperature of the polymer helps us to understand the mechanical, chemical and thermal properties of the polymer. The degree of crystallization of the polymers should be around 30 - 80%. When adding another matrix, like RH into polymer, polymer blend lowers its melting and the crystallization temperature.

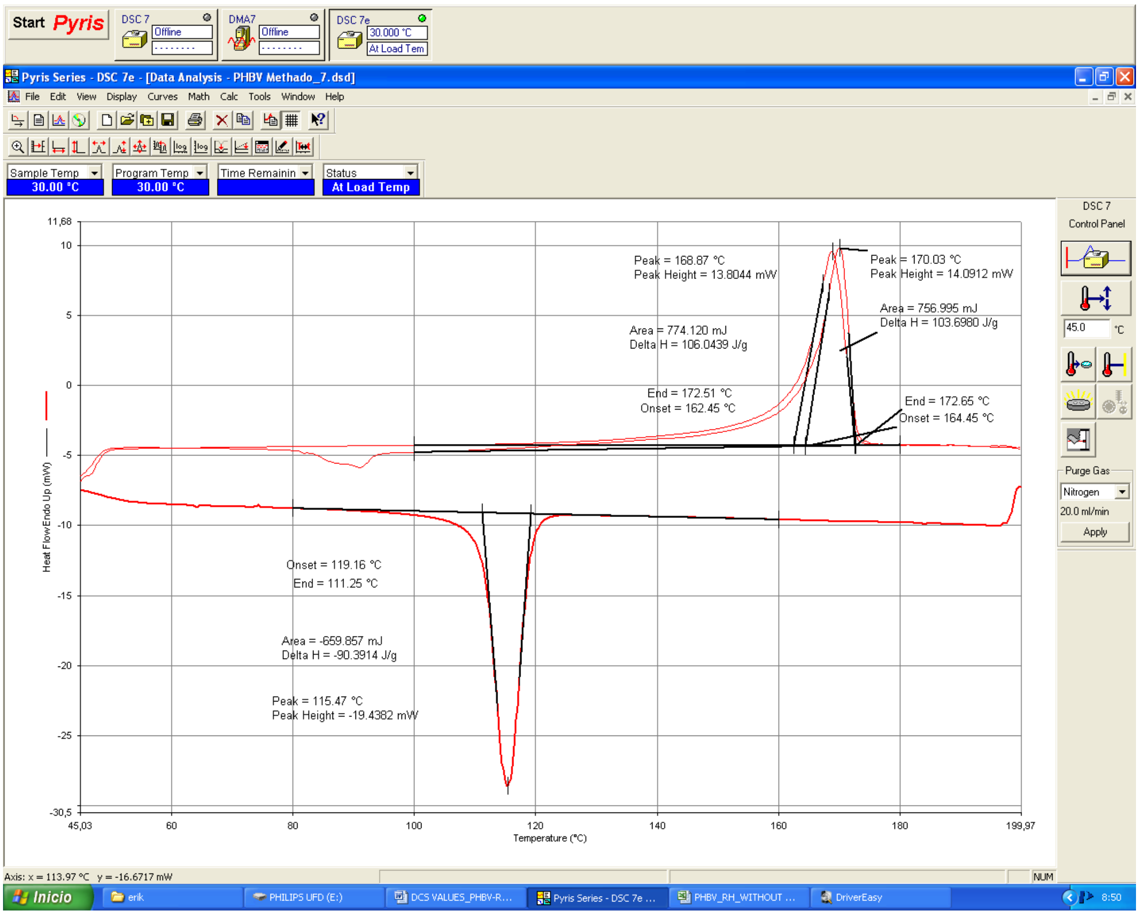


Figure 31 DSC curve of PHBV Mezclado (Pyris Software version 9.0.2.0193)

Ideal DSC curve would have three curves (called Heating 1 and 2, Cooling 1) that are similar in Figure 31 because the program that was used measured three different steps. These steps can be seen in Figure 30, where phases 2-3 are Heating 1, phases 4-5 are Cooling 1 and phases 6-7 are Heating 2. Using the programs functions, temperature peak and ΔH of the curve can be determined.

3.2.8 Thermoforming

Thermoforming of the PHBV and RH films were investigated with Illig SB 53-c Skin Packaging and Blister Forming machine (Figure 32). Thermoforming is a technique, where heat is applied to the polymer until it starts to melt and then it is subjected to pressure controlled vacuum. Polymer then takes the shape of the mould. Based on the shape of the polymer mould after thermoforming, it can be said whether the polymer is good enough for thermal processing.

Figure 32 Illig SB 53-c Skin Packaging and Blister Forming machine

When the machine was started, the real temperature T_{real} of the heating element was determined using a digital thermometer and a timer. This was done in order to check whether the temperature display was showing accurate results. The real temperature T_{real} should be between 92°C and 98°C.

Temperature was measured in the intervals of 5 seconds. Used nominal temperature was 600°C. According to the measurements, calculated T_{real} = 93 – 98 °C (Attachment 1). The results were accurate enough, so the thermoforming of the films could be done.

Thickness of the film was determined with Positest DFT. Measuring points were in the shape of a cross, the middle of the cross being the center of the film. Using a stamp and ink, a grid was made on the film. The sample was cut with scissors into a smaller rectangle. When thermoforming the films, different pressures and treatment times (vacuum and heat treatment) were tested. If the films had small holes in them, then the time of heat treatment was shortened. If the shape of the thermoformed film was uneven, then the vacuum pressure was raised and/or the time of the vacuum treatment cut shorter.

4 RESULTS

This chapter is a short review about the findings that were measured from the films. Under each title there is also a conclusion about the success of the NaOH treatment or something else regarding the titled measurement.

4.1 NaOH treatment

The surface and the shape of alkaline treated husks were observed with SEM and microscope. After NaOH treatment, the surface morphology of both husks is modified. Based on the SEM pictures, the best results were achieved with 10% NaOH treated RH. It doesn´t seem to matter whether RH was treated in 10% NaOH for 24 hrs or 36 hrs, as it can be seen by comparing Figure 20 (page 28) and Figure 24 (page 30). As the studies made by Bergeret – Benezet – Tran - Papanicolaou – Koutsomitopoulou (3, p.57), Tran (24, p.58) and Mohammadi (25, p.58) suggest, the roughness of RH was increased. Some of the SEM pictures were poor in quality because the RH samples were not dry enough. More time in the oven would have fixed this problem.

4.2 Melt blending

Melt blending of the untreated RH was successful. RH seemed to be blended evenly in the PHBV. In the Figure 33 below, there are polymer “hats” that were formed during the melt blending process. The shape of these hats indicate the flow of the polymer and if the temperature used for melt blending the polymer is inappropriate, the polymer starts to smell burnt. Hat no.1 is the most optimal shape because it has a narrow top which tells that the flow of the polymer is great and it has a bottom that is not too thick. Hat no. 2 has a thicker shaft that tells the polymer is thicker and the flow of the polymer is uneven. This could be because of the accumulation of the unmelted PHBV particles because the hat smelled like burnt. Hat no. 3 has also a thicker shaft which indicates that there has been an accumulation of RH particles and the flow of the particles has been uneven.

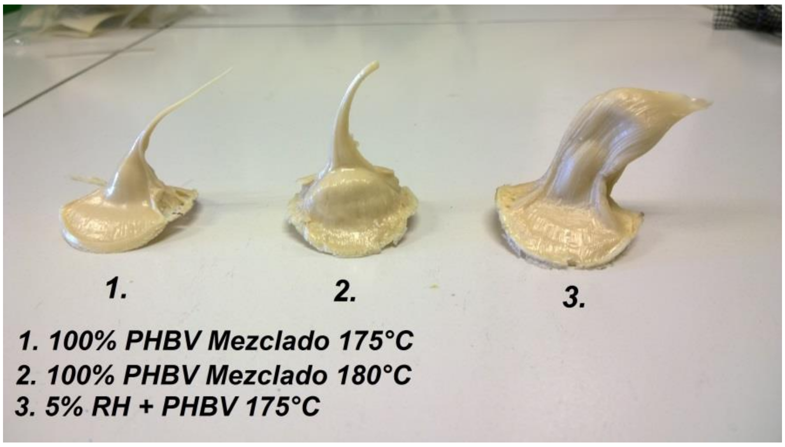


Figure 33 Polymer "hats"

Melt blending of the treated RH ended up being a failure (Figure 34). When NaOH treated RH was mixed with PHBV, it became liquid after mixing and it started seeping out from the holes of the machine. It did not behave the same way as the untreated RH did during the melt blending process. The melt blending of the treated RH was done twice and both times it liquefied. All the treated RH was lost and because of the lack of time, another batch could not be done. It is highly possible that the NaOH treatment did something to the chemical structure of RH.

Figure 34 The aftermath of melt blending the NaOH treated RH

4.3 Film pressing

Because the NaOH treated RH was lost, the NaOH treated films could not be pressed and their morphology determined. The measured average thickness of the untreated RH films was 101 ± 17 µm. Morphology of the films was investigated with SEM. If there is a gap between RH and PHBV particle it usually means that there is very little adhesion or none at all (Figure 35).

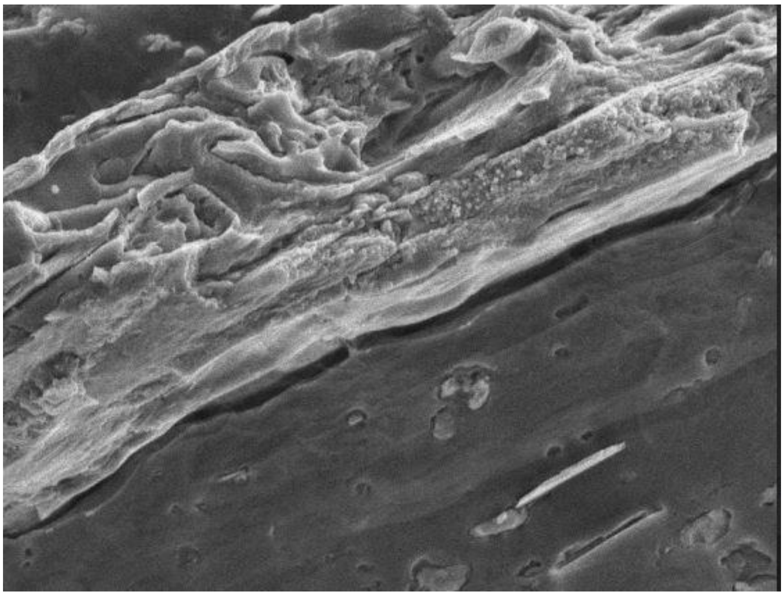


Figure 35 Example of poor adhesion

Poor adhesion usually occurs in polymers, when there is no rough surface on the other matrix where the second matrix could hang onto. In Figure 35 there is a small gap between the PHBV and RH that is formed during the film pressing. When the heated material is cooled down, it shrinks a little bit. This shrinking forms a gap between two matrixes, if there is no adhesion. If this same film was put under a stress, it would break much more easily because the adhesion between two matrixes is poor.

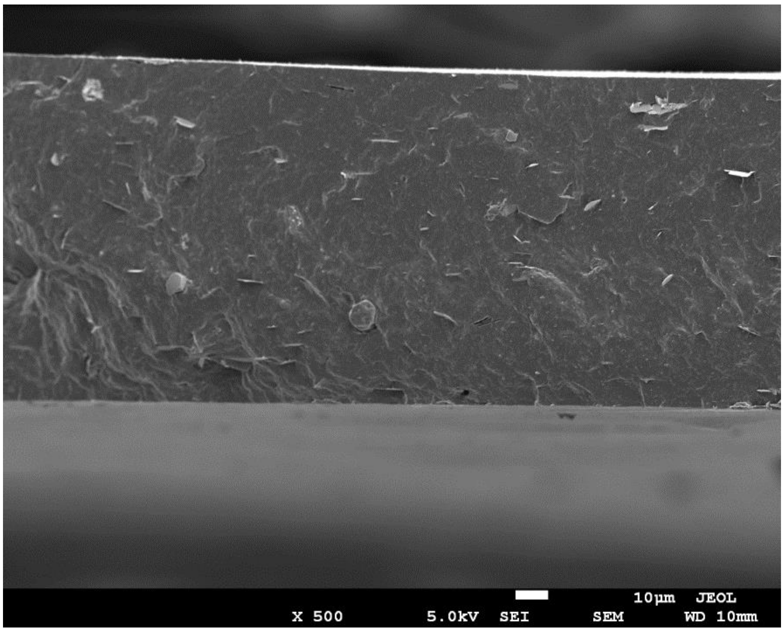


Figure 36 PHBV + 5% untreated RH (x500)

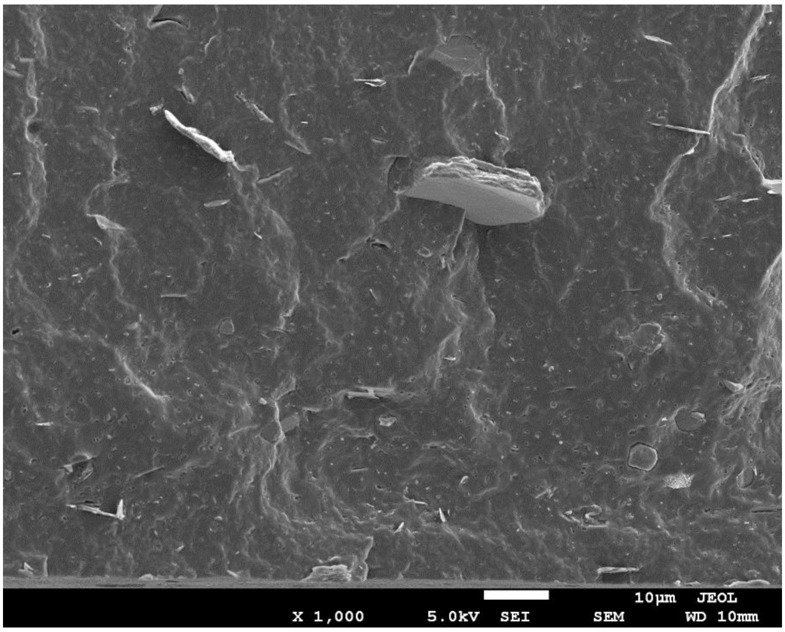


Figure 37 PHBV + 5% untreated RH (x1000)

In the Figures 36 and 37 it can be seen that the PHBV + 5% untreated RH does not have too many fiber-like particles in it. In an ideal case Figure 36 should look like it would have lots of small hairs coming out of it. This kind of ideal structure would, in theory, increase the mechanical properties of the biocomposite. The adhesion between RH and PHBV in the mix seems to be great because there is no gap between the two matrixes.

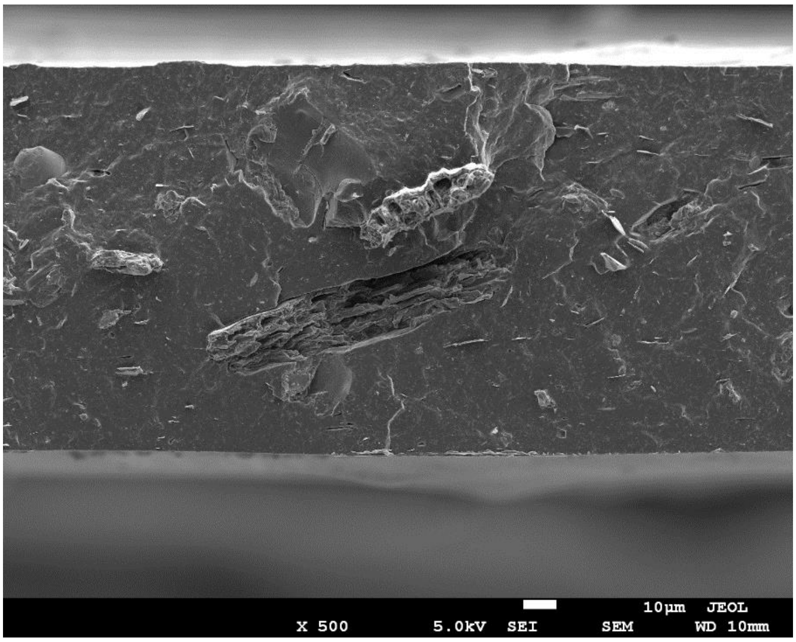


Figure 38 PHBV + 10% untreated RH (x500)

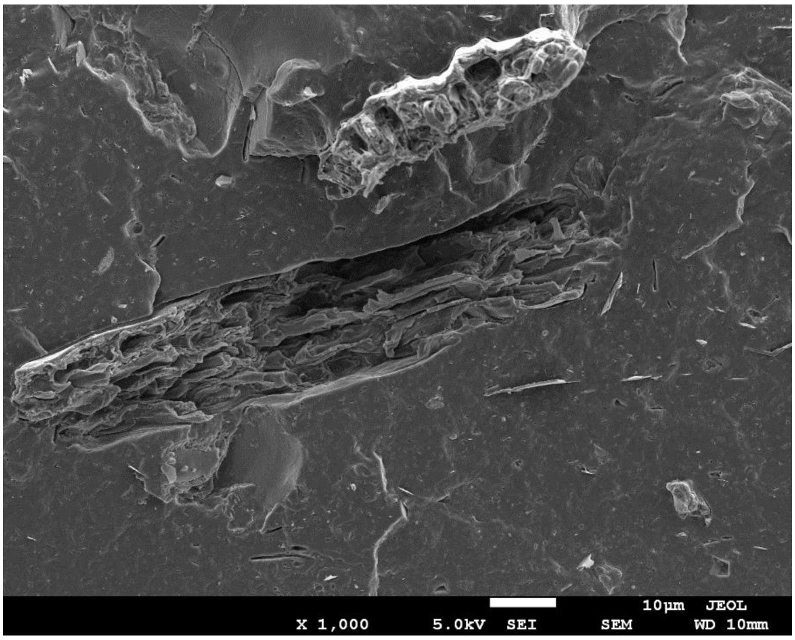


Figure 39 PHBV + 10% untreated RH (x1000)

PHBV + 10% untreated RH seems to have the same problem as 5% untreated RH. There are no fiber-like particles. Adhesion between the particles seems to be great. If the NaOH treated RH could have been melt blended, it could have had a better surface and film morphology compared to untreated RH.

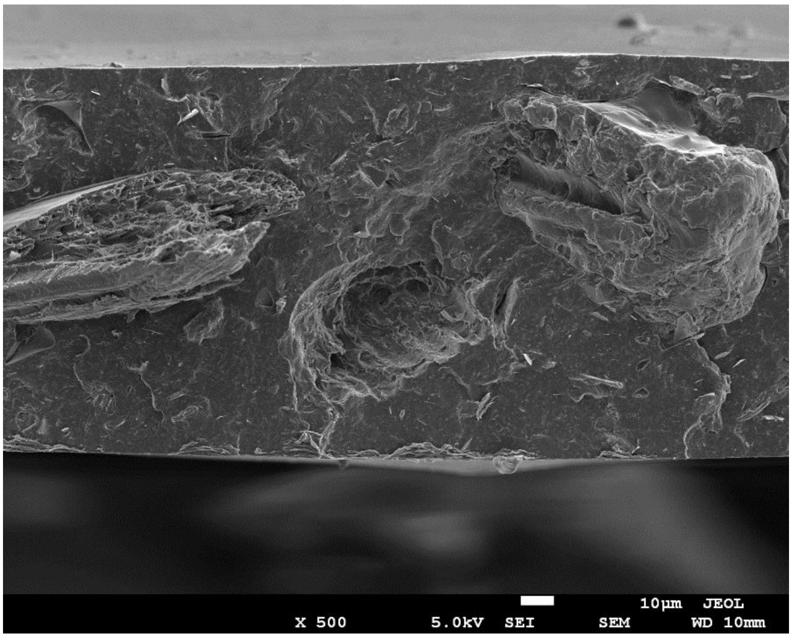


Figure 40 PHBV + 15% untreated RH (x500)

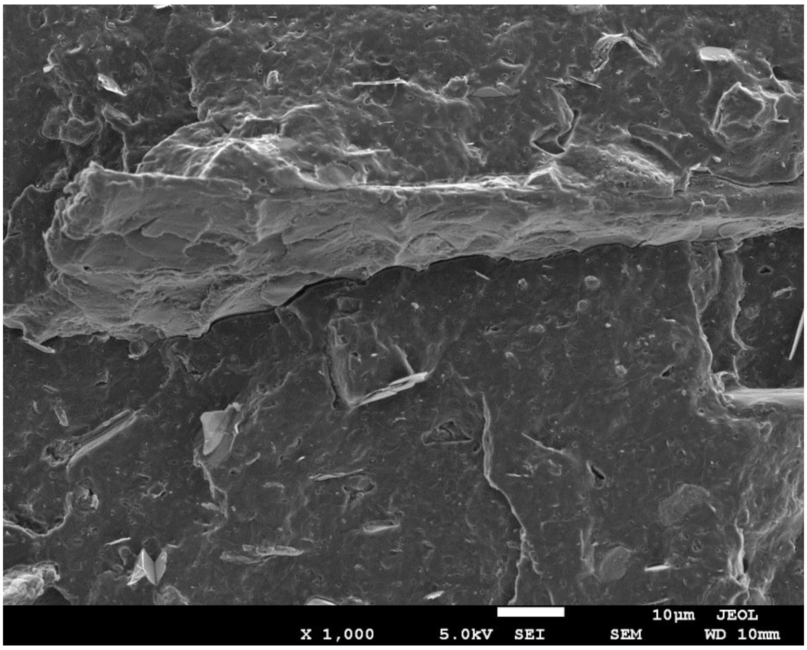


Figure 41 PHBV + 15% untreated RH (x1000)

Figure 40 shows two massive sized particles of RH. These particles are going to be harmful during the thermoforming because when half of the film’s thickness is made of a solid piece, it will lower the mechanical stress needed to break the film.

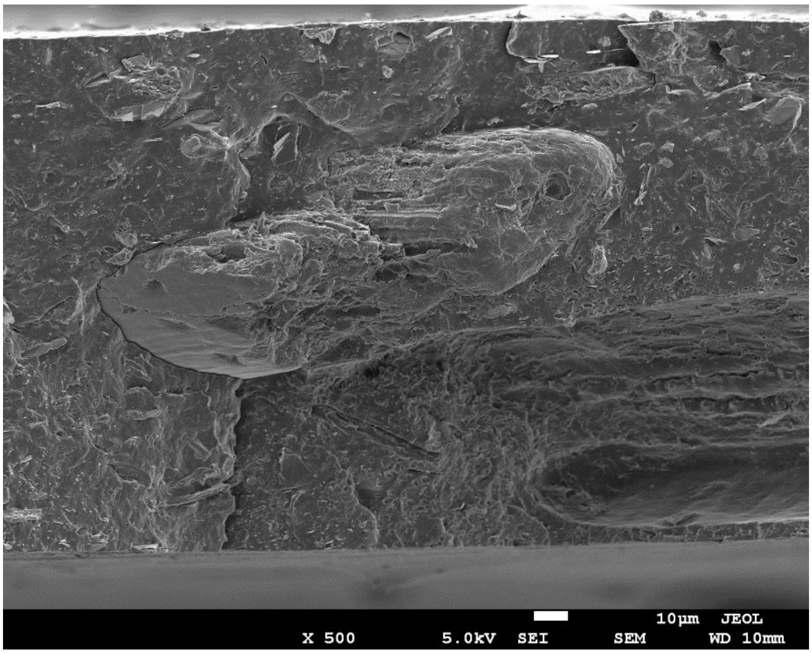


Figure 42 PHBV + 20% untreated RH (x500)

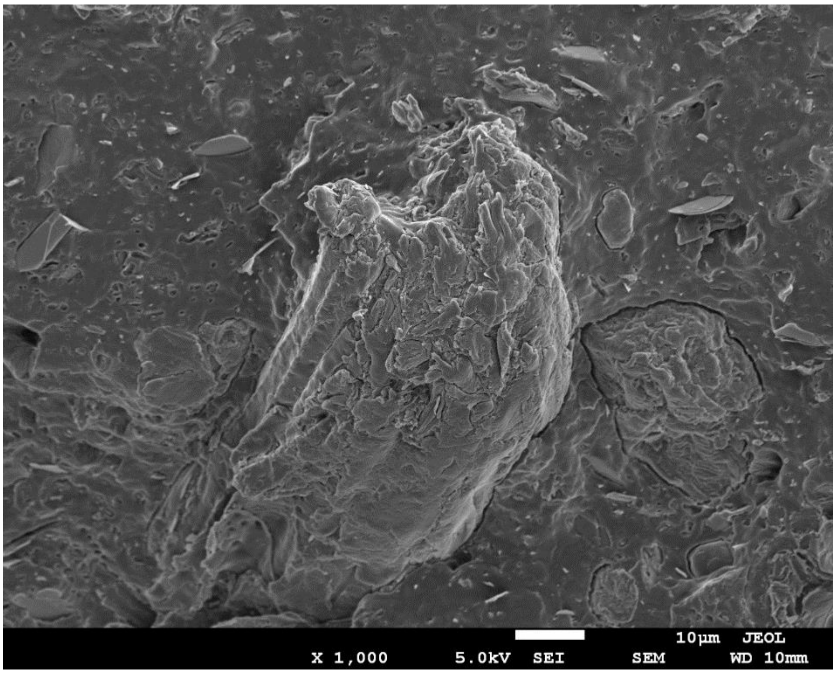


Figure 43 PHBV + 20% untreated RH (x1000)

As the Figures 42 and 43 above show, there are no fiber-like particles in the film. None of the untreated RH blends had problems with their adhesion on the two matrixes.

4.4 Determination of tensile properties

According to the measurements, the modulus of elasticity was improved with the introduction of untreated RH to the films. When comparing the results to pure PHBV Mezclado, the untreated RH (after one day of degradation in the desiccator) had the maximum improvement of 20% in the modulus of elasticity (Attachment 2**)**. After 15 days of degradation in the desiccator, the untreated RH had only the maximum improvement of 5% in the modulus of elasticity (Attachment 3).

Young's modulus (modulus of elasticity) can be calculated using the Formula 1. Tables 3 and 4 below show the percentage, how much the modulus of elasticity was improved when compared to the modulus of elasticity of pure PHBV Mezclado.

Table 3 Improvement (%) of the modulus of elasticity after 1 day of degradation

Blend	%
5% RH	20,2
10% RH	7,4
15% RH	15,3
20% RH	10,3

Table 4 Improvement (%) of the modulus of elasticity after 15 days of degradation

Blend	%
5% RH	4,6
10% RH	5,2
15% RH	0,6
20% RH	-4,3

As Table 3 shows, there was an improvement in the modulus of elasticity, when untreated RH was used as a filler material in PHBV based biopolymer. After 15 days of degradation, the chemical bonding between molecules breaks down due to the hydrolysis. In Table 4, with the blend of PHBV+20% RH (w/w), marked as red, there was a decrease in the modulus of elasticity. This decrease could be the result of too thick RH particles that pierce the film and make it more vulnerable for hydrolysis.

4.5 Differential Scanning Calorimetry (DSC)

The degree of crystallization of these polymers should be around 30 - 80%. If the degree of crystallization was higher, it would indicate that the polymer blend is really brittle and it could not stand heating. As the Figure 44 shows, the polymer blends are well within that zone. Small line on top of the column tells the amount of error (%) in the results.

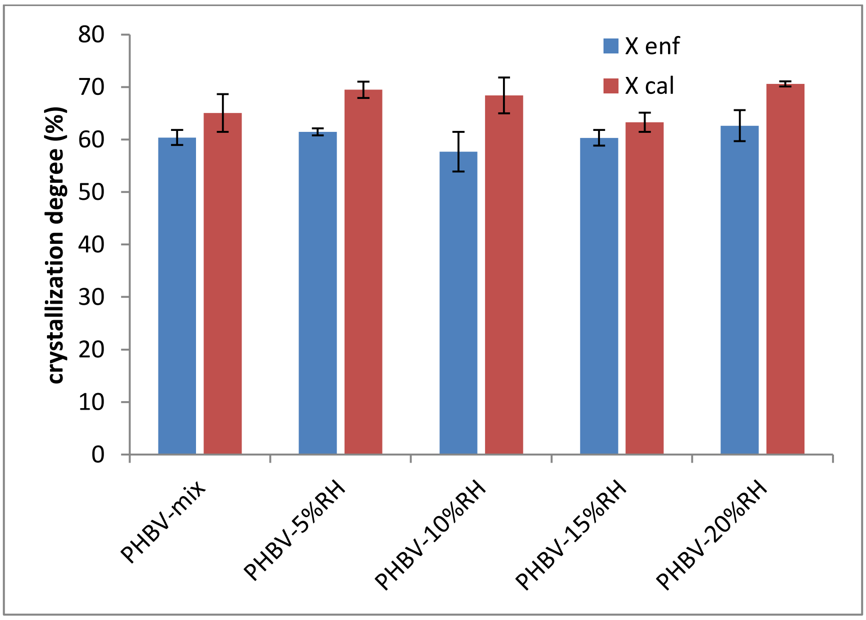


Figure 44 Crystallization degree of PHBV blends

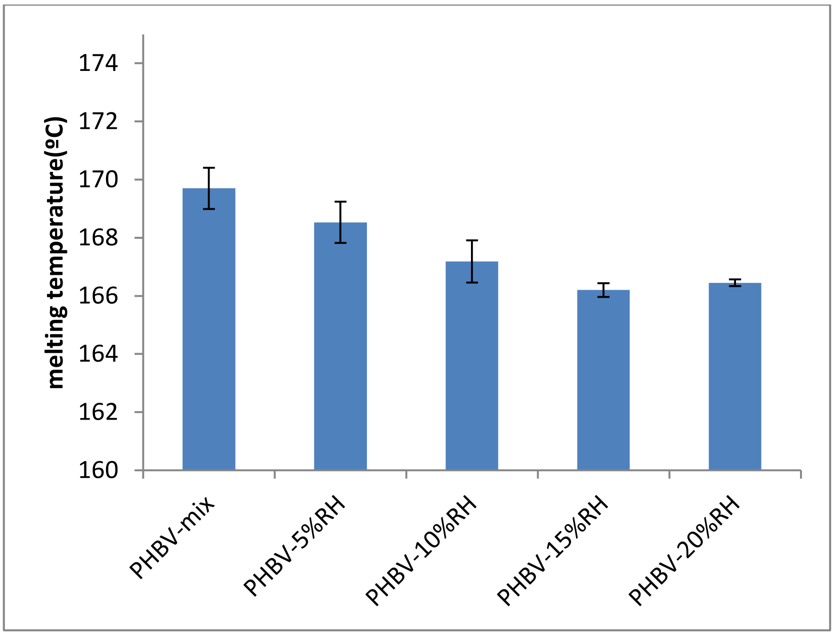


Figure 45 Melting temperature of PHBV blends

Figure 45 shows the temperature needed for melting the polymer blend. The temperature needed for melting the polymer lowers, if the polymer is a blend. This happens because the structure of the polymer is not anymore copolymer (made completely out of two elastomers, see Figure 5). When RH is introduced into the polymer blend, it will make the structure of PHBV even more random. This lowers the intermolecular forces between the polymer chains, which causes the drop in the melting temperature.

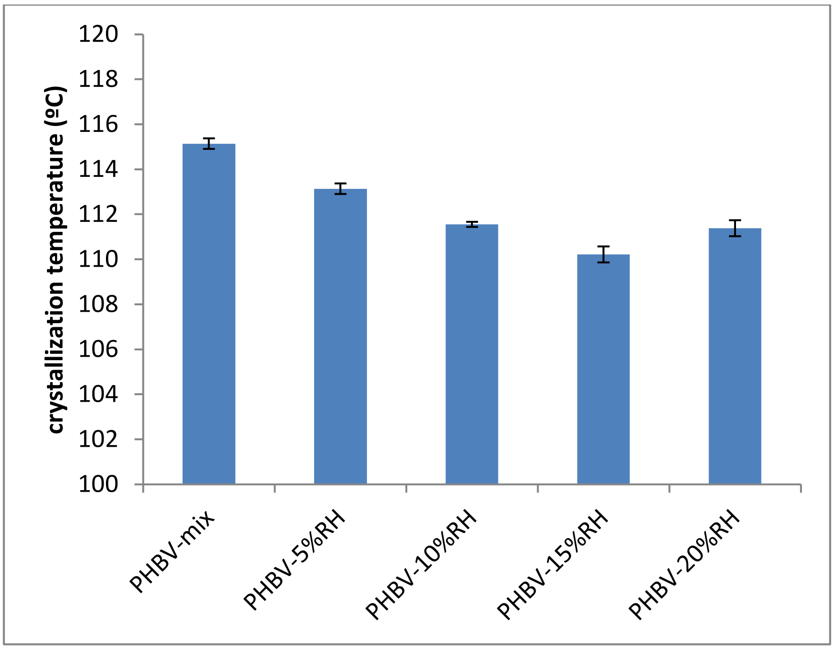


Figure 46 Crystallization temperature of PHBV blends

Crystallization temperature of PHBV blends should be lower compared to pure PHBV because there is added matrix (RH) in the blends which will lower the crystallization temperature. As it can be seen in Figure 46 above, the crystallization temperature of PHBV blends follows this trend.

4.6 Thermoforming

Results of thermoforming the films were disappointing. The PHBV + RH films were badly deformed and full of holes, which made them unusable for testing the thickness of the thermoformed films. Different conditions of thermoforming were tested, but none of them worked for the polymer blend of RH and PHBV. There was too much variation in the results, so no conclusion could not be drawn on which blend was the best for thermoforming.

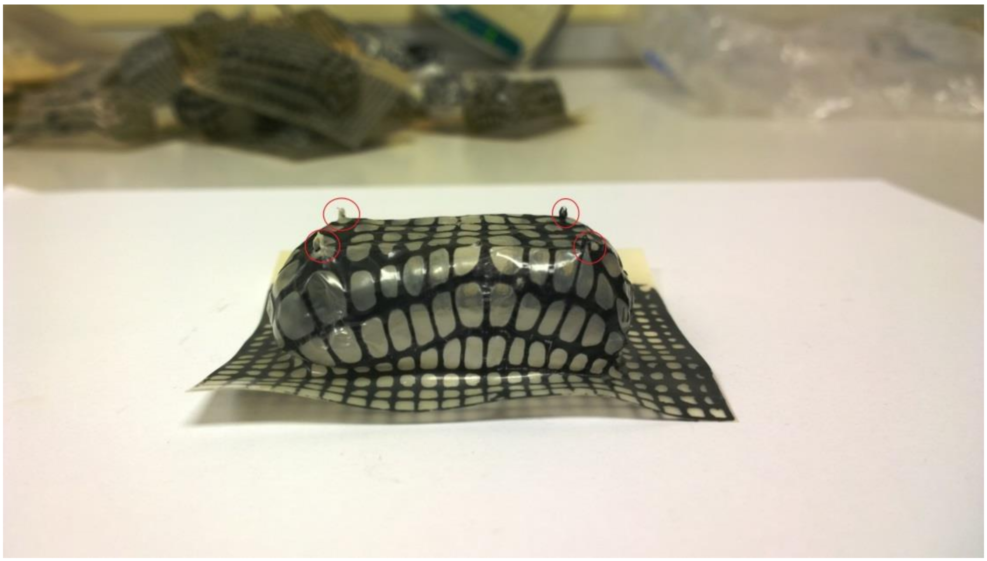


Figure 47 PHBV film after thermoforming

In Figure 47 the mold injection points (red rings), where the vacuum treatment has sucked the air from the mould can be seen. This is the most optimal form of the film that can be achieved with the equipment that was used. There are no holes and the film has the same shape as the mould.

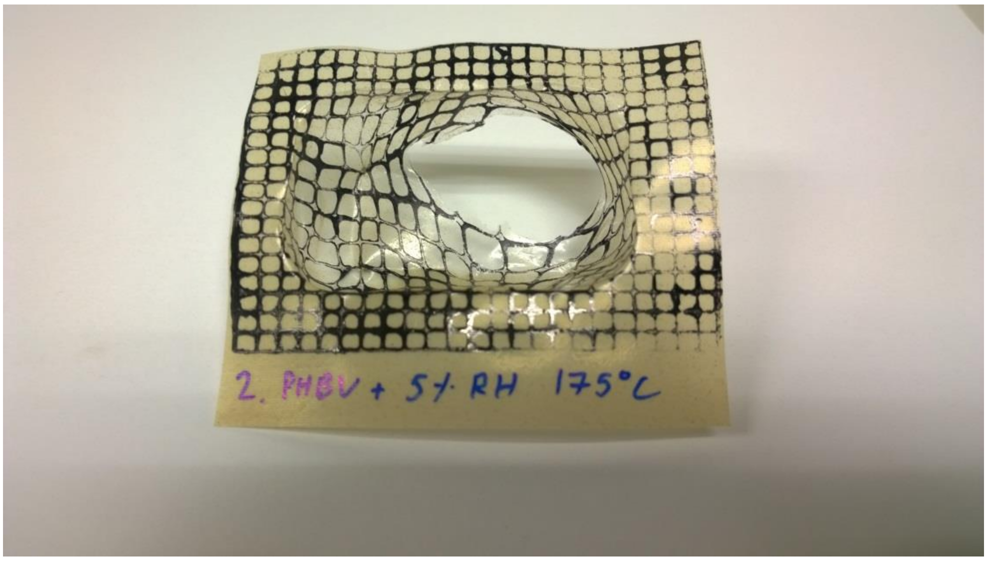


Figure 48 Thermoformed PHBV+ 5% (w/w) RH film

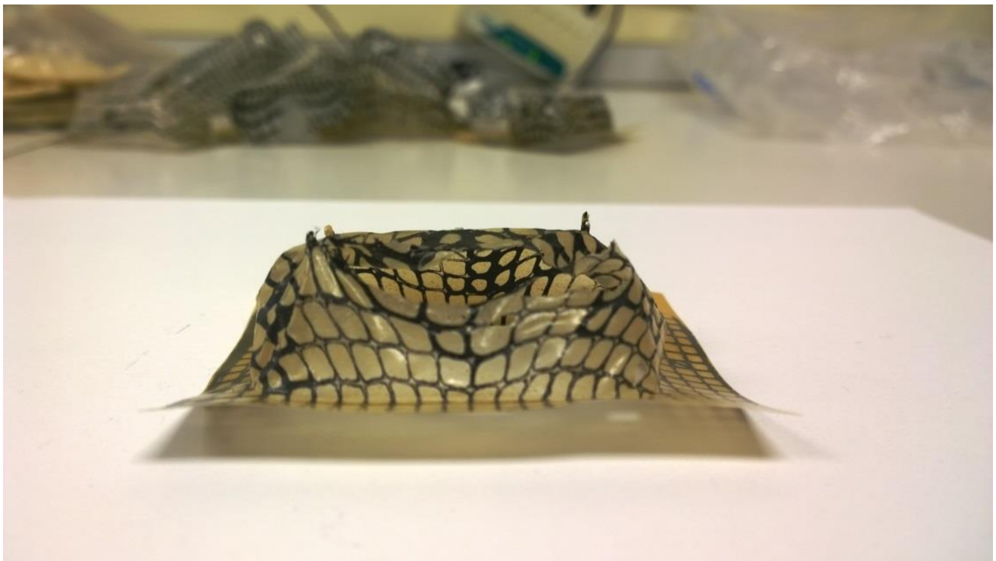


Figure 49 Thermoformed PHBV+ 5% (w/w) RH film, another angle

In Figures 48 and 49 can be seen a thermoformed film, that is deformed and ruptured. All the films had similar holes in them. The cause of this was observed with SEM, which is the enormous particle size of RH compared to the thickness of the films. The points where the RH particles pierced the film were also the same spots that gave up while thermoforming. Also, it should be noted that the thickness of the films was not even, mainly because of the process used to press them.

5 SUMMARY

This thesis is about researching the usage of rice husk (RH) as a strengthening fiber in PHBV based biocomposite that is biodegradable. This biocomposite consists of two matrixes: 1.) biodegradable polymer (PHBV) and 2.) natural fiber that improves the mechanical properties of polymers (rice husk). The aim of this study was to make a biodegradable biocomposite, made of PHBV and RH that should have better mechanical properties compared to pure PHBV.

Two different types of RH (untreated and NaOH treated RH) were tested to see whether the chemical treatment of RH would improve its mechanical properties or not. NaOH treated RH was not suitable for film pressing. NaOH treatment of RH lowered PHBV's viscosity at 175°C and it turned into liquid during the melt blending process. Due to lack of time, another batch of NaOH treated RH could not be done.

The adhesion between untreated RH and PHBV was great. This might be the main factor for the improved mechanical properties. Even though RH was mixed within the PHBV homogenously, the particles did not spread evenly. This could be observed from the SEM pictures. According to the results from the determination of the tensile properties, the modulus of elasticity improved 20% (max.) compared to pure PHBV with the samples that were measured after one day of degradation. After 15 days of degradation in the desiccator, the modulus of elasticity was improved only slightly, with the increase of 5% (max.) in the modulus of elasticity.

The degree of crystallinity of RH and PHBV polymer remained almost the same as the pure PHBV Mezclado. Melting temperatures of the RH blends were lowered, due to the addition of RH into the polymer. This caused the structure of the polymer to be a random copolymer, which lowers the melting temperature.

Untreated RH films less thick than 140 µm cannot handle the mechanical stress caused by the thermoforming. Almost all the films were ruptured from the corners or they were unevenly formed. This was caused mainly by the RH particles that were too big compared to the thickness of the films. RH particles were almost half the thickness of the films, when investigated with SEM. In order to make films that could be thermoformed, the films would have to be thicker. This would also ease the process of making these films. Grinding the RH into particles smaller than 140 μm cannot be done without a significant amount of work.

The untreated RH films are not transparent, which could be a problem with the packaging of certain products like fruits. Customers want to see the product they are buying, so it could not be used in applications as stated before. Untreated RH films could be used as a thick, opaque plastic coating on the products that do not need to have a `window` on their side for the customers to see the product itself. There are plenty of goods that could be wrapped in opaque RH films.

By improving the process of making these films, some of the problems regarding the polymer recycling could be relieved. There are still some things that needs to be figured out, but the results of this thesis are encouraging. Research group PI-MA will continue its work to find out innovative answers for this kind of problems.

REFERENCES

1. Food and Agriculture Organization of the United Nations. 2013. Search conducted with following info: (Country: World + Total; Year: 2013; Item: Rice, paddy; Element: Production Quantity). Available at: http://faostat.fao.org/site/567/default.aspx#ancor (Search day 20.10.2014)

2. Rozainee, M. – Ngo, S.P – Johari, A. – Salema, A.A. – Tan, K.G. 2009. *”The Utilisation of Rice Husk Waste and Its Ash Part 1”*. The Ingeniur Vol 41 Mar-May 2009, page 46-50. Available at: http://www.academia.edu/438079/Utilisation_Of_Rice_Husk_Waste_And_Its_Ash_Part_1_

3. Bergeret, A. - Benezet, J.C. - Tran, T.P.T. - Papanicolaou, G.C. - Koutsomitopoulou, A. 2013. *”Valorization of agricultural by-products in poly(lactic acid) to developbiocomposites”*. Thakur, V.K. (Ed.).

4. Bower, David I. 2002. *”An Introduction to Polymer Physics”*. New York: Cambridge University Press, page 8-20.

5. Ophardt, Charles E. 2003. ”Addition Polymers”. Available at: http://www.elmhurst.edu/~chm/vchembook/401addpolymers.html (Search day 28.1..2014).

6. Ophardt, Charles E. 2003. ”Condensation Polymers”. Available at: http://www.elmhurst.edu/~chm/vchembook/402condensepolymers.html (Search day 28.1..2014).

7. Lower, Stephen. 2010. *“Polymers and Plastics”*. Available at: http://chemwiki.ucdavis.edu/Wikitexts/Simon_Fraser_Chem1%3A_Lower/06._States_of_Matter/Polymers_and_Plastics

8. Ring, W. – Mita, I. – Jenkins, A.D. – Bikales, N.M. 1985. *”Source-based Nomenclature for Copolymers”*. IUPAC Macromolecular Division Commission on Macromolecular Nomenclature. http://pac.iupac.org/publications/pac/pdf/1985/pdf/5710x1427.pdf

9. Pyykkö, Kimmo. 2008. *”Moottorin imukäyrien valmistaminen muovin rotaatiovalua käyttäen”*. Bachelor´s thesis. Tampere: Tampere University of Applied Sciences, Degree Programme in Mechanical and Production Engineering. https://publications.theseus.fi/bitstream/handle/10024/8702/Pyykk%C3%83%C2%B6.Kimmo.pdf?sequence=2

10. Verma, N.K. – Khanna, S.K. – Kapila, B. 2011. *”Classification of Polymers”*. Comprehensive Chemistry XII, 15th edition, pages 1542 – 1551.

11. Fried, Joel R. 2014. *”Polymer Science and Technology”*. Prentice Hall, 3rd edition, pages 1-6.

12. *”Plastics”*. 2007. Nobel Media AB 2014. Available at: http://www.nobelprize.org/educational/chemistry/plastics/readmore.html (Search day 27.11.2014).

13. Shanks, Robert – Kong, Ing. 2012.*”Thermoplastic Elastomers”*. Available at: http://cdn.intechopen.com/pdfs-wm/34065.pdf

14. Tarr, Martin. 2014.*”Polymer Types”*. Available at: http://www.ami.ac.uk/courses/topics/0210_pt/ (Search day 27.11.2014).

15. Javadi, Alireza – Pilla, Srikanth – Gong, Shaoqin – Turng, Lih-Seng. 2010. *“Biobased and Biodegradable PHBV- Based Polymer Blends and Biocomposites: Properties and Applications”*. Handbook of Bioplastics and Biocomposites Engineering Applications, pages 373-396.

16. Soulestin, J. – Prasantha, K. – Lacrampe, M.F. – Krawczak, P. 2011. *“Bioplastics Based Nanocomposites for Packaging Applications”*. Handbook of Bioplastics and Biocomposites Engineering Applications, pages 77-120.

17. Rudnik, Ewa. 2008. *“Compostable Polymer Materials”*. Elsevier Ltd, 1st edition, page 21.

18. Santiaguel, Alaric Francis. 2013. *“A Second Life for Rice Husk”*. Rice Today Vol. 12, No. 2 (April – June 2013). Available at:

http://es.scribd.com/doc/135034710/RT-Vol-12-No-2-A-Second-Life-for-Rice-Husk#fullscreen=1

19. *“What is lignin”*. 2010. Lignoworks 2014. Available at: http://www.lignoworks.ca/content/what-lignin

20. Hannay, F. 2002. *“Rigid Plastics Packaging: Materials, Processes and Applications”*. Rapra Technology, vol. 13, No. 7, pages 23 - 26.

21. *”Plastics”*. 2014. US Environmental Protection Agency. Available at: http://www.epa.gov/osw/conserve/materials/plastics.htm (Search day 21.09.2014)

22. C.J. Moore, G.L. Lattin, A.F. Zellers. 2005.”Density of Plastic Particles found in zooplankton trawls from Coastal Waters of California to the North Pacific Central Gyre”. Algalita Marine Research Foundation.

23. *“When Will Oil Run Out”*. 2014. Institution of Mechanical Engineers. Available at: http://www.imeche.org/knowledge/themes/energy/energy-supply/fossil-energy/when-will-oil-run-out

24. Tran, Thi Phuong Thao - Bénézet, Jean-Charles – Bergeret, Anne. 2014. *“Rice and Einkorn wheat husks reinforced poly(lactic acid) (PLA)biocomposites: Effects of alkaline and silane surface treatments of husks”*. Elsevier B.V.

25. Mohammadi-Rovshandeh, Jamshid - Pouresmaeel-Selakjani, Peyman - Davachi, Seyed Mohammad - Kaffashi, Babak - Hassani, Atieh - Bahmeyi, Alireza. 2014. *“Effect of Lignin Removal on Mechanical, Thermal, and Morphological Properties of Polylactide/Starch/Rice Husk Blend Used in Food Packaging”*. Journal of Applied Polymer Science.

26. Tran, Thanh Duy - Nguyen, Mao Dang - Thuc, C. N. Ha - Thuc, H. Ha - Tan, Tai Dang. 2013. *“Study of Mechanical Properties of Composite Material Based on Polypropylene and Vietnamese Rice Husk Filler”*. Journal of Chemistry.

27. Singh, Sanjeev - Mohanty, Amar K. - Sugie, Tomohiko - Takai, Yoshihiro - Hamada, Hiroyuki. 2008. “*Renewable resource based biocomposites from natural fiber and polyhydroxybutyrate-co-valerate (PHBV) bioplastic”*. Elsevier B.V. Composites: Part A 39 (2008) 875–886.

28. ENMAT Y1000 Technical data sheet. Available at: http://www.ecojo.co.il/images/pdf/rawmaterials/ENMAT_Y1000_Technical_Data_Sheet.pdf

29. Höhne, G.W.H. – Hemminger, W.F. – Flammersheim, H.-J. 2003. *“Differential Scanning Calorimetry”*. Springer Science & Business Media, 2nd Edition.

ATTACHMENTS

Attachment 1 Results from the determination of the real temperature T_{real}

Test	10s	15s	20s	25s	30s	35s	40s	45s	50s
1	61	71	80	87	92	96	99	101	102
2	60	72	83	89	94	98	100	103	105
3	69	81	89	95	100	103	106	108	109
4	70	82	91	96	101	106	108	110	112
5	60	73	83	90	95	99	102	104	105
6	65	79	89	96	101	105	107	110	111
7	69	81	91	98	103	106	109	112	113
			T_{real}	93°C	98°C				

$$\frac{87+89+95+96+90+96+98}{7}=93$$

$$\frac{92+94+100+101+95+101+103}{7}=9$$

Attachment 2 Results of the tensile properties (RH blends after 1 day of degradation)

	PHBV Mezclado	**PHBV + 5% RH**	**PHBV + 10% RH**	**PHBV + 15% RH**	**PHBV + 20% RH**
1	1554,73	2790,52	1136,40	1284,85	1876,56
2	1593,69	2980,64	943,11	1837,34	2249,97
3	1686,09	1416,17	1477,04	1080,86	1117,33
4	1635,56	1485,39	1241,70	2099,51	1054,01
5	1362,18	1980,16	2037,63	2007,66	819,95
6	1486,48	1538,88	2900,30	1672,52	2331,10
7	1447,10	1618,87	1243,52	1916,43	1079,17
8	1576,12	1603,76	2529,03	1135,29	3259,95
9	1484,87	1611,32	1380,98	1787,74	1755,75
10	1714,94	1690,59	1763,60	1651,30	1598,71
11	1372,28	1718,45	1930,49	3505,26	-
12	-	1694,86	1340,82	-	-
13	-	1574,58	-	-	-
14	-	3265,79	-	-	-
Media	**1537,64 MPa ± 118,20 MPa**	**1926,43 MPa ± 609,80 MPa**	**1660,38 MPa ± 593,13 MPa**	**1816,25 MPa ± 656,94 MPa**	**1714,25 MPa ± 752,29 MPa**

Attachment 3 Results of the tensile properties (RH blends after 15 days of degradation)

	PHBV Mezclado	**PHBV + 5% RH**	**PHBV + 10% RH**	**PHBV + 15% RH**	**PHBV + 20% RH**
1	4198,68	4416,45	4428,44	4430,98	3658,09
2	3917,80	3903,34	4053,52	3923,91	4044,52
3	3957,50	4077,62	4568,83	3739,07	3519,19
4	4052,73	3933,18	4546,53	4283,75	3456,05
5	4315,37	4341,43	4033,58	4000,59	4007,78
6	4069,73	4783,20	4915,04	4277,01	3077,98
7	4151,94	4552,07	4377,35	3937,31	4657,05
8	4195,30	4452,93	4053,64	3853,20	4190,13
9	4164,19	4098,86	4010,74	4317,47	4262,80
10	3259,87	3883,30	3843,16	3952,48	3962,32
11	4254,73	-	4365,45	-	-
12	-	-	4078,65	-	-
Media	**4048,90 MPa ± 288,05 MPa**	**4244,24 MPa ± 99,85 MPa**	**4272,91 MPa ± 310,88 MPa**	**4071,58 MPa ± 234,32 MPa**	**3883,59 MPa ± 459,34 MPa**