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TESTING OF WATER VAPOUR PERMEABILITY OF FILMS MADE OF POLY (HYDROXY-ALKANOATE) AND ZEIN

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Abstract: Marine waste presents a global problem, and it mainly composed of different plastic products, mostly in very tiny fragments. The one way to deal with marine waste is to increase the usage of biodegradable plastic materials. The main aim of the MarineClean project (full name of the project is Marine debris removal and preventing further litter entry) is to reduce the sea pollution by the development of marine waste removal equipment and by promoting marine degradable packaging. Not many biodegradable plastic materials degrade in marine waters, but one of them is poly(hidroxyalkanoate) (PHA), the material chosen for the MarineClean project. In the project, some tests were also done with edible material made of zein, corn protein. In order to test the suitability of marine degradable material for making of food packaging, the testing of the water vapour transmission rate has been made.
Keywords: poly(hidroxyalkanoate), zein, water vapour transmission rate

1. INTRODUCTION

Plastic materials are the most popular packaging material in the world, mainly because of their versatile properties and light weight. On the other hand, plastic waste has caused increasing environmental concerns, resulting in a strengthening of various regulations aimed at reducing the amounts of waste generated. One of the problems is that conventional, fossil-based plastics are virtually all non-biodegradable, and some are difficult to recycle or reuse due to being complex materials having varying levels of contamination. One of the biggest environmental problems is marine debris that may originate from activities on land or at sea. Land sourced material include plastic bags, bottles, fibreglass, plastic pellets and insulation etc. while sea sourced material include abandoned or lost fishing gear, items lost from offshore platforms and solid and non-biodegradable material sourced from ships. The problems caused by marine debris are multifaceted and essentially rooted in inadequate solid waste management practices, product designs that do not consider life-cycle impacts, consumer choices, lack of waste management infrastructure, littering and the public's poor understanding of the potential consequences of their actions. [1]

The European project CIP Eco-innovation entitled *MarineClean* (full name of the project is Marine debris removal and preventing further litter entry) was proposed with the main aim to reduce the sea pollution. One of the areas of activities is the design of marine degradable and/or edible packaging. For this purpose a biobased, biodegradable material based on poly(hydroxyalkanoate) (PHA) was selected. Also, some tests were done with edible material made of zein, corn protein.

2. POLY(HYDROXYALKANOATE) (PHA)

Poly(hydroxyalkanoate)s (PHAs) are polyesters synthesized by a variety of bacteria as an intracellular storage material of carbon and energy. [2] Due to their biodegradability and biocompatibility these biopolyesters may easily find numerous applications. The properties of PHAs are dependent on their monomer composition, and it is, therefore, of great interest that recent research has revealed that, in addition to PHB, a large variety of PHAs can be synthesized by microbial fermentation. The monomer composition of PHAs depends on the nature of the carbon source and microorganisms used. [3] Since the first finding of PHA in 1926, more than 100 different monomer units have been identified as constituents of PHA in above 300 different microorganisms including 3-hydroxyalkanotes of 3 – 12 carbon atoms with large variety of R-pendant groups, 4-hydroxyalkanoates of 4 – 8 carbon atoms, 5-hydroxypentanoates, 5-hydroxyhexanoate and 6-hydroxydodecanoate. However, only a few of these PHAs have been produced in amounts sufficient to enable the characterization of their material properties and to develop potential applications. Poly(3-hydroxybutyrate) [P(3HB) or PHB] is a homopolymer of 3-hydroxybutyrate and is the most widespread PHA in natural condition. [4] PHB is a typical highly crystalline thermoplastic whereas the medium chain lengths PHAs are elastomers with low melting points and a relatively lower degree of crystallinity. A very interesting property of PHAs with respect to food packaging applications is their low water vapour permeability which is close to that of PE-LD. [3]

One of the unique properties of PHA materials is their biodegradability in various environments. The rate of biodegradation of PHA materials depends on many factors, notably those related to the environment (temperature, moisture level, pH, and nutrient supply) and those related to the PHA materials themselves (composition, crystallinity, additives, and surface area). [5] PHA is a high-molecular-weight solid polymer that cannot be transported through the cell wall, so microorganisms such as bacteria and fungi excrete extracellular PHA-degrading enzymes (PHA depolymerases) that hydrolyze the solid PHA into the water-soluble monomer and oligomers. These low-molecular-weight degradation products are then transported into the cell and subsequently metabolized as carbon and energy sources (Figure 1). [2]

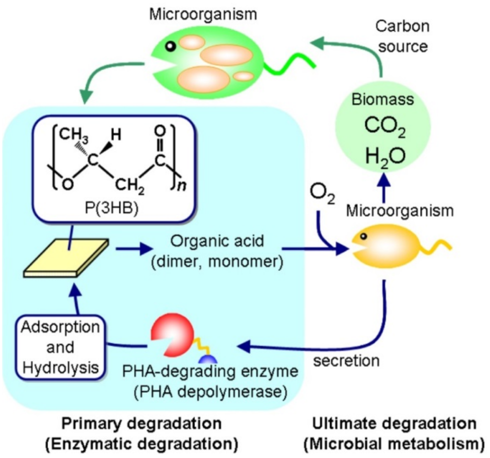

Figure 1 – Biosynthesis and biodegradation process of PHA in a natural environment [2]

PHAs have rich properties depending on the structures. Homopolymers, random copolymers, and block copolymers of PHA can be produced depending on the bacterial species and growth conditions. With over 150 different PHA monomers being reported, PHAs with flexible thermal and mechanical properties have been developed. Such diversity has allowed the development of various applications, including environmentally friendly biodegradable plastics for packaging purposes, fibers, biodegradable and biocompatible implants, and controlled drug release carriers.[6] Figure 2 presents biodegradable beach toys made of PHA that degrade in marine environment. [7]

Figure 2 – Biodegradable beach toys made of PHA

For the purposes of *MarineClean* project, a marine degradable film under the brand name *EcoOcean*, is produced by the *EcoCortec*. Its basis is poly(hydroxybutyrate) (PHB) and it is intended for the production of films, foils, and bags using the procedure of tubular film extrusion. *EcoOcean* film and bags contain 77% biobased content and they are fully marine biodegradable. *EcoOcean* is designed to biodegrade in marine environments, anaerobic digestion, natural soil and water environments, backyard composting systems, and municipal composting facilities (in areas where these facilities are available). [8]

EcoOcean films are durable in use and shelf stable, yet biodegradable in ambient temperature environments. The material has high melt strength and its physical properties are near PE-LLD and include heat sealability, excellent tensile properties, moisture and heat resistance, UV resistance and good weatherability. [9]

The crystalline behavior provides valuable information for interpreting the water vapour permeation properties of the PHA membranes. The water vapour permeability is related to the chemical structure and the morphology of the PHA membranes. In a comparison with the packaging materials available in the market, PHA has similar water barrier property as PET, especially for poly(3-hydroxybutyrate) (PHB). PHA is a promising material for disposable packaging applications as it is also biodegradable. However, its brittleness and melt instability resulted from slow crystallization restrict the commercial applications of PHB. [10]

3. ZEIN

Zein comprises a group of alcohol-soluble proteins (prolamins) found in corn endosperm. It can be extracted with aqueous alcohol and dried to a granular powder. [11] Zein has been examined as a possible raw material for polymer application since the early part of the 20th century. It resembled bees' wax and can be soft, ductile, tenacious, and elastic. It had some of the properties of wheat gluten and was analogous to resin. Renewed interest in zein as a polymeric material has been stimulated, in part, by the perceived negative impact of plastic on solid waste disposal. Zein offers several potential advantages as a raw material for film, coatings, and plastics applications. It is biodegradable and it is annually renewable. The annual surpluses of corn provide a substantial raw material resource. However, there are also some problems with the use of zein as a plastic material. Zein is a biological material and, like most biological materials, it is affected by water. This, coupled with the fact that water is a plasticizer for zein, means that zein's properties are subject to change with humidity. [12] Zein films have water vapour permeability (WVP) values lower than or similar to those of other protein films, cellulose ethers, and cellophane. However, their WVP is notably higher than that of LDPE or ethylene-vinyl alcohol copolymer (EVOH). [11]

Many older uses of zein were lost to synthetic polymers because of superior properties and lower cost of the synthetic polymers. In this day of environmentally friendly products, however, zein again may find a niche that synthetic polymers cannot fill. But for zein to realize its full potential, research must finds ways to overcome two main problems: prohibitive cost and poor resistance to water. [12] Since zein films are completely safe to ingest, it is the perfect coating for foods and pharmaceutical ingredients. [13] During the *MarineClean* project, edible packaging on a basis of zein was developed. Edible packaging was produced and tested on edibility for marine animals at the *National Institute of Biology, Marine Biology Station Piran*. Sensory analysis was done at TC *PoliEko* but negative feedback was gained during presentation of the material to the consumers. The consortium therefore decided not to push this material on the market because it would not gain success at the moment.

4. BARRIER PROPERTIES OF PLASTIC FILMS

The determination of the barrier properties of a polymer is crucial to estimate and predict the product-package shelf-life. The specific barrier requirement of a package system depends upon the food characteristics and the intended end-use applications. Generally plastics are relatively permeable to small molecules such as gases, water vapour, organic vapours, and liquids, and they provide a broad range of mass transfer characteristics, ranging from excellent to low barrier values, which are important in the case of food products. Water vapour and oxygen are two of the main permeants studied in packaging applications, because they may move from the internal or external environment through the polymer package wall, resulting in possible negative changes in product quality and shelf-life. [14]

The water vapour barrier properties for the packaged food product, whose physical and chemical deteriorations are related to its equilibrium moisture content, are of great importance for maintaining or extending its shelf-life. The water vapour barrier is quantified by the water vapour permeability coefficients (WVPC) which indicate the amount of water vapour that permeates per unit of area and time in a packaging material ($kg \cdot m/m^2 \cdot s \cdot Pa$). For fresh food it is important to avoid dehydration while for bakery or delicatessen it is important to avoid water permeation. The water vapour transmission rate (WVTR) is expressed in $cm^3/m^2 \cdot s$ (or $g/m^2 \cdot d$). [14]

A major challenge for the material manufacturer is hydrophilic behaviour of many biobased polymers as a lot of food applications demand materials that are resistant to moist conditions. It is possible to produce biobased materials with water vapour transmittance rates comparable to the ones provided by some conventional plastics, but if a high water vapour barrier material is required, very few biobased materials apply. [3]

Blown films comprise one of the first product categories to be developed based on fossil oil derived biodegradable polyesters. They have successfully been applied as garbage bags and related applications. In many food packaging applications, water vapour barriers as well as gas barriers are required. No single biobased polymer can fulfill both these demands. In this case, the use of co-extrusion can lead to laminates which meet the objectives. For example, materials which are based on thermoplastic starch can be film blown in a co-extrusion set-up with polymers like PLA and PHB/V as coating materials. [3]

Normally, barrier materials (such as non-biodegradable and biodegradable plastics) have the ability to restrict the passage of gases, vapours, and organic liquids through their boundaries. In simpler terms, barrier materials prevent substances inside the barrier from escaping, and outside substances from entering the barrier. Therefore, mass is the best indicator of the amount of substances moving in and out of the barrier. Low-density polyethylene is gaining market share in food industrial applications. It is flexible, transparent, resists tearing, and acts as a moisture barrier. The water vapour transmission rate (WVTR) is one of the key indicators for determining a plastics wrap's effectiveness in preventing food spoilage. It is defined as a rate at which water vapour can move from one side of the barrier to the other. The transmission rate of gases and vapours depends on both the solubility of the gases and their rate of diffusion through the barrier (which depends on the configuration of the barrier polymer). [15]

Permeability is a function of both the permeance and the thickness of the barrier material. Permeation, which includes the rate at which a gas passes through the barrier material, is affected by the characteristics of the polymer, such as its chemical makeup. Permeability is also affected by the molecular organization of the polymer, such as crystallinity: crystallites are impermeable, so a polymer with a higher degree of crystallinity will have a lower amount of permeation, resulting in it being a better barrier. Permeability is also affected by temperature, humidity, and pressure. [15]

5. TESTING OF WATER VAPOUR TRANSMISSION RATE

The moisture or water vapour transmission rate measures the rate at which water vapour passes through thin films of material. Typically, the thicker the film is, the slower will be the rate of transmission. The water vapour transmission rate of a particular film is based on how fast vapour passes through the film under controlled conditions. The relationship between the WVTR and the thickness of the film is inverse and approximately linear for large areas; as a result, doubling the thickness of the film reduces the WVTR value by half. [16]

Figure 3 – Testing of water vapour transmission rate

Samples run with modified version of ASTM E96 – *Standard Test Methods for Water Vapour Transmission of Materials*. The test was performed as follows. The aluminum test cup is filled with silica gel desiccant beads. The sample is then clamped across the mouth of the cup (Figure 3). The fully assembled cup is then placed in a humidity controlled chamber, and weight gain is measured over time.

The test was run at 23°C and 50% relative humidity in the chamber, and a total run time of at least 24 hours. Diameter of testing cup mouth: 9.525 cm (test area *A*: 0.007126 m^2). The test was repeated twice with the use of the same film test pieces.

The official method requires that film samples be sealed to the edges of the cup with melted wax. The cells in the test use screw clamps and a rubber gasket to seal the film. For high barrier films (e.g. PE) the wax seal is likely to produce more repeatable results. With bioplastics and other more permeable materials, comparable results have been obtained with such cells. However, since a modified method was used, comparisons with published results should be made with caution.

The mass of water loss from the cups were monitored as a function of time. The water vapour transmission rate was calculated using the following equation:

$$WVTR = \frac{W/_t}{A} \quad (1)$$

where: *WVTR* – water vapour transmission rate, $g/m^2 \cdot d$; *W* – weight change, g; *t* – time, d; *W/t* – slope of the straight line (weight loss per unit time), g/d; *A* – test area, m^2

Results of testing of water vapour transmission rate for PE-LD film, *EcoOcean* film and zein film are given in table 1.

Table 1 – Comparison of water vapour transmission rates for polyethylene film, *EcoOcean* film and zein film

Measured / calculated values	PE-LD film	*EcoOcean* film	Zein film
Average thickness of the film, *e*, μm	10.5	63.5	237.5
Water vapour transmission rate, *WVTR*, $g/(m^2 \cdot d)$	16.8	36.5	23.8
WVTR normalized to 100 μm thick film, $g/(m^2 \cdot d)$	1.8	23.2	57.5

Zein film sample was significantly thicker than polyethylene and *EcoOcean* film. Also, zein film was significantly harder to produce by extrusion, and compared to PHA film it was stiff and brittle. Additionally, it swelled during testing as shown by some warping of the film surface. Literature reports for water vapour transmission rate of polyethylene film are usually higher than what was observed, but many of those tests are run at higher temperature and/or higher relative humidity, so it is difficult to do a direct comparison of the numbers. Also, literature reports for water vapour transmission rate of PHA should be close to that of PE-LD, but testing didn't support that statement.

6. CONCLUSION

Packaging is one of the largest markets for the polymer industry. Fossil-based plastics, mainly polyolefins and polyesters, dominate the food packaging industry. Due to their non-biodegradability and improper waste management they tend to accumulate in lands and waters, so their replacement is sought in bio-based, biodegradable plastics. Currently, less than 1% of plastic packaging is derived from bio-based sources, mainly because of their higher price and lower properties. Besides mechanical and processing properties, biodegradable films do not have adequate barrier properties for being used directly in food packaging applications. Testing of water vapour transmission rate showed that polyethylene film provides significantly better barrier for moisture than biodegradable films based on poly(hidroxyalkanoate) and zein.

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