

Deliverable 2.3

Assessment of the efficiency of active packaging and bioplastics

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1. EXECUTIVE SUMMARY

This report presents the findings of a project aimed at assessing the efficiency of active packaging and bioplastics in preventing egg hatching in milled rice samples contaminated with adult insects. The study involved various analyses and methodologies to determine the effectiveness of different packaging materials.

The commercial bioplastic Mater-Bi was tested against traditional petro-plastics, specifically BOPP (biaxially oriented polypropylene), in milled rice samples contaminated with adult insects. Following CO₂ measurements, it was observed that Mater-Bi did not provide adequate protection; holes appeared quickly, allowing insects to pass through.

Unable to identify commercial solutions matching the functionality of BOPP, we explored the development of active packaging utilizing Natural Deep Eutectic Solvents/NADES. The newly developed active packaging film was characterized for its hydrophilic/hydrophobic properties with comparisons made to Mater-Bi and BOPP materials.

The results provide insights into the limitations of current bioplastics and highlight the potential of innovative active packaging solutions in enhancing rice based food protection.

2. INTRODUCTION

The fundamental purpose of food packaging is to maintain food quality and safety from production to final consumption by preventing any unwanted biological and chemical changes. Hence, the packaging should function as a barrier to protect the food from environmental influences such as oxygen, moisture, light, dust, pests, volatiles, and both chemical and microbiological contamination [1]. A new class of materials known as "bioplastics" has been developed as a result of efforts to find sustainable alternatives to plastics derived from petroleum. Biodegradable, biobased, or both types of bioplastics are possible. Bioplastics can be categorized as compostable or biodegradable depending on whether they come from synthetic or natural sources, which are unrenewable or renewable, respectively. Biodegradable polymers derived from renewable resources possess the capacity to decompose naturally. Although these polymers have a positive effect on the environment, they typically have certain functional shortcomings, like poor barrier and tensile strength [2].

3. BIOPOLYMERS/BIOPLASTICS

Biopolymer polysaccharides are made up of monosaccharides joined by glycosidic bonds. Due to their hydrophilicity, polysaccharide-based films have low environmental impact and a comparatively small carbon footprint. On the other hand, they are characterized by weak mechanical properties and high permeability to gases in moist environments. Furthermore, natural polysaccharides typically break down before they melt, negating the possibility of processing them thermally and leaving only wet processing methods like coating and solution casting. The structure of the monomer units and the glycosidic bonds separating the monomers distinguish distinct kinds of polysaccharides from one another. Significantly varied polymer properties including crystallinity, branching, and polymer charge result from these variations. Some of the most widely used polysaccharides for food packaging are chitosan, cellulosic material, starch, alginate, pectin, agar and cyclodextrins [2, 3].

4. NEED TO DEVELOP ACTIVE PACKAGING WITH DEEP EUTECTIC SOLVENTS

Deep eutectic solvents (DESs) are a result of tackling the quest for greener solvents that are cheap, biodegradable, facile to synthesize, offering 100% atom economy and possessing flexibility in tuning physical and chemical properties [4,5]. Typically, DES is a liquid system formed from a eutectic mixture of Lewis or Brønsted acids and bases that results in the dip of the melting point of the solvent when compared to its solid individual components [6]. Hydrophobic NADESs are a recent discovery and their applications in the last few years have been centered around extraction, environmental and chemical / materials purposes [7,8]. This study will profit from the tunability offered by choosing the starting components of hydrophobic NADESs to promote the antioxidant properties of films for food packaging.

For the production of emulsions, high-intensity methods are widely used in distinct applications [9,10]. These methods incorporate energy-intensive mechanical devices, such as high-pressure homogenizers (colloidal mills, rotor-stator mixers and jet dispersers), ultrasonicators and microfluidizers, that ensure droplet breakdown by generating intense impact, shear, cavitational or turbulent flow profiles. Among the high-intensity methods, ultrasound-assisted emulsification methods are able to produce smaller emulsion droplets using a relatively lower energy consumption and additionally decreasing the risks of contamination by the equipment [11]. Ultrasonicators using high-frequency sound waves (20 kHz and above) can generate intense disruptive forces from a tip immersed into a liquid sample. Particularly, in the case of the formation of nanoemulsions by ultrasound emulsification, the two underlying mechanisms are the droplet breakdown of the dispersed phase into the continuous phase via acoustic waves, followed by the droplet size reduction due to acoustic cavitation and implosion [10,12].

In order to facilitate the advantages of hydrophobic NADESs in an aqueous medium and to harness the bioactivity of hydrophobic starting compounds, oil-in-water emulsions need to be formulated. The formulation of hydrophobic DES-in-water emulsions by ultrasound emulsification combines the tunability of deep eutectic solvents along with the advantages of emulsions such as increased surface area. Incorporating these emulsions into films for food packaging enhances properties such as antioxidant properties, and reduced permeability to oxygen and water, of the films.

5. METHODOLOGY FOR ACTIVE PACKAGING

The aim of this project is the synthesis of hydrophobic alcohol-based DESs for food packaging applications. Natural components having intrinsic antioxidant properties were used to synthesise novel hydrophobic DESs. These DESs were then introduced into emulsions which were subsequently cast to form **essential oil based-films**.

Thymol, a terpene was the main component explored to synthesize DESs along with other natural components. DESs were prepared using varying compositions of the individual components and their stability was observed at room temperature. The most stable DESs were further used to form emulsions. Pectin, a biopolymer was introduced into the aqueous phase of the emulsion along with a plasticiser to form hydrophobic DES-in-water emulsions by the process of ultrasound emulsification. Films without DESs were also cast to use as a control. The concentrations of the biopolymer and plasticisers used were optimised based on the formation of the films in the subsequent step. The emulsions formulated by ultrasound emulsification were cast using a film applicator and subjected to evaporation at a controlled temperature of 35 °C in an oven to form films. The films formed from emulsions of both the methods will be studied in detail for their intrinsic structure and surface properties. These films will be further studied for their mechanical, anti-oxidant (2,2-Diphenyl-1-picrylhydrazyl (DPPH) and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) methods) and barrier properties (water vapour, gases, UV-Vis) targeting food packaging.

6. CHARACTERIZATION OF ACTIVE PACKAGING AND BIOPLASTICS

An active packaging film based on essential oils, a commercial bioplastic "Mater-Bi" (completely biodegradable and compostable in accordance with EN 13432, Portugal), and a traditional petro-plastic "BOPP" (BOPP 30µm TRANSP + PE 70µm TRANSP) were used in this study. The films were characterized by: 1-Static contact angle measurements of water to define the film's hydrophilicity/hydrophobicity nature (Table 1) and 2- Pure gas permeabilities to CO₂, O₂ and N₂, measured by the classical time-lag

(Table 2). The pure gas permeabilities to CO_2 , O_2 and N_2 of essential oil-based film was not measured because the film was not mechanically stable.

Table 1:

	Essential oil-based film	Mater-Bi	ВОРР
Static contact angle measurements of water	43.6°	71.6°	90.6°

Tabela 2:

	P _{CO2} (Barrer)	P ₀₂ (Barrer)	P _{N2} (Barrer)
BOPP	(6.17 ± 0.93) x 10 ³	(5.10 ± 1.66) x 10 ³	(1.21± 0.71) x 10 ³
Mater-Bi	(6.78 ± 1.68) x 10 ³	(6.04 ± 0.56) x 10 ³	(0.91 ± 0.11) × 10 ³

The essential oil-based film was clearly hydrophilic, with a static contact angle measurement of water less than 90° due to the predominance of the hydrophilic biopolymer chitosan. The commercial bioplastic "Mater-Bi," commercialized by Silvex, Portugal [14], is completely biodegradable and compostable. In contrast, the traditional petro-plastic "BOPP" (BOPP 30µm TRANSP + PE 70µm TRANSP) is hydrophobic, owing to its biaxially oriented polypropylene- BOPP [13] and polyethylene (PE) composition, both of which are hydrophobic materials.

7. CONCLUSIONS

Packaging is crucial for maintaining food quality and safety from production to final consumption. Future research should focus on developing active packaging and bioplastics with enhanced barrier properties to propose effective solutions for scaling up their use in the rice industry.

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